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2011 – Istanbul University, Istanbul, Turkey

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Without the authors and participants ISTE- 2011 would of course have been impossible. We would like to sincerely thank all of you for coming, presenting and joining in the academic activities. We would also like to thank all of those who contributed to the reviewing process of the "ISTEC - 2011" conference papers.

We have lots of participants from 25 different countries. These countries are Turkey, Algeria, Poland, South Korea, Malaysia, Libya, Egypt, Saudi Arabia, Nigeria, Turkish Republic of Northern Cyprus, Romania, India, Morocco, Taiwan, Indonesia, Macedonia, Canada, Jordan, Pakistan, United Arab Emirates, Oman, Brazil, Russia, Italy, Uganda.

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## KEYNOTES

<b>Keynote Speaker</b>	<b>Topic</b>
<b>Prof.Dr. Rıdvan Karapınar</b>	<b>Optical Response of a Nematic Liquid Crystal Display</b>
<b>Dr. Huriye Arıkan</b>	<b>Women of Mathematics</b>

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*Özhan ÖZTUĞ*

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# A CASE STUDY: ADAPTIVE CONTROL USING FAST AND ROBUST ADAPTATION FOR NONLINEAR SYSTEMS

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**Abstract** — This paper surveys the recent literature in Applied Nonlinear Control. No attempt has been made to provide mathematical or algorithmic details in literature; instead, general outline of some techniques have been given. The goal of this paper is to serve as a resource for new researchers in the field and provides the background of nonlinear control for specific analysis. Also, a case study was present the novel L1 adaptive output feedback control methodology[1]-[2] for uncertain systems in the presence of time-varying unknown nonlinearities, unmodeled dynamics with disturbances. The adaptive controller ensures uniformly bounded transient and asymptotic tracking for the system's both signals, input and output simultaneously. The performance bounds can be systematically improved by increasing the adaptation rate.

**Keywords** : Adaptive, nonlinear, robust, linearization, Lyapunov

## I. Introduction

The development of nonlinear methods was a remarkable achievement of the 1980's. Within the last decade, researchers from the areas as robotics, flight control, process control and biomedical engineering have shown their interest in the application and development of nonlinear control systems. Compared with the methodologies used in linear, nonlinear systems have much more complex behaviors that cause the analysis becomes more difficult. First, nonlinear equations, unlike linear ones, cannot in general be solved analytically, and therefore a complete understanding of the behavior of a nonlinear system is very difficult. Second, the Laplace transform and Fourier transform do not apply to nonlinear systems. In real world, physical systems are inherently nonlinear. Thus, all control systems are nonlinear to a certain extent and there is no unique method or procedure can fully predict the behavior of nonlinear systems.

## II. General Methods of Nonlinear Control

In the past few years, a number of major results have been obtained in nonlinear controls. Here, we would like to briefly review some commonly used methodologies [3], [14]:

### 2.1 Feedback linearization

Feedback linearization deals with techniques for transforming original system models into equivalent models of a simpler form. The basic idea is to transform a nonlinear system into a linear system (i.e., of canceling the nonlinearities), and then use the well-known linear design techniques to complete the control design. The approach has been used to solve a number of practical nonlinear control problems. It applies to important classes of nonlinear systems (so-called input-state linearization or input-output linearization to partial linearization). This well known techniques can also be used as model-simplifying devices for robust control and adaptive control. Although Feedback linearization is commonly used in early research, it has the following limitations: 1).Typically requires a full state measurement; 2).It can not be used for all nonlinear systems; and 3).With parameter uncertainty or disturbances in system, it does not guarantee the robustness.

### 2.2 Sliding Control

Sliding control provides a systematic approach to the problem of maintaining stability in the face of modeling imprecision. The methodology is based on the notational simplification. Although performance can be achieved in the presence of arbitrary

parameter inaccuracies, uncertainties in the model structure lead to a trade-off between tracking performance and parametric uncertainties. In practice, this corresponds to replacing a switching chattering control law by its smooth approximation. Generally speaking, the ideas of feedback linearization, sliding mode, backstepping and adaptive controls are commonly used methods in nonlinear systems with limitations.

### 2.3 Variable Structure Control

The stability problem was resolved in the early 80's, most of the existing schemes use the same controller structure, which often suffers from poor transient responses during the initial adaptation stage. Attempts to remedy this situation include the variable structure control systems and multiple models with switching and tuning [4]-[6]. The design of VSC system requires the appropriate switching functions and sliding modes. Up to now, these steps are reasonable only when the system is in one of the canonical forms [7]. This often means that only special cases have been treated.

### 2.4 Neural-Network and Fuzzy Control

The concept of Neural Networks (NN) in Control derived to find faster and simpler solutions for highly nonlinear control problems with constrained and uncertain environments. Moreover, NN have the ability to keep learning during their operation. In recent years, it is effectively used in uncertain, nonlinear, and some types of time-varying systems. Youping [8] proposes a neural controller for unknown nonlinear systems based on backstepping. This controller works for a general class of input-output linearizable systems with no zero dynamics, minimum-phase systems. Another robust cerebellar model articulation controller (RCMAC) [9] is designed for unknown nonlinear systems, on-line tuned by the derived adaptive laws based on Lyapunov sense. The developed control scheme has the advantages that it can tune the parameters of RCMAC even unknown system dynamics and achieve specified robust tracking performance. Besides neural networks, the "model-free" concept of fuzzy logic is broadly use in recent research such as [10], the gain parameters of PI controller integrates with the fuzzy system are adapted by proposing adaptation laws, such that the ideal control law for nonlinear systems can be estimated. In NN and fuzzy logic systems, the design procedures of are based on rigorous nonlinear derivations and stability proofs, and yield a multi-loop intelligent control structure with NN in some of the loops. The weight tuning algorithms were given that do not require complicated initialization procedures, work on-line in real-time, and offer guaranteed tracking and bounded NN weights and control signals.

With all the existing methods listed above, there are more brilliant ideas not present here to save the paragraph. For the case study we proposed in adaptive control theory, the most important features are the guaranteed robustness in the presence of fast adaptation, achieved via continuous feedback. The separation between adaptation and robustness, inherent to L1 adaptive control architecture, was possible to achieve by appropriate modification of the control objective with the understanding that uncertainties in any feedback loop remedy for only within the bandwidth of the control channel. This problem reformulation led to a solution that allows for tracking both in transient and steady-state input and output of an auxiliary linear closed-loop reference system. Moreover, fast adaptation proved to be beneficial both for performance and robustness, while the trade-off between those in resolved via the selection of the underlying filtering structure, which can be straightforwardly addressed via conventional methods from classical and robust control.

## III. A Case Study for L1 Adaptive Control

Generally, a L1 adaptive control system can be schematically represented by [11, figure 1]. It is composed of four parts: the system containing unknown parameters, the output predictor for compactly specifying the desired output of the system, a feedback control law containing adjustable parameters, and an adaptation mechanism for updating the adjustable parameters. In this section, before we quickly jump into the analysis of L1 adaptive controller, we would like to recall some interested topics in the designing of adaptive control systems.

### Topic 1: What Kind of Uncertainty We Face

Model imprecision may come from actual uncertainty about the plant, simplified representation of system dynamics or neglecting structural modes. From a control point of view, modeling inaccuracies can be classified into two major kinds:

- 1). Parametric uncertainties; and
- 2). Unstructured uncertainties

The first kind corresponds to inaccuracies on the terms actually included in the model, while the second corresponds to inaccuracies on the system order, relative degree or unmodeled dynamics.

### Topic 2: Relax the Assumptions in Adaptive System

The four assumptions made regarding the plant transfer function, for the solution of the adaptive control problem in general case are listed below:

- 1). Sign of the high frequency gain: The sign of the high frequency gain is required to prove global stability using Lyapunov's direct methods.

- 2). Knowledge of relative degree: For a scalar transfer function, the relative degree is the difference between the number of poles and zeros. The knowledge of the relative degree is a key assumption in classical adaptive control laws since it defines the set of reference models which lead to differentiator free compensators.
- 3). An upper bound on the order of plant is known: The knowledge of the order of the plant was needed to determine a controller structure with enough freedom to generate the desired control input to the plant. In particular, if an upper bound on the order of the plant is specified as  $n$ , the controller has to be of dimension  $2n$ .
- 4). Zeros of the plant transfer function lies in the right-half of the complex plant: This property assures that the state of the overall system does not grow in an unbounded fashion even while the output error tends to be zero.

The efforts made to develop a systematic procedure for the adaptive controller while relaxing the four assumptions is still an active area. In author's option, it is not possible to deal in a coherent fashion with the different efforts that are in progress. While there are many existing methods [12]-[13] to relax these limitations, the stability and performance of the system must not sacrifice.

Many nonlinear controller designs, including model reference adaptive control [15], use Lyapunov functions and Babalet's Lemma for stability and asymptotic analysis but provides no characterization of transients. Transient performance is always critical in real world applications. The historical crash of X-15A-3 on November 15, 1967 [16] and the resulting death of pilot Michael Adams were due to deficiencies of the stable, albeit non-robust, adaptive flight control system. Control signals of high-frequency, large transient errors, or slow convergence rate of tracking errors are a few examples of undesired transients. The output constraints are in fact a transient performance, which requires the output signal to rigorously be within pre-specified bounds without overshoot. Another deficiency in conventional adaptive control and the derived neural network control is its inability to deal with time-varying uncertainties. In fact, these two challenges are coupled together. With both direct and indirect adaptive control, some of the adaptive parameters need to converge to a set of values to ensure output performance. In the indirect approach, persistent excitation is further required for the convergence of the adaptive estimates. However, the transient of this convergence cannot be characterized as illustrated in Figure 2(a), which directly leads to an uncharacterized transient of the closed-loop performance. In the case of a time-varying (TV) plant, the true unknown parameter value is time-varying, as illustrated in Figure 2(b). Hence, there is no guarantee of the convergence of the adaptive estimates especially when the transient in 2(a) is unspecified and nonlinear. It can be projected that the overall process may lead to instability in the case of overshoot and nonlinear behavior of the convergence in Figure 2(a).

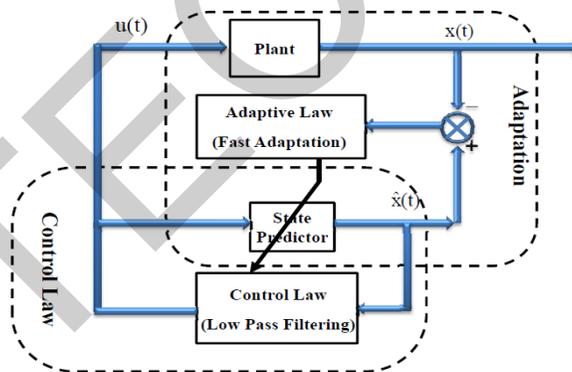


Figure 1: L1 Adaptive control architecture

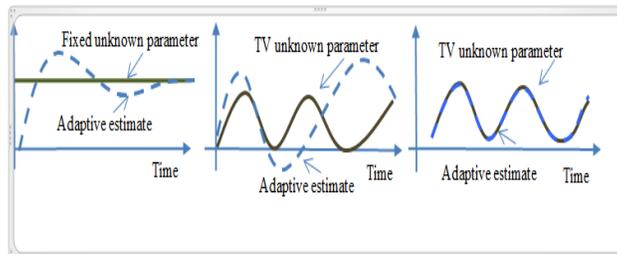


Figure 2: Transient of conventional adaptive control with (a) Fixed unknown parameter, (b) Time varying unknown parameter, and (c) L1 adaptive controller with time varying unknown parameter

#### IV. Conclusion

Nonlinear control designs are increasingly important in a wide range of technologies. Physically characteristics are concerned in

nonlinear systems, such as nonlinear uncertainties, unmodeled dynamics, deterministic and stochastic disturbances when creating a structure-specific methodology applicable to broader systems. Generally speaking, the theoretical analysis of nonlinear systems is based on a number of assumptions such as the linearity of the plant, prior knowledge of structural modes. With the knowledge of given nonlinear systems, controller design can divide into two categories. The first deals the basis of analytical approaches when knowing the nominal model of given systems. If the method can not meet the demanded specifications, advanced controls such as robust control and adaptive control should be considered. The second category uses fuzzy logic, neural-network, optimal control integrated with learning algorithms. In this project, we attempt to provide the novel L1 adaptive control architecture that has guaranteed transient response in addition to stable tracking for uncertain systems in the presence of unknown state and time-dependent nonlinearities. The control signal and the system response approximate the same signals of a closed-loop reference system, which can be designed to achieve desired specifications. Moreover, we have shown the simulation of examples that L1 adaptive control is the resolution of many benchmark issues in nonlinear systems. This is an area where discoveries of new structures may lead to significant breakthrough.

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# A CASE STUDY: AN APPLICATION OF HYBRID SYSTEMS WITH MEMORY ON TUMOR SYSTEM

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## ABSTRACT

Dynamics of cancer involve some complex interactions like immune system responses. Many different models of immune response to tumor growth exist in the literature. Most of the available models are first principles models which have problems in determining the model parameters. For potential use in treatment planning, a model should be able to adopt to subject by subject variability and unknown factors. A common solution to this problem is inferring the parameters and determining system behaviour from empirical observation. In inferential modeling case we first select a model class and infer the parameters from the observations. In this case, hybrid systems are suitable for use in inferential modeling due to their analytical and computational advances. By hybrid systems with memory phenomena, representation of factors which may depend on whole history rather than a combination of historical events can be efficiently modeled.

**Keywords:** piecewise linear systems, hybrid systems, memory, regulatory gene networks, tumor.

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# A NEW SYNTHESIS METHOD OF MANGANESE DIOXIDE BY $Mn^{2+}$ IONS COMPLEXATION AND ELECTRO-OXIDATION IN A FILMOF POLYPYRROLE BENZOIC ACID

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## Abstract

This work involves the synthesis of manganese dioxide  $MnO_2$  by an original method based on the inclusion of manganese dioxide in the films of poly [pyrrole benzoic acid] by complexation of manganese ions in the polymer film. The deposition of films of poly [pyrrole benzoic acid] on the surface of the carbon electrode is produced by the electrochemical oxidation of the monomer in acetonitrile medium. The incorporation of particles of manganese dioxide is performed by immersing the modified electrode in an aqueous solution containing manganese ions, followed by electro-oxidation to precipitate the manganese dioxide particles in the polymer film. The presence of manganese dioxide ( $Mn^{4+}$ ) in the polymer films is confirmed by the presence of the oxidation peak of incorporated manganese. Several parameters affect the amount of incorporated manganese dioxide as the pH of the medium, the film thickness and the immersion time. The best results were obtained with concentrations of manganese ions in the order of  $10^{-2}$  M, with an immersion time of 10 minutes and a weak acidic pH (pH = 5.8).

**Keywords:** Modified electrodes, Manganese dioxide, Functionalized polypyrrole.

## 1. INTRODUCTION

In this paper, we describe a novel method and easiest way to elaborate a new composite material based on a glassy carbon electrode modified with a polymer film of poly (pyrrole-benzoic acid) containing manganese ions. The electrochemical oxidation of the complex formed (polymer-manganese) will lead to the formation and precipitation of manganese dioxide in the polymer film. We may expect from this procedure a better dispersion of the metal in the polymer film and the formation of particles of smaller sizes [1-5].

## 2. EXPERIMENTAL

After the deposition of poly [4 - (pyrrol-1-yl methyl) benzoic acid] on a glassy carbon electrode obtained by controlled potential electrochemical oxidation of the monomer in acetonitrile solution  $10^{-1}$  M  $LiClO_4$  as electrolyte, the modified electrode is either oxidized in aqueous  $10^{-1}$  M in  $Na_2SO_4$  and containing  $10^{-2}$  M in  $MnSO_4$ , or it is immersed in an aqueous solution in a metal salt of  $MnSO_4$   $10^{-2}$  M for a few minutes to complex ions manganese by the polymer film due to the protons of  $H^+$  that are present in the carboxyl group of polypyrrole. The electrode is then washed with distilled water several times to remove excess metal cations associated with the non-polymer, and then immersed in an aqueous solution of  $10^{-1}$  M in  $Na_2SO_4$  to oxidize the manganese ions in complexed dioxide manganese. This process can be repeated several times. Both deposition techniques of manganese dioxide on the surface of the modified electrode are shown in Figure 1.

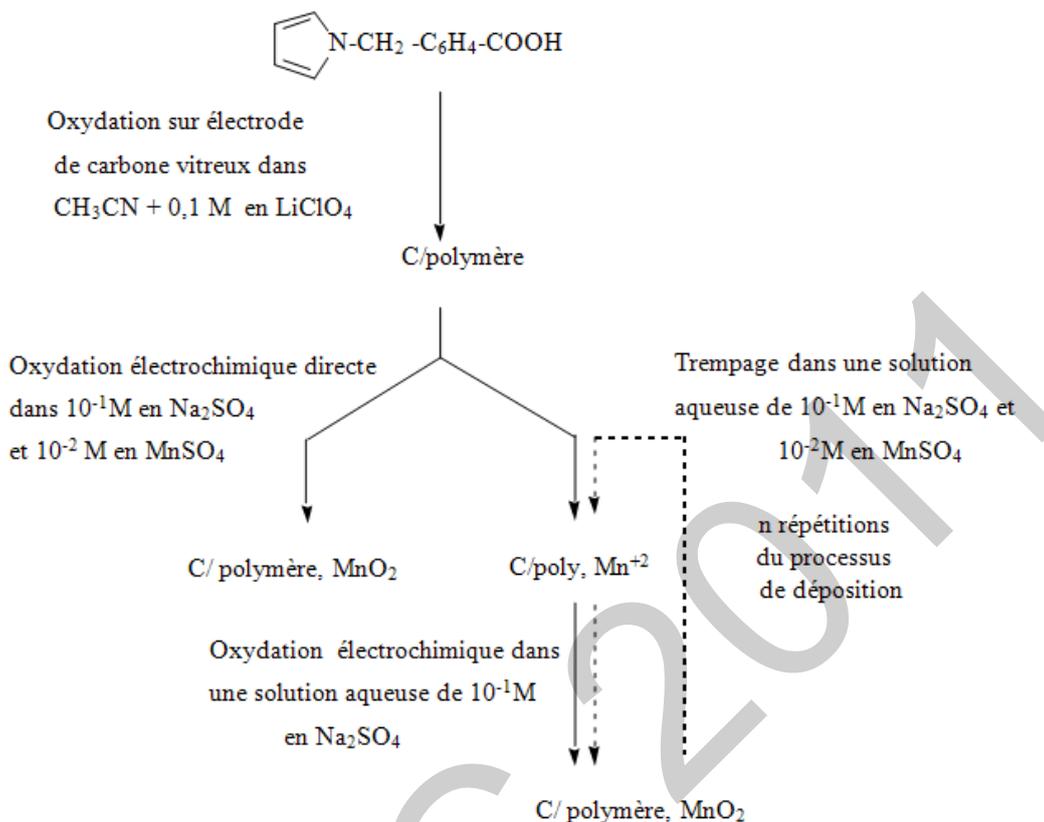
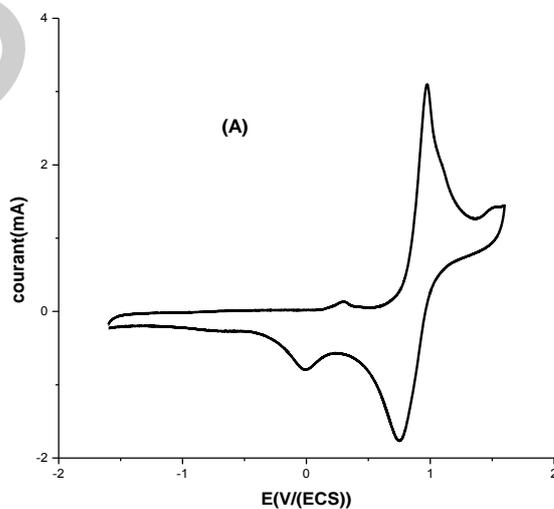


Figure 1: Techniques of preparing a glassy carbon electrode modified with MnO<sub>2</sub> particles.

### 3. Study of the electrochemical behavior of manganese (II) on glassy carbon

The electrochemical behavior of manganese (II) was studied on a glassy carbon electrode of 0.07 cm<sup>2</sup> ( $\phi = 3$  mm) of area by digital cyclic voltammetry in an aqueous solution containing 10<sup>-2</sup> M of MnSO<sub>4</sub> and 10<sup>-1</sup> M of Na<sub>2</sub>SO<sub>4</sub>, see Figure 2. The obtained curve is characterized by the presence of two oxidation peaks in the vicinity of 0.3 V/ECS and 0.97 V/ECS corresponding, respectively, to the oxidation of manganese II ions in Manganese III and manganese IV. In the return sweep is also observed two peaks in the vicinity of 0.75 V/SCE and -0.01V/ECS corresponding to the reduction of oxidized species.

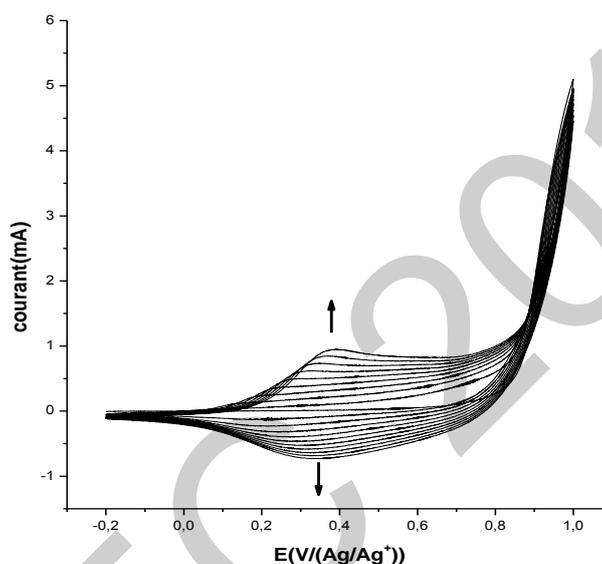


**Figure 2:** Cyclic voltammetry curves for oxidation-reduction of manganese II plotted on glassy carbon electrode ( $s = 0.07 \text{ cm}^2$ ) in an aqueous solution  $10^{-2} \text{ M}$  of  $\text{MnSO}_4$  and  $10^{-1} \text{ M}$   $\text{Na}_2\text{SO}_4$  at the speed of  $v = 100 \text{ mV/s}$ .

#### 4. Incorporation of manganese dioxide in poly [4 - (pyrrol-1-ylmethyl) benzoic acid]

##### 4.1 The electropolymerization of 4 - (pyrrol-1-ylmethyl) benzoic acid

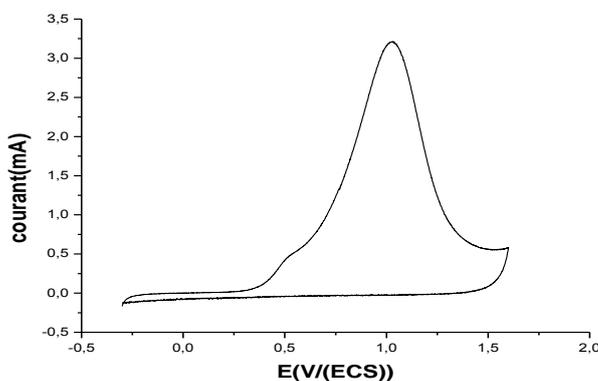
The electrochemical behavior of the monomer was studied by cyclic voltammetry on glassy carbon electrode ( $\Phi = 3 \text{ mm}$ ) in an acetonitrile medium ( $\text{CH}_3\text{CN}$ ),  $10^{-1} \text{ M}$  of lithium perchlorate ( $\text{LiClO}_4$ ) and  $4 \times 10^{-3} \text{ M}$  of 4-(pyrrol-1-yl methyl) benzoic acid. The presence of an irreversible oxidation peak around  $0.95 \text{ V}/(\text{Ag}/\text{Ag}^+)$  corresponding to the oxidation of monomer (polymerization) and consequently to the formation of poly 4-(pyrrol-1-yl methyl) benzoic acid deposited on the surface of the electrode. The record shows a subsequent increase in current waves of oxidation and reduction peaks observed around  $0.4 \text{ V}$ , indicating that the polymer is starting to be deposited on the surface of the electrode. The current intensity of the peaks is seen to stabilize after several cycles, see Figure 3.



**Figure 3:** Electropolymerization of monomer by successive scans on a glassy carbon electrode ( $s = 0.07 \text{ cm}^2$ ) in  $\text{CH}_3\text{CN}$  in  $0.1 \text{ M}$   $\text{LiClO}_4$  and  $4 \times 10^{-3} \text{ M}$  of monomer at the speed of  $v = 100 \text{ mV/s}$ .

##### 4.2 Electrochemical study of manganese II on an electrode modified by the polymer film

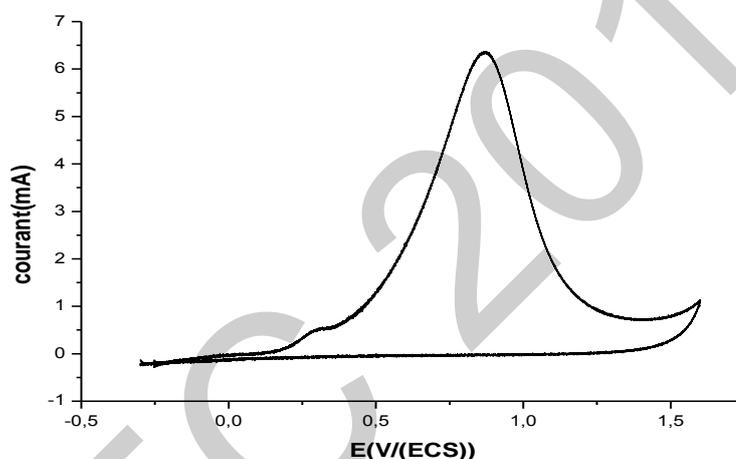
The electrochemical behavior of manganese II on an electrode modified with a film of poly 4-(pyrrol-1-yl methyl) benzoic acid in a solution in  $10^{-1} \text{ M}$  of  $\text{Na}_2\text{SO}_4$  as a supporting electrolyte and  $10^{-2} \text{ M}$  of  $\text{MnSO}_4$  was performed by cyclic voltammetry with a digital scan speed of  $100 \text{ mV/s}$ , Figure 4. The curve obtained is characterized by an intense oxidation peak near  $1.02 \text{ V}/\text{SCE}$  and by the lack of reduction peak of manganese IV. This is probably due to the formation of a variety of non-active manganese dioxide which could be the gamma variety.



**Figure 4:** Diagram of cyclic voltammetry of manganese II on glassy carbon electrode modified with a polymer film directly in an aqueous solution  $10^{-1}$  M of  $\text{Na}_2\text{SO}_4$  and  $10^{-2}$  M in  $\text{MnSO}_4$  at  $v = 100$  mV/s.

#### 4.3 Study of complexation of manganese II in the film of the polymer

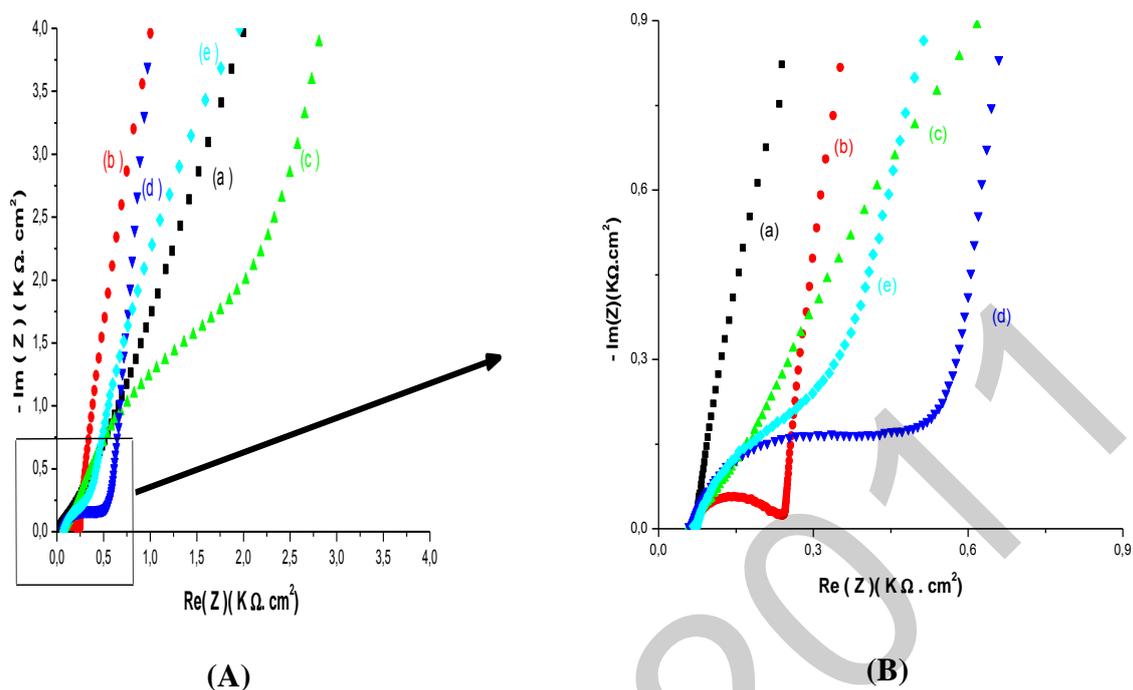
In order to study the complexation of manganese II, we first deposited a film of poly 4-(pyrrol-1-yl methyl) benzoic acid on the surface of a glassy carbon electrode ( $\Phi = 3$  mm), then the modified electrode was dipped in a solution of  $10^{-2}$  M of  $\text{MnSO}_4$  for 5 minutes to allow the complexation of Mn II by the polymer film with carboxylic groups present in the polymer structure. The complexing site of the carboxylic acid allows the interchange the ions of  $\text{H}^+$  by those of  $\text{Mn}^{2+}$ . Afterwards, the electrode was washed several times with distilled water in order to eliminate the excess of manganese II which are not associated with the polymer. A cyclic voltammetry was then carried out in the solution, described previously, in a potential range between -0.3 and 1.6 V/SCE. The obtained curve exhibits an intense peak corresponding to the oxidation of Mn II complexed into Mn IV on the surface of the modified electrode at a potential 0.87 V/ECS (Figure 5). The absence of the reduction peak of  $\text{Mn}^{4+}$  observed at 0.74 V/ECS in the study on a glassy carbon electrode may be due to the dispersion of  $\text{MnO}_2$  in the solution.



**Figure 5:** Cyclic voltammetry curve of manganese II on glassy carbon electrode modified with a polymer film in an aqueous solution  $10^{-1}$  M of  $\text{Na}_2\text{SO}_4$  after immersion for 5 minutes in a solution of  $10^{-2}$  M of  $\text{MnSO}_4$  at  $v = 100$  mV/s.

#### 5. Characterization of the composite material by impedance spectroscopy

In Figure 6 are shown the impedance diagrams of the different electrodes. The impedance diagrams are composed of an arc of circles at high frequencies corresponding to a charge transfer process and of a straight line at low frequencies corresponding to a diffusion regime (Figure 6(A), curves b, c, d, e), except the case prior to deposition the electrode diagram presents a line all across the spectrum characteristic of a diffusion process (Figure 6(A), diagram a). After an increase in the range of frequencies between 0 and  $7 \text{ k}\Omega\text{cm}^2$ , we observe that the glassy carbon electrode has the best electrical properties, Figure 6(B), diagram a). The impedance diagram of the electrode after deposition of metallic manganese has an arc and then a very steep right slope corresponding to a blocking system. Although the electrical properties of the material decreases after deposition of the polymer film (Figure 6(B), diagram c) and the complexation of manganese (Figure 6(B), diagram d), the latter becomes more important after oxidation of manganese in the film polymer (Figure 6(B), diagram e).



**Figure 6:** (A) - Impedance diagrams of an aqueous 0.1 M  $\text{Na}_2\text{SO}_4$  in the frequency range between 100 kHz and 10 MHz on an electrode (a) bare glassy carbon electrode, (b) electrode covered with a layer of manganese in an applied potential to 0.86 V/ECS, (c) polymer film alone, (d) glassy carbon electrode modified with a film of poly [4 - (pyrrol-1-yl methyl) benzoic acid] and then soaked in a solution of  $10^{-2}$  M of  $\text{MnSO}_4$  for 30 minutes, (e) glassy carbon electrode modified with a polymer film and then dipped in a solution of  $10^{-2}$  M of  $\text{MnSO}_4$  for 30 minutes and oxidized at the potential of 0.86 V/ECS in the absence of  $\text{MnSO}_4$ . (B) After expansion of the frequency domain.

## 5. Conclusion

In conclusion, we have presented here in this paper a new method of preparing a new modified electrode by inclusion of particles of manganese dioxide in a film of poly [pyrrole benzoic acid] for applications in electrochemical generators as a cathode in Leclanche batteries and in electrocatalysis. The polymer film is deposited on the surface of a carbon electrode by electrochemical oxidation of the monomer. The incorporation of particles of manganese dioxide is obtained by complexation of manganese ions by the carboxylic sites of the polymer followed by electrooxidation to precipitate them into the polymer film.

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# A NOTE ON THE CLASSICAL ELASTIC CURVES IN AN 3-DIMENSIONAL SPACE

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**Abstract:** In this paper the mathematical idealization of the classical variational problem in 3-dimensional indefinite-Riemannian Manifolds is studied for the curve  $\alpha$  which is timelike and spacelike, parameterized by the arc-length. The geodesic curvature and torsion of an elastic curve are evaluated if they exist as the solutions of the differential equations for all different cases. Due to elastic curve definition, the minimum principle theorem is applied to elastic energy function which is defined as the integral of the squared geodesic curvature of the curve.

**Keyword:** Elastic curve, Minimum principle, Spacelike, Timelike,

## 1 Introduction

The classical curve known as the *elastica* is the solution to a variational problem proposed by Daniel Bernoulli to Leonhard Euler in 1744, that of minimizing the bending energy of a thin inextensible wire [1]. The mathematical idealization of this problem is that of minimizing the integral of the squared curvature for curves of a fixed length satisfying given first order boundary data.

For a curve  $\alpha(s)$  in a Riemannian manifold  $M$  two quantities are defined: the length  $L(\alpha)$  and the total square curvature  $E(\alpha)$ . A curve  $\alpha$  is called as an elastica if it is a critical point of the functional  $E$  restricted to the space of curves a fixed length  $L_0$ . The notion of elastica is quite old. But modern approaches to it in differential geometry are rather new. J. Langer and D. A. Singer classified all closed elastica in the Euclidean space [5]. Also N. Koiso treated the case of Euclidean spaces and found a unique long time solution of an initial value problem that converges to an elastica in [7]. In [4] N. Koiso is studied elastica restricted in a submanifold.

The complete classification of elastica with constant slant in the complex projective plane is obtained in [6].

In [2] the classical techniques of the calculus of variations are used to derive the equations of the elastica, also in that study the classical variational problem in Euclidean space and its generalization to Riemannian manifolds are considered. The case sectional curvature  $G=0$  has been studied by the authors in [10]. In this paper the classical variational problem is studied in 3-dimensional indefinite-Riemannian manifold.

## 2 Preliminaries

Let  $M_\gamma$  be an 3-dimensional indefinite-Riemannian manifold of index  $\gamma(0 \leq \gamma \leq 3)$  isometrically immersed into an  $m$ -dimensional indefinite-Riemannian manifold  $\overline{M}_i$  of index  $i$  for  $m \geq 3$ . Then  $M_\gamma$  is called an 3-dimensional indefinite-Riemannian submanifold of  $M_i$

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Especially if  $\gamma = 1$ , then  $M_1$  is called a Lorentzian submanifold of  $M_i$ . We denote the metrics of  $M_\gamma$  and  $\bar{M}_i$  by the symbol  $\langle , \rangle$  and the covariant differentiation of  $M_\gamma$  (resp.  $\bar{M}_i$ ) by  $\nabla$  (resp.  $\bar{\nabla}$ ). Then we have the Gauss formula

$$\bar{\nabla}_X Y = \nabla_X Y + B(X, Y), \tag{1}$$

where  $X$  and  $Y$  are tangent vector fields of  $M_\gamma$  and  $B$  is the second fundamental form of  $M_\gamma$ .

Let  $\alpha(t)$  be a regular curve on an 3-dimensional indefinite-Riemannian manifold  $M_\gamma$ . We denote the tangent vector field  $\alpha'(t) = X$ . When  $\langle X, X \rangle = \pm 1$ ,  $\alpha$  is called a unit speed curve.

### 3 The elastica in an 3-dimensional indefinite-Riemannian manifold

In this paper we will formulate a generalized variational problem, that of the elastica in an 3-dimensional indefinite-Riemannian manifold. By this we mean a curve which is an extremal for the integral of the squared (geodesic) curvature among curves with specified boundary conditions. Here we summarize the machinery needed for calculations.

In what follows,  $M$  is an smooth 3-dimensional indefinite-Riemannian manifold, with indefinite-Riemannian metric  $g(X, Y) = \langle X, Y \rangle = x_1 y_1 + x_2 y_2 - x_3 y_3$ , where  $X = (x_1, x_2, x_3)$  and  $Y = (y_1, y_2, y_3)$ , that is, a symmetric bilinear form on tangent vectors  $X$  and  $Y$  at each point. The covariant derivative  $\nabla_X Y$ , measures the derivative of a vector field  $Y$  in the direction of a vector  $X$ .

*Definition* A vector field  $V$  is called spacelike if  $\langle V, V \rangle > 0$  or  $V = 0$ , timelike if  $\langle V, V \rangle < 0$  and lightlike if  $\langle V, V \rangle = 0$  and  $V \neq 0$ .

For vector fields  $X$  and  $Y$  the equality of mixed partial derivatives is replaced by the bracket formula:

$$\nabla_X Y - \nabla_Y X = [X, Y] = XY - YX,$$

Let  $\alpha(t)$  be an immersed curve in  $M$ , then it has velocity vector  $V = vT$  and squared geodesic curvature

$$\kappa^2 = P \nabla_T T P^2,$$

Set the Frenet frame for a family of curves  $\alpha_w(t) = g(w, t)$  by  $(T, N, B)$ , therefore we can write

$$W(w, t) = \frac{\partial \alpha}{\partial w},$$

$$V(w, t) = \frac{\partial \alpha}{\partial t} = v(w, t)T(w, t),$$

So  $V$  is velocity and  $v = \frac{ds}{dt}$  is speed, and  $W$  represents an infinitesimal variation of the curve.  $s$  is the arc-length parameter along a curve.

The basic formulas needed in calculating the Euler equations are as follows:

$$0 = [W, V] = [W, vT] = W(v)T + v[W, T], \tag{2}$$

So  $[W, T] = \frac{W(v)}{v} T = gT$ .

$$2\tau W(v) = W(v^2) = 2\langle \nabla_W V, V \rangle = 2\langle \nabla_V W, V \rangle = 2v^2 \langle \nabla_T W, T \rangle, \tag{3}$$

So,  $W(v) = -gv$ ,  $g = -\langle \nabla_T W, T \rangle$ .

$$W(\kappa^2) = 2\langle \nabla_T \nabla_T W, \nabla_T T \rangle + 4g\kappa^2 + 2\langle R(W, T)T, \nabla_T T \rangle, \tag{4}$$

Here the curvature tensor  $R$  is given by

$$R(X, Y)Z = \nabla_X \nabla_Y Z - \nabla_Y \nabla_X Z - \nabla_{[X, Y]} Z.$$

The proof of equation (6), is mentioned in [2].

In what follows,  $\alpha : [0, 1] \rightarrow M$  is a curve of length  $L$ . Now for fixed constant  $\lambda$  let

$$\begin{aligned} F^\lambda(\alpha) &= \frac{1}{2} \int_0^L \kappa^2 + \lambda ds = \frac{1}{2} \left( \int_0^L \kappa^2 ds + \lambda L \right) \\ &= \frac{1}{2} \int_0^1 (\mathbf{P} \nabla_T \mathbf{T} \mathbf{P}^2 + \lambda) v(t) dt, \end{aligned}$$

For a variation  $\alpha_w$  with variation field  $W$  we compute

$$\begin{aligned} \frac{d}{dw} F^\lambda(\alpha_w) &= \frac{1}{2} \int_0^L W(\kappa^2) v + (\kappa^2 + \lambda) W(v) dt \\ &= \frac{1}{2} \int_0^1 W(\kappa^2) - (\kappa^2 + \lambda) g ds \\ &= \frac{1}{2} \int_0^1 \langle \nabla_T \nabla_T W, \nabla_T T \rangle + 2g\kappa^2 \\ &\quad + \langle R(W, T)T, \nabla_T T \rangle - \frac{1}{2} (\kappa^2 + \lambda) g ds. \end{aligned}$$

One of the symmetries of the curvature tensor allows us to replace  $\langle R(W, T)T, \nabla_T T \rangle$  with  $\langle R(\nabla_T T, T)T, W \rangle$ . Now integrate by parts, using  $g = -\langle \nabla_T W, T \rangle$ , we get

$$\begin{aligned} \frac{d}{dw} F^\lambda(\alpha_w) &= \int_0^1 \langle \nabla_T \nabla_T W, \nabla_T T \rangle - \langle \nabla_T W, 2\kappa^2 T \rangle \\ &\quad + \langle R(\nabla_T T, T)T, W \rangle + \frac{1}{2} \langle \nabla_T W, (\kappa^2 + \lambda) T \rangle ds \\ &= \int_0^L \langle E, W \rangle ds + [\langle \nabla_T W, \nabla_T T \rangle + \langle W, -(\nabla_T)^2 T + \Lambda T \rangle]_0^L, \end{aligned}$$

where

$$E = (\nabla_T)^3 T - \nabla_T(\Lambda T) + R(\nabla_T T, T)T,$$

and  $\Lambda = \frac{\lambda - 3\kappa^2}{2}$ .

## 4 The Frenet equations

Let  $\alpha$  be a curve in 3-dimensional indefinite-Riemannian manifold  $M$  with speed  $v(t) = |\alpha'(t)|$ , curvature  $k$ , torsion  $\tau$  and Frenet frame  $\{T, N, B\}$ . The Frenet equations are written down as follows [9]:

$$\nabla_T T = \varepsilon_2 \kappa N, \quad \nabla_T N = -\varepsilon_1 \kappa T + \varepsilon_3 \tau B, \quad \nabla_T B = -\varepsilon_2 \tau N,$$

where  $\varepsilon_1 = \langle T, T \rangle$ ,  $\varepsilon_2 = \langle N, N \rangle$  and  $\varepsilon_3 = \langle B, B \rangle$ .

### 4.1 The Timelike Case

Let  $\alpha(t)$  be a timelike curve in 3-dimensional indefinite--Riemannian manifold  $M$ . If the normal vector field  $N$  and the binormal vector field  $B$  are spacelike, then we have the following Frenet formulas along  $\alpha(t)$  :

$$\alpha'(t) = vT, \nabla_T T = \kappa N, \nabla_T N = \kappa T + \tau B, \nabla_T B = -\tau N, \quad (5)$$

where  $\kappa$  and  $\tau$  are curvature and torsion of  $\alpha$ , respectively.

## 5 Acknowledgment

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# A STUDY OF COVARIANCE ESTIMATION TO APPLY CARRIER-SMOOTHED-CODE FILTER IN GNSS

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## ABSTRACT

By estimating the process and measurement noise covariances based on filter residuals, adaptive filtering is frequently used to improve system reliability for various engineering applications. In order to apply this method to global navigation satellite system (GNSS) applications, this paper proposes an efficient method for carrier-smoothed-code (CSC) filtering which is advantageous for GNSS applications. The proposed adaptive CSC method estimates the noise covariances of carrier-phase measurements and pseudorange measurements based on innovation sequences for time propagations and measurement updates, respectively. Performance of the proposed method was evaluated by applying field-collected real GPS measurements. Analysis on experiment results shows that the proposed method improves position reliability and accuracy compared with traditional CSC filtering.

## INTRODUCTION

Accuracy, continuity, availability, and reliability are four important factors that should be considered for advanced global navigation satellite system (GNSS) applications. Among the four important factors, utmost care should be given to reliability since it directly affects human safety. Thus, the main concern of utilizing GNSS nowadays is how to obtain reliable measurements in various adverse environments shown in Fig. 1.

The reliability of GNSS can be harmed due to many factors such as abnormal atmospheric conditions, malfunction of the receiver's software and hardware, the receiver's surrounding environments, and wrong parameters in unhealthy ephemeris information. If the reliability is insufficient to meet the system requirements, abnormal measurements or parameters can drive the vehicle relying on GNSS receivers into various dangerous situations. Thus, the reliability has been and will be one of the most serious problems over wide application area of GNSS.

Adaptive filtering (Magill 1965; Mehra 1970, 1971) is used in various engineering applications to improve system reliability by estimating the process and measurement noise covariance utilizing the residual of the filter. Traditionally, the Kalman filtering (Kalman 1960) has been the most popular method to obtain optimal estimates and has been widely used in real-time dynamic data processing. For the reason, there have been a lot of research works for adaptive Kalman filtering (Mohamed and Schwarz 1999).

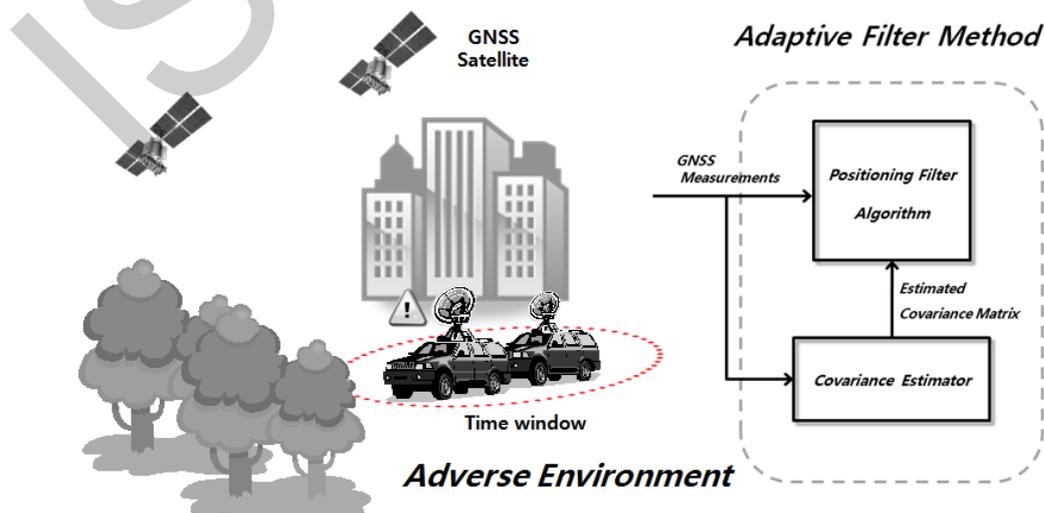


Fig. 1 Improving the reliability utilizing adaptive filter in urban area

In GNSS applications, However, the carrier-smoothed-code (CSC) filtering proposed by Hatch (1982) has been recognized to be more effective than Kalman filtering due to the unique characteristic that carrier-phase measurements can be utilized for more accurate time propagation than high-speed inertial sensor outputs. By the time propagation based on carrier-phase measurements, estimation errors do not increase in proportion to the length of time interval without measurement updates. To apply adaptive filtering in CSC filter for more improved reliability, it is required to estimate both pseudorange and carrier-phase measurement noise covariance.

This paper proposes a new covariance estimator for adaptive CSC filtering under structural stochastic assumptions. The proposed method estimates the noise covariance of carrier-phase measurements for time propagations and pseudorange measurements for measurement updates based on innovation sequences. Performance of the proposed method was evaluated by using GPS experimental data.

### ADAPTIVE DOUBLE DIFFERENCING POSITION DOMAIN HATCH FILTER

The proposed covariance estimator is designed to apply double differencing position domain (DD PD) Hatch Filter. The DD PD Hatch filter is effective in real-time kinematic differential positioning where satellite visibility changes frequently. More details on the position-domain carrier-smoothed-code principle can be found in (Lee et al. 2005; Kim and Lee 2008).

Fig.2 shows the proposed adaptive DD PD Hatch filter. As shown in figure, the carrier-phase noise covariance is estimated by utilizing received real measurements and *a posteriori* error covariance. The pseudorange noise covariance is estimated by utilizing real measurements and *a priori* error covariance. Since the proposed method does not need to operate a number of filters and to change original filter algorithm, it can be easily applied to existing system.

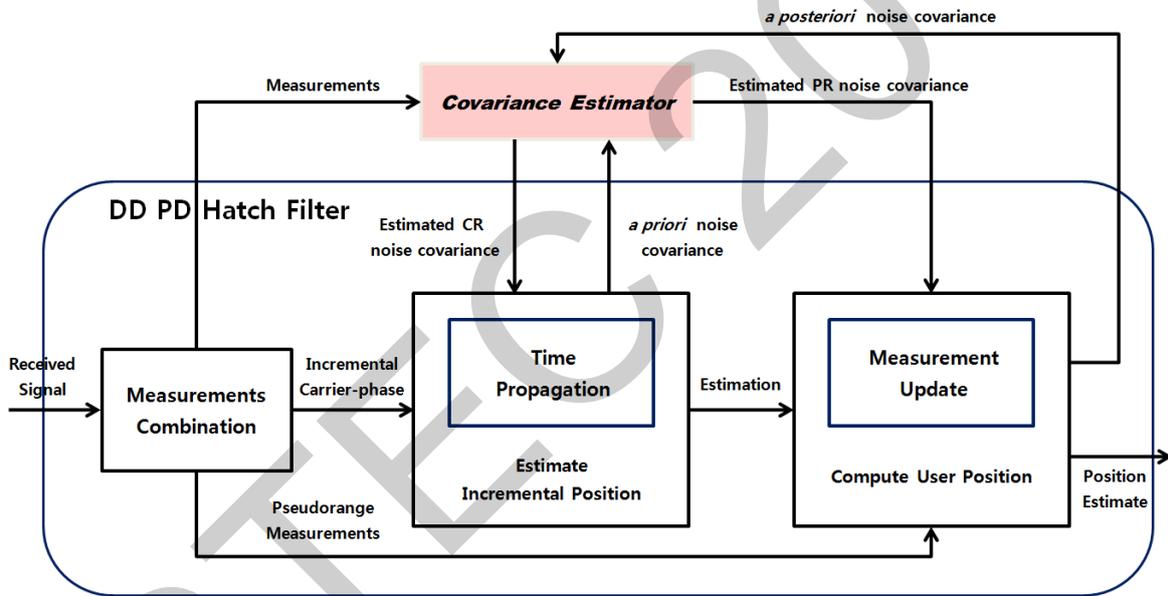


Fig. 2 Adaptive double differencing position domain Hatch filter

#### Carrier-phase Noise Covariance Estimation for Time Propagation

Since the CSC filter does not utilize a dynamic model, the carrier-phase measurement noise instead of the process noise describing modeling uncertainty is introduced as the error source for time propagations. Thus, the carrier-phase noise covariance needs to be estimated for more accurate time propagation. The proposed adaptive method is based on innovation-based adaptive estimation (IAE). To implement IAE, noise covariance is obtained by innovation sequence which is computed by the residual of the filter after time propagation. For the purpose, the innovation sequence is formed by differencing the real measurement and the estimated filter state. In the proposed method, the innovation sequence for time propagation  $Z_{\Phi,k}$  is modeled by

$$Z_{\Phi,k} = \Omega_{k+1}^* - H_{k+1}^* \Delta \hat{X}_k \tag{1}$$

where  $\Omega_{k+1}^*$  indicates the real indirect measurement,  $H_{k+1}^*$  indicates the observation matrix,  $\Delta \hat{X}_k$  indicates the estimated position increment based on filter states and \* indicates double differenced form. By Eq. (1), innovation sequence covariance can be modeled by

$$E\{Z_{\Phi,k}Z_{\Phi,k}^T\} = (I - H_{k+1}^*H_{k+1}^{*+})R_{\Phi,k}(I - H_{k+1}^*H_{k+1}^{*+})^T + (I - H_{k+1}^*H_{k+1}^{*+})\Delta H_k^*\hat{P}_k\Delta H_k^{*T}(I - H_{k+1}^*H_{k+1}^{*+})^T \quad (2)$$

where,

$$R_{\Phi,k} = E\{(N_{k+1} - N_k)(N_{k+1} - N_k)^T\}$$

$$\hat{P}_k = E\{\delta\hat{X}_k\delta\hat{X}_k^T\}$$

$N_k$  : carrier phase measurement noise

As shown in Eq. (2), the covariance is composed of the carrier-phase noise covariance  $R_{\Phi,k}$ , the *a posteriori* error covariance  $\hat{P}_k$  and the observation matrix. Thus, the  $R_{\Phi,k}$  can be estimated by the following equation.

$$R_{\Phi,k} = \left[ E\{Z_{\Phi,k}Z_{\Phi,k}^T\} - (I - H_{k+1}^*H_{k+1}^{*+})\Delta H_k^*\hat{P}_k\Delta H_k^{*T}(I - H_{k+1}^*H_{k+1}^{*+})^T \right] \left[ (I - H_{k+1}^*H_{k+1}^{*+})(I - H_{k+1}^*H_{k+1}^{*+})^T \right]^{-1} \quad (3)$$

By Eq. (3), the carrier-phase noise covariance affected by receiver's surrounding environment can be obtained in real-time.

### Pseudorange Noise Covariance Estimation for Measurement Update

The conventional double differenced pseudorange residuals are formed by subtracting the single differenced residuals of the reference channel from the other single differenced residuals. In addition, a new type of double differenced residuals  $Z_{dSD}$  can also be formed by subtracting between the residuals of successive channels.

$$Z_{DD} = \begin{bmatrix} z_{sd}^1 - z_{sd}^r \\ z_{sd}^2 - z_{sd}^r \\ \vdots \\ z_{sd}^{n-1} - z_{sd}^r \end{bmatrix}, \quad Z_{dSD} = \begin{bmatrix} z_{sd}^1 - z_{sd}^2 \\ z_{sd}^2 - z_{sd}^3 \\ \vdots \\ z_{sd}^{n-1} - z_{sd}^n \end{bmatrix} \quad (4)$$

Based on the residual sets, the innovation matrix can be obtained by

$$\bar{C}_{\rho,k} = \begin{bmatrix} \sigma_1^2 + \sigma_r^2 & \sigma_r^2 & \cdots & \sigma_r^2 \\ \sigma_r^2 & \sigma_2^2 + \sigma_r^2 & & \vdots \\ \vdots & & \ddots & \sigma_r^2 \\ \sigma_r^2 & \cdots & \sigma_r^2 & \sigma_{n-1}^2 + \sigma_r^2 \end{bmatrix} \quad (5)$$

where,

$$\bar{R}_{dSD} = E\{Z_{dSD}Z_{dSD}^T\}$$

$$\bar{R}_{DD} = E\{Z_{DD}Z_{DD}^T\}$$

$$\bar{C}_{dSD} = \text{diag}(\bar{R}_{dSD}) = [\sigma_1^2 + \sigma_2^2 \quad \sigma_2^2 + \sigma_3^2 \quad \cdots \quad \sigma_{n-1}^2 + \sigma_n^2]$$

$$\bar{C}_{DD} = \text{diag}(\bar{R}_{DD}) = [\sigma_1^2 + \sigma_r^2 \quad \sigma_2^2 + \sigma_r^2 \quad \cdots \quad \sigma_{n-1}^2 + \sigma_r^2]$$

$$\bar{C}_{dSD}^i = \sigma_i^2 + \sigma_{i+1}^2$$

$$\sum_{k=i}^{i+1} \bar{C}_{DD}^k = \sigma_i^2 + \sigma_{i+1}^2 + 2\sigma_r^2$$

$$\sigma_r^2 = \frac{1}{2} \left( \sum_{k=i}^{i+1} \bar{C}_{DD}^k - \bar{C}_{dSD}^k \right)$$

The pseudorange noise covariance can be obtained by differencing between the innovation matrix and the *a priori* error covariance as follows.

$$R_{\rho,k} = \bar{C}_{\rho,k} - H_k^* \bar{P}_k H_k^{*T} \tag{6}$$

For more reliability, the estimated covariance can be computed through averaging within the pre-defined time interval.

### FIELD EXPERIMENT

To evaluate the performance of the proposed adaptive filtering, a field experiment was performed. For the experiment, two static GPS receivers were used. The measurements were processed in kinematic mode assuming that rover is not stationary. One GPS receiver was dual frequency for reference and the other was low cost single frequency for rover. The baseline between the reference and rover receivers were set approximately 7.9 km. All the raw measurements of the reference and rover receivers were logged in the standard RINEX (Receiver INdependent EXchange) format.

Fig. 3 shows the area where the experiment was performed and the number of visible satellites for the rover during the stationary experiment. As shown in Fig. 3, sufficient number of satellites were visible throughout the experiment.

Fig. 4 shows the estimated standard deviations of carrier-phase and pseudorange measurements. In this experiment, it was assumed that the carrier-phase noise terms from different channels satisfies the standard deviation and independent to each other since carrier-phase measurements are less susceptible to multipath errors which causes different noise characteristics between channels. Thus, the one standard deviation value accounting for carrier-phase noise characteristic was computed and applied to all the channels. However, the standard deviations for pseudorange measurements were computed for each satellite channel due to different multipath effects on different channels. The initial values for pseudorange and carrier-phase noise terms were set as 1.5 m and 0.015 m, respectively.

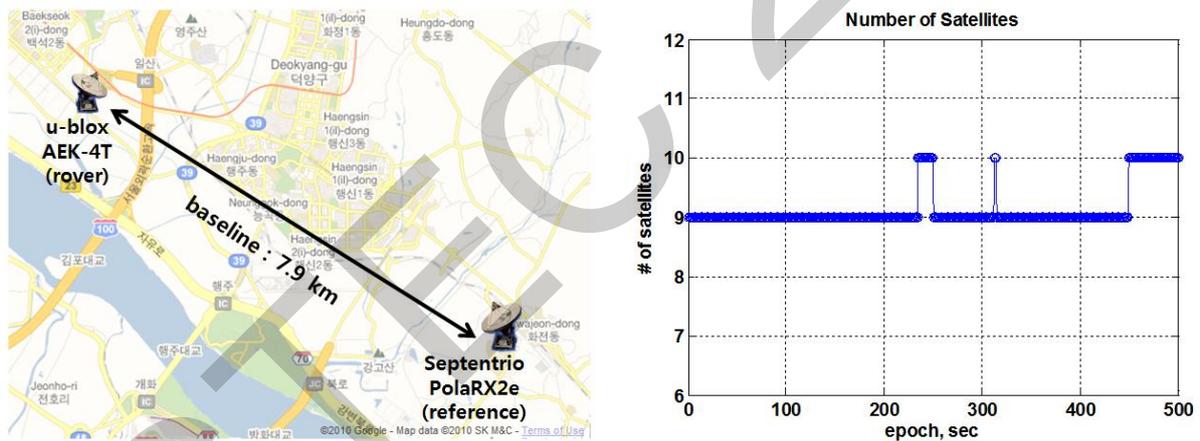


Fig. 3 Experiment area and the number of visible satellites

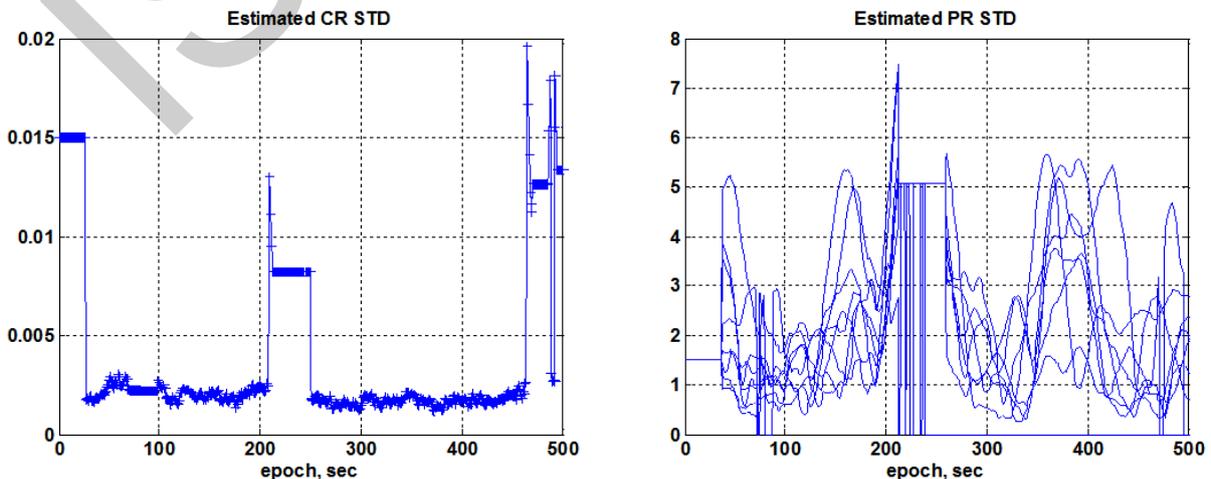


Fig. 4 Estimated standard deviation values for carrier-phase and pseudorange noise terms

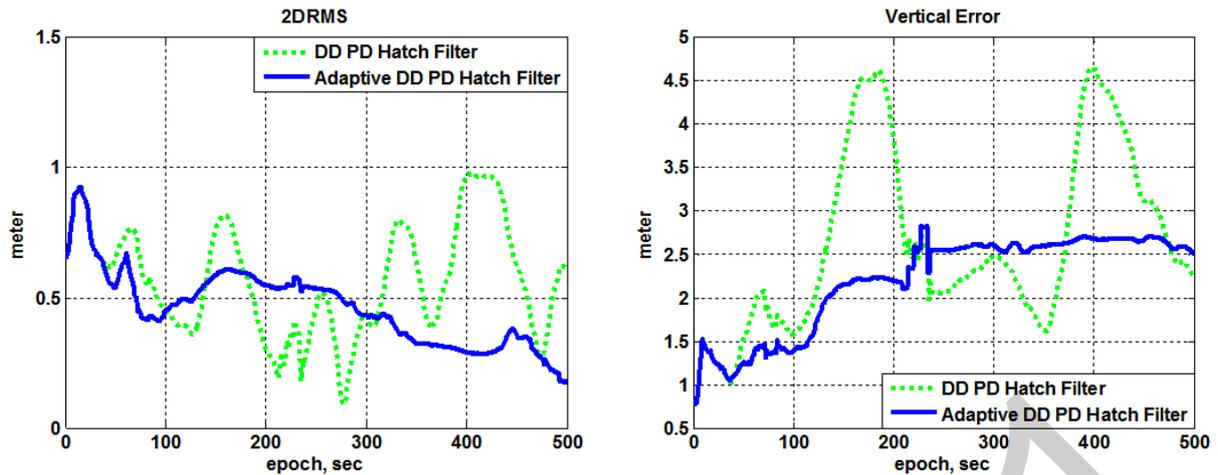


Fig. 5 Comparison of 2DRMS and vertical error between the proposed adaptive filter and the traditional filter

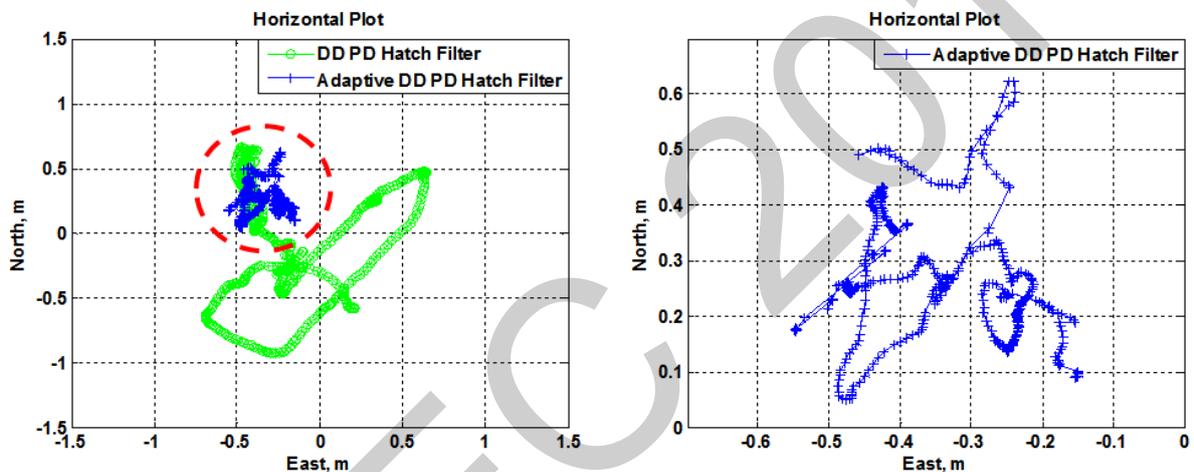


Fig. 6 Comparison of position estimate distributions between the proposed adaptive filter and the traditional filter

Fig. 5 shows the two 2DRMS and vertical errors of the same receiver and Fig. 6 shows the position estimates of the same receiver with or without covariance estimation in steady-state of the filter. In Fig. 6, the two lines marked with circles and crosses correspond to the traditional CSC filter and the proposed adaptive CSC filter, respectively. Fig. 5 and Fig. 6 show the positioning accuracy improvement by utilizing the proposed adaptive method.

### Conclusions

In this study, the new type of adaptive covariance estimator was proposed for improved CSC filtering. The proposed method estimates the noise covariances of carrier-phase measurements and pseudorange measurements based on innovation sequences for time propagations and measurement updates, respectively. Performance of the proposed method was evaluated by applying field-collected GPS experimental data. Through the experiment, it was shown that proposed adaptive CSC filter provide more accurate and precise position estimates than traditional CSC filter.

### Acknowledgements

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# ACCURATE DETERMINATION OF RETENTION INDICES IN PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

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## Abstract

A method for calculating the retention indices in gas chromatography, based on cubic spline interpolation, does not require the presence in the sample of complete homologous series of n-alkanes. Applying a few plasticizers eluted in a column shows that the indices thus obtained are distributed more linearly than those calculated conventionally.

## I - INTRODUCTION

The Kovats index has been extended to programmed temperature gas chromatography (PTGC) by several authors. A compound X eluted between two reference n-alkanes of chain lengths (Z) and (Z + i) have a retention index for programmed elution expressed as:

$$(1) \quad I_X = 100 Z + 100 i [\text{Tr}(X) - \text{Tr}(Z)] / [\text{Tr}(Z + i) - \text{Tr}(Z)]$$

Where Tr is the retention temperature of the three compounds considered.

The linearity between the retention temperature and the number of carbon atoms thus assumed can be derived theoretically if a number of restrictive assumptions are made [2].

The practical verification of the supposed linearity was first attempted. The retention temperatures were obtained from a theoretical model [3] which makes use of a transcendental integral:

$$(2) \quad b \cdot t_M = \int_{T_0}^{T_r} [1 + A \exp \overline{\Delta H}_v^0 / RT]^{-1}$$

Where  $T_0$  is the column temperature at time 0, which is the moment of injection of the solute and start of heating at a constant rate b. The  $t_0$  is the retention time of a non-sorbed sample (methane), R is the constant gas,  $\overline{\Delta H}_v^0$  is the standard evaporation enthalpy of the solute from the solution in the stationary phase, and A is an entropy term. Both of these thermodynamical values, required for the calculation of the solute retention temperature, were obtained by measuring the isothermal retention times over an interval of sixty degrees, using a  $10^\circ$  spacing.

We describe the basic elements of the cubic spline interpolation necessary to write the computer program, which applied to the calculation of PTGC indices of some plasticizers, eluted on a column packed with OV17 on (60-80mesh) Chromosorb Q. Since retention temperature is the most valuable parameter in PTGC, correlations, between retention indices and retention temperatures are established.

## II – SOLUTION THERMODYNAMIC PARAMETERS OF SOLUTES

The solute retention times  $t_r$  were expressed for isothermal chromatography by equation (3) in terms of thermodynamic parameters of solution.

$$(3) \quad (t_r - T_M) / t_M = A \exp \overline{\Delta H}_v^0 / RT$$

By measuring the retention time over an interval of sixty degrees, using a  $10^\circ$  degrees spacing, we could easily obtain the standard molar partial enthalpy of solution  $\overline{\Delta H}_v^0$  and the values of the entropy term A. Both of these thermodynamical values [Table I] were quite constant throughout the experimental range.

**Table I.** Solution thermodynamic parameters of standard n-paraffins and their measured ( $T_{Rm}$ ) and calculated ( $T_{Rc}$ ) retention temperatures.

n-alkanes	$\overline{\Delta H_v^0}$ (K Cal/mol)	$A \times 10^6$	$T_{Rm}$ ( $^{\circ}C$ )	$T_{Rc}$ ( $^{\circ}C$ )	
Decane		8.100	29.80	113	109.7
Tridecane		11.000	7.09	143	139.8
Tetradecane		11.800	4.52	155.5	152
Pentadecane		12.500	3.84	169	168.8
Hexadecane		13.000	3.04	181	178.2
Heptadecane		13.250	2.56	191.5	186
Octadecane		13.700	2.33	198	192.8
Eicosane		15.000	1.24	215	216.4
Docosane		17.500	0.14	232	234.3
Hexacosane		18.600	0.199	266	267
Octacosane		19.600	0.13	280	283.5
Triacontane		20.300	0.11	294	297.5

### III – COMPUTATION OF THE RETENTION TEMPERATURES OF THE N-ALKANES

Equation (3) was resolved numerically by Newton’s method, with the help of a micro computer , when  $b.t_M = 4.05$ . The computed values ( $T_{Rc}$ ), wwhich were compared to the mmeasured retention temperatures ( $T_{Rm}$ ), are shown in Table I. The regression line of  $T_{Rc}$  on  $T_{Rm}$  was established by yhe least square method and is :

$$(4) \quad T_{Rc} = 9.452 + 1.040 T_{Rm}$$

The analysis of variance shows that the slop of the above regression line is very significant ( $F_{obs} = 539.4$ ).

### IV – COMPUTATION OF THE RETENTINS INDICES USING A NON-LINEAR INTERPOLATION

Among methods commonly used for generating smooth curves, the cubic spline interpolation was considered to be the most suitable.

Below we present only an outline of the application of cubic spline interpolation to the calculation of retention indices. For further details we refer to two books (a,b) covering the most important aspects of the subject.

Let  $a = X_0 < X_1 < \dots < X_N = b$ , (with  $N > 2$ ), be a partition of the interval  $[a,b]$  where a function  $f$  is defined. This function,  $f$ , admits a unique interpolating natural cubic spline. The cubic splines are functions composed of third order polynomials pieced together in the data points. The fact that they are of class  $C^2 [a,b]$  is their essential property.

The numerical construction of a spline is faciliated by applying to the cubic polynomials:

$$(5) \quad S_j(x) = a_j + b_j(x - x_j) + c_j(x - x_j)^2 + d_j(x - x_j)^3, \quad 0 \leq j \leq N - 1$$

the conditions:

$$\begin{aligned} S(x_j) &= f(x_j) & 0 \leq j \leq N \\ S_{j+1}(x_{j+1}) &= S_j(x_{j+1}) & 0 \leq j \leq N - 2 \\ S'_{j+1}(x_{j+1}) &= S'_j(x_{j+1}) & 0 \leq j \leq N - 2 \\ S''_{j+1}(x_{j+1}) &= S''_j(x_{j+1}) & 0 \leq j \leq N - 2 \end{aligned}$$

and the natural limit conditions:

$$S''(x_0) = S''(x_N) = 0$$

### V – RESULTS AND DISCUSSION

The values of solution thermodynamic constants,  $\overline{\Delta H_v^0}$  and  $A$ , of plasticizers (Table II) were obtained by measuring the retention time at different temperatures [equation (3)]. Both of these thermodynamic values were quite constant throughout the temperature range between 1000 an 3000.

From the values of  $\overline{\Delta H_v^0}$  and  $A$  in Tables I and II, the retention temperatures of the n-alkanes and plasticizers were calculated as functions of the product  $b.t_m$  by numerical integration of equation (2). From these retention temperatures, retention indices could be determined for any program.

Programmed retention indices thus calculated ( $I_c$ ) were compared to the measured ones ( $I_m$ ) when  $b.t_m = 4.05$ . The regression lines of  $I_c$  vs.  $I_m$ , established by the least square method are:

$$I_c = 6.599 + 0.997 I_m; \quad (F_{obs} = 128.04)$$

and

$$L_C = 10.756 + 0.998 I_m; \quad (F_{obs} = 110.54)$$

respectively for linear and spline interpolation

The analysis of variance shows that the slopes of the above regression lines are very significant.

Table II. Solution thermodynamic values for some plasticizers, and programmed retention indices determined by using computed retention temperatures.

Plasticizer	$\overline{\Delta H}_v^0$ Symbol	(K Cal/mol)	$A \times 10^6$	$I_L$	$I_S$
Trimethyl phosphate	TMPH	9.400	17.30	1102	1106.7
Dimethyl adipate	DMA	11.700	7.70	1445	1447.9
Dimethyl phtalate	DMP	12.800	5.13	1707	1696.1
Diethyl phtalate	DEP	13.900	2.70	1888	1906.2
Dimethyl sebacate	DMS	14.100	2.09	1872	1896.3
Diallyl phtalate	DAP	14.800	1.71	2038	2017.0
Dibutyl adipate	DBA	14.600	1.53	1943	1935.0
Diethyl sebacate	DES	14.800	1.37	1960	1966.4
Dibutyl phtalate	DBP	15.800	1.27	2219	2187.4
Bts(methyleneglycol) phtalate	BMGP	16.500	0.79	2347	2365.4
Dioctyl adipate	DOA	18.800	0.13	2541	2540.4
Dicyclohexyl phtalate	DCHP	19.800	0.15	2897	2944.6
Dioctyl phtalate	DOP	21.200	0.03	2801	2820.1
Bis(butyleneglycol) phtalate	BBGP	18.800	0.32	2857	2801.6

## VI – CONCLUSION

In practice the relationship between the carbon number of homologs and their retention temperature is not strictly a linear one, as supposed by linear interpolation. Also, retention indices calculated in a classical way are not appropriate for reference use, or for storing in a reference library.

A method has been described for the calculation of programmed retention indices based on cubic spline interpolation, which does not require the presence of consecutive normal paraffins in the sample. For the mathematical procedure the standards do not necessarily have to belong to homologous series.

Using the method for the determination of linear PTGC retention indices of some plasticizers, separated on column packed with OV17 on Chromosorb Q (60-80 mesh), several conclusions have been made:

- (1) Retention indices computed by the spline and by the linear techniques may differ by as much as 49 index units, when the retention index of the compound varies with temperature.
- (2) The spline technique yields results more consistent with the scheme of retention indices.
- (3) Spline-calculated indices have smaller standard deviations, and are generally more constant at different heating rates.
- (4) In general, spline-calculated indices are either consistent with the concept of significant temperature, or they are in good agreement with isothermal indices.

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# ADA UYDU GÖRÜNTÜLERİNİN MEKANSAL VERİTABANLARI İÇİN VEKTÖREL MODELLENMESİ

## VECTOR MODELLING OF ISLAND SATELLITE IMAGES FOR SPATIAL DATABASES

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### ÖZET

Rasterdan vektöre dönüşüm diğer bir ifade ile vektörizasyon; Coğrafi Bilgi Sistemi (CBS) ve Uzaktan Algılama görüntü işleme uygulamalarında, mühendislik çizimlerini analog biçimden sayısal ortama aktarmada önemli bir işleve sahiptir. Bu çalışmada mekansal veri tabanları için görüntünün kenarlaştırma yöntemiyle rasterdan vektöre çevrilmesi ve vektör modeller üzerinden mekansal sorguların gerçekleşmesi ele alınmıştır. İlk olarak Sobel operatörü ile gri görüntüdeki kenarlar bulunup Otsu eşikleme yöntemi ile ikili seviyeye çevrilmiştir. Daha sonra dört yönlü tarama yapılarak şeklin sınırlarını gösteren noktalar tespit edilip elde edilen noktaları içine alacak minimum çevrime sahip dışbükey “paket sarma” algoritması ile bulunmuştur. Son olarak dışbükeyi ifade eden poligonun noktaları mekansal veri tabanına kaydedilip mekansal sorgulamalara hazır hale getirilmiştir. Uygulama gerçek bir ada uydu görüntüsü üzerinde yapılmıştır ve mekansal veritabanı olarak PostgreSQL’in PostGIS modülü kullanılmıştır. Önerilen tekniğin etkinliği simülasyonlarla incelenmiştir.

**Anahtar Sözcükler:** Vektörizasyon, Raster Veri, Vektör Veri, Mekansal Veritabanları, Veri Modelleme

### ABSTRACT

Raster-to-vector conversion, i.e. vectorization, has key functionalities in Geographic Information Systems (GIS), image processing for Remote Sensing, and conversion of technical drawings (analog to digital) in engineering applications. This study presents a technique to convert a raster image into a vector data as object sets by using edge-detection algorithms, which enables spatial queries on image data. In this architecture, we first apply Sobel operator to grayscale image to find out the edges, and then, convert the edges into binary-level with Otsu threshold technique. In the next step, we apply 4-way scan to find out the border pixels of the image, and create a convex hull covering those pixels by aid of Gift Wrapping algorithm. Finally, points of the convex-hull are stored into the database as a polygon and corresponding image is made ready for the spatial queries. The proposed technique is applied on a real-world island image, and PostgreSQL with its PostGIS module is used as a spatial database. The efficiency of the proposed technique is examined by the simulations.

**Keywords:** Vectorization, Raster Data, Vector Data, Spatial Databases, Data Modeling

### 1.GİRİŞ

Bilgisayarlarda görüntü; raster grafik denilen gri renk ton değerlerini içeren iki boyutlu bir dizi formatında veya vektör grafik denilen nokta, doğru, poligon gibi matematiksel olarak ifade edilen geometrik primitifler yolu ile olmak üzere iki şekilde temsil edilir. Her iki gösterimin birbirlerine göre avantajları olmasına rağmen birçok uygulamada birlikte kullanılabilir (Chock, Cardenas & Klinger, 1981). Rasterdan vektöre dönüşüm diğer bir deyişle vektörizasyon; Coğrafi Bilgi Sistemi ve Uzaktan Algılama görüntü işleme uygulamalarında, mühendislik çizimlerini analog biçimden sayısal ortama aktarmada, doküman analizi ve tanımda önemli bir işleve sahiptir. Grafik bilgi sistemlerinde çizgi en temel veri elemanlarından biri olması sebebiyle raster bir görüntüdeki çizgilerin doğru bir şekilde elde edilmesi çok önemlidir (Zhong, 2002). Vektörizasyon işleminin başarısı raster görüntünün kalitesi ve detayların belirginliği ile doğru orantılıdır.

Yapılan uygulamalar genelde internet tabanlı olduğundan çok büyük veri setlerinin transferi ve analizini gerektirmektedir. Raster görüntüde (örneğin TIFF görüntü) görüntüyü oluşturan bütün piksellerin lokasyon ve renk bilgileri tutulduğu için dosyanın boyutu çok büyük olmaktadır. Aynı görüntünün vektörel temsilinde (örneğin text dosyasındaki x,y dizileri) görüntünün matematiksel tanımlaması tutulduğu için dosya boyutu orijinalinden onlarca hatta binlerce kat daha küçük boyuta sahip olabilmektedir. Görüntülerde alan, çevre, uzunluk, komşuluk, yakınlık gibi mekansal sorgulamalar raster bilgiden çok vektörel bilgi gerektirdiğinden bu tür sorgu ve analizlerin vektör görüntüsü üzerinde yapılması büyük miktarda hesaplama ve performans kazanımı ile sonuçlanmaktadır.

Raster görüntülerde çözünürlük ve renk derinliği arttıkça dosya boyutu artmaktadır. Örneğin 2"x3" büyüklüğünde çözünürlüğü 300 dpi ve renk derinliği 24-bit olan bir görüntünün boyutu 12Mb'in üzerinde olurken bu görüntünün vektör formatında boyutu 96 bit kadar olmaktadır. Görüntü bilgisayarda oluşturulurken veya taranırken dosyanın büyük boyutta olması bilgisayarın işlemci ve hard diskinin çok daha fazladan çalışmasına neden olur. Büyük boyutlu (1Mb'tan fazla) dosyalar internet üzerinden transfer edilirken her iki tarafta da yüksek hızlı internet bağlantısının olmasını gerektirir. Vektör formatında hem işlemciyi yormamış hem de sınırlı bant genişliğinde veri transferini sağlamış olur. Ayrıca veri tabanlarının sınırlı boyutta olmasından dolayı vektör formatta çok daha fazla bilgi depolanabilir.

Şu ana kadar yapılan çalışmalar rasterden vektöre dönüşümde etkin ve yüzde yüz çözüm sunamamıştır. Bunun birçok sebebi vardır ve mimari bölümünde açıklanmıştır. Bu çalışmada raster görüntülerin vektörizasyonuna yönelik yeni bir yöntem geliştirilmiştir. Yöntem, raster görüntünün Sobel operatörü yardımıyla kenar bulma işleminden geçirilip Otsu eşikleme yöntemiyle ikili resme çevrilip dört-yönlü tarama ile elde edilen sınır nokta setlerini Paket Sarma (Gift Wrapping) algoritması ile minimum çevrime sahip dışbükeyi bulma temeline dayanmaktadır. Çalışmada ada görüntüsü üzerinde adanın ne kadar büyüdüğü/küçüldüğü veya ne kadar yer değiştirdiği gibi mekansal sorgulama işlemleri test edilip çok daha hızlı ve etkin bir şekilde yapılabilmesi sağlanmıştır.

Örnek uygulama olarak ada görüntülerinin seçilmesinin nedeni, adanın bir nesne olarak ayırt edilebilir ve şekil olarak poligon ile tanımlanabilmesinin kolaylığındandır. Diğer random uydu görüntülerinde neyin ada, neyin göl, neyin ülke sınırları, neyin il sınırları olduğunun temsilinin nesne bazlı olarak ayırt edilmesi zordur. Makalemizin geri kalan kısmı şu şekilde özetlenebilir: 2. bölüm ilgili çalışmaları kapsamaktadır. 3. bölümde kenarlaştırmaya dayalı vektörizasyonun genel mimarisi sunulmuştur. 4. bölümde gerçekleştirilen simülasyonlar ve değerlendirilmesi ele alınmıştır. 5. bölümde ise yöntemin sonuçları tartışılmış ve gelecek çalışmalara yer verilmiştir.

## 2.İLGİLİ ÇALIŞMALAR

Raster görüntülerdeki çizgilerin elde edilmesine yönelik birçok yöntem geliştirilmiştir. Yöntemleri; düz çizgiyi eğimi ve kesişim noktalarına göre parametrize eden Hough dönüşüm tabanlı (Duda & Hart, 1972), inceltme tabanlı (Tamura, 1978; Haralick,1992; Nalwa, 1993), kontur tabanlı (Martínez-Pérez, Jiménez & Navalón, 1987) , grafik yürütme tabanlı (Di Zenzo & Morelli, 1989) , ağ desen tabanlı (Lin, Shimotsuji, Minoh, & Sakai, 1985) ve ayrık piksel tabanlı (Liu & Dori, 1999b) metotlar olmak üzere altı sınıfa ayırabiliriz. Birincisi hariç diğer metotlarda orta eksen bulma, çizgi izleme/zincir kodlama ve vektör azaltma/poligonlaştırma işlemleri vardır (Liu & Dori, 1999a).

Orta eksen bulma ile raster görüntüdeki çizgilerin çekirdek çizgi tespitleri yapılarak orta eksen haricindeki bilgiler atılarak azaltılmış olur. Daha sonra çizgi izleme işlemi ile her bir pikselin ilerleme yönleri belirlenerek noktalar zinciri üretilir. Son kısımda da kritik olmayan noktalar bu zincirden çıkartılarak vektör doğrular elde edilir.

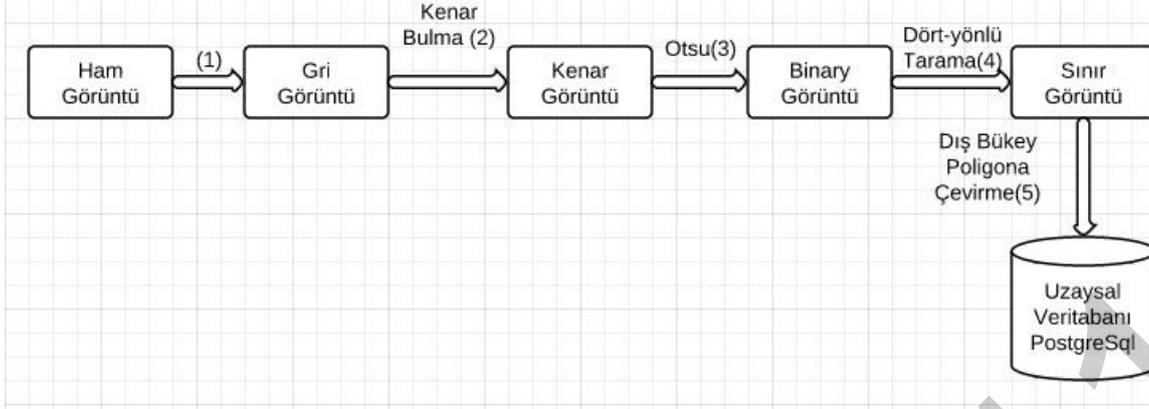
Hough dönüşüm tabanlı metotlarda gürültülü çizgilere ait olan noktalar için de polar koordinat düzleminde doruklar oluşturması beklendiğinden gürültülü görüntülerdeki çizgileri de tespit edebilmektedir. Ayrıca kavisli çizgiler için uygun değildir. İnceltme tabanlı metotların yüksek zaman karmaşıklığı, çizgi kalınlığı gibi şekil bilgilerinin kaybolması, kesişimlerde bozulma, yanlış ve sürpriz dallanmalar gibi dezavantajları vardır. Daha çok çizgisel görüntülerin vektörizasyonunda kullanılmakta olup görüntü alanının küçük çizgi kalınlığının önemli olmadığı karakter tanıma uygulamalarında kullanılmaktadır. Kontur tabanlı, grafik yürütme tabanlı ve ağ desen tabanlı metotların ise çok kesişim ve eğik çizgilerin olduğu çizimlerde kullanılması uygun değildir.

Ayrıca vektörizasyon için literatürde biri matematiksel diğeri istatistiksel olmak üzere iki yaklaşım vardır. Birincisi kenar bulma yardımıyla görüntüden elde edilen piksellerin zincir kodlamasına dayanır. Kavis ve segmentleri bulmak için (Kalmykov, 2007; Yang, 2002; Zhang, Song, Dai, & Lyu, 2006), elips ve eğrileri bulmak için (Chen., Yong, Zheng, & Sun, 2004; Wan & Ventura, 1997) çalışmaları örnek olarak verilebilir. Zincir kodları interpolasyon yöntemleri kullanılarak geometrik pirimitiflere dönüştürülür. Görüntü gürültülü ise bu yöntemler tatmin edici sonuçlar vermez. İstatistiksel yöntemler de ise nesnenin sınır değeri için olası bir model tanımlanır. Snake kontur modelinde nesnenin sınırları kapalı parametrik bir eğriye benzetilir (Kass, Witkin, & Terzopoulos, 1987). Aktif kontur modelinde ise nesnenin sınırları parametrik bir eğriye benzetilir (Amit, 2002). Dinamik poligon modelinde sınırlar kesişmeyen poligonlara benzetilir (Pievatolo & Green, 1998).

Bahsi geçen çalışmaların çoğu büyük ölçüde doğrusal çizgilerden oluşan görüntüler için uygun sonuçlar vermektedir. Uygulamamızda ada görüntüleri ile ilgilenildiğinden bu görüntüler diğer mühendislik çizimlerindeki gibi yalnızca düz çizgilerden oluşmadığı için yeni bir yöntem geliştirilmesi ihtiyacı hissedildi. Geliştirilen sistemim mimarisi aşağıda anlatıldığı gibidir.

## 3.MİMARİ

Raster ada görüntüsünde Sobel operatörü ile kenarlar bulunup Otsu eşikleme yöntemi ile ikili seviyeye çevrilmiştir. 4-yönlü tarama yapılarak şeklin sınırlarını gösteren noktalar elde edildikten sonra bu noktaları kapsayan dışbükey “paket sarma” algoritması ile bulunmuştur. Son olarak dışbükeyi ifade eden poligonun noktaları mekansal veri tabanına kaydedilmiştir. Algoritmanın temel mantığı şekildeki gibidir:



Şekil 1. Algoritmanın Akış Şeması

İlk olarak ham ada görüntüsü, resmi daha sonra işleyecek algoritmaların işini kolaylaştırmak için gri seviyeye çevrilmiştir (adım 1, Şekil 3). Görüntüdeki önemli yapısal kısımların muhafaza edilip daha az anlamlı bilgilerin filtrelenmesi yoluyla işlenecek veri sayısını azaltmak sebebiyle kenar bulma tekniklerinden birinci dereceden türev hesabına dayalı Sobel operatörü (Sobel, 1978) ile gri görüntü kenar görüntüsüne çevrilmiştir.

Görüntü kirlilikleri kenar bulma algoritmalarının başarısını etkilemektedir. Uydu görüntülerinde görüntü kirlilikleri genelde havanın kapalı, bulutlu olmasından veya düşük olasılıkla da olsa farklı cisimlerden ortaya çıkar. Görüntülerin de kenar gibi algılanmaması için seçilen görüntülerin temiz olmasına dikkat ettik.

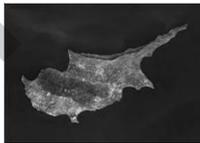
Eşikleme işleminin başarımı daha sonraki görüntü işleme yöntemlerinin başarımını doğrudan etkilediğinden eşik değerlerinin otomatik olarak ve sahnedeki bilgiyi mümkün olduğunca ortaya çıkaracak şekilde belirlenmesi büyük öneme sahiptir. Ayrıca görüntünün özelliklerinin bölgeden bölgeye değişebileceğini dolayısıyla görüntünün her bir bölgesinde farklı bir eşik değerini kullanma gereksinimini, piksellerin yerleşimi ve aralarındaki ilişkileri hesaba katması gerekmektedir.

Uygulamamızda kenar saptama işleminden geçmiş görüntüdeki adayı resmin geri kalanından ayırmak için piksellerin gri seviye değerlerinin tüm imgedeki dağılımlarının yanı sıra yerel özelliklerini de göz önüne alan Otsu eşikleme (Otsu, 1979) yöntemi kullanılmıştır (adım 3, Şekil 5).

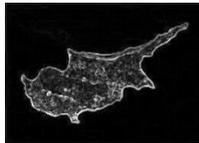
Otsu eşikleme filtresinden geçen resmin adayı temsil eden her bir pikseli 1, geri kalan kısmı 0 olarak kodlanmıştır. İmge üzerinde yataydan başlayarak satır satır soldan sağa tarandığında her satırda ilk rastlanan 1 değerli pikselleri adanın sol sınır değerlerini sağdan sola doğru tarandığında her satırda ilk rastlanan 1 değerli pikselleri de adanın sağ sınır değerlerini verir. Yine imge üzerinde dikey taramalar yaparak imgenin her sütun için rastlanan yukarıdan aşağıya tarandığında ilk 1 değerli pikselleri adanın üst sınır, aşağıdan yukarıya tarandığında ilk rastlanan 1 değerli pikselleri de alt sınır değerlerini verir (adım 4, Şekil 6).



Şekil 2. Ham Kıbrıs Ada'sı görüntüsü



Şekil 3. Gri seviye Kıbrıs Ada'sı görüntüsü



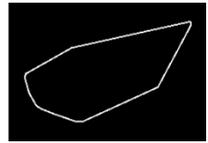
Şekil 4. Kıbrıs Ada'sı Kenar görüntüsü



Şekil 5. Kıbrıs Ada'sı Eşik görüntüsü



Şekil 6. Kıbrıs Ada'sı Eşik görüntüsü



Şekil 7. Kıbrıs Ada'sının Vektör görüntüsü

Resimdeki adaları matematiksel olarak poligonlarla temsil edilir ve poligon verisi, başlangıç ve bitiş noktaları aynı olan sıralı (x,y) nokta setlerinden oluşur. Uygulanan kenar saptama algoritması adayı temsil eden noktaları doğru olarak bulsa dahi bunların sıralı olarak düzenlenmesi gerekmektedir.

Düzlemdeki bütün noktaları kapsayan en küçük alana sahip poligonu bulmak için Paket Kaplama algoritması (Jarvis, 1973) kullanılmıştır. Bu algoritma ile daha önce bulunan sınır değerlerini ifade eden ama sıralı olmayan bütün noktaları kapsayacak şekilde sıralı hale getirilerek raster olan ada görüntüsü bu aşamadan sonra vektörel biçimde ifade edilmektedir. (adım 5, Şekil 7)

Kullanılan veri modeline göre veritabanı yönetim sistemleri hiyerarşik, ağ, ilişkisel, nesne ve nesne ilişkisel veritabanı modelleri olarak kategorilere ayrılırlar. Nesne ilişkisel veritabanlarında her nesne bir sınıfı temsil eder ve sınıf içerisinde nesneye ait veriler ve fonksiyonlar bir arada tutulur. Mekansal nesnelere ait verileri saklayabilen ve sorgulayabilen mekansal veri tabanları nesne ilişkisel veritabanı modelini kullanır.

Tipik veri tabanları nümerik ve karakter veri tiplerini anlayabilirken, mekansal veri tabanlarında mekansal veri tiplerini (nokta, çizgi ve poligon) analiz edebilir. Bu veri tipleri geometri ya da özellik olarak bilinir. Mekansal veriler; nokta, çizgi ve alansal olarak ifade edilebilen coğrafi haritalar, nehirler, yollar, adalar veya piksel gruplarından oluşan uydu görüntüleri, sayısal yükseklik modelleri ve hava fotoğrafları olabilir. Mekansal veri tabanları üzerinde Kocaeli'nin nüfusu kaç, Kocaeli'de toplam kaç tane ilçe var, A harfi ile başlayan ilçelerini listeleyin gibi tipik SQL sorgularına ek olarak mühendislik fakültesine en yakın iki restoran nerededir (yakınlık/proximity), Kocaeli'de şehirlerarası otobüs terminali hangi ilçededir (içerme/containment), Türkiye'ye komşu ülkeler hangileridir (bitişiklik/adjacency) ve Kocaeli'nin hangi ilçeleri üzerinden tren yolu geçer (kesişim-örtüşme /intersection-overlap) gibi mekansal sorgulamalar yapılabilir.

Veritabanları için nesne ilişkisel veri modelini kullanan ve SQL standart sorgu dilini destekleyen veritabanı yönetim sistemi PostgreSQL, diğer birçok gelişmiş veritabanından olduğu gibi dışarıdan kendisine bağlanan istemciler ile belirli bir dilde konuşup anlaşabilmek için bir sunucu/istemci protokolüne sahiptir. PostgreSQL veritabanına ulaşmak için PostgreSQL'in soket bağlantısı üzerinden basit okuma/yazma sistem çağrılarında bulunmak gibi bir iç işleyişi ile ilgili hiçbir çalışma mekanizmasından haberdar olmak zorunda kalınmadan, programlama dilinin sunduğu API kütüphanesinden faydalanılarak kolaylıkla veritabanı ile etkileşime geçip, ilgili sorgulamalar gerçekleştirilebilir. Biz de çalışmamızda Java programlama dilinin sunduğu "pgjdbc" API kütüphanesinden yararlandık.

Vektörel biçime çevirdiğimiz ada görüntüsü geometrik olmayan (adanın ismi, alanı ve çevresi) ve geometrik olan (poligon) özellikleri ile PostgreSQL veritabanına kaydedildi. Geometri veri tipi ve bu tipi kullanan fonksiyonlarla işlem yapabilmek için PostgreSQL'e mekansal PostGIS eklentisi eklendi.

#### 4. GERÇEKLEŞTİRİLEN TESTLER VE DEĞERLENDİRİLMESİ

Uygulamamızda daha çok alan ve çevre hesapları yaptığımızdan PostGIS fonksiyonları yardımıyla veritabanına kaydedilen ada görüntüsünün alanı ve çevresi hesaplandı. Hesaplanan değerlerden ve verilen harita ölçek değerine göre adanın gerçek alan ve çevre dönüşümü;

$$\text{Gerçek Uzunluk} = \text{Ölçek} * \text{Veritabanındaki Poligondan Hesaplanan Harita Uzunluğu} \quad (1)$$

$$\text{Gerçek Alan} = \text{Ölçek (Payda)}^2 * \text{Veritabanındaki Poligondan Hesaplanan Harita Alanı} \quad (2)$$

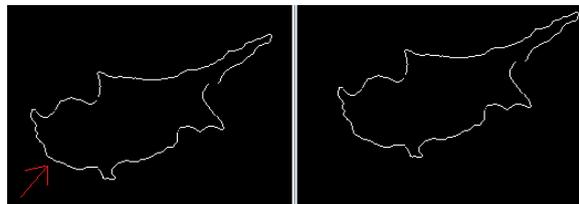
formülleri ile bulundu. Veritabanına kaydedilen vektörel yapıdaki adanın alan ve çevre uzunluklarını hesaplayan mekansal sorgular da şu şekildedir:

```
SELECT Round(ST_Area(poligononce)) AS Alan, Round(ST_Area(poligonsonra)) AS AlanSon,area AS Gercek FROM dbpoligon Where ad= 'kibris'
```

```
SELECT Round(ST_length(ST_Boundary(poligononce))) AS CevreOnce,Round(ST_length (ST_Boundary(poligonsonra))) AS CevreSon, cevre AS Cevre FROM dbpoligon WHERE ad='kibris'
```

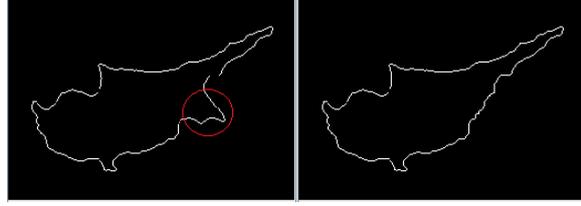
Raster Kıbrıs Ada görüntüsü vektörleştirilip depremden dolayı kayma derecesi tespiti (senaryo 1), erozyon (senaryo 2) ve dolgu (senaryo 3) gibi bazı senaryolar test edildi.

Senaryo 1'de Kıbrıs Ada'sı üzerinde öteleme işlemi ile yapay bir deprem varlığı elde edildi. Daha sonra ötelemeden önceki ve sonraki resimlerden elde edilen poligonların ağırlık merkezleri karşılaştırılarak ne kadar km'lik bir kayma olduğuna bakıldı.



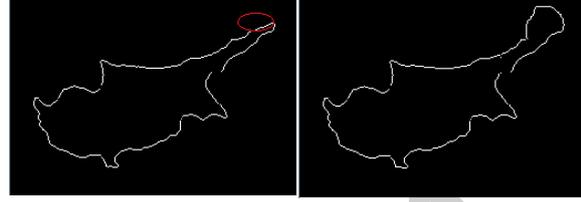
Şekil 8. Senaryo 1'in şekille ifadesi

Senaryo 2’de Kıbrıs Ada’sının bir kısmı silinerek yapay bir erozyon elde edildi. Daha sonra alan ve çevre sorgulamaları yapılarak ne kadar azalma olduğu araştırıldı.



Şekil 9. Senaryo 2’nin şekille ifadesi

Senaryo 3’te Kıbrıs Ada’sına bir kısmı eklenerek yapay bir doldurma/dolgu elde edildi. Daha sonra alan ve çevre sorgulamaları yapılarak ne kadar artma olduğu araştırıldı.



Şekil 10. Senaryo 3’ün şekille ifadesi

SENARYOLAR	Önceki Alan(km <sup>2</sup> )	Sonraki Alan(km <sup>2</sup> )	Önceki Çevre(km)	Sonraki Çevre(km)
Senaryo1	15715	15715	543	543
Senaryo2	15715	14016	543	535
Senaryo3	15715	17380	543	557

Tablo 1. Gerçekleştirilen simülasyonların sonuçları

Kıbrıs Ada’sının gerçek alanı 9251 km<sup>2</sup> çevresi ise 648 km’dir. Adayı dışbükey poligon olarak temsil ettiğimizden adanın alanı 15715 km<sup>2</sup> çevresi ise 543 km olarak gözükmektedir. Dışbükey poligon, sınır değerlerini içine alan en küçük alana sahip poligon olduğundan gerçekte var olmayan kısımlar da hesaba katmaktadır. Bu gerçek göz önüne alınarak Tablo 1’de gösterilen testlerden Senaryo1’de sadece öteleme yapıldığından alan ve çevre değişikliği gözükmemektedir. Kayma miktarı kaymadan önceki ve sonraki ada görüntülerinin ağırlık merkezlerinin karşılaştırılmasıyla 25 km olarak saptandı. Senaryo2’deki yapay erozyondan dolayı alanda 1699 km<sup>2</sup> çevrede 8 km’lik bir azalma, Senaryo3’te ise yapay doldurmadan kaynaklanan 1665 km<sup>2</sup>’lik bir alan ve 14 km’lik bir çevre artması görülmektedir. Senaryo2’de erozyon ve Senaryo3’te doldurma yapıldığından herhangi bir kayma olmamıştır.

## 5. SONUÇLAR

Bu çalışmada mekansal veri tabanları için gerçek bir ada görüntünün kenarlaştırma yöntemiyle vektörleştirilmesi ve vektör modeller üzerinden mekansal sorguların gerçekleşmesi ele alınmıştır. Uygulama gerçek bir ada uydu görüntüsü üzerinde yapılmış ve önerilen tekniğin etkinliği simülasyonlarla incelenmiştir. İnternet dünyası ve bununla ilgili teknolojilerin gelişmesi ile uydu görüntüleri ve diğer raster resimlerin web tabanlı dağıtık sistemlerde uygulamaları hızla artmıştır. Bu tür uygulamalarda sınırlı network bant genişliği ve internet alt yapısı, yüksek boyutlu resimlerin etkin transferi ve işlenmesine olanak vermemektedir. Önerilen yaklaşım görüntü boyutunu aşırı derecede düşürdüğü için web servis tabanlı dağıtık uygulamalara büyük katkı sağlayacaktır.

Bu çalışmada raster ada görüntülerinin vektörizasyonuna yönelik olarak geliştirilen kenar görüntüden dışbükey poligon elde edilmesine dayalı model ile mekansal sorgulamalar yapıp başarılı sonuçlar elde edileceği gösterilmiştir. Test sonuçlarında da görüldüğü üzere yöntem özellikle seçilen görüntüde 2. dereceden fazla kıvrımlı yapıya sahip olmayan yani algoritmanın dört-yönlü tarama adımında tüm yönlerden (doğu-batı-kuzey-güney) de ulaşılabilen ada görüntüleri üzerinde çalışmaktadır. Adayı içbükey poligon olarak temsil etmek gerçek görüntüye daha çok benzeyecektir. Ayrıca bu çalışmada havanın kapalı, bulutlu olmasından veya düşük olasılıkla da olsa farklı cisimlerden ortaya çıkan kirliliklerin olduğu görüntüler kenar bulmada hatalara neden olduğundan seçilmemiştir. Vektör görüntüdeki adanın dünya üzerinde nereyi temsil ettiği nokta-enlem/boylam projeksiyonları yapılarak enlem/boylam uzaklıklarından daha gerçek sonuçlar bulunabilir. Gelecek çalışmada adayı içbükey bir poligon olarak temsil edip projeksiyonlarla zengin bir çalışma yapılması hedeflenmektedir.

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# ALKALİ SİLİS REAKSİYONUNDA YÜKSEK FIRIN CÜRUFU ETKİSİNİN ARAŞTIRILMASI

## THE INVESTIGATION OF THE EFFECT OF GRANULATED BLAST FURNACE SLAG ON THE ALKALI-SILICA REACTION OF MORTARS

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### ÖZET

Gerek ülkemizde, gerekse diğer ülkelerde birçok betonarme yapı elemanında hasarlar meydana getiren ASR, oldukça kompleks kimyasal bir reaksiyondur. Reaksiyonlar sonunda oluşan su emme özelliği olan jel, şişerek genişlemektedir. Deneysel çalışmada mineral katkı olan yüksek fırın cürufunun çimento ile kısmi yer değişimi %50'ye kadar %5'lik adımlarla yapılmıştır. Harçlı beton elemanlarda hızlandırılmış harç çubuğu deney yöntemi kullanılarak Sakarya bölgesinde kullanılan agregada ASR oluşumları izlenmiştir.

Şahit numunede alkali silis reaksiyonunu 16 gün sonunda standartların belirlediği değerin çok üzerinde %76 civarında genleşme görülmüştür. Mineral katkı olarak yüksek fırın cürufu kullanımında; kullanım yüzdesi %30-%50 dolayında olduğunda ASR'yi azalttığı görülmüştür.

Bu verilere göre betonun durabilitesi açısından zararlı olan alkali silis reaksiyonu mineral katkı olan yüksek fırın cürufu ile standart seviye aralığına azaltılabilmektedir. Mineral katkıların atık olmaktan çıkması, ekonomiye fayda sağlaması açısından kullanımının yaygınlaşması uygun olacaktır.

**Anahtar Kelimeler:** Alkali Silis Reaksiyonu(ASR), Yüksek Fırın Cürufu(YFC), Reaksiyon, Durabilite.

### ABSTRACT

Alkali-silica reaction is pretty complex reaction causes damages on the reinforced concrete structures not only in Turkey but also all over the world. The gel occurs after the alkali-silica reaction swells up due to this reaction and causes expansion on the concrete surfaces. In this study, as a mineral additive granulated blast furnace slag used and replaced with cement with various replacement rates from 5% to 50%. Accelerated mortar bar test method used on the mortars which containing Sakarya region aggregates to investigate alkali-silica reaction.

Control specimen exhibited worse performance than other specimens and showed 76% expansion above the standard values at the end of 16 days. The use of granulated blast furnace slag exhibited very well performance in the range of 30%- 50% and reduced the effect of alkali-silica reaction.

Test results indicated that as a mineral additive granulated blast furnace slag reduced the effect of alkali-silica reaction in terms of durability aspect. The use of granulated blast furnace slag utilizes not only mineral additive aspect but also as a waste material which using this mineral additive should protect our environment by depleting a hazardous material by using in the production of concrete.

**Keywords:** Alkali-silica reaction, granulated blast furnace slag, reaction, durability.

## 1. Giriş

Beton veya betonarme yapı herhangi bir şekilde tahrip olmadan veya özelliklerinde bir azalma meydana gelmeden, belirli bir süre kendinden beklenen fonksiyonu yerine getirmelidir. Böyle bir durum ancak betonun dayanıklılığı sayesinde elde edilir. Betonarme veya beton yapı elemanlarının, zamanla bozulup işlevlerini beklenen servis ömürlerine ulaşmadan yitirmelerine birçok faktör sebep olabilir. Yapı elemanının dayanıklılığını belirleyen etkenler arasında, beton bileşimini oluşturan malzemelerin fiziksel ve kimyasal yapısından kaynaklanan iç etkiler ve çevreden kaynaklanan dış etkiler sayılabilir. Bazı

durumlarda, beton bileşimini oluşturan malzemelerin kendi aralarında veya çevreden gelen zararlı maddelerle kimyasal reaksiyonlara girebildiği, böylece beton hacim sabitliğinin bozulması nedeniyle yapı elemanının zarar gördüğü bilinmektedir.

Alkali silis reaksiyonuna çimentodaki alkali ile, agregalardaki aktif silis ve nem neden olur. Aktif silis, alkali ile nemin bir araya gelmesiyle reaksiyona girerek jel kıvamında alkali silikat bileşikler oluştururlar. Bu bileşikler beton içinde şişme yapar ve betonun çatlamasına neden olurlar. Beton yapılarında ASR'nin hasara neden olan etkisi genişleme deformasyonudur.

Düşük alkali içeren çimento kullanılsa bile;

\* Betonda su nemin hareketi sonunda belli noktalarda alkali konsantrasyonu oluşursa,

\* Agregada aşırı derecede reaktif ise,

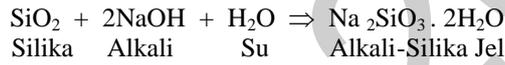
\* Betonda kullanılan mineral ve kimyasal katkıları, karma suyu ve agregadan yeterli miktarda alkali ilavesi söz konusu oluyorsa,

\* Çimento dozajının çok yüksek olması nedeniyle beton alkalinitesi çok yükseliyorsa, ASR tehlikesi söz konusu olabilir (Farny, Kosmatka,1998).

### 1.1. Alkali Silis Reaksiyonu Oluşumu

Bazı çimentoların içinde fazla miktarda bulunan sodyum oksit ( $\text{Na}_2\text{O}$ ) ve potasyum oksit ( $\text{K}_2\text{O}$ ) gibi alkali oksitler, beton boşluk çözeltisinde sodyum hidroksit ( $\text{NaOH}$ ) ve potasyum hidroksit ( $\text{KOH}$ ) oluştururlar ve aktif silis içeren agregalarla reaksiyona girerek, zamanla betonu çatlatan bir jel oluşumuna sebep olurlar (Neville,1981). ASR'nin oluşturduğu reaksiyon ürünleri aşırı derecede su emme ve genişleme özelliği olan ürünlerdir. Bu ürünler, suyu emdikçe şişip betonda içsel çekme gerilmeleri oluşturarak agregaya ile onu çevreleyen çimento pastasının çatlamasına neden olur (Farny, Kosmatka,1998).

Reaksiyonun neden olduğu genişleme belli bir sınırı aştığında beton için potansiyel bir tehlike oluşturur (Neville,1981). Beton boşluk çözeltisinde bulunan hidroksil ( $\text{OH}^-$ ) ve alkali iyonları ile beton agregası bünyesindeki bazı reaktif silis içeren malzemeler arasında oluşan reaksiyon aşağıda verilmiştir (Neville,1981).



Jelin oluşumu ve genişmesi eş zamanlı değildir. Bu nedenle jelin varlığı mutlaka ciddi boyutta ASR tahribatı oluşturacak anlamı taşımaz. Jel ileriki safhalarda su emerek hacmini artırır (Neville,1981).

ASR'nin meydana gelmesi ve hasara neden olması için aşağıdaki koşulların sağlanması gerekir;

- Betonda yeterli alkali (%0.6 fazla alkali içerik)
- Agregada zararlı etkiye neden olacak miktarda reaktif silika
- Yeterli nem

Yeterli miktarda nem bulunmasının önemi, kimyasal reaksiyon sırasında ortaya çıkan alkali-silika jelin bünyesine su emme kabiliyeti ile genişleme basıncı oluşturması ve böylece çekme gerilime neden olmasıdır. Bu nedenle ASR nedeniyle önemli ölçüde hasar, ıslak muhafaza koşullarında ve gerçek uygulamada nemli çevre koşullarında meydana gelir (Neville,1981). ASR'nin görünür dış belirtisi harita şekilli çatlaklardır (Şekil 1).



Şekil 1. Yol Bariyerinde Gözlenen ASR Çatlakları

## 2. Deneysel Çalışma

### 2.1. Çalışma Kapsamında Kullanılan Malzemeler

#### 2.1.1. Agregası

Deneysel çalışmada kullanılan agregası Sakarya Pamukova bölgesinde faaliyet gösteren kum çakıl ocağından temin edilmiş olup, 0-7 mm aralığındadır.

Agregası üzerinde öncelikle ASTM C289, TS 2517'ye uygun Kimyasal Analiz metodu yöntemiyle Aktif Silis miktarı bulunmuş ve zararlı bölgede olduğu tespit edilmiştir (Tablo 1).

Tablo 1. TS 2517'ye Uygun Yapılan Kimyasal ASR Raporu

Numunede istenen Tayinler	Alkali Agregası Reaktivitesi
<b>Analiz Sonuçları:</b> Sonuçlar aşağıdaki gibidir.	
<b>Harcanan NaOH</b>	350 (mmol/L)
<b>Çözünen Silis (SiO<sub>2</sub>)</b>	700 (mmol/L)
<b>Sonuç : TS 2517</b>	<b>III. Bölge Zararlı Agregası</b>

#### 2.1.2. Yüksek Fırın Cürufu

Yüksek Fırın Cürufu demir üretimi sırasında ortaya çıkan bir yan üründür. Ham demir üretiminde atık malzeme olarak elde edilen yüksek fırın cürufu, yüksek fırınlarda daha hafif olmasından dolayı ham demirin üzerinde kalır. Demir filizi gangi, kok ve kireç taşının yanma sonrası atıkları YFC'nu meydana getirir. YFC yavaş soğutulduğunda kristal bir yapı kazanır.

Bu haliyle bazalta benzer mekanik özelliklere sahiptir ve beton agregası olarak kullanılabilir. Öte yandan hızlı soğutma uygulaması sonucunda camı yapıda cüruf elde edilir. Bu tür cüruflar granüle yüksek fırın cürufu olarak adlandırılırlar (Tokyay ve diğ. 2002). YFC'nin hidrolik bağlayıcı özellik kazanabilmesi; cürufun kimyasal kompozisyonu, inceliği ve içerisindeki camı yapı miktarına bağlıdır (Tokyay ve diğ. 2002). Cürufu betonun dayanımı, cüruf inceliğine, aktivite indeksine ve karışım içerisindeki cüruf/çimento oranına bağlıdır (Malthora, 1987). YFC ince öğütülmüş olarak beton içerisinde kullanıldığında, işlenebilirliği artırdığı, daha az su absorbe ettiği, terlemeyi azalttığı görülmüştür (Neville, 1999).

Deneysel çalışmada kullandığımız CEM I 42,5 R tipi çimento ve yüksek fırın cürufu Bolu Çimento AŞ'den temin edilmiş olup analiz değerleri tabloda verilmiştir (Tablo 2).

Tablo 2. CEM I 42.5 R tipi çimento ve Yüksek Fırın Cürufu Analiz Değerleri

	CEM-1 42.5 R	Öğütülmüş Cüruf
SiO <sub>2</sub> (%)	19,95	35,27
Al <sub>2</sub> O <sub>3</sub> (%)	5,12	14,81
Fe <sub>2</sub> O <sub>3</sub> (%)	3,75	2,13
CaO (%)	63,82	28,79
MgO (%)	1,64	8,32
SO <sub>3</sub> (%)	3,36	0,51
Na <sub>2</sub> O (%)	0,22	0,50
K <sub>2</sub> O (%)	0,46	1,17
Na <sub>2</sub> O Eşdeğer	0,52	1,27
Kızdırma Kaybı (%)	1,11	0,21
Serbest CaO (%)	1,23	-
45 Mikron elek üstü (%)	1,9	0,20
90 Mikron elek üstü (%)	-	-
Özgül Ağırlık	3,13	2,95
Blaine inceliği (cm <sup>2</sup> /gr)	3971	5074

## 2.2. Deney Metodu ve Çalışma İçeriği

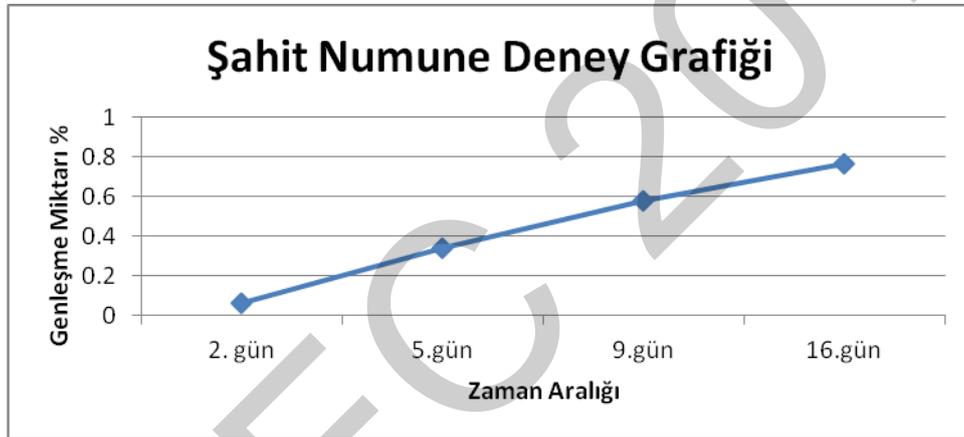
Deneyisel çalışmada ASTM C-1260 Hızlandırılmış Harç Çubuğu Yöntemi uygulanmıştır. Yukarıda analiz değerleri verilen yüksek fırın cürufu ile çimento %5, %10, %15, %20, %25, %30, %35, %40, %45 ve %50 oranlarında yer değişimi yapılarak, her gruptan 4'er numune hazırlanmıştır. Numunelere ait ilk boy 1. gün, 2.gün, 5.gün, 9.gün, 16. günlük periyotla numunelerin boy değişim ölçümleri yapılmış, bu sonuçlara bakılarak değerlendirme yapılmıştır (TS 3322- ASTM C-1260). ASTM C-1260 standardında yer alan değerlendirme kriterleri aşağıdaki gibidir.

- %0,2' den fazla genleşme olmuşsa agrega potansiyel reaktif olarak değerlendirilir.
- %0,1 - %0,2 arası genleşme olmuşsa zararsız veya potansiyel reaktif olabilir. Bu durumda genleşmelerin 28 güne kadar kaydedilmesi önerilmektedir
- %0,1'nun altında genleşme oluşuyorsa çoğu zaman agrega zararsız sayılabilir.

Deneyisel çalışmada şahit numunemizde alkali silis reaksiyonunu açıkça gözledik. 16 gün sonunda standartların belirlediği değerin çok üzerinde (% 0.76) civarında genleşme görülmüştür. Dolayısıyla kimyasal metotta belirlenen zararlı bölge sonucuna ulaşılmıştır. Numunelere ait genleşme sonuçları Tablo 3 ve Şekil 2'de oluşan çatlaklar ise Şekil 3'te sunulmuştur.

Tablo 3. Şahit Numune okuma değerleri

2. gün	5.gün	9.gün	16.gün
0,0599	0,3372	0,5785	0,7631



Şekil 2. Şahit Numune 16 günlük Boy Genleşme Yüzdeleri

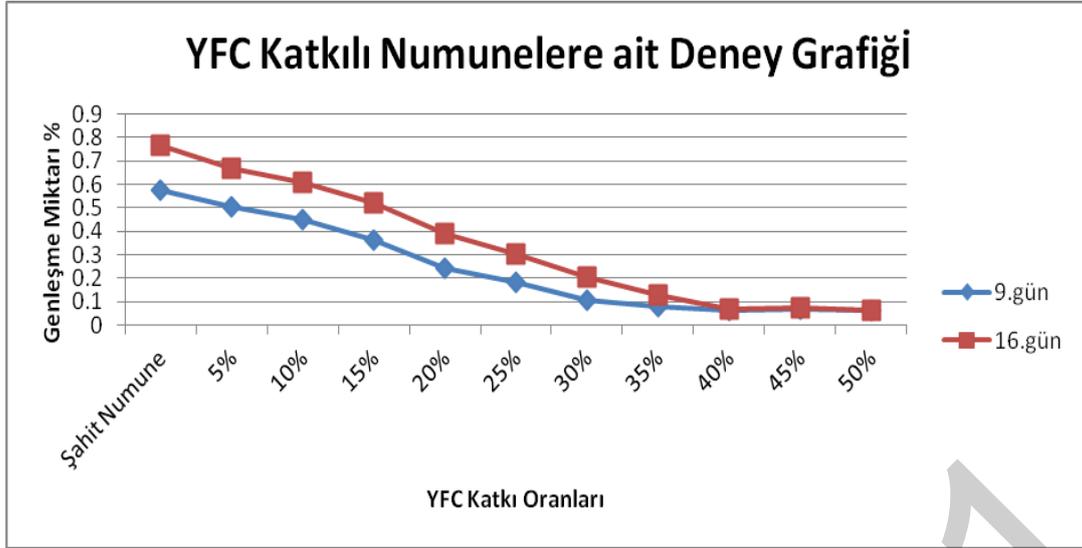


Şekil 3. Şahit Numune 16 günlük Boy Genleşme Çatlakları

Yüksek Fırın Cürufu katkı olarak hazırlanan numunelerde izlenen genleşme değerleri Tablo 4'te bu değerlerden elde edilen grafik ise Şekil 4'te sunulmuştur.

Tablo 4. YFC Katkılı Numunelere ait okuma değerleri

	Şahit Numune	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
9.gün	0,57855	0,50271	0,45156	0,361525	0,244407	0,182203	0,109661	0,077627	0,063475	0,069322	0,064181
16.gün	0,76731	0,66771	0,60661	0,522373	0,392161	0,300847	0,202542	0,130932	0,068983	0,073898	0,065085



Şekil 4. YFC Katkılı Numunelerde 16 günlük Boy Genleşme Grafiği

### 3. Sonuçlar

Deney sürecinde yapılan ölçümlerinin sonucunda; oluşturduğumuz grafiklerde şahit numuneye göre, katkıli numunelerde alkali silis reaksiyonu oluşumunun azaldığı tespit edilmiştir. Değişik oranlarda oluşturulan YFC katkıli numunelerimizde 16 gün sonunda gözlenen verilerin yorumu aşağıdaki gibidir.

- Mineral katkı olarak kullandığımız yüksek fırın cürufu ile çimento arasındaki yer değişimi % 30 olduğunda ASR'yi standart seviyede azaltmış, % 35, %40, %45 ve %50 oranında katkı kullanıldığında ASR oluşumunu standartların altında düşürdüğü tespit edilmiştir.
- Bu verilere göre; betonun durabilitesi açısından zararlı olan alkali silika reaksiyonu mineral katkı olan YFC ile belirli bir oranda azaltılabilmektedir.
- Deney süresi sonunda kontrol numunesi genleşmelerini %0.1 değerinin altına düşüren minimum katkı miktarı, kullanılabilir "emniyetli miktar" olmaktadır.
- Doğru karışımlarla hazırlanan betonlarda durabilite yönünden çok yönlü kazanımlar elde edilecektir. Buda betonarme yapıların servis ömrünü uzatacaktır.

### 4. Teşekkür

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## AN ECONOMIC SYSTEM INSPIRED BY THE HUMAN BODY

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### Abstract

In this study, by drawing analogy between various prevalent economic systems in the world and the results of their application in different countries, the researchers propose a new system called "An Economic System Based on Islamic Principles" which is inspired by the human body. The proposed system emphasizes the originality of human, Islamic values and is built on the basis of justice and non-discrimination. To determine which economic system in the world is superior, the human body was considered which is not created by the mankind. The governing rules of human body were analyzed and certain desirable economic rules were derived. Structures of the human body, the heart, cardiovascular system and the control of the brain over these regulates the body's the economic system that can be an appropriate model to design an optimal economic system. The results confirm the validity of the proposed system. And eventually five fundamental economic principles are concluded.

### Introduction

Although the economy in the eighteenth century AD, a new discipline in Great Britain and France appeared, but took two centuries to reach the threshold of scientific rationality. Before that, intuition, public opinion and mass beliefs in place were consistent with economic ideas and economic theories were unclear and vague. It has been not long time ago since anyone could use equations and certainly without the need for complex algorithms, detailed mathematical models (even without making a mistake) and integral part of today's computers that are taught in economics courses at accredited universities to teach.

No doubt, the bad and wrong economic policies during the twentieth century have brought in the damage to all nations and more sacrifices compared to any other contagious disease on the left. Communized program land in Russia during the twenties, in China during the fifties and sixties of the twentieth century in Tanzania, hundreds of millions of farmers suffered from hunger and famine. Arbitrary banning of printing money, Weimar Germany was unstable and gave rise to Nazism. Nationalizing corporations and firing investors and entrepreneurs out of work during the forty AD, Argentina's economy and a decade later, Egypt annihilated. Points "Raj" (exclusive license) in India, firms had to obtain various licenses, before they start their economic development for decades to stop construction and left millions in poverty and misery.

Even in larger scale, the twentieth century witnessed a battle between two economic systems, i.e., free market capitalism and state socialism. In the socialist system, public and collective form of property, competition and production of pre- planning was banned. In a market system, private ownership was established, to encourage competition and production is determined by entrepreneurs not government bureaucrats are. Faced with the question of what economic system was superior, nations hesitated and economists remained bipartisan.

But today the situation is completely different .When the Soviet Union disintegrated, Socialist model, which was embodied in the Soviet Union fell, it disintegrated or more because it was proved that the socialist economic system is not functioning properly. Now there is only one economic system: free market capitalism. In all countries the public sector to privatization has been assigned, money is out of government control and management has been given to independent central banks. Thanks to the deregulation of markets and open borders, competition has been made and the rate of tax giving is reduced, that has been encouraging entrepreneurs and creates new jobs.

The results were unique. Open economy and promote trade, helped to rebuild Europe after 1990 And 800 million people were out of poverty that many of them live in China, Brazil and India. Even in Africa and the Middle East Arabic, nations that accepted capitalism started to escape the terrible underdevelopment that had long dominated them. Behind all this unprecedented growth, not only the socialism state collapsed, but also the scientific

revolution in economics exists, although people still doesn't understand the whole of it, but has been increasingly embraced by policymakers around the world. This transformation began in the sixties and brings the consensus of economists who eventually founded the firm about what constitutes good policy.

There is little agreement among economists that which institutions are necessary and still less agreement on how to create them. For example, the relationship between democracy and economic development opposed to show any clear description, it seems intends to act in its own way to be transformed. Analysts also have different views about the culture; history and religion in creating the institutional conditions for growth and prosperity are less on these days. Until the sixties, many sociologists, welcomed the Max Weber's cultural determinism, believed that culture is the cornerstone of economic development. According to Weber, Confucianism is incompatible with economic growth, but growth in South Korea and Taiwan today has refuted the theory. Some say Islam prevents the development, but Turkey, Malaysia, Indonesia, are growing rapidly.

### Method

To achieve the desired appropriate economic system through the comparison of the three socialist, liberal and capitalist economic systems, and the comparison of the three systems with the Islamic economy system, we achieved an economic system inspired by the human body. Every system has always embodied in a set of principles that will underpin the specific framework for the economic activity. On the one hand, this set of principles on specific philosophical insight is based on economic activity, and on the other hand, the interactions of these principles form the framework for economic activities that are directed to the appropriate system.

Thus, every economic system has three components:

Economic philosophy is set of principles and methods of analysis that will determine the economic variables. Economic philosophy provides the intellectual basis; because includes the ideas about the production, distribution and consumption, and incorporate the principles and rules of operation that gives a boost in the form of certain theories. The economic philosophy role plays the religious position in life, man and God. The economic philosophy of Marxist ideas appears in the form of class struggle and conflict of interest, revolution and the dictatorship of the proletariat and all the principles and rules of this philosophy comes from the working class. Struggle and conflict, is the conflict philosophy that were manifested in the will and desire of the Greeks and Romans God's; and also another interpretation of the concept of divine vengeance, which tends to be attributed to the culture of Judaism and Christianity; the God that always wants to beat and terrorize and murder the man and let him not realizing the his materials and gratification.

In capitalism, the economic philosophy of "freedom" and will embody the invisible hand. The concept is that it should not be any hindrance to the realization of man's efforts to protect personal interests, and if people are given freedom to do what they want, will be coordinated between the parties. Thus, we see that the capitalist economic philosophy is based on the lack of attention to God. In this philosophy, if there is no God, the world does not need a creator, and if God exists, its removal, that created the world and set it; then trends hermitage and retirement and does not address what has created and does not interfere in the actions of creatures. The socialist system of ownership of assets particularly is limited to the assets which are used to produce goods and services. Prohibition laws are designed to fuse property assets, which everyone can be a landlord of the house and have access to needed goods. Karl Marx had believed that private ownership of the means of production, emergence and intensification of the economic elite social classes. Hence socialism is seeking to achieve a non-class community and reduction of economic inequality. On the other hand the pursuit of individual interests, especially the most profit, is in contrary with the collective spirit of socialism that has been followed. Values and social norms of socialism condemn what capitalism called, "the spirit of entrepreneurship", and that's why a private business is considered as the "black market". Socialism rejected the idea that free market economy will take care of the economic growth. Instead, rather than abandoning the market approaches to his socialist government, design, supervision and financial controls are in their hands. Socialism also rejected the idea that capitalists are producing goods that consumers are required; in capitalism, consumers don't understand the information necessary for evaluation of consumer products and are captured in the trap of advertising that capitalism has made them. Therefore it plays a small role in the national-socialist propaganda.

The second element of each economic system reveals itself in the set of rules and regulation, social institutions and legal framework that brings into the system behavior. This element consists of these issues: Set the ownership and possession of the means of production by the total public directly, or by the government due to it governs, the rules for behavior, and the lawful limits to the goods and services that are accessible, forms of economic transactions that people can do, and this set of rules apply norms of behavior for the ones who make economic decisions which the producer and consumer are also included. In capitalism we see that the "freedom" may require a minimum of government intervention and requires an absolute right to private property and freedom of occupation and freedom for all types of economic transactions and relationships and special criteria of the authenticity and genuineness of the schools are getting the benefit. In this system, as long as all kinds of manufactured goods are sold, as with all useful word meanings, both economically and morally, this product is useful.

In Marxism, ownership as a fundamental right belongs to the proletarian class which is represented by the dictatorship. This type of ownership through government ownership of the means of production and domination of the government engendered on what should be produced, how and to whom will be generated (be distributed). Interest and public interest is a fundamental standard for the system that has been imposed. Due to it, and all economic transactions between the authority determines but in Liberalism, economic liberalism maintained keeping economic freedom and privacy protection of private property and capitalism, and minimal government intervention in economic activities of individuals, or of any foreign government intervention in the economy and people.

The third element of any economic system is methodology. The method of each system is based on the basis of the system and the foundation also is made up of basic principles and rules of its special forms. In any system, there is a set of rules that following the course of action to ensure the system is necessary. In perfect competition, the rules are about the freedom of market entry and exit, and freedom of information and the size of economic units. In monopoly capitalism or large capitalism these rules give opportunity to manufacturers to determine more prices than some of the costs and openness of the raw material markets, and management of goods in their markets and restrictions on technology transfer do not visualize, unless that is contrary to the interest of the large producer. In the Marxist system, we find the rules of centrally planned program that administrative staff, led by a dictatorial leader who embodies the labor government, are doing. In short, production is controlled through this social method. A way that determines the types and quantities of manufactured goods, prices and wage levels. Each economic system is moving toward desired result and the favorable result has a relationship with the underlying philosophy; also is based on the top social priorities, such as increased welfare or justice in the distribution, individual freedom or independence, or maintain economic growth and ethics. In one hand, the evaluations of any adjustment will based on the philosophy and principles and methods of operation with the human nature, and on the other hand, its performance in achieving the priorities that are at the head of the system will evaluate it.

### **Procedure**

After we reached the differential of the economic systems, none of them realized as the full and proper procedures for handling the country's economic system. With a look at the human body and its structure that is not human-made, and only God is aware of the principles and its structure, we offer a new economic system model that brings us the amazing results.

If you consider the human body as a road map, we see that there are roads that will lead you to the downtown, the "heart". Three major parts of the circulatory system are: Blood vessels that routes blood travels, heart that pumps or pushes blood through body and blood that carries important "stuff" through body. This stuff is the essential ingredients that keep human alive. The blood is pumped by the heart through the body and circulates nutrients to all body. Meantime, there are white blood cells that fight and kill germs that may enter the bloodstream. Platelets prevent bleeding due to the injuries. All of these devices are related to each other all the time and with no interruption.

If we get a close look in economy systems, we find much resemblance with human body. Human body has a heart that controls everything that goes through artery and arterioles (routs) and it doesn't let any harm happens. White blood cells protect the body against attacks by foreign forces and Platelets avoid wasting essential materials for the body and weakening. The economic system should have a very strong controller like the heart of the body, must have an organization that controls incoming and outgoing of the system like white blood cells, and also should

have a structure to avoid ruination as what platelets do. At the end all of these organizations should have a very regular and strong relationship and feedbacks.

### Results

Comparing 4 different economic systems and comparing them with the human body, these results obtained:

1. Command (management) awake and alert (like the human heart)
2. A dynamic and active economic system ( create a centralized economic structure)
3. A widespread economic system includes public sector and private sector.
4. Precise control over all economic structures
5. Conservation and vindication of resources, property and economic facilities
6. Regular feedback and the relationship between economic systems and structures

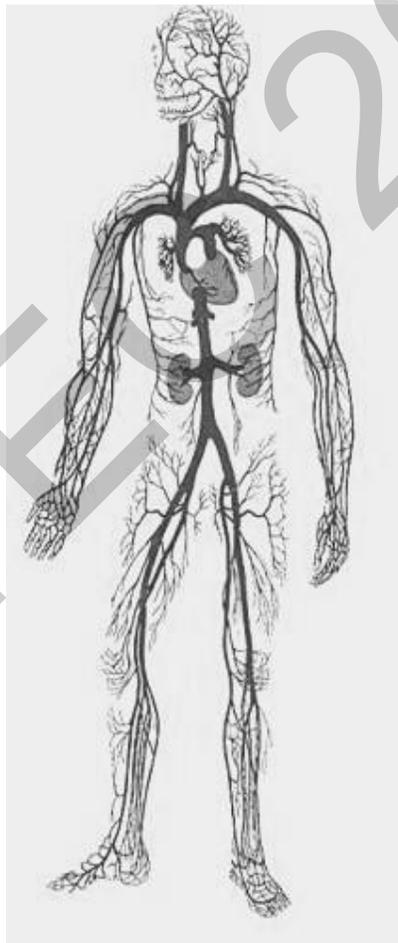


Figure1: The blood circulation system and how it goes through the body

## Conclusion

Due to the differences of each economic system that have been used separately in different countries and The results that are visible in all the countries, we came to conclusion that none of these systems are effortlessly, and have always had problems which dealing with them is very difficult.

In this research, due to the similarities in the human body with other economic organizations, we came to conclusion that as for human body that is not created by mankind, a new economic system can be introduced and due to the human body that only God knows how to make it, this economic system is absolutely perfect and if can be used as completely due to the needs of the community, this system is very suitable for modern societies.

In fact the Islamic economic system that nowadays is used in some countries such as Iran or Malaysia is somehow similar to the one we recommend. But even in those countries the Islamic economic system is not perfectly used. The new model that is based on the human body should consider justice in distribution of wealth and property. The subjective possession should be noticed and used. on one hand, the heart that flow blood throughout the body and all the organs have some of it, the society should distribute the wealth and properties among the people with justice and on the other hand the system should have a very strong and powerful custody which doesn't let the wealth goes somewhere else outside the society. If countries consider this economic system as part of their society, we hope that many problems which they face nowadays would be solved.

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# AN EMPIRICAL INVESTIGATION OF CUSTOMER SATISFACTION

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## ABSTRACT

*This research has proposed a conceptual framework to investigate the effects of customers' perceived service quality and perceived product quality on customer satisfaction. To test the conceptual framework, structural equation modeling has been used to analyze the data collected from 1530 customers shopping from 102 stores belonging to four Turkish supermarket chains in Istanbul. The results of the study indicate that perceived service quality and perceived product quality are significantly related to customer satisfaction. Customer Satisfaction Index was also obtained and investigated according to supermarket chains.*

**Keywords:** Dimensionality, Customer satisfaction index, Service quality, Product quality

## 1. INTRODUCTION

Customer satisfaction is a key issue for organizations in today's competitive market place. To improve product and service quality, and maintain customer loyalty within a highly competitive marketplace, it became a central concern for companies and organizations. A key motivation for the growing emphasis on customer satisfaction is that high customer satisfaction lead to a stronger competitive position resulting in higher market share and profit (Fornell, 1992). Customer satisfaction is also generally assumed to be a significant determinant of repeat sales, positive word-of-mouth, and customer loyalty. Satisfied customers return and buy more, and they tell other people about their experiences (Fornell, et al., 1996). Thus, dynamic structure and intense competition in retail markets especially in supermarkets increase the need for supermarket retailers to use strategies focused on customer satisfaction (Okumuş & Temizerler, 2006). The supermarket sector is characterized by increased competition, an enhanced opportunity to analyze markets, and greater shopper expectations. These aspects suggest that customer satisfaction management is especially critical and supermarket managers recognize that customer satisfaction plays a key role in a successful business strategy.

Customer satisfaction is well known and established concept in several disciplines and different types of satisfaction have been identified. In line with Oliver (1989) we perceive satisfaction as a post-consumption evaluation or "A pleasurable level of consumption related fulfillment" (Blomer, 2002). In this study we define the customer satisfaction is an affective reaction (Menon & Dubé, 2000) in which the customers' needs, desires and expectations during the course of service and product quality experience have been met or exceeded (Lovelock, 2001). Supermarkets offer a variety of products and services simultaneously so that, for the customer, there is more to visiting a store than the mere acquisition of consumption products. Differences in the "shopping experience" between retail outlets (e.g., store ambience, disposition of associates, store services) are often as important to the customer as differences in the physical characteristics of the products offered (e.g., quality) (Gómez, McLaughlin, Wittink, 2004).

The antecedents of customer satisfaction have been widely studied in the case of service companies. Results of most of the published studies identify positive influences of the perception of service quality on customer satisfaction. However, there is only a very limited number of studies examining the relationship both of the service and product quality on customer satisfaction in the supermarkets. In this study, a conceptual framework is proposed that analyses the effects of perceived service quality and perceived product quality on customer satisfaction in the supermarkets. To test the framework, structural equation modeling techniques are applied to a representative sample of four major supermarket chains in Istanbul. This paper is organized as follows: in the next section, we discuss and develop the conceptual model. We then describe the data, and we elaborate the statistical model. We conclude with the presentation of results and a discussion of possible extensions for future research.

## 2. METHODS

### 2.1. CONCEPTUAL MODEL OF CUSTOMER SATISFACTION

The conceptual framework of this study builds upon the works from several disciplines such as retailing, consumer behaviour, marketing, and psychology. The conceptual models found in the literature mainly dealt with the image in consumer/shopping behaviour, store selection, store image and different levels of evaluations embedded in satisfaction structure (Noyan & Gölbaşı Şimşek, 2011). We test the conceptual model introduced below on data collected by four large supermarket chains from their own shoppers. The proposed model has three latent variables, Perceived Service Quality (PSQ) and Perceived Product Quality (PPQ) are exogenous constructs, and Customer Satisfaction (CS) is endogenous construct based on the various areas in which the survey questions were asked. The aim of this paper is to improve empirical knowledge about the impact of supermarket satisfaction. Two distinct dimensions of perceived quality are identified: quality of service and quality of product. Our prime interest is in assessing some disregarded antecedents of customer satisfaction in terms of perceived service quality and perceived product quality.

## 2.2. DATA AND MEASURES

Data were collected from a sample of costumers of four supermarkets belonging to same Turkish store chain in Istanbul. 1530 correctly –filled-out questioners were collected across at least 15 customers per store for each of about 102 stores. The sample was found to be representative for the costumers of the local supermarket chain in terms of gender, age, number of household members ad net house hold income. The design of the questionnaire was based on multiple-item measured scales that have been validated and found to be reliable in previous research. All determinants were measured on ten-point Likert scales ranging from completely disagree to completely agree. The measurement items of the different constructs and their origin are shown in Table 1. Table 1 provides the results of the measurement model after the unreliable items were eliminated.

### *Reliability and Validity of Measures*

At the first step, Exploratory Factor Analyses (EFA) were carried out using Maximum Likelihood (ML) extraction method with Promax rotation. ML factor analysis proceeds on the assumption that the data have a multivariate normal distribution, which in turn implies that each individual variable is normally distributed. Violation of this assumption may lead to distorted factor analytic results. West and Curran (1995) suggested that the ML can produce useful results as long as the skewness of each observed variable is less than 2.0 and kurtosis is less than 7.0. It can be seen from Table 1 that all the items of PSQ, PPQ, and CS meet these criteria.

**TABLE 1. DESCRIPTIVE STATISTICS FOR THE ITEMS OF LATENT VARIABLES (N=1530)**

	Items	Mean	Std. Deviation	Skewness	Kurtosis
<b>Service Quality Perceptions ( Cronin et al., 2000)</b>					
Q1	Staff have knowledge about products and campaigns.	7.78	1.849	-1.015	.915
Q2	Staff have enough experience to help customers.	7.77	1.833	-.952	.782
Q3	Staff are affable.	7.80	1.831	-.991	.932
Q4	Staff are polite and respectful.	7.81	1.813	-.946	.770
Q5	Staff are easy to reach.	7.82	1.748	-.920	.761
Q6	Easy to communicate with staff.	7.75	1.805	-1.001	1.058
Q7	Staff give understandable responses to questions.	7.75	1.842	-.934	.738
Q8	Staff are reliable.	7.79	1.759	-.887	.697
Q9	There is a sales person who is ready to help at any moment.	7.50	1.994	-1.010	.904
Q10	Staff strive to understand my needs.	7.65	1.831	-.887	.718
Q11	Cashiers are careful.	7.76	1.829	-.997	1.063
<b>Product Quality Perceptions (Sirohi et al., 1998)</b>					
Q12	The products of vegetable-fruit department are very high in quality.	7.43	1.959	-.934	.754
Q13	The products of meat-fish department are very high in quality .	7.46	1.855	-.837	.612
Q14	Hot/frozen ready-made foods are very high in quality.	7.50	1.782	-.739	.385
Q15	The products of bakery department are very high in quality.	7.48	1.851	-.743	.269
Q16	Packaged-frozen products are very high in quality.	7.51	1.785	-.703	.307
Q17	Not packaged dried foods (dried beans, pasta, grain,...) are very high in quality.	7.60	1.808	-.899	.842
Q18	Milky products are very high in quality.	7.62	1.766	-.727	.244
Q19	There are no out-of-date products on shelves.	7.36	1.895	-.758	.346
Q20	In general, products of this supermarket are very high in quality.	7.85	1.784	-.950	.776
Q21	The products of vegetable-fruit department are very high in quality.	7.58	1.752	-.772	.618
<b>Customer Satisfaction (Brumly,2002)</b>					
Q22	I think, shopping with this supermarket is a good decision.	7.16	1.766	-.391	-.176
Q23	This supermarket takes customer satisfaction as a goal.	7.20	1.716	-.414	-.180
Q24	I am satisfied with preferring this supermarket.	7.20	1.753	-.401	-.324
Q25	I am satisfied with shopping this supermarket.	7.28	1.748	-.406	-.333
Q26	In general, I am satisfied with this supermarket.	7.23	1.757	-.444	-.163
Q27	I am satisfied with pricing to product quality by this supermarket.	7.13	1.856	-.477	-.105
Q28	I am really satisfied with this supermarket.	7.22	1.820	-.501	-.002

Factor analysts have developed a wide range of techniques that may be used to decide the number of factors to extract. Empirical investigations have shown that these techniques not always point to same number of factors and experts have recommend that analysts (a) consider the information provided by several techniques, and (b) make a final decision on the number of factors against the background of the theoretical meaningfulness and interpretability of the factors obtained (Preacher & MacCallum, 2003).

The following techniques and criteria were used to decide the number of factors to retain. These empirical criteria include the popular eigenvalues-greater-than-one (eigenvalues $>1$ ) criterion (KG; Guttman, 1954; Kaiser, 1960) and the scree test (Catell,1978), as well as the less commonly applied techniques of parallel analysis (PA; Horn,1965) and the minimum average partial test (MAP; Velicer,1976). From the result of simulation studies of Zwick&Velicer (1982,1986) and Glorfeld (1995), KG rule tends to underestimate and PA overestimate the number of factors. It is better to extract too many rather than too few factors. Underextraction leads to distortion of the extracted factors. In contrast, overextraction generally does not distort the character of the major factors (Wood, Tataryn & Gorsuch, 1996). Fortunately, there is increasing consensus among statisticians that two less well-known procedures, PA and MAP test, are superior to other procedures and typically yield optimal solutions to number of factor problem (Wood et al., 1996; Zwick & Velicer, 1982, 1986). These procedures are statistically based, rather than being mechanical rules of thumb. In PA, the focus is on the number of factors that account for more variance than the components derived from random data. The MAP test uses a principal components analysis followed by an examination of a series of matrices of partial correlations. Specifically, on the first step the first principal component is partialled out of the correlations between the variables of interest, and the average squared coefficient in the off diagonals of the resulting partial correlation matrix is computed. On the second step, the first two principal components are partialled out of the original correlation matrix and the average squared partial correlation is again computed. These computations are conducted for (number of items-1) steps, where p is the number of variables. The number of components is chosen to be the step number in the analyses that resulted in the average squared partial correlation. O'connor (2000) wrote codes for SAS and SPSS for the PA and MAP procedures. After examination all of the above procedures, scree plot in Figure 1, KG rule and PA analysis with its results given in Table 2, and the MAP test showed three factors solution.

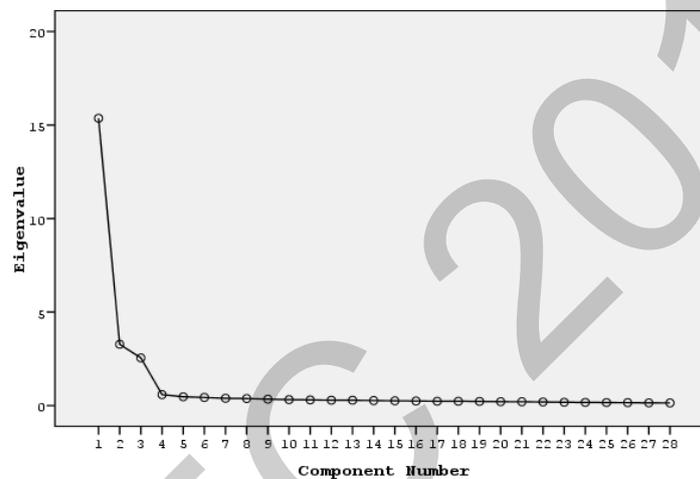


FIGURE 1. SCREE PLOT

TABLE 2. RAW DATA EIGENVALUES, MEAN & 95 % RANDOM DATA EIGENVALUES

Root	Raw Data	Means	95%
1	15.362805	1.25872	1.28798
2	3.276793	1.22092	1.24454
3	2.547975	1.19358	1.2114
4	0.585774	1.17214	1.18694
5	0.471483	1.15014	1.16676
6	0.434512	1.13256	1.14657
7	0.388863	1.11386	1.13045
8	0.377663	1.09594	1.11087
9	0.342143	1.07905	1.09317
10	0.318059	1.06347	1.07933
11	0.30225	1.04796	1.06116
12	0.288822	1.03206	1.04577
13	0.285798	1.01695	1.02958
14	0.26725	1.00077	1.01468
15	0.255466	0.98555	0.99751
16	0.243713	0.97171	0.98197
17	0.231403	0.95881	0.97387
18	0.230225	0.94329	0.95594
19	0.22358	0.92805	0.94083

20	0.210547	0.91341	0.92491
21	0.204868	0.89917	0.91362
22	0.194927	0.88424	0.8966
23	0.178643	0.86899	0.88017
24	0.171382	0.85126	0.86496
25	0.160737	0.83492	0.84892
26	0.156878	0.81655	0.83146
27	0.146141	0.79659	0.8155
28	0.1413	0.76935	0.79237

Going forward to three factors solution, Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy was .977 indicating higher sampling adequacy. The first factor accounted for 54.867 %, the second factor accounted for 11.703% and third factor accounted for 9.100% of the total variance. These three factors accounted for 75.670% of the total variance. The communality values of observed variables ranged from .595 to .835. Pattern loadings are shown in Table 3, which are noticeable higher on underlying factor indicating construct validity from the exploratory points of view.

**TABLE 3. PATTERN LOADINGS**

items	Factors		
	PSQ	PPQ	CQ
Q1	<b>.874</b>	.028	-.046
Q2	<b>.889</b>	.016	-.021
Q3	<b>.901</b>	-.031	.019
Q4	<b>.898</b>	-.030	.018
Q5	<b>.903</b>	-.023	.014
Q6	<b>.905</b>	-.022	.005
Q7	<b>.909</b>	-.007	.009
Q8	<b>.854</b>	.001	.033
Q9	<b>.797</b>	.044	-.011
Q10	<b>.831</b>	.044	-.021
Q11	<b>.755</b>	.055	.037
Q12	-.046	<b>.877</b>	-.021
Q13	-.021	<b>.892</b>	-.023
Q14	.025	<b>.906</b>	-.053
Q15	.031	<b>.885</b>	-.024
Q16	.013	<b>.886</b>	-.013
Q17	.020	<b>.824</b>	.010
Q18	.005	<b>.818</b>	.039
Q19	-.058	<b>.813</b>	.019
Q20	.116	<b>.610</b>	.132
Q21	.056	<b>.788</b>	.056
Q22	.003	.051	<b>.864</b>
Q23	.012	.064	<b>.843</b>
Q24	.009	.019	<b>.892</b>
Q25	-.009	.007	<b>.914</b>
Q26	-.018	.019	<b>.889</b>
Q27	.028	-.072	<b>.901</b>
Q28	.004	-.027	<b>.911</b>

The second goal of the study in order to reach acceptable measurement model, was to confirm that each measure taps facets of the three latent constructs (convergent validity) and that the constructs are distinct from each other (discriminant validity). Confirmatory Factor Analysis (CFA) was used for establishing the validity of the constructs.

Unidimensionality is a necessary condition for reliability and construct validation (Mak & Sockel, 2001, p.271). The unidimensionality of the constructs was analyzed by specifying a measurement model for each construct. According to Jöreskog and Sörbom (1993), a goodness of fit index (GFI) of 0.90 or above suggests that each of the construct is unidimensional.

Convergent validity is examined by using the Bentler-Bonett normed fit index (NFI) (Bentler & Bonett, 1990). As seen from the Table 4, all of the construct have GFI and NFI values above 0.90 indicating that all of the construct are unidimensional and,

convergent validity was achieved for all the construct. Acceptable model fits are indicated by goodness of fit indices, and RMSEA (Root Mean Square Error of Approximation) values below 0.08 and, SRMR (Standardized Root Mean Square Residual) below 0.05 represent an acceptable model fit (Browne & Cudeck, 1992)

**TABLE 4. GOODNESS OF FIT INDICES FOR UNIDIMENSIONAL CONSTRUCTS**

Latent Constructs	GFI	NFI	RMSEA	SRMR
PSQ	0.94	0.97	0.085	0.019
PPQ	0.91	0.96	0.11	0.029
CS	0.98	0.99	0.064	0.011

In assessing discriminant validity the factor correlation matrix given in Table 5 was examined, and showed that three factors did not overlap substantially. To test discriminant validity, CFA was performed on selected pair of scales, allowing correlation between two construct. The analysis was rerun with the correlation the two constructs fixed at 1. A chi-square difference tests were conducted for these unrestricted and restricted models. The results suggest that for three pairs of constructs, the two-factor solutions were better than the single factor solutions ( $p < 0.01$ ).

**TABLE 5. INTERCORRELATIONS OF THE LATENT CONSTRUCTS**

	PSQ	PPQ	CS
PSQ	1		
PPQ	0.61	1	
CS	0.57	0.62	1

The factor loadings and construct reliabilities for the measurement model are presented in Table 6. The individual item loadings (lambdas) on the constructs were all highly significant ( $p < 0.001$ ,  $t$  value  $> 10$ ) with values ranging from 0.733 to 0.901. All the individual scales exceeded the recommended minimum standards proposed by Bagozzi and Yi (1988) in terms of construct reliability (composite reliability greater than 0.70). Şimşek & Noyan's (2012) generalized theta coefficient  $-\theta_G$  for composite reliability of the total scale was 0.9614, which indicates high reliability of total scores.

**TABLE 6. STANDARDIZED CFA COEFFICIENTS AND CONSTRUCT RELIABILITY**

Constructs	Items	Loadings	t	Item Reliability ( $R^2$ )	Constructs Reliability
PSQ	Q1	0.850	*	0.723	0.968
	Q2	0.876	46.401	0.768	
	Q3	0.885	47.252	0.783	
	Q4	0.882	46.959	0.778	
	Q5	0.890	47.788	0.792	
	Q6	0.885	47.295	0.783	
	Q7	0.900	48.882	0.810	
	Q8	0.860	44.788	0.739	
	Q9	0.792	38.933	0.628	
	Q10	0.825	41.662	0.681	
	Q11	0.784	38.247	0.614	
PPQ	Q12	0.815	*	0.665	0.956
	Q13	0.851	40.543	0.724	
	Q14	0.880	42.735	0.774	
	Q15	0.881	42.821	0.776	
	Q16	0.878	42.603	0.771	
	Q17	0.818	38.184	0.668	
	Q18	0.823	38.581	0.678	
	Q19	0.753	33.951	0.567	
	Q20	0.733	32.707	0.537	
	Q21	0.837	39.569	0.701	
CS	Q22	0.879	*	0.773	0.959
	Q23	0.870	48.589	0.757	
	Q24	0.897	51.869	0.804	
	Q25	0.901	52.513	0.813	
	Q26	0.871	48.698	0.759	
	Q27	0.845	45.779	0.714	
	Q28	0.875	49.154	0.765	

\*Fixed parameter for scaling purpose

*Structural Model*

The reliability and validity analysis results indicate that the scales for the constructs appear to have satisfactory measurement qualities. After measurement model was built, a structural model with latent variables considered adding proposed structural paths between latent constructs. The proposed model was analyzed via ML estimation using covariance matrix of observed variables as input. Table 7 reports goodness of fit indices, parameter estimates and their t- values for the structural model. The overall ( $\chi^2_{(347)} = 1935.72, p < 0.01$ ), which is expected given the large sample size (Bagozzi & Yi, 1988). All other goodness of fit indices are within the acceptable ranges (GFI=0.91, AGFI=0.90, SRMR=0.031, CFI=0.96, NFI=0.96, NNFI=0.96, RMSEA=0.058 and, CN=325.81). All of the fit indices indicate that the proposed model exhibits good fit to the data.

**TABLE 7. SUMMARY OF THE RESULTS FROM PROPOSED MODEL**

Path	Estimate	Standard Error of Estimate	Standardized Estimate	t-value
PSQ → CS	0.307	0.027	0.311	11.563*
PPQ → CS	0.415	0.027	0.427	15.290*
Squared Multiple Correlation (SMC) = 0.44				
$\chi^2_{(347)} = 1935.72, p < 0.01$				
Goodness of Fit Index (GFI) = 0.91				
Adjusted Goodness of Fit Index (AGFI) = 0.90				
Standardized Root Mean Square Residual (SRMR)= 0.031				
Comparative Fit Index (CFI) = 0.96				
Normed Fit Index (NFI) = 0.96				
Non-Normed Fit Index (NNFI) = 0.96				
Root Mean Square Error of Approximation (RMSEA) = 0.058				
Critical N (CN) = 325.81				
*p<0.01				

In accordance with the parameter estimates shown in Table 7, Perceived service quality and Perceived product quality have direct positive and significant effects on Customer satisfaction. From standardized estimates, the effect of Perceived service quality was lower than the effect of Perceived product quality, their effects on Customer satisfaction were comparable in terms of magnitude. From the SMC value in Table 8, 44% variance of Customer satisfaction was explained by Perceived service quality and Perceived product quality, which indicates a fairly high level of explanatory power.

**3. DISCUSSION AND CONCLUSIONS**

The main purpose of this study was carried out modeling Customer Satisfaction using Perceived Service Quality and Perceived Product Quality as exogenous latent constructs. A well fitting structural and accompanying measurement models were developed. It was concluded that Perceived Service Quality and Perceived Product Quality affect Customer Satisfaction positively, and their effects on Customer Satisfaction were comparable in terms of effect sizes. Therefore, policy makers in Turkish retailing sector should be consider Service Quality as well as Product Quality to provide satisfied customers. We also obtained Customer Satisfaction Index (CSI) using the Structural Equation Modeling (SEM) approach. To investigate positions of four different supermarkets chain (labeled by A,B,C and, D), they were grouped into two classes as economy class and non-economy class supermarkets according to their customer profile, brand and variety of products. As for the analysis of group (classes of economy vs. non-economy) differences, Kruskal-Wallis Tests were performed following evidence on factorial invariance. Table 8 shows the test results and suitable descriptive statistics of supermarkets.

**TABLE 8. COMPARISONS OF FOUR DIFFERENT SUPERMARKET CHAINS**

Index	Groups	N	Mean Rank	Rank Order	Chi-Square	df	p
PSQ	Economy A	405	712.25	4	23.641	3	.000
	Economy B	405	853.86	1			
	Non-Economy C	450	741.34	3			
	Non-Economy D	270	753.10	2			
PPQ	Economy A	405	710.30	4	29.955	3	.000
	Economy B	405	711.06	3			
	Non-Economy C	450	850.88	1			
	Non-Economy D	270	787.66	2			
CS	Economy A	405	836.42	1	17.314	3	.001
	Economy B	405	771.01	2			
	Non-Economy C	450	722.47	4			
	Non-Economy D	270	722.58	3			

According to Kruskal-Wallis Tests, the group differences of PSQ, PPQ and, CS indexes were found statistically significant (p<0.01). As seen from the above Table, economy class supermarkets have higher Customer Satisfaction Index while they have lower Perceived Product Quality Index. On the other hand, non-economy class supermarkets with lower Perceived

Service Quality Index have lower Customer Satisfaction Index. The second conclusion can be made from the above results that, the single strategy (such as Service Quality or Product Quality going alone) is not enough to achieve customer satisfaction. And it is clear that, some other determinants of customer satisfaction in addition to PSQ and PPQ should be required.

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# AN ETHNOBOTANICAL SURVEY OF MEDICINAL PLANTS IN THE HODNA (SOUTH EAST OF ALGERIA)

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**ABSTRACT:** This study aimed to identify wild plants collected for medical purposes by the local people of HODNA, located in the south east Region of Algeria, and to establish the uses and local names of these plants, using ethnobotanical survey list, information is gathered through personal interviews with traditional medical practitioners, community elders and patients. Field study was carried out over a period of approximately three years (2008–2010).

A total of 104 plants belonging to 47 families were identified in the region and employed in the traditional medical practice of the people. Ailments such as diabetes, eczema and leishmaniose are mostly treated with the medicinal plants. Details pertaining to the preparation and administration of plant drugs are provided.

The survey provides a veritable source of information for traditional medical practitioners and medicinal plant researchers. These medicinal plants may be incorporated into the healthcare delivery system of the country.

**Keywords:** Ethnobotany; Medicinal plants; Hodna region; Algeria.

## 1. Introduction

Algeria is one of the richest countries in the world in terms of plant diversity<sup>1</sup>. HODNA region located in the south east of Algeria has a rich flora, due to its variable climate and high number of ecological zones. This diversity in flora provides a rich source of medicinal plants, which has long been utilized by the local people, and hence accounts for the accumulation of remarkable medicinal folk knowledge in the region. Documentation of the indigenous knowledge through ethnobotanical studies is important for the conservation and utilization of biological resources<sup>2</sup>. Majority of the Algerian people living in rural areas traditionally use plants. Generally, they use plants for nourishment and medical purposes. The traditional knowledge in Hodna region is passed verbally from generation to generation and valuable information can be lost whenever a traditional medical practitioner passes without conveying his traditional medicinal plants knowledge. As a result, the need to perform ethnobotanical researches and to document the medicinal plants and the associated indigenous knowledge must be an urgent task.

## 2. MATERIALS AND METHODS

### 2.1 Study area

The region of M'sila, occupies a privileged position in the central part of northern Algeria. As a whole, it is part of the highlands of central and covers an area of 18,718 km<sup>2</sup> and it is located at an altitude of 500 m, is situated between 35° 42' 07" N 4° 32' 49"E . The climate of the investigation area is continental, due in part to the Saharan influences. Summer is hot and dry while winter is very cold, with low and irregular rainfall; it is of the order of 100 to 250 mm /year<sup>3, 4</sup>. Morphology and its geographical position gives this region a unified ecological aspect represented by the predominance of the steppe, which covers 1.2 million ha (63% of the total area) of the state. The areas used for agriculture accounts for 20% of the total area devoted mainly to cereals, to arboriculture and market gardening.

### 2.2 Ethnobotanical surveys

The surveys were conducted during the period 2008-2010. A questionnaire was administered to the local people (traditional medical practitioners, community elders and patients), through face-to-face

interviews. During the interviews, demographic characteristics of the study participants and local names, utilized parts and preparation methods of the plants were recorded. The ethnobotanical surveys were conducted in the entire M'sila region in order to have as much information regarding the traditional use of medicinal plants by local people because of their knowledge entnomédicinales.

### 3. Results and discussion

Informants identified 104 plants belonging to 47 families that are used for the treatment of various diseases (Table 1).

Table 1: Some medicinal plants reported in M'sila.

Family	Scientific name	local name	Plant part use	Mode of uses
Lamiaceae	<i>Marrubium vulgare</i> L	Merriout	aerial	Infusion
	<i>Teucrium polium</i> L	Khyatta	aerial	Decoction, powder
	<i>Salvia officinalis</i>	Souak en abi	aerial	Decoction, powder
	<i>Ajuga iva</i> Schreber	Chendgoura	aerial	Infusion, decoction
	<i>Ocimum basilicum</i>	Lehbak	aerial	infusion, decoction
Asteraceae	<i>Artemisia obsinthium</i> L	Chadjret meriem	aerial	Infusion, decoction, maceration
	<i>Cynara scolymus</i> L.	khorchouf	leave	powder
	<i>Cynara cardunculus</i> L.	Khorchouf lakhla	leave, root	decoction
	<i>Artemisia herba alba</i> .Asso	Chih	aerial	infusion, maceration
	<i>Cichorium intybus</i>		aerial	decoction
	<i>Erigeron canadensis</i>	Chicoria Chih errabii	aerial	infusion
Poaceae	<i>Stipa Tenacissima</i> L.	Halfa	leave	Powder, decoction
	<i>Hordeum vulgare</i> L	Chair	seed	powder
Liliaceae	<i>Allium sativum</i> L.	Thoum	bub	Mastication
	<i>Allium cepa</i> L.	El basla		maceration
Cupressaceae	<i>Juniperus oxycedrus</i>	Tagua	leave	Tisane
Myrtaceae	<i>Eucalyptus globulus labil</i>	Calitous	leave	Infusion
Geraniaceae	<i>Geranium robertianum</i> L.	Ibrat erraii	whole plant	Decoction
Brassicaceae	<i>Lepidium sativum</i> L.	Habb errechad	Seeds, leaves	Powder, decoction
		ou horf		
Oleaceae	<i>Olea europaea</i> .L	Zitoune	leaves, oil	decoction
Fabaceae	<i>Trigonella faenum_graecum</i> L	Helba	seed	decoction
Moraceae	<i>Morus nigra</i>	Toute	leaves	decoction
Zygophyllaceae	<i>Peganum harmala</i>	Harmel	seeds	Decoction, infusion, powder
			aerial	

Medicinal plants are usually used internally or externally which depends on the illness. The internal use of the medicinal plants consisted mainly of drugs used to relief stomach ache, back ache and muscle pain as well as constipation, cough, asthma and kidney stones. The external use of medicinal plants in this area consisted mainly of drugs for inflammation and irritations of the skin (skin cracks, bruises, frostbite, scorpion bite and insect bite).

Decoction or infusion is almost the common method of preparation of medicinal plants to be used internally, however, without knowing neither the real differences between the two methods nor their effect on the final product. Other methods of preparation and use were recorded like direct applications in the form of powdered plant material, paste or in the form of vapor inhalation. Almost all the external remedies prepared from medicinal plants are prepared in olive oil, mainly in the form of decoction.

It was noted that the Lamiaceae family is number one species identified (13.28%). The plant parts most commonly used are the aerial parts (29.31%), leaves (15.51%), flowers (12.64%)...

#### 4. CONCLUSION

The survey shows that a large number of medicinal plants are used in M'sila (Hodna) for treating different ailments. The knowledge of the use of plants to treat diseases has been with the people for generations but has not been recorded. This knowledge remains mostly with the traditional medical practitioners who are mostly old people. In addition to their medicinal uses, some of these plants have other uses. The local population should be educated on sustainable methods of harvesting plants to treat diseases today without compromising their availability for future use.

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# AN INTEGRATION METHOD FOR L1 GPS RECEIVER AND MEMS IMU BASED ON DUAL FILTERS

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**Abstract:** To combine a GPS receiver and an inertial measurement unit, loosely-coupled and tightly-coupled integration methods have been most-widely utilized. The loose-coupled method is advantageous in implementation simplicity but bears theoretically undesirable filter-driven-filter problem and the tightly-coupled method is advantageous in theoretical soundness but imposes computational burden since large number of system states need to be utilized by the integration filter. This paper proposes a new integration method adopting dual filter architecture. In the proposed integration method, one filter is based on carrier-smoothed-code filtering in position domain and the other filter is based on traditional Kalman filtering. In the proposed dual filter integration method, computational burden is reduced by distributed processing and the filter-driven-filter problem is avoided since raw measurements are utilized as the input to each filter. The accuracy of the proposed method is evaluated by an experiment utilizing field-collected real measurements.

**Keywords:** GPS, inertial measurement unit, integration, filter.

## 1. Introduction

As compared with positioning systems, navigation systems need to estimate velocity and attitude in addition to position. For the reason, it can be understood that navigation is more complex problem than positioning with a theoretical point of view since more state need to be estimated. For positioning, Global Positioning System (GPS) receivers are widely used nowadays. By a GPS receiver, any user can easily obtain position information with meter- or centimeter-level accuracy. However, due to the intrinsic weakness of radio signals to signal path blocking, multipath, interference, and jamming (Colombo 1986; Akim and Tuchin 2003; Jefferson and Bar-Sever 2000), it is not guaranteed to obtain reliable positioning results at any time.

As compared with GPS receivers, inertial navigation systems (INSs) provides velocity and attitude in addition to position. An INS processes signals from a set of self-contained inertial sensors or an inertial measurement unit (IMU). Inertial sensors are advantageous for navigation since they are not affected by radio signal environment (Titterton 1997; Farrell and Barth 1999; Hong et al. 2004).

In addition, they can track detailed high-speed dynamics. However, their errors grow exponentially with time if aiding sensors are not utilized to bound error magnitudes. For the reason, the integration of an IMU with a GNSS receiver has been considered as the ideal combination for navigation applications. By the integration, the advantageous characteristics of two different sensors can be combined to provide accurate position, velocity, and attitude at high output rate with feasible accuracy.

To integrate an IMU and a GPS receiver, the loosely-coupled (LC) and tightly-coupled (TC) methods have been widely utilized. The LC method is advantageous in implementation simplicity but bears theoretically undesirable filter-driven-filter problem and the TC method is advantageous in theoretical soundness but imposes computational burden since large number of system states need to be utilized by the integration filter.

Motivated by the comparison result, this paper proposes a new integration method adopting dual filter architecture. In the proposed integration method, one filter is based on carrier-smoothed-code (CSC) filtering in position domain and the other filter is based on traditional Kalman filtering. In the proposed dual filter integration method, computational burden is reduced by distributed processing and the filter-driven-filter problem is avoided since raw measurements are utilized as the input to each filter. The accuracy of the proposed method is evaluated by an experiment utilizing field-collected real measurements.

## 2. Summary of Strapdown Inertial Navigation

An INS can be classified into one of the two categories. One is the gimbled-INS (GINS) and the other is the strapdown INS (SINS). A GINS utilizes a stabilized platform where gyroscopes and accelerometers are mounted. The stabilized

platform is torqued to maintain its attitude independently of the vehicle movements utilizing gyroscope outputs. By integrating the accelerometer outputs, the velocity and position of the vehicle are obtained. The attitude is obtained by measuring angles between the stabilized platform and the vehicle body. As compared, an SDINS does not utilize the stabilized platform. Instead, an IMU containing gyroscopes and accelerometers is directly attached to the vehicle's body. The attitude of the vehicle is computed by processing gyroscope outputs. By integrating the accelerometer outputs transformed by the attitude, the velocity and position of the vehicle are obtained. The simplest SINS equations are summarized as follows.

Latitude, Longitude, Height :

$$\dot{L} = \frac{V_N}{R_L + h}, \quad \dot{l} = \frac{V_E}{R_l + h \cos L}, \quad \dot{h} = -V_D \quad (1)$$

Velocity :

$$\dot{V}^n = [\dot{V}_N \quad \dot{V}_E \quad \dot{V}_D]^T = C_b^n f^b - [2(\omega_{ie}^n \times) + (\omega_{en}^n \times)]V^n + g^n \quad (2)$$

Attitude :

$$\dot{C}_b^n = C_b^n (\omega_{ib}^b \times) \quad (3)$$

where

$\omega_{ib}^b$  : angular rate provide by strapdown gyroscopes

$f^b$  : specific force provide by strapdown accelerometers

$g^n = [0 \quad 0 \quad g_0]^T$  : gravity

$(\omega_{ab}^c \times)$  : skew-symmetric matrix constructed by  $\omega_{ab}^c$

$$\omega_{ie}^n = [\Omega_N \quad 0 \quad \Omega_D]^T = [\Omega \cos L \quad 0 \quad -\Omega \sin L]^T \quad (4)$$

$$\omega_{en}^n = [\rho_N \quad \rho_E \quad \rho_D]^T = \left[ \frac{V_E}{R_l + h} \quad -\frac{V_N}{R_l + h} \quad -\frac{V_E \tan L}{R_l + h} \right]^T \quad (5)$$

$$R_L = \frac{R_0(1-e^2)}{(1-e^2 \sin^2 L)^{3/2}}, \quad R_l = \frac{R_0}{(1-e^2 \sin^2 L)^{1/2}} \quad (6)$$

$g_0$  : gravity constant

$\Omega$  : earth rotation rate

$R_0$  : earth radius constant

$e$  : eccentricity of the earth

Though GINSs are highly-accurate, less accurate SINSs are more widely utilized nowadays due to several factors such as low cost, easy maintenance, and modularity brought by micro-electromechanical systems (MEMS) technology.

### 3. GPS/INS Integration by Dual Filters

To combine a GPS receiver and an inertial measurement unit, Kalman filters are widely utilized for optimal sensor integration. Based on the continuous-time modeling by Eqs. (1-6), the initialization, the time propagations and the measurement updates of discrete-time Kalman filters are implemented as follows.

Time Propagation :

$$\bar{X}_{k+1} = F_k \hat{X}_k : a \text{ priori state estimate} \quad (7)$$

$$\bar{P}_{k+1} = F_k \hat{P}_k F_k^T + Q_k : a \text{ priori error covariance} \quad (8)$$

Measurement Update :

$$Z_k = Y_k - H_k \bar{X}_k : \text{indirect measurement (measurement residual)} \quad (9)$$

$$K_k = \bar{P}_k H_k^T (H_k \bar{P}_k H_k^T + R_k)^{-1} : \text{Kalman gain} \quad (10)$$

$$\hat{X}_k = \bar{X}_k + K_k Z_k : a \text{ posteriori state estimate} \quad (11)$$

$$\hat{P}_k = (I - K_k H_k) \bar{P}_k (I - K_k H_k)^T + K_k R_k K_k^T : a \text{ posteriori error covariance} \quad (12)$$

According to the difference in measurement types and Kalman filter states, the integration methods are classified into the LC and TC integration methods. In the LC method, position solutions provided by GPS receivers are utilized as the measurement  $Y_k$  and the Kalman filter includes position error, velocity error, attitude error, accelerometer bias, and gyroscope drift as the filter states (Pitman 1962; Benson 1975; Lee et al. 1998).

$$X_k = X_{INS} = \left[ \delta L \quad \delta l \quad \delta h \quad \delta V_N \quad \delta V_E \quad \delta V_D \quad \psi_N \quad \psi_E \quad \psi_D \quad \nabla_x \quad \nabla_y \quad \nabla_z \quad \varepsilon_x \quad \varepsilon_y \quad \varepsilon_z \right]^T \quad (13)$$

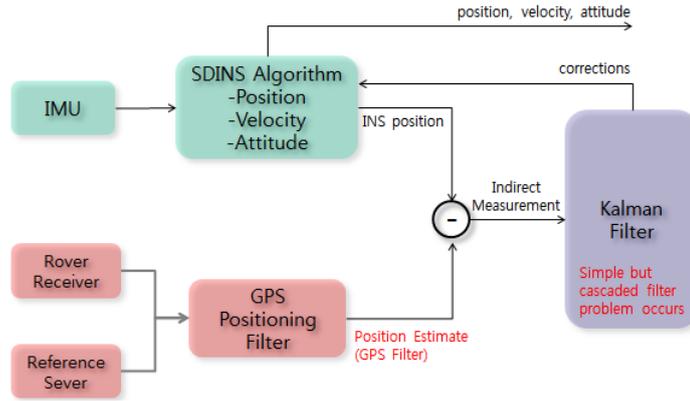


Fig. 1 Configuration of loosely-coupled GPS/SINS integration

The configuration of the LC method is shown in Fig. 1. The indirect measurement  $Z_k$  is formed by differencing the GPS position solution and the position estimate provided by INS as follows.

$$Z_k = \begin{bmatrix} L_{GPS} \\ l_{GPS} \\ h_{GPS} \end{bmatrix} - \begin{bmatrix} \bar{L} \\ \bar{l} \\ \bar{h} \end{bmatrix} = \begin{bmatrix} \delta \bar{L} \\ \delta \bar{l} \\ \delta \bar{h} \end{bmatrix} + \varepsilon_k \quad (14)$$

$\varepsilon_k$  : error contained in the GPS position solution at the  $k$  – th time step

One critical problem of the LC integration is that the GPS position error  $\varepsilon_k$  is not white due to the pre-filtering performed in the GPS receiver or the temporally-correlated atmospheric errors contained in GPS position solutions. This causes a filter-driven-filter or cascaded-filter problem. As a result, the following condition is not satisfied which corresponds to the fundamental assumption imposed on the measurements utilized by Kalman filters.

$$E(\varepsilon_k \varepsilon_{k+1}) \neq O \quad (15)$$

where the symbols  $E(\bullet)$  and  $O$  denote the statistical expectation and the zero matrix of appropriate dimension.

In the TC method, GPS pseudoranges and carrier phases are utilized to form the measurement vector  $Y_k$  instead of the position solution provided by the GPS receiver. The TC Kalman filter includes the pseudorange and carrier phase errors in addition to the inertial navigation errors.

$$X_k = \begin{bmatrix} X_{INS}^T & X_{GPS}^T \end{bmatrix}^T \quad (16)$$

$$X_{GPS} = [\delta b \ \delta PR_1 \ \delta PR_2 \ \dots \ \delta PR_{N_s} \ \delta CR_1 \ \delta CR_2 \ \dots \ \delta CR_{N_s}]^T \quad (17)$$

$\delta b$  : GPS clock bias

$\delta PR_j$  : pseudorange error with respect to the  $j$  – th satellite

$\delta CR_j$  : carrier phase error with respect to the  $j$  – th satellite

$N_s$  : total number of satellites

The indirect measurement  $Z_k$  is formed by differencing the GPS measurements and their equivalents computed based on state estimates.

$$Z_k = \begin{bmatrix} PR_1 \\ PR_2 \\ \vdots \\ PR_J \\ CR_1 \\ CR_1 \\ \vdots \\ CR_J \end{bmatrix}_{GPS} - \begin{bmatrix} PR_1 \\ PR_2 \\ \vdots \\ PR_J \\ CR_1 \\ CR_2 \\ \vdots \\ CR_J \end{bmatrix} = H_k \bar{X}_k + v_k \quad (18)$$

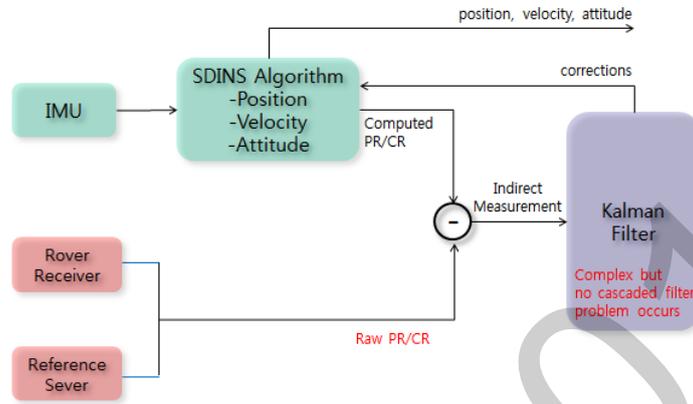


Fig. 2 Configuration of tightly-coupled GPS/SINS integration

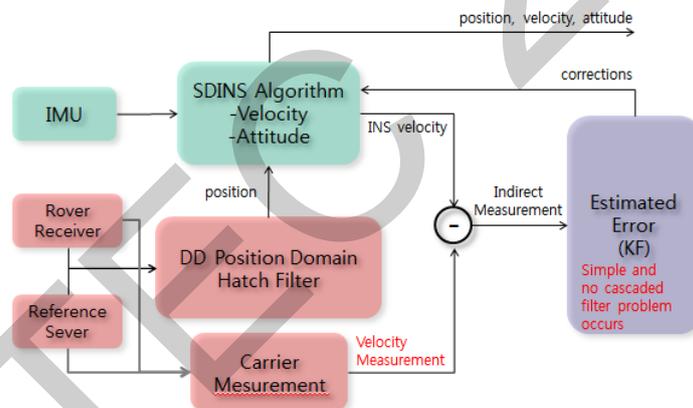


Fig. 3 Configuration of proposed GPS/SINS integration based on dual filters

- $PR_j / CR_j$  : pseudorange/carrier phase with respect to the  $j$ -th satellite provided by the GPS receiver
- $\overline{PR}_j / \overline{CR}_j$  : pseudorange/carrier phase estimate with respect to the  $j$ -th satellite compute by state estimates
- $v_k$  : error contained in the GPS measurements at the  $k$ -th time step

The configuration of the TC integration method is shown in Fig. 2. Due to the utilization of raw measurements and the inclusion of GPS errors into the filter states, the troublesome filter-driven-filter problem can be eliminated.

$$E(v_k v_{k+1}) = 0 \quad (19)$$

However, as shown in Eq. (16), the total number of filter states are largely increased. At maximum, the number of states can be increased to  $15(INS)+2*32(GPS)=79$ . This increased number of states would impose heavy burden to navigation computers.

As explained until now, both the LC and TC integration methods bear advantages and disadvantages at the same time. This study is motivated to find an appropriate integration method to combine only the advantages and remove disadvantages of the conventional GPS/INS integration methods. One key idea to solve this problem was found in CSC

filtering (Hatch 1982; Hwang and Brown 1990; Lee et al. 2005; Lee et al. 2008). The CSC filtering is unique in precise GPS applications and it is more beneficial than the Kalman filtering if only positioning accuracy is concerned. Without measurements updates, Kalman filter errors increase monotonically. However, CSC filter errors do not increase due to the precise time propagation based on carrier phase measurements instead of incomplete dynamic modeling or inertial sensor outputs.

Based on the background explained above, this paper proposes a new GPS/INS integration method for low-cost L1 GPS receivers and MEMS IMUs. The proposed method utilizes two different filters as shown in Fig. 3. In the proposed method, the CSC filter takes the role of accurate position estimation and the Kalman filter estimates the rest of INS error states. The INS computes only the velocity and attitude at high rate. The high rate INS velocity, combined with accurate but low rate GPS position, enables generating high rate position outputs. By distributing filter states into two filters as

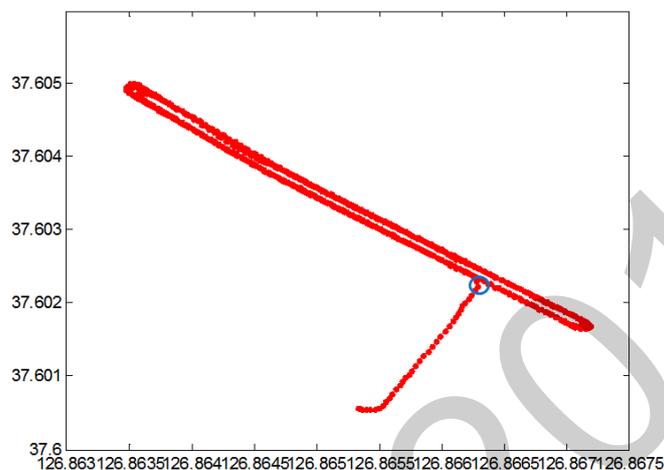


Fig. 4 Trajectory for experiment

explained, computational burden of the proposed method is reduced when compared with that of the TC method. Since the Kalman filter utilizes accurate GPS velocity formed by carrier-phase measurements, the filter-driven-filter problem also does not occur.

#### 4. Experiment

To evaluate the proposed integration method, an experiment was performed utilizing field-collected real measurements. For the experiment, two Ublox AEK-4T receivers are utilized for differential positioning. A low-grade Xsens IMU was utilized to provide inertial measurements. The experiment was performed during 40 minutes. To process outputs from the two GPS receivers and the single IMU, a software was developed by modifying GAFAS engine (Lee 2005).

The focus of this experiment is to assess the accuracy of high rate position estimates combining the dual filter outputs. At each integer multiple of seconds, the double differencing (DD) position domain (PD) Hatch filter (Kim 2008) generates the low rate GPS position estimates. Meanwhile, the SINS algorithm processes high rate MEMS IMU outputs to generate high rate velocity estimates by the velocity-aided Kalman filter. Whenever a position estimate by the DD PD Hatch filter is generated, it is utilized as the initial value of the high rate position estimates. Until the next DD PD Hatch filter output, the position estimates are extrapolated by the SINS velocity.

During the experiment, satellite visibility was good enough to obtain cm-level position estimates by the DD PD Hatch filter. Thus, if the high rate INS velocity estimates were accurate, the trajectory extrapolating the low rate GPS position estimates by the INS velocity would be continuous without abrupt jumps. If the INS velocity estimates were not accurate enough, many abrupt jumps would result in the high rate GPS/INS trajectory. Fig. 4 shows the whole experiment trajectory and Fig. 5(a) shows the magnified trajectory corresponding to the area marked by the circle in Fig. 4. As shown in Fig. 5(a), the low rate GPS trajectory and the high rate GPS/INS trajectory cannot be discriminated due to the low resolution of the figure though magnified.

Fig. 5(b) shows the more magnified details of the area marked by the rectangle in Fig. 5(a) so that the two different trajectories can be discriminated sufficiently. In Fig. 5(b), the trajectory combining straight lines corresponds to the low rate GPS position estimates and the continuous trajectory corresponds to the high rate GPS/INS position estimates. As shown in Fig. 5(b), the high rate GPS/INS trajectory does not show discontinuous jumps which would appear if the velocity estimates by the Kalman were not accurate. The accurate velocity can only be obtained when the Kalman filter achieves the accurate estimation of the other states such as attitude, accelerometer bias, and gyro drift.

## 5. Conclusions

This paper proposed a new GPS/INS integration method based on dual filter architecture. In the proposed integration method, one filter is based on carrier-smoothed-code filtering and the other filter is based on traditional Kalman filtering. In the proposed dual filter integration method, computational burden is reduced by distributed processing and the filter-driven-filter problem is avoided since raw measurements are utilized as the input to each filter. The accuracy of the proposed method is evaluated by an experiment utilizing field-collected real measurements. By the experiment result, it was shown that the proposed integration method can provide accurate position estimates at high output rate even when low cost L1 GPS receivers and MEMS inertial sensors are utilized.

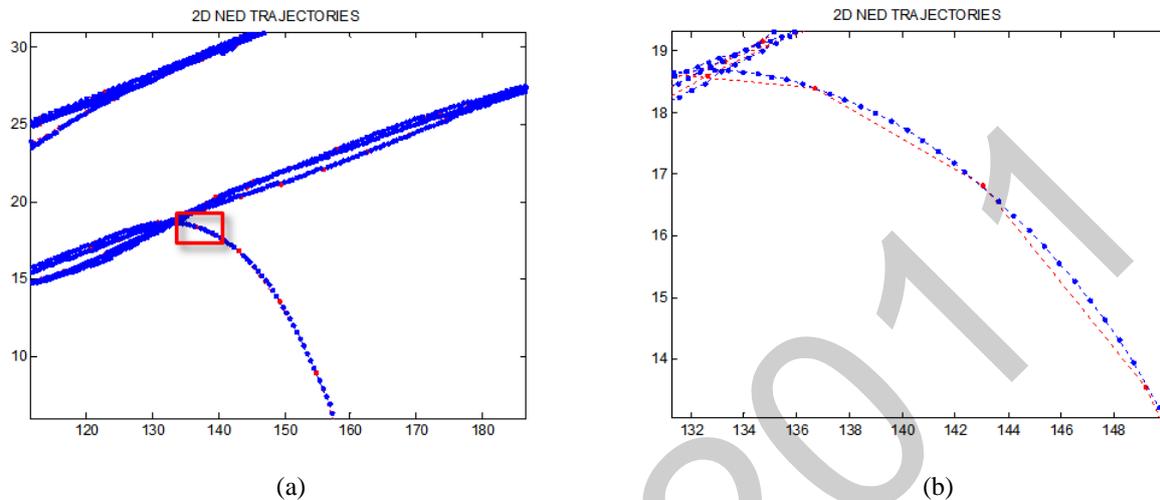


Fig. 5 Magnified trajectory to check the accuracy of high rate position outputs

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## ANTIBACTERIAL ACTIVITY AND PHYTOCHEMICAL SCREENING OF THE METHANOLIC AND ETHANOLIC EXTRACTS OF *LIPPIA CITRIODORA*.

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### ABSTRACT:

The methanolic and ethanolic extracts of *Lippia citriodora* were tested for their antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Helicobacter pylori* and *Pseudomonas aeruginosa*. Our results showed that the ethanolic extract was the most active against these pathogens. Its phytochemical screening indicated that it contained mainly five flavonoids. Among them, the quercetin-3-O-glucoside was the most active against the five microbial species tested, but the synergism between the identified apigenin, quercetin-3-O-glucoside and kaempferol-3-O-glucoside gave a best minimal inhibitory concentrations.

**Keywords:** *Lippia citriodora*, extracts, antibacterials, flavonoids.

### INTRODUCTION:

Several plants were widespread for their many therapeutic and pharmaceutical virtues, especially anti-infectious and preventive against different diseases. These benefits provide form their big content on bioactive compou (Cushnie, Hamilthoh, & Lamb, 2003; Siess, Le Bon, & Canivence, 2000). In our work, we had tried to determinate the antibacterial activity of *L. citriodora*. Then, we had realised a phytochemical screening in order to determinate the principal bioactive compounds presents in the methanolic and ethanolic extracts. This activity had been selected because of its great medicinal relevance (Hamil et al., 2003).

### MATERIAL AND METHODS:

The plant came from the area of El Aouana, Jijel (Algeria). This verbenaceae was identified in the botanical department as the voucher specimen Mo-S03 (University Mentouri, Constantine, Algeria). The bacteria used came from the laboratories of microbiology and infectious in Mohammed Ben-Yahia's hospital (Jijel, Algeria).

**Preparation of the extracts:** The plant materials (powdered) were extracted with methanol by using a Soxhlet apparatus and with aquous ethanol (80 %) by maceration. The obtained extracts were filtered and evaporated respectively to give the crude dried extract.

**The antibacterial activity:** We used the diffusion method on agar (Osato 2009). This activity was carried out on Muller-Hinton (Institute Pasteur, Algiers, Algeria) with incubation at 37°C during 12 H.

**The phytochemical screening:** We carried out a separation of the compounds present in the ethanolic extract by partitions between solvents (Markham, 1982). Then, a phytochemical screening was carried out using chemical methods and thin-layer chromatography (TLC) (Wagner & Bladt, 1996) and the isentification of flavonoids was carried out using a series of spectral analyses (Mabry, Markham, & Thomas 1970; Markham, 1982; Voirin, 1983). In the case of the identification of the glycosyl flavonoids, an acid hydrolysis was realized by heating in the presence of HCl in a bath water. The aglycone was recovered by confrontation (partition) with diethylic ether and was identified by UV- visible spectrophotometry and Co-TLC with control substances. The remaining carbohydrates were then concentrated and subjected to Co-TLC. The revelation was carried out by malonate of aniline and heating at 100% in the incubator.

### RESULTS:

**The extracts antibacterial activity:** The results showed that the ethanolic extract was more active than the methanolic extract (table I). In fact, the first one was able to inhibit the growth of *S. aureus*, *K. pneumoniae* and *H. pylori* with minimal inhibitory concentrations (MICs) of 0,190 mg/ml, 0,170 mg/ ml and 0,100 mg /ml respectively (Table 1).

Table 1: MICs values recorded by each extract (mg/ml).

	<i>E. coli</i>	<i>S. aureus</i>	<i>K. pneumoniae</i>	<i>P. aeruginosa</i>	<i>H. pylori</i>
Ethanolic extract	-	0,190	0,170	-	0,100
Methanolic extract	-	-	0,260	-	0,180

**The phytochemical screening:** The phytochemical analysis of the separate compounds showed that the ethanolic extract contained mainly phenol acids and flavonoids. Only five flavonoids were present in sufficient quantities for the identification by the spectral analysis: The first compound was thus a luteolin mono-substituted. Its acid hydrolysis released glucose and luteolin. It was thus a luteolin-O-7-glucoside. For the second compound, it released two glucoses and a luteolin. It was thus a luteolin-O-3', 7-diglucoside. The third compound was an aglycone apigenin. The forth and fifth compounds were successively quercetin and kaempferol mono-substituted. Their acid hydrolysis released glucose and quercetin for the fourth compound and glucose and keampferol for the fifth. So, they were successively quercetin-3-O-glucoside and kaempferol-3-O-glucoside (Table 2).

Table 2: MICs values recorded for the identified flavonoids (mg/ml).

	Luteolin-7-O-glucoside	Luteolin-3', 7-O-diglucoside	Apigenin	Kaempferol-3-O-glucoside	Quercetin-3-O-glucoside	Synergism
<i>E. coli</i>	-	-	0,100	0,105	0,090	0,0070
<i>S. aureus</i>	0,080	0,080	0,075	0,075	0,075	0,0090
<i>K. pneumoniae</i>	0,100	0,105	0,090	0,090	0,060	0,0065
<i>P. aeruginosa</i>	-	-	0,090	0,095	0,070	0,0060
<i>H. pylori</i>	0,060	0,060	0,040	0,040	0,035	0,0030

**The flavonoids antibacterial activity:** These five flavonoids identified gave an inhibition of all the species with MICs varying between 0,105 mg/ml and 0,035 mg/ml. Only the luteolin-7-O-glucoside and the luteolin-3',7-O-diglucoside did not have an action on the growth of all the tested species. The aglycone apigenin and kaempferol-3-O-glucoside inhibited three species with the same MICs: *S. aureus*, *K. pneumoniae* and *H. pylori*. For the two other species, these molecules gave slightly different MICs. But the quercetin-3-O-glucoside gave for each bacteria the lowest MIC. Yet, the synergism between these three most active flavonoids gave a best antimicrobial activity against the five species (Table 2).

#### DISCUSSION:

The high antibacterial effect of the ethanolic extract of *L. citriodora* is due to its high content on flavonoids. In this work, the phytochemical analysis of the separate compounds showed that the ethanolic extract contained mainly phenol acids and flavonoids. In fact these compounds are known for their strong antimicrobial activity (Cushnie, Hamilthoh, & Lamb, 2003; Martini, Katerere, & Eloff, 2004). Other studies carried out before showed that discovered flavonoids were frequently present at various medicinal plants (Okamura, Haraguchi, Hashimoto, & Yagi 1994; Fecka & Turek, 2007).

The antibacterial activity of the identified flavonoids was more significant than that of the ethanolic and methanolic extracts. This could be explained by the fact that the active compounds were present in big amount in the ethanolic extract. Only *E. coli* and *P. aeruginosa* were not sensitive to all our extracts. They had in particularly shown a resistance to the ethanolic extract and the identified luteolins whatever the nature of their substitutions. A previous work gave similar results for all the tested bacteria except for *E. coli*. Indeed, this species was perfectly sensitive to the luteolins extracted from the olives '*alcaparra*'. This indicated that our plant was not adapted to treat the infections caused by these bacteria (Sousa et al. 2006). The synergism of the aglycone apigenin, quercetin-3-O-glucoside and kaempferol-3-O-glucoside was the most active against the studied microorganisms. However, *H. pylori* was the most sensitive species to the all the tested extracts. The lowest MIC recorded for this species was of 3µg/ml. This could indicate that weak concentrations in these extracts were sufficient to limit, and even to eliminate completely the infections caused by this microorganism. So, the flavonoids of *L. citriodora* allowed the inhibition of some microorganisms that may be causal agents of human urinary, intestinal, gastric and respiratory tract infections; indicating thus that they could be used to cure these diseases. The extracts of this plant gave an inhibition of *H. pylori* with very low concentrations, but required stronger values to stop the growth of *E. coli* and *P. aeruginosa*.

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## ANTIBACTERIAL AND ANTIFUNGAL EFFECTS OF THREE ZINGIBERACEAE ESSENTIAL OILS ON SOME SELECTED MICROBIAL ISOLATES

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### ABSTRACT

Essential oil from three Zingiberaceae species were extracted using dichloromethane, and isolated by hydro-distillation. Volatile components of all extracts were analyzed by gas chromatography - mass spectrometry. (GC-MS). Results showed that cycloisolongifolene, 8,9-dehydro-9-formyl (35.29%) and dihydrocostunolide (22.51%) were the major compounds present in *Curcuma aeruginosa* oil. Similarly caryophyllene oxide (18.71%) and caryophyllene (12.69%) were the major compounds found in *Curcuma mangga* oil whilst 2,6,9,9-tetramethyl-2,6,10-cycloundecatrien-1-one (60.77%) and  $\alpha$ -caryophyllene (23.92%) were found in *Zingiber cassumunar* oil, respectively. GC-MS analyses had identified a total of 58 compounds in the three Zingiberaceae species, with 16 compounds belonging to *C. aeruginosa*, 27 compounds from *C. mangga*, and 15 compounds from *Z. cassumunar*. These essential oils were rich in sesquiterpenes and monoterpenes. In terms of antimicrobial activity, *C. mangga* essential oil displayed the highest and most broad-spectrum activity amongst the three essential oils by inhibiting the growth on all bacteria and fungi. *C. aeruginosa* displayed moderate antimicrobial activity and inhibited all microorganisms except the *Pseudomonas aeruginosa*. However, *Z. cassumunar* oil had the least activity as it shown a weak inhibition on *Streptococcus aureus* and *P. aeruginosa*. The results of this study suggest that the essential oils of *C. mangga* and *C. aeruginosa* have potent antimicrobial properties that may be useful in many applications such as for food preservation, pharmaceuticals and natural therapies.

**Keywords:** Antibacterial; Antifungal; *Curcuma aeruginosa*; *Curcuma mangga* ; *Zingiber cassumunar*;

### INTRODUCTION

Plant oils and extracts have been used for a wide variety of purposes for many thousands of years (Jones, 1996). For the past decade the essential oils have been screened for their potential uses in herbal medications. Anwar et al. (2009) suggested that the spread of drug-resistant pathogens is one of the biggest threats to successful treatment of microbial diseases. Similarly, the consumption of food contaminated with food-borne microorganisms can pose a serious threat to human health.

Essential oils are becoming increasingly popular as natural antimicrobial agents to be used for a wide variety of purposes. At present essential oils are used by the flavoring industry for flavor enhancement and for their antioxidant effect. However, the potential use of these oils as natural antimicrobial agents has been less explored (Consentino et al., 2003). In Malaysia about 3,200 species of higher plants are reported to have medicinal values and some of them have been used in various traditional health treatment (Jantan, 1998). According to Chen et al., (2008) many Zingiberaceous plants have been reported for their biological usage such as antifungal, antioxidant, insecticidal, and anti-inflammatory activities. The more common species from this family such as ginger (*Zingiber officinale*) and turmeric (*Curcuma longa*) which have been extensively studied. Our study on the antimicrobial activity of the essential oils of three Zingiberaceae species namely *C. aeruginosa*, *C. mangga* and *Z. cassumunar* was because we found no report on these species which are grown in east Malaysia until to-date.

## METHODS AND PROCEDURES

### 2.1 Plant materials

Rhizomes of *C. aeruginosa*, *C. mangga* and *Z. cassumunar* were obtained fresh from a local wet market in Kuantan, Pahang. These plants were identified by a botanist from the Universiti Putra Malaysia.

### 2.2 Essential oil extraction

Fresh rhizomes were thoroughly washed and dried at room temperature. Rhizomes were chopped into small cubes and weighed. A sample of 966 g, 1806 g, and 1687 g of each *C. mangga*, *C. aeruginosa*, and *Z. cassumunar* rhizomes respectively, were subjected to steam distillation for a minimum of 6 hours using a Clevenger-type apparatus at atmospheric pressure of 101.33 kPa. Distillate (aqueous phase) was extracted with dichloromethane (DCM). The organic phase was dried over anhydrous sodium sulphate, filtered, and the solvent was then separated from the oil using the rotary evaporator. The essential oils were stored at 4°C until used.

### 2.3 GC-MS analysis

The analyses of the volatile compounds were carried out using the Perkin Elmer AutoSystem XL gas chromatograph equipped with Elite-5 fused-silica capillary column (inner diameter 30 m x 0.32 mm, 0.25 µm film thickness), which was directly coupled to the TurboMass Gold mass spectrometry of the same company (Perkin Elmer Inc., Connecticut, USA). The equipment were conditioned and programmed according to the required parameters. The carrier gas was helium at a flow rate of 5 mL/min. The initial temperature was set at 50°C with continuous increment of 4°C/min until reaching final temperature at 250°C. Consequently, 5 µL of the essential oil which was dissolved in 495 µL of solvent (1:100 v/v), was injected into the column automatically. DCM was used as a solvent to dissolve both oils of *C. mangga* and *C. aeruginosa* whilst absolute ethanol was used to dissolve *Z. cassumunar* oil. The essential oil components were identified by comparing their mass spectra with the National Institute of Standard and Technology (NIST) mass spectral database library. The composition of the oil was reported as relative percentage of the total peak area, using the following calculation: Relative % of peak area = (Area of the peak / Total peak area) x 100

### 2.4 Antimicrobial screening

#### 2.4.1 Test microorganisms

Six microbial isolates which were obtained from the Institute of Medical Research Kuala Lumpur was used in this study. They were two Gram-positive bacteria (*Bacillus cereus* ATCC11778 and *Staphylococcus aureus* ATCC25923), two Gram-negative bacteria (*Escherichia coli* ATCC35218 and *Pseudomonas aeruginosa* ATCC27853), and two fungi (*Candida albicans* ATCC10231 and *Cryptococcus neoformans* ATCC90112).

#### 2.4.2 Disc-diffusion method

The disc-diffusion method was employed for the determination of antimicrobial activity of the essential oils, according to the methods suggested by the National Community for Clinical Laboratory Standards (NCCLS, 2001).

#### 2.4.3 Determination of minimum inhibitory concentration (MIC)

Essential oils that showed significant antimicrobial activity in the disc-diffusion method were chosen for determination of MIC using the broth microdilution method against the same microorganisms, as described by Skočibušić et al. (2006) with slight modifications. Broth microdilutions were performed in Mueller Hinton Broth (MHB), with the exception of the fungal strains in Potato Dextrose Broth [PDB].

#### 2.4.4 Determination of minimum bactericidal or fungicidal concentration (MBC/MFC)

To determine MBC/MFC, all wells that showed no visible growth were sub-cultured on either MHA (for bacteria) or PDB (for fungi) using sterile cotton swabs. The agar plates were then incubated at the appropriate temperature and time. The lowest concentration of oil or antibiotic on the plate that exhibits complete killing of the microorganism was considered as the MBC or MFC. MBC or MFC is defined as the lowest concentration of the essential oil or antibiotic at which inoculated bacteria or fungi were completely destroyed.

## RESULTS AND DISCUSSION

### 3.1 Essential oil yields

Steam distillation of the rhizomes produced different yields of oils from the three plants. All essential oils possess strong and characteristic aromatic fragrances. The rhizomes of *Z. cassumunar* gave the highest yield of oil (0.30% w/w), followed by *C. aeruginosa* (0.19% w/w) and *C. mangga* (0.12% w/w), as tabulated in Table 1.

Table 1. Yield and appearance of the essential oils.

Botanical name	Common name	*Yield (% w/w)	Color or appearance
<i>Curcuma aeruginosa</i>	Pink and blue ginger	0.19	Thick black
<i>Curcuma mangga</i>	Mango ginger	0.12	Thick yellow
<i>Zingiber cassumunar</i>	Cassumunar ginger	0.30	Clear yellow

\*[Weight of the essential oil (g) / Weight of the rhizomes (g)] x 100

### 3.2 Chemical composition of *C. aeruginosa* essential oil

GC-MS analysis of the *C. aeruginosa* oil has identified 16 compounds in the oil. Sesquiterpenes dominated the chemical composition of the oil, as it made up 94.08% of the oil, while the rest of its chemical profile was made up of oxygenated monoterpenes (5.92%). Zwaving & Bos (2006) reported that the essential oils of *C. aeruginosa* rhizomes from Indonesia and India contain high percentages of curcumanolides A, B (11.4%), curcumenol (9.9%), dehydrocurdione (9.4%), and isocurcumenol (8.5%). Jarikasem et al. (2003) found that the rhizomes from Thailand contain curzerenone (41.63%) and eucalyptol (9.64%) as the major compound.

### 3.3 Chemical composition of *C. mangga* essential oil.

Twenty seven compounds were identified in the *C. mangga* essential oil of which sesquiterpenes (52.67%) and monoterpenes (31.44%) were the major compounds. Wong et al., (1999) has reported *C. mangga* essential oil from a different area in Malaysia were consisted mainly of monoterpenes instead of sesquiterpenes. Myrcene (78.68%) was the majoritary compound in their sample, with small traces of (E)- $\beta$ -ocimene (5.1 %),  $\beta$ -pinene (3.7%), and pinene (2.9%).

### 3.4 Chemical composition of *Z. cassumunar* essential oil

*Z. cassumunar* essential oil shown the presence of 15 compounds which consisted mainly of sesquiterpenes (98.78%) and small amounts of monoterpenes (1.22%). The sesquiterpenes dominating the oil were 2,6,9,9-tetramethyl-2,6,10-cycloundecatrien-1-one (60.77%) and  $\alpha$ -caryophyllene (23.92%). Caryophyllene oxide made up 6.44% of the oil, while the rest of the components were only present in small individual abundances or trace amounts.

### 3.5 Common compound in the essential oils

Caryophyllene (C<sub>15</sub>H<sub>24</sub>), which is a bicyclic sesquiterpene, was found to be the only common compound present in all three species investigated in this study. It was present in small amounts in all three essential oils, with the highest percentage in *C. mangga* oil (12.69%), followed by *Z. cassumunar* (2.03%) and *C. aeruginosa* (1.01%).

### 3.6 Antimicrobial activity

The antimicrobial activity of the essential oils against selected microorganism were assessed by the presence or absence of inhibition zones and determining the MIC and MBC/MFC values. In general, the three Zingiberaceae essential oils displayed varying degrees of antimicrobial activity against the tested microorganisms. Results of the disc-diffusion assay [Table 2] indicated that *C. mangga* essential oil had the strongest activity, whilst *C. aeruginosa* had moderate activity, and *Z. cassumunar* showed no activity against most of the microorganisms tested. *S. aureus* was the most sensitive bacteria since it was inhibited by all essential oils, and *P. aeruginosa* was the most resistant bacteria since the oils showed either weak or no inhibition towards it.

Table 2. Antimicrobial activity of the three *Zingiberaceae* plants essential oils by the disc-diffusion method.

Microorganisms	Zone of inhibition of (mm)			Positive control	Negative control
	<i>C. aeruginosa</i>	<i>C. mangga</i>	<i>Z. cassumunar</i>		
<b>Gram-positive</b>					
<i>B. cereus</i>	7.0 ± 0.0	10.0 ± 0.0	-	17.0	-
<i>S. aureus</i>	9.3 ± 0.4	13.5 ± 0.7	8.5 ± 0.0	23.0	-
<b>Gram-negative</b>					
<i>E. coli</i>	7.5 ± 0.0	9.0 ± 0.0	-	23.0	-
<i>P. aeruginosa</i>	-	7.0 ± 0.0	7.5 ± 0.0	13.0	-
<b>Fungi</b>					
<i>C. albicans</i>	8.8 ± 0.4	14.8 ± 0.4	-	18.0	-
<i>C. neoformans</i>	7.0 ± 0.0	10.3 ± 0.4	-	10.5	-

*C. mangga* essential oil showed a broad-spectrum activity as it was the only oil that successfully inhibited the growth of all tested microorganisms. For this oil, the Gram-positive bacteria were more sensitive towards it compared to the Gram-negative bacteria, as bigger ZOI was produced. The two fungi *C. albicans* and *C. neoformans* were also highly susceptible towards the *C. mangga* oil, with ZOI ≥10 mm (strongly inhibitory). Overall, *C. albicans* was the most sensitive microorganism as the largest ZOI (14.8 ± 0.4 mm) was produced, and this was followed by *S. aureus* (13.5 ± 0.7 mm).

On the other hand, *Z. cassumunar* essential oil only displayed weak or no antimicrobial activity. It failed to inhibit the growth of the Gram-positive *B. cereus*, Gram-negative *E. coli*, as well as the two fungi, *C. albicans* and *C. neoformans*. It has been reported that the DCM and methanol extracts of *Z. cassumunar* rhizome and root were also inactive against *E. coli* and *C. albicans* (Habsah, 2000). However, the *Z. cassumunar* oil in the present study was slightly inhibitory towards *P. aeruginosa* (7.5 ± 0.0 mm), which was resistant or slightly resistant to the other essential oils. This oil also displayed moderate activity against the Gram-positive *S. aureus* (8.5 ± 0.0 mm).

### 3.7 MIC and MBC/MFC of *C. mangga*

Essential oils that showed significant ZOI (≥10 mm) against tested microorganisms in the disc-diffusion assay were chosen for further determination of the MIC and MBC/MFC, using the broth microdilution assay. Since only the *C. mangga* essential oil showed significant ZOI of ≥10 mm, it is the only oil that was further investigated. The microorganisms that showed high sensitivity towards the *C. mangga* oil were the Gram-positive bacteria (*B. cereus* and *S. aureus*), and the fungi (*C. albicans* and *C. neoformans*).

MIC and MBC/MFC results [Table 3] indicate that the *C. mangga* oil had different levels of activity against the microorganisms. The inhibitory properties of the oil were observed within a range of concentrations from 0.02 to 33.30 µL/mL. In liquid medium the essential oil was active against all the Gram-positive bacteria and fungi. It is noted that the MIC and MBC/MFC value of the *C. mangga* oil was the same, which suggests that the oil is both inhibitory and bactericidal or fungicidal at a single concentration.

Table 3. Antimicrobial activity of *C. mangga* essential oil against sensitive microorganisms by the broth microdilution method.

Microorganisms	<i>C. mangga</i> essential oil		Positive control	
	MIC (µL/mL)	MBC/MFC (µL/mL)	MIC (mg/mL)	MBC/MFC (mg/mL)
<b>Gram-positive</b>				
<i>B. cereus</i>	11.1	11.1	0.002	0.12
<i>S. aureus</i>	1.2	1.2	0.01	0.12
<b>Fungi</b>				
<i>C. albicans</i>	3.7	3.7	0.12	0.37
<i>C. neoformans</i>	0.1	0.1	0.37	0.37

Positive control: Tetracycline or nystatin

Maximum activity of the *C. mangga* essential oil was observed against the fungi *C. neoformans*, which had the lowest MIC and MFC value of 0.1  $\mu\text{L}/\text{mL}$ . This is followed by *S. aureus* (1.2  $\mu\text{L}/\text{mL}$ ) and *C. albicans* (3.7  $\mu\text{L}/\text{mL}$ ). *B. cereus* needed the highest MIC and MBC value, which was 11.1  $\mu\text{L}/\text{mL}$ . This suggests that it was the least susceptible microorganism in this assay, as it needed a higher oil concentration before it can be inhibited and completely killed.

The susceptibility of the microorganisms in this assay was different to that observed in the disc-diffusion assay. In the disc-diffusion assay, the susceptibility of the microorganism was *C. albicans* > *S. aureus* > *C. neoformans* > *B. cereus*, with *C. albicans* being the most susceptible microorganism. However, in the broth microdilution assay, the susceptibility was as follows: *C. neoformans* > *S. aureus* > *C. albicans* > *B. cereus*, with *C. neoformans* being the most susceptible. These differences occurred due to the variation in diffusibility of the essential oil compounds in the disc-diffusion assay. Rios et al. also observed similar inconsistencies between disc-diffusion assay and MIC determination, and concluded that the disc-diffusion method is not reliable enough to be used as a definitive method for determining the strength of antimicrobial activity [21]. The determination of MIC and MBC/MFC is regarded as a more precise evaluation of antimicrobial property, since those determinations are more sensitive than the agar disk diffusion assay.

### CONCLUSION

Steam distillation had successfully yielded 0.19%, 0.12%, and 0.30% of the *C. aeruginosa*, *C. mangga*, and *Z. cassumunar* essential oil respectively. The oils were found to have different fragrances and appearance. GC-MS analyses identified a total of 58 compounds in the three Zingiberaceae species, with 16 compounds belonging to *C. aeruginosa*, 27 compounds from *C. mangga*, and 15 compounds from *Z. cassumunar*. It was found that the essential oils were rich in sesquiterpenes and monoterpenes.

In terms of antimicrobial activity, *C. mangga* essential oil displayed the highest and most broad-spectrum activity amongst the three essential oils, by successfully inhibiting the growth of all bacteria and fungi. *C. aeruginosa* displayed mild antimicrobial activity and inhibited all microorganisms except the Gram-negative *P. aeruginosa*. *Z. cassumunar* oil had the least activity as it only showed weak inhibition of *S. aureus* and *P. aeruginosa*. The results of this study suggest that the essential oils of *C. mangga* and *C. aeruginosa* have potent antimicrobial properties that may be useful in many applications, such as food preservation, pharmaceuticals, and natural therapies. However, further phytochemical and pharmacological studies are necessary to isolate the bioactive compound(s) and study their mechanisms of action.

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# ANTIMICROBIAL AND ANTIOXIDANT ACTIVITIES OF THAI LOCAL FRUIT EXTRACTS: APPLICATION OF A SELECTED FRUIT EXTRACT, *PHYLLANTHUS EMBLICA* LINN. AS A NATURAL PRESERVATIVE IN RAW GROUND PORK DURING REFRIGERATED STORAGE

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## ABSTRACT

Crude methanolic extracts of Thai local fruits including *Ardisia polycephala* Wall. (pirangasa), *Elaeocarpus hygrophilus* Kurz. (makoknum), *Limonia acidissima* Linn. (maquid or elephant apple), *Phyllanthus emblica* Linn. (makampom or Indian gooseberry), *Garcinia schomburgkiana* Pierre. (madan) and *Averrhoa carambola* Linn. (mafueng or star fruit) were tested for their antimicrobial and antioxidant activities. Fruit extracts of madan, makampom and makoknum had higher antimicrobial activity, while the extracts of makampom, pirangasa and makoknum had stronger antioxidant activity compared to the others. Then, the extract of makampom (0.25–2.0%) was used as a natural preservative in raw ground pork during refrigerated storage at 4°C. This extract at 2.0% was the most effective to decrease the number of total viable counts and total *Pseudomonas* in raw ground pork. After 12-day storage at 4°C, total viable counts and total *Pseudomonas* in ground pork samples added with 2.0% makampom extract had low survival rate of 23.27% and 2.06%, respectively. These raw ground pork samples had acceptable appearance with 5.52 pH value. Moreover, addition of 2.0% makampom extract was the most effective to delay lipid oxidation by slowing down the increasing of thiobarbituric reactive substance (TBARS) value of raw ground pork. Then, the chilled raw ground pork added with 2.0% makampom extract was used to produce a seasoned ground pork product. After duo-trio testing, some of 12 taste panels could not detect flavor of this fruit extract in the product.

**Keywords:** fruit extract, *Phyllanthus emblica*, antimicrobial, antioxidant

## INTRODUCTION

Fruit is important as a natural source of antioxidant. Many fruits are rich in some active compounds such as phenolic compounds, vitamins,  $\beta$ -carotene and others which have an important role in antioxidant activity. Some tropical fruits have been reported to have antioxidant activity such as star fruit (*Averrhoa carambola*) (Lim et al., 2007) and Indian gooseberry (*Phyllanthus emblica* or makampom) (Pinsuwan et al., 2007). Epidemiological studies have shown that many phytonutrients in fruits have potentially protective effects against many diseases including cancer, diabetes and cardiovascular diseases caused by oxygen radicals. Phytochemical antioxidants might prevent the oxidative damage (Blasa et al., 2010). In addition, some fruits was reported to have antimicrobial activity (Mayachiew and Devahastin, 2008). However, antioxidant and antimicrobial activities of some other Thai local fruits was unknown.

Fruit of *P. emblica* is available in several countries of Southeast Asia. Its extract has been reported to possess antioxidant, antimicrobial, antidiarrheal and spasmolytic activities (Pinsuwan et al., 2007; Mayachiew and Devahastin, 2008; Medmood et al., 2011). Therefore, it is interesting to study the use of *P. emblica* fruit extract as a source of natural preservatives in raw ground pork.

## MATERIALS AND METHODS

### Microorganisms

Fifteen microbial strains (6 species of bacteria, 4 species of yeasts and 5 species of molds) were used in this study. *Bacillus cereus* DMST 5040, *Escherichia coli* DMST 4212, *Listeria monocytogenes* DMST 11256, *Pseudomonas fluorescens* DMST 20076 and *Salmonella* Typhimurium DMST 0562 were obtained from the culture collection of the Department of Medical Sciences, Ministry of Public Health, Thailand. *Staphylococcus aureus* TISIR 118, *Candida lipolytica* TISTR 5655, *Pichia membranaefaciens* TISTR 5093, *Rhodotorula glutinis* TISTR 5159, *Zygosaccharomyces rouxii* TISTR 5044, *Aspergillus flavus* TISTR 3041, *Aspergillus parasiticus* TISTR 3276, *Aspergillus ochraceus* TISTR 3557, *Fusarium moniliforme* TISTR 3175 and *Rhizopus stolonifer* TISTR 3199 were obtained from the Microbiological Resources Centre for Southeast Asian Region (Bangkok MIRCEN).

### Culture preparation

The bacterial cultures (*B. cereus*, *E. coli*, *L. monocytogenes*, *P. fluorescens*, *S. Typhimurium* and *S. aureus*) were subcultured twice onto Nutrient Agar (NA, Difco) and incubated for 24 h at 37°C, except for *P. fluorescens* incubated at 30°C. Yeast cultures (*C. lipolytica*, *P. membranaefaciens*, *R. glutinis* and *Z. rouxii*) were subcultured twice onto Saboraud Dextrose Agar (SDA, Difco) and incubated at 30°C for 48 h. A loopful of each bacteria and yeast in agar slant was inoculated into NB and SDB, respectively. After incubation, microbial cells were collected by centrifugation at 3000  $\times$ g for 15 min,

washed twice and resuspended in 0.1% peptone water. Turbidity was adjusted to match the turbidity of 5 McFarland standard to obtain an inoculum concentration of  $10^7$  CFU/ml.

To prepare spore suspension of mold, each mold culture was grown in Potato Dextrose Agar (PDA, Difco) at 30°C for 7 days. Conidia were harvested by adding with 5 µl of sterile 0.01% Tween 80 in culture tubes, and the agar surface was scraped. Conidial concentration was adjusted to  $10^6$  conidia/ml using haemocytometer.

### Extraction of Thai local fruits

Six species of Thai local fruits including fruits of *Ardisia polycephala* Wall. (Thai name: pilungasa), *Averrhoa carambola* Linn. (common name: star fruit or Thai name: mafueng), *Elaeocarpus hygrophilus* Kurz. (common name: Spanish plum or Thai name: makoknum), *Garcinia schomburgkiana* Pierre. (Thai name: madan), *Limonia acidissima* Linn. (Thai name: makwit) and *Phyllanthus emblica* Linn. (common name: Indian gooseberry or Thai name: makampom) were purchased at retail in Bangkok, Thailand. These plants were extracted using methanol as a solvent.

To prepare crude methanolic extracts of Thai local fruits, all fruits were washed, cut into small pieces, freeze-dried and powdered. Then, 10 g of each dried fruit were soaked in 100 ml methanol, and shaken at 200 rpm for 24 h at ambient temperature. The mixtures were then filtered. The filtrates were evaporated using vacuum rotary evaporator (BÜCHI Rotavapor R-200/205, Model R205V800, Switzerland), and air dried. Stock solutions of crude methanolic extracts were prepared by diluting 0.2 g dried extracts with 1 ml of 10% dimethyl sulphoxide (DMSO) solution.

### Screening of fruit extracts using disk diffusion test

The disk diffusion test was performed using the standard procedure as described by Jorgensen et al. (1999). The inoculum suspension (100 µl) of each microbial strain was added and swabbed onto the surface of Mueller-Hinton Agar (MHA, Difco) for bacteria, SDA for yeasts and PDA for molds. Sterile 6-mm filter paper discs (Whatman) were aseptically placed on MHA, SDA and PDA surfaces. Crude methanolic extracts (15 µl) were immediately added to discs. A 15-µl aliquot of 10% DMSO was also added to a sterile paper disc as a negative control. The plates were incubated at 37°C for 24 h for bacteria, except for *P. fluorescens* incubated at 30°C and at 30°C for 72 h for yeasts and molds. Antimicrobial activity was evaluated by measuring inhibition zone diameters. The experiment was done in triplicate.

### Determination of the minimum inhibitory concentrations using agar dilution test

The minimum inhibitory concentrations (MICs) of all fruit extracts against 15 microbial strains were determined using an agar dilution method (Collins et al., 2001). Each fruit extract was diluted to obtain 5 concentrations (200, 140, 102.4, 51.2 and 25.6 mg/ml). Then, 19 ml appropriate agar medium (MHA, SDA or PDA) was poured into each petridish to obtain final concentrations (10, 7, 5.12, 2.56 and 1.28 µg/ml). Negative control was performed using distilled water. Penicillin G (at final concentration of 2000, 1000, 500, 250, 125, 62.5 and 31.25 unit/ml) and fluconazole (at final concentration of 0.1, 0.08, 0.04, 0.02 and 0.01 mg/ml) were tested as positive controls. After surface drying, a loopful of each microbial suspension (spore suspension for molds) was inoculated at the centre of each agar plate. After incubation at appropriate temperature and time, the growth of each microbial strains at different concentrations of fruit extracts was recorded. The lowest concentration of a fruit extract that completely inhibited visible growth of each microbial strain was recorded as the MIC.

### Determination of antioxidant activity

#### Free radical scavenging activity assay (DPPH method)

The free radical scavenging activity of fruit extracts was measured according to the method of Brand-Williams (1995). Each stock solution of extracts and  $\alpha$ -tocopherol (10,000 µg/ml, a positive control) were prepared and diluted to the concentrations of 1,000, 500, 100, 10, and 1 µg/ml in methanol. Seventy five microliter of each diluted extract at five concentrations were added to 2.925 ml of a 0.025 g/L DPPH (2, 2-diphenyl-1-picrylhydrazyl) solution in methanol. The reaction mixtures were then incubated in the dark for 30 min. The absorbance at 515 nm was measured at 0 and 30 min of incubation using a UV-Visible spectrophotometer (UNICO, 2800A). To prepare standard curve of DPPH, the absorbance of DPPH at different concentrations was measured at 515 nm. The remaining DPPH concentration in the reaction mixture was calculated from the DPPH standard curve, and the percentage of the remaining DPPH was calculated using the following equation:

$$\%DPPH_{REM} = [DPPH]_T / [DPPH]_{T=0}$$

Where  $[DPPH]_T$  and  $[DPPH]_{T=0}$  were the concentration of DPPH at steady state and zero time, respectively. The percentages of the remaining DPPH in each reaction mixture of five different concentrations of all extracts were then plotted against µg of extract / mg of DPPH to obtain the amount of antioxidant or extract necessary to decrease the initial DPPH by 50% ( $EC_{50}$ ). The  $EC_{50}$  values of all extracts were calculated by the following linear regression of plots, and the antiradical efficiency ( $AE=1/EC_{50}$ ) values were also calculated.

$$[\%DPPH_{REM}] = b [\mu\text{g antioxidant/ mg DPPH}] + a.$$

#### Ferric reducing antioxidant power (FRAP) assay

Antioxidant activity of fruit extracts was determined according to the FRAP method previously described by Lado et al. (2004). To do FRAP assay, 1 mg/ml fruit extract (50 µl) was mixed with 1.5 mL FRAP reagent (25 ml of 300 mM acetate buffer, 2.5 mL of 10 mM TPTZ (2,4,6-tri-2-pyridyl-2-triazine, Fluka, Sigma-Aldrich, Switzerland) in 40 mM HCl and 2.5 mL

of 20 mM FeCl<sub>3</sub>.6H<sub>2</sub>O), and incubated at 37°C for 5 min. The absorbance was measured at 594 nm using UV-visible spectrophotometer (UV1601, Shimadzu Scientific Instruments (Oceania) Pty. Ltd., Australia) against blank (FRAP reagent without the sample). The concentration of Fe<sup>2+</sup>-TPTZ (reducing capacity) was calculated by comparing the absorbance at 594 nm with the standard curve of the Fe (II) standard solutions (ferrous sulfate heptahydrate). Alpha-tocopherol was used as a positive control.

#### Determination of total phenolic content

Total phenolic content was determined according to the method of Tepe et al. (2005). Each fruit extract (0.1 ml of 10,000 µg/ml crude methanolic extract) was transferred to a flask containing 46 ml distilled water. Folin-Ciocalteu's phenol reagent (Fluka, Sigma-Aldrich, Switzerland) (1 ml) was added, shaken thoroughly, and allowed to stand for 3 min. Then, 3 ml of 2% Na<sub>2</sub>CO<sub>3</sub> was added, and allowed to stand for 2 h with intermittent shaking. Then, the absorbance was measured at 760 nm using UV-visible spectrophotometer (UV1601, Shimadzu Scientific Instruments (Oceania) Pty. Ltd., Australia). Standard curve of gallic acid (Fluka, Sigma-Aldrich, Spain) was prepared using the similar procedure. The results were expressed as µg GAE (gallic acid equivalents) /mg extract.

#### Application of a selected fruit extract for extending shelf-life of chilled ground pork

A fruit extract with high antimicrobial and antioxidant activities was selected for use as a natural preservative in ground pork during refrigerated storage. Six treatments of ground pork (80% lean meat mixed with 20% pork fat) were prepared. These were treatment 1 (ground pork without fruit extract added, control), treatment 2 (ground pork added with 0.02% BHT, butylated hydroxytoluene) and treatment 3-6 (ground pork added with 0.25, 1.0, 1.5 and 2.0% of a selected fruit extract, respectively). All ground pork samples were added with cell suspension (10<sup>7</sup> cells/ml) of *P. fluorescens* DMST 20076 (10 µl/ 25 g ground pork) to get a final cell concentration of 10<sup>7</sup> cells/ g ground pork. Then, all samples were stored at 4°C for 12 days. At day 0, 1, 3, 7 and 12 days of storage, total viable counts, total psychrotrophic bacteria and total *Pseudomonas* in chilled ground pork samples were analysed by spiral plating technique using the Spiral Plater (Autoplate 4000, Spiral Biotech company, USA) onto Plate Count agar (PCA, incubated at 37°C for 24 h), PCA (incubated at 4°C for 10 days) and *Pseudomonas* isolation agar (PIA, incubated at 30°C for 24 h), respectively. Measurement of pH and color values were also performed using pH meter (Testo 205, Germany) and color value meter (Konica Minolta model CR – 300, Japan), respectively, while TBARS (thiobarbituric reactive substances) values were analysed by using a method of Kirk and Sawyer (1991). Three replicates of experiments were performed.

#### Statistical analysis

Data were analysed by using analysis of variance to determine if significant differences (P<0.05) existed between mean values and using Duncan multiple range test to compare between treatment means.

#### Use of chilled ground pork for production of a seasoned pork product

This study was aimed at comparing a seasoned pork product made from fresh ground pork without a fruit extract (a control sample) and those made from chilled ground pork added with a selected fruit extract and stored at 4°C for 0, 3 and 7 days. This product contained 87.97% ground pork (with or without the fruit extract), 0.44% sucrose, 4.1% soy sauce, 0.88% tasty sauce, 0.15% salt, 1.47% milk, 2.35% oyster sauce, 1.47% chopped garlic with white pepper, 0.95% olive oil and 0.59% tapioca flour. All ingredients were mixed together. Then, a sensory analysis (a duo-trio test) was performed in triplicate by 12 untrained taste panels to establish differences between the control sample and the seasoned pork samples made from chilled ground pork stored at different period of time.

To do duo-trio test, the seasoned pork samples including the control sample and the sample made from ground pork added with a fruit extract were divided to small pieces (15 g/piece), and each piece was rounded to a circular shape with 1 inch thick. All samples were fried in palm oil at 160-170°C for 10 min. Then, the cooked samples were served to the 12 untrained panelists. Each panel needed to evaluate 3 samples independently. One sample was coded as "R" and the other two samples were coded with 3 digit numbers. These panels were asked to evaluate "which sample of these two samples was similar to the "R" sample?". The number of the taste panels giving the correct answer was evaluated if the significant differences existed by using a statistical table for duo-trio test (Roessler et al., 1978).

## RESULTS AND DISCUSSION

#### Antimicrobial activity

Extracts of madan, makoknum and makampom exhibited wider inhibition zone against most of bacteria tested by disk diffusion test. However, all fruit extracts could not inhibit growth of all mold species tested, but makoknum and madan extracts could produce inhibition zone only yeast species, *R. glutinis* (Table 1). Madan, makoknum and makampom extracts were selected for MICs determination. Among all fruit extracts tested, fruit extract of madan showed the broadest antimicrobial action to all bacterial species tested (Table 2). Interestingly, it could effectively inhibit foodborne bacterial pathogens (*L. monocytogenes* and *S. Typhimurium*) with the MIC of 2.56 mg/ml. The only yeast species susceptible to madan extract was *R. glutinis*. However, its antimicrobial activity may be due its organic acids. Suntornsuk et al. (2002) reported that the amount of vitamin C in madan fruit juice was 4.6 mg/100 g.

Fruit extract of makampom also exhibited strong inhibitory to some bacteria, especially *P. fluorescens* and *S. aureus* with 2.56 mg/ml MIC (Table 2). Mayachiew and Devahastin (2008) also found that *P. emblica* fruit extract inhibited *S. aureus*

with MIC of 13.97 mg/ml. Several components of *P. emblica* fruits may act as antimicrobial agents. They reported that this fruit extract contained gallic acid, hydrolysable tannin and ascorbic acid (11.21%).

Table 1 Antimicrobial activity of Thai local fruit extracts using disk diffusion test

Microbial species	Diameter of inhibition zone (mm) <sup>a</sup> ± SD					
	<i>Artisia polycephala</i> (pilungasa)	<i>Averrhoa carambola</i> (mafueng)	<i>Elaeocarpus hygrophilus</i> (makoknum)	<i>Garcinia schomburgkiana</i> (madan)	<i>Phyllanthus emblica</i> (makampom)	<i>Limonia acidissima</i> (makwit)
<b>Bacteria</b>						
<i>Bacillus cereus</i>	- <sup>b</sup>	-	11.7 ± 0.3	11.0 ± 0.5	9.4 ± 0.5	-
<i>Escherichia coli</i>	-	-	-	8.5 ± 0.5	-	-
<i>Listeria monocytogenes</i>	-	-	9.4 ± 0.1	-	-	-
<i>Pseudomonas fluorescens</i>	-	-	11.5 ± 1.2	10.0 ± 0.3	9.8 ± 0.6	-
<i>Salmonella Typhimurium</i>	-	-	9.0 ± 0.0	11.3 ± 0.2	-	-
<i>Staphylococcus aureus</i>	-	-	8.7 ± 0.3	10.8 ± 0.3	10.3 ± 0.6	-
<b>Yeasts</b>						
<i>Candida lipolytica</i>	-	-	-	-	-	-
<i>Pichia membranaefaciens</i>	-	-	-	-	-	-
<i>Rhodotorula glutinis</i>	-	-	14.7 ± 1.1	21.7 ± 1.1	-	-
<i>Zygosaccharomyces rouxii</i>	-	-	-	-	-	-

<sup>a</sup>Data are mean of three replications.

<sup>b</sup>No inhibition was observed.

Table 2 Minimum inhibitory concentrations of Thai local fruit extracts

Microbial species	Minimum inhibitory concentrations of Thai local fruit extracts (mg/ml)				
	<i>Elaeocarpus hygrophilus</i> (makoknum)	<i>Garcinia schomburgkiana</i> (madan)	<i>Phyllanthus emblica</i> (makampom)	Penicillin G*	Fluconazole
<b>Bacteria</b>					
<i>Bacillus cereus</i>	>10	5.12	5.12	250	>0.10
<i>Escherichia coli</i>	>10	5.12	>10	125	>0.10
<i>Listeria monocytogenes</i>	>10	2.56	>10	62.50	>0.10
<i>Pseudomonas fluorescens</i>	7	5.12	2.56	>2000	>0.10
<i>Salmonella Typhimurium</i>	5.12	2.56	>10	250	>0.10
<i>Staphylococcus aureus</i>	>10	5.12	2.56	31.25	>0.10
<b>Yeasts</b>					
<i>Candida lipolytica</i>	>10	>10	>10	>2000	0.02
<i>Pichia membranaefaciens</i>	>10	>10	>10	>2000	0.08
<i>Rhodotorula glutinis</i>	>10	5.12	>10	>2000	>0.10
<i>Zygosaccharomyces rouxii</i>	>10	>10	>10	>2000	0.10

\* Units/ml for penicillin G

### Antioxidant activity

Among all fruit extracts tested, makampom (*P. emblica*) fruit extract had the highest antioxidant activity by DPPH method (EC<sub>50</sub> of 501.71 µg extract /mg DPPH) and strongest reducing capacity (4.86 mmol/L) by FRAP method, followed by pilungasa, makoknum, madan, mafueng and makwit (Table 3). The lower EC<sub>50</sub> value of the extract indicates its higher antioxidant activity (Brand-Williams et al., 1995). Their antioxidant activities were related to their phenolic contents. Makampom contained the highest phenolic content (4,220 µg GAE/mg dry extract). Pinsuwan et al. (2007) reported that the alcoholic extract of *P. emblica* possessed high antioxidant capacity with EC<sub>50</sub> of 1.55 µg/ml and high phenolic content (454.7 mg gallic acid equivalent/g). In addition, Lou et al. (2009) isolated six compounds from *P. emblica* fruit and identified as cinnamic acid, quercetin, 5-hydroxymethylfurfural, gallic acid, β-daucosterol and ellagic acid.

Fruit of pilungasa (*A. polycephala*) was found to possess high antioxidant activity and high phenolic contents. Ahamad et al. (1977) reported that phytochemical constituents in leaves of pilungasa were baurenol, α-amyrin and β-amyrin. Ruangchakpet and Sajjaanantakul (2007) reported that *E. hygrophilus* (makoknum) fruit at 6 month maturity had high total phenolics (345.8 mg gallic acid/ 100 g fresh weight) and flavonoid content (49.0 mg catechin/100 g fresh weight). The highest gallic acid content (103.6 mg/100 g fresh weight) was found at 6 month maturity.

Compared to other fruits, mafueng had not much antioxidant activity and total phenolics. Samee et al. (2006) also reported that star fruit (mafueng) had lower antioxidant activity, compared to other fruits tested. Lim et al. (2007) report that star fruit contained antioxidant activity (IC<sub>50</sub> of 3.8 mg/ml by DPPH method) and total phenolics of 131 mg/100 g fresh fruit.

Table 3 Antioxidant activity and total phenolic content of Thai local fruit extracts

Fruit extracts	DPPH method	FRAP method	Total phenolic content
	EC <sub>50</sub> (µg extract / mg DPPH) <sup>a</sup> ± SD	Reducing ability (mmol/L) <sup>a</sup> ± SD	(µg Gallic Acid Equivalents (GAE)/mg dry extract) <sup>a</sup> ± SD
<i>Ardisia polycephala</i> (pilungasa)	739.38 ± 15.61	4.72 ± 0.12	1,270 ± 208.71
<i>Averrhoa carambola</i> (mafueng)	17,308.33 ± 339.25	1.27 ± 0.11	116.67 ± 48.21
<i>Elaeocarpus hygrophilus</i> (makoknum)	2,082.49 ± 46.91	2.79 ± 0.08	263.33 ± 108.74
<i>Garcinia schomburgkiana</i> (madan)	6,952.48 ± 638.97	2.60 ± 0.05	210 ± 80.32
<i>Phyllanthus emblica</i> (makampom)	501.71 ± 16.61	4.86 ± 0.14	4,220 ± 121.62
<i>Limonia acidissima</i> (makuit)	27,773.4 ± 846.18	0.50 ± 0.01	166.67 ± 39.80
α-tocopherol	467.55 ± 16.79	4.89 ± 0.08	<sup>b</sup>

<sup>a</sup>Data are mean of three replications.  
<sup>b</sup>Data are not determined.

**Application of a selected fruit extract as a natural preservative in chilled ground pork**

Makampom extract was selected for use as a natural preservative to extend shelf-life of chilled ground pork. Total microbial counts in ground pork added with 1.5 and 2.0% makampom extract decreased as storage time increased. After 7 days of storage at 4°C, ground pork added with 1.5-2.0% of this fruit extract had lower survival populations of total microorganisms (29-36% survival) than the samples added with lower concentrations of this extract (0.25-1.0% survival) (Figure 1a). Of all, samples added with 2.0% makampom extract had the lowest percentage of *Pseudomonas* survival cells (Figure 1b). However, the number of total psychrotrophs in all treatments of chilled ground pork increased by 0.13-0.51 log unit after 12-day storage. Unlike other treatments, the number of total psychrotrophs in ground pork samples added with 1.5-2.0% makampom extract slightly decreased after 1 day of storage, then gradually increased as the storage time increased (Figure 1c).

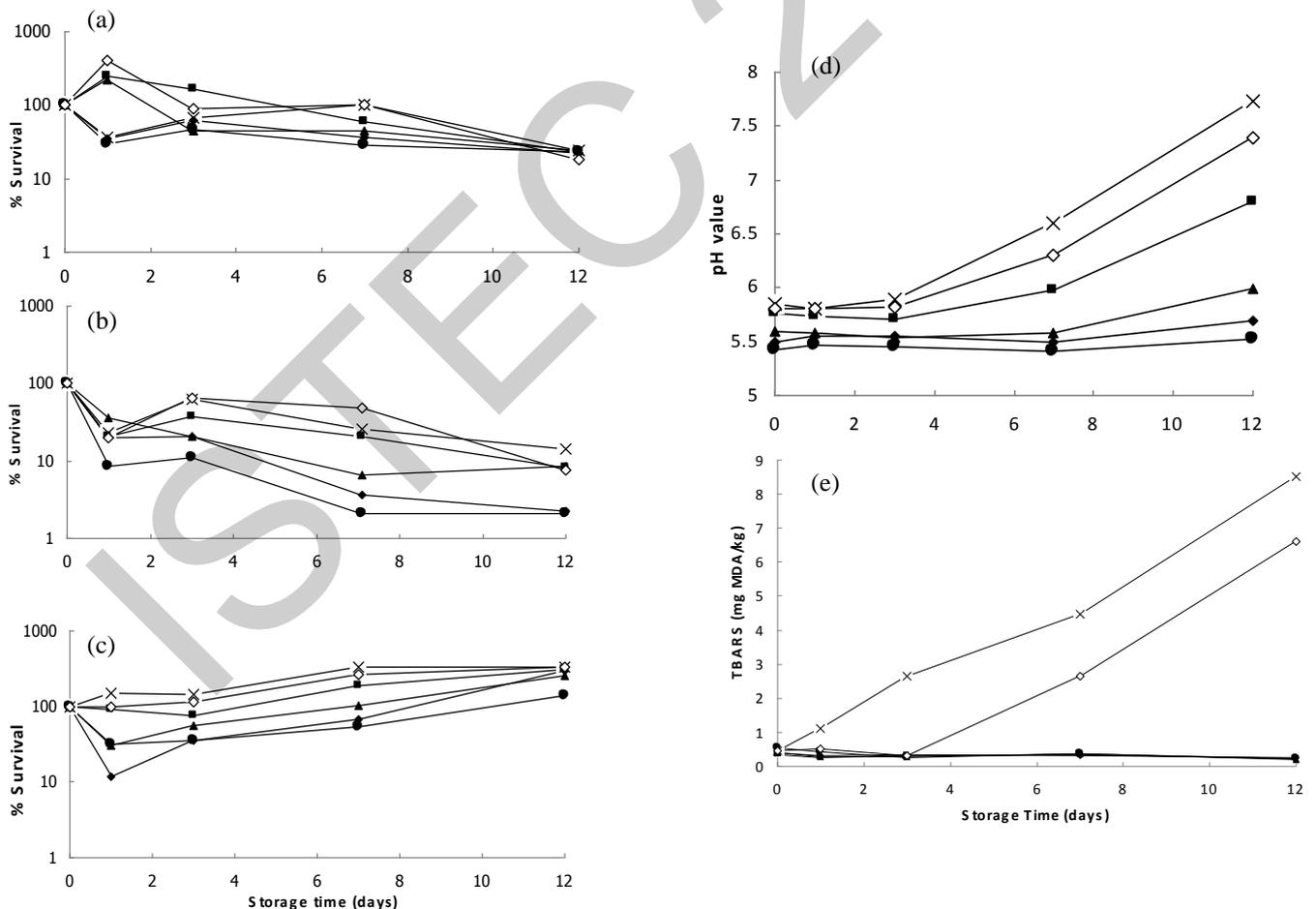


Figure 1 Survival of total microorganisms (a), total *Pseudomonas* (b) and total psychrotroph (c), pH values (d), and thiobarbituric reactive substances (TBARS) values (e) in ground pork added with some preservatives during refrigerated storage (Symbol: ×, control (no preservative added); ■, 0.25% makampom extract; ▲, 1.0% makampom extract; ◆, 1.5% makampom extract; ●, 2.0% makampom extract, and ◇, 0.02% BHT)

Decreasing of total microbial counts and *Pseudomonas* counts in the samples added with 1.5-2.0% makampom extract was probably due to its active compounds. This indicated that this extract could delay spoilage of chilled ground pork up to 7 days, while the control samples could be kept at 4°C for only 3 days before changing appearance. Medmood et al. (2011) found that crude extract of *P. emblica* fruit contained alkaloids, tannins, terpenes, flavonoids, sterols and saponins.

At the beginning of storage, pH values of ground pork samples without any preservative (control, pH 5.84) and the samples added with BHT (pH 5.81) were higher than the pH values of the samples added with 0.25-2.0% makampom extract (pH 5.76-5.43). The pH values of all pork samples slightly changed or remained constant until 3 days of storage, then increased until the end of storage. The pH values of the control samples and the samples added with 0.02% BHT increased more rapidly (to neutral pH level) than the samples of other treatments. Among all treatments of ground pork, the pH values of ground pork samples added with 1.5 and 2.0% makampom extract were the lowest (5.68 and 5.52, respectively) after 12-day storage (Figure 1d). In the control samples, increasing of pH to neutral level was related with the high number of total viable counts which indicated their spoilage. At 12-day storage, the control samples had green surface with stink odor, while the appearance of the samples added with 1.5-2.0% makampom extract was almost similar to fresh ground pork.

TBARS values of the control samples and the samples added with 0.02% BHT significantly increased more rapidly as the storage time increased ( $P < 0.05$ ), compared to other samples. The TBARS values of the samples added with 0.25-2.0% makampom extract slightly changed at each storage time, but no significant different was found between those of the samples with each concentration of the extract ( $P > 0.05$ ). Among all treatment samples, the TBARS values of the samples added with 0.25-2.0% makampom extract were the lowest (0.20 – 0.26 mg MDA/kg) at the end of the storage (Figure 1e).

#### *Use of chilled ground pork added with a selected fruit extract to produce a seasoned pork product*

Makampom extract at 2.0% was the most suitable to extend shelf-life of chilled ground pork. Therefore, the ground pork added with 2.0% makampom extract and stored for 0, 3 and 7 days at 4°C was used to produce the seasoned pork product ( $a_w$  0.97). After duo-trio test, only 5, 4 and 8 panels (out of 12 panelists) could discriminate between the control samples (pH 5.67) and the samples made from ground pork added with 2.0% makampom extract and stored for 0, 3 and 7 days at 4°C (pH 5.58), respectively. Based on the table of Roessler et al. (1978), it can be concluded that the taste panels could not discriminate between the control samples and the treated samples, when using probability level at 0.05. This indicates that the taste panels could not detect the flavor of 2.0% makampom extract added. Thus, the flavor of this extract should not cause product unacceptability. It is possible to use makampom extract as a natural preservative to extend shelf-life of chilled ground pork.

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# APPLICATION OF IMAGE ENHANCEMENT METHODS ON FUSED IMAGES PRIOR TO CLASSIFICATION OF SATELLITE IMAGES

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## Abstract

Fusion methods increase spatial resolution providing more details of the satellite image. Higher resolution fused images with colour information might be helpful for classification algorithms. However, spectral distortions and artificial structures called artifacts are the main problems of fusion methods need to be fixed for proper application of classification algorithms. Enhancement of fused images could improve overall accuracy results of classification algorithms. In this study, an image enhancement method is applied on wavelet-based fused image to reduce colour distortions for diminishing error rates while increasing overall accuracy with better kappa statistics values. While Principal Component Analysis (PCA) based image enhancement method found successful by the application of Support Vector Machines classification by about 1 % accuracy enhancement, Maximum Likelihood Classification results did not improve.

**Keywords:** *Satellite image classification, image enhancement, fusion method, PCA-based enhancement, image enhancement.*

## 1. Introduction

Fusion process is combination of high resolution panchromatic image with low resolution multi-spectral image. Panchromatic image is a single band image whereas multi-spectral image has different number of bands depending on the sensor type. Panchromatic image has better resolution without colour information while multi-spectral image is a lower resolution image with colour information. Fused images provide better spatial resolution. However, spectral distortions by introducing new colors or artificial structures called artifacts cause decrease in overall accuracy values especially with nonlinear classification methods such as Support Vector Machines. Enhancement methods are proposed and tested to decrease classification errors caused by spectral distortions present in the fused image. PCA-based image enhancement technique is found successful by increase in overall accuracy and kappa values for especially nonlinear classification algorithms.

The remainder of the paper is organized as follows: Section (2) focuses on brief mathematical background for the subject. Section (3) emphasizes conclusions.

## 2. Theory

PCA-based image enhancement approach: As a preparation for Principal Components Transform, fused image bands, pan band and multispectral bands are merged. By combination of the bands, collecting all the information about the image is achieved. Total of 9 bands are formed by the transformation. As expected first four or five bands carry most of the information and remaining bands include noise, so they can be discarded.

PCA transformation steps can be described as below [1]:

1. Get image.
2. Calculate mean and covariance matrix.
3. Calculate Eigen vectors from the co-variance matrix.
4. Find Eigen values.

5. Order the covariance matrix by Eigen value highest.
6. Eigen vectors with highest Eigen value is the Principal Component, which contains significant information.
7. Lowest Eigen value components can be discarded.

In simplest terms; Principal Components Analysis is a transformation method to eliminate redundancy with representative data with the greatest variance and uncorrelated set of variables called principal components. The number of principal components is at most equal to number of original variables [2].

$E \text{ cov } E^T = V$  and  $P_e = \sum_{k=1}^n d_k E_{ke}$  are main formulas for Principal Components calculations. E stands for Eigen values matrix, cov stands for covariance matrix, V stands for Eigenvectors matrix sorted form the greatest to the lowest, T stands for transpose, P stands for output of principal component value at the specified band, k is used for representing a particular input band, n is total number of bands, and d input data file at the specified band [3]. Selected number of PC bands was fed into classification algorithms.

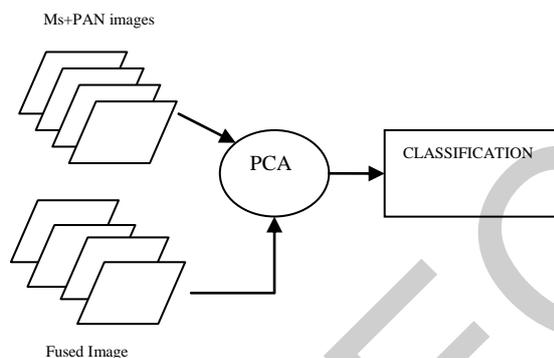


Figure 1. PCA-based Image Enhancement

### 3. Conclusion

Confusion matrix provides valuable information about accuracy of each classification method. The success of classifier on each individual class could be observed by using confusion matrix [4]. Overall accuracy and kappa values [5] are primary accuracy assessment metrics used for comparison purposes in the study. Maximum Likelihood Classification results did not improve by the application of proposed image enhancement method. However, with Support Vector Machines classification algorithm, an accuracy improvement of about 1 % is recorded. Enhanced fused image has overall classification accuracy of 94.43 % while the fused image has 93.3 % overall accuracy. Kappa values changed from 91.63 % to 93.03 % with application of enhancement method with Support Vector Machines classification algorithm. Thus, it can be concluded that nonlinear classification algorithms such as with Support Vector Machines are more affected by enhancement methods than linear or moderately nonlinear classification algorithms like Maximum Likelihood Classification.

Smooth join of the enhanced image and fused image results in an image with better spectral quality in addition to spatial enhancements providing higher classification accuracy results. The final images are visibly enhanced with relatively low noise level compared to the original image. The image fusion and image enhancement methods could be integrated into existing classifier systems as optional processing steps. United approach is especially effective for advanced applications [6].

Class separability is better after enhancements compared to the original reference fused satellite image. Using the classified result of the original fused image as a benchmark, improvement in the overall accuracy of classification results of the enhanced fused images are observed. Higher classification accuracy is possible with the integration of image fusion and image enhancement methods into classification process.

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# APPLICATIONS OF ARTIFICIAL NEURAL NETWORKS IN THE SURFACE ENGINEERING: A SHORT REVIEW

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## ABSTRACT

Surface engineering's main goal is to make possible the design and manufacture of materials with a combination of bulk and surface properties unobtainable in a single material. It employs appropriate surface technologies to achieve optimal surface property in the most cost effective manner. Surface engineering deals with many phenomena such as friction and wear which are not easy to be modeled theoretically thus mathematical modeling acquires more importance. On the other hand artificial neural networks are non-linear statistical data modeling tools generally used to model complex relationships or to find patterns in data. Therefore artificial neural networks are an appropriate choice for utilization in the surface engineering. In this paper different applications of artificial neural networks were classified and reviewed. In addition new trends in participations of artificial neural networks and surface engineering were discussed.

Keywords: Artificial Neural Networks, Surface Engineering, Tribology, Mathematical Modeling

## INTRODUCTION

Surface engineering term invoked by Bell and co-workers in 1983, to provide emphasis to the multi-disciplinary activities concerned with the science and technology of engineering surfaces. Its main goal is to make possible the design and manufacture of materials with a combination of bulk and surface properties unobtainable in a single monolithic material. The skill in surface engineering is to manipulate appropriate surface technologies to achieve optimal surface property designs, for specific applications, in the most cost effective manner (TYRKIEL, 1995).

In the field of Surface engineering complex and nonlinear phenomena are involved consequently analytical models are very difficult and even impossible to obtain. However, for performance enhancement of mechanical systems precise modeling and prediction of various processes like as the friction, corrosion and wear are required. Artificial Neural Networks (ANN) due to their capabilities of nonlinear behavior learning from experimental data and generalization are good candidates to create such models.

## ARTIFICIAL NEURAL NETWORKS

By developing ever more powerful computers, it is continue to be difficult to use them efficiently for tasks that are quite simple for humans. For example human could recognize alphabet letters easily or make a distinction between people's faces. Obtaining more experience leads human to do these tasks more easily and with fewer mistakes. While these simple tasks for human are difficult to be programmed and utilized on computers.

An artificial neural network is a mathematical or computational model that is inspired by the structure and functional aspects of biological neural networks. A neural network is a connected group of artificial neurons and data that flow through the network during the learning stage changes its structure. Modern neural networks are non-linear statistical data modeling tools. They are usually used to model complex relationships between inputs and outputs or to find patterns in data.

## SURFACE ENGINEERING

Surfaces of industrial parts are the most important and critical sections, because most failures initiate on the surface. Therefore, the level of protection and strengthen of surfaces are very sensitive issues and determine the quality, life length, productivity and cost effectiveness of the products. Surface engineering involves the application of traditional or new heat treatment technologies or other types of operations such as surface coating methods on critical engineering parts in order to achieve properties which either none of the ingredients of the inner section or the surface possesses. The motivation for the development of surface engineering partly originates from the rapid advances in technologies such as lasers and electron beams, chemical heat treatments, different layer deposition techniques. In addition, origins and principles of surface engineering must be searched in the traditional heat treatment technologies including rapid cooling hardening, carbonizing and nitriding of iron alloys.

## FORMING AND MACHINING EFFECTS ON THE SURFACE (ROUGHNESS)

Surface parameters such as roughness, waviness and texture are mainly influenced by various parameters of the production processes. Occasionally by creating small changes in parameters of a process, significant results could be obtained. So many studies have been carried out in this field, but in order to brief the topics, only the influences of production processes' parameters on the surface roughness will be discussed.

Surface roughness plays an important role in determining how a part will interact with the environment. Rough surfaces have higher friction coefficients and wear more quickly than smooth surfaces. High surface roughness may easily form nucleation sites for cracks or corrosion. Although roughness is usually unwanted, it is difficult to be controlled in manufacturing. Decreasing the roughness of a surface will typically increase its producing cost. In several studies, the neural network approach is applied for the prediction and control of surface roughness in a computer numerically controlled lathe (Karayel, 2009), mill (Zain, 2010) (Benardos, 2002) (Oktem, 2006) and also in nontraditional machining processes like as waterjet (Çaydaş & Hasçalık, 2008) and electric discharge machining (Rao G, Rangajanardhaa, Hanumantha, & Sreenivasa, 2009).

The study done by Karayel in Sakarya University could be mentioned as a good sample for this kind of applications. Karayel's work was based on the prediction and control of surface roughness in CNC lathe using artificial neural network. At the first place the researcher carried out experiments on the CNC lathe to obtain the data used for the training and testing of a neural network. The experiment parameters were depth of cutting, cutting speed, and feed rate. A feed forward multilayered neural network was developed and the network model was trained using the back-propagation algorithm. The predicted surface roughness originated from the developed model, were very close to the experiment values. Hence, it is possible to control the surface roughness as the developed control system is used.

## MODELING OF SUPERFICIAL HEAT TREATMENT AND COATING PARAMETERS

Appropriate heat treating needs precise control over parameters such as temperature, time held at a certain temperature and cooling rate (Rajan, Sharma, & Ashok, 1992). Demands for cheaper products along with higher quality make many investigators study the effects of process parameters in heat treatment, carbonizing and nitriding. As an example, in 2001 Malinova et al. studied the influences of the nitrocarburizing parameters and steel composition on the microhardness profile. They used a model which was based on a feed-forward artificial neural network. Good correspondence between predicted and experimental data was observed (Malinova, Malinov, & Pantev, 2001). Another researcher Zhecheva designed an artificial neural network models for simulation and predictions of microhardness profiles of titanium alloys following gas and plasma nitriding. The model has shown a good performance which could be used for calculating microhardness profiles after nitriding at temperatures between 700 and 1100 °C for periods of time between 1 and 100 h (Zhecheva, Malinov, & Sha, 2005).

Coatings consist of a large number of processes and materials and in order to obtain the functional coatings, combinations of processing parameters have deliberately to be chosen. These selections are changed by cost and effects on the coating properties. Better understanding of the physical, chemical and thermodynamical aspects of coating methods could be helpful to select the parameters, improve systems, coating of new materials and using new technologies. Though, this understanding is strongly constrained by the complexity of the processes and the related treatments. Artificial neural networks have been used in many studies to find out these complexities. For instance, among the different coating methods, thermal spraying is a flexible technique to manufacture coatings which offers a large choice of processes and materials (Guessasma, Montavon, & Coddet, 2004). Numerous studies have been done on the modeling, simulation and optimization of thermal spraying using ANN methods. As an example, Guessasma in 2004 applied an artificial neural network methodology to analyze and predict microstructure features of alumina, titania coating. Studied factors were alumina, titania, porosity and unmelted particle contents (Guessasma & Coddet, 5157-5164).

## CLASSIFICATION OF INDUSTRIAL PARTS SURFACES

Classification is growing as one of the most dynamic research areas of artificial neural networks. A classification problem occurs when an object needs to be assigned into a predefined group. Many problems in the surface engineering can be treated as classification problems. Examples include image processing and acoustic characterization for online production process control (Zhang, 2000).

Many researchers have used digital image processing to evaluate and improve surfaces quality by online or offline control of the process parameters. Many of the fundamental requirements during conventional surface evaluation do not exist in digital image processing. In this case only image is used for evaluation without any component. Therefore Practical use of digital image for surface evaluation faces many challenges. One of studies in this ground is Priya and Ramamoorthy work in 2007; they used image processing to estimate surface roughness. In the conventional roughness measurement method, alignment of component with the stylus movement is very helpful. While, in digital roughness measurement method, measured surface should be kept horizontally when the image is being taken. They have estimated the surface roughness by using digital images of machined surfaces at varying angles (Priya & Ramamoorthy, 2007).

## TRIBOLOGICAL APPLICATIONS OF ANN

Numerous studies use artificial neural networks to model and predict tribological aspects of mechanical systems such as wear and friction (frangu & ripa, 2001). LiuJie et al. used ANN to study the effects of PV factor and contact temperature on the dry sliding tribological behavior of PEEK-CF30 composite. By data sets obtained from a pin-on-disc machine, relationship models of friction coefficient and weight loss of PEEK-CF30 versus PV factor and contact temperature were built with training a back propagation network. The results show that the models can precisely predict friction coefficient and wear weight (LiuJiea, Davimb, & Cardoso, 2007). An ability of artificial neural networks in classification is another major advantage that could be used to recognize faults in bearings, machinery. Vyas and Satishkumar in 1998 used a back-propagation learning algorithm for prediction of faults in rotating machinery. Vibration signals of the rotor-bearing system are employed to train the network as well. They achieved an overall success rate up to 90% (Vyas & Satishkumar, 2001).

## CONCLUSION

Researchers apply artificial neural networks for two main reasons: modeling and classification. ANN is one of the small numbers of methods that could be applied to solve surface engineering problems. Complexity and nonlinearity of surface engineering and tribological phenomena make modeling very problematic. In summary, ANN outstanding to its learning process and nonlinear behavior is an adequate method for modeling these kinds of systems. However, they often contain many weights that must be estimated, they require large training sets. For the purpose of classification, Non-adaptive unsupervised networks are able to reconstruct their patterns when they are presented with noisy samples and can be used for image recognition. Some of the potential applications of classification with ANN methodology could be online inspection of products surfaces and online control of wear and friction. At the end, it is concluded that ANN is so applicable in surface engineering and would have wildy been utilized in this field.

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# ASYMMETRIC ENCRYPTION / DECRYPTION WITH PENTOR AND ULTRA PENTOR OPERATORS

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## ABSTRACT

Finding new approaches for asymmetric encryption / decryption process represents a milestone in cryptographic research and development. In this paper we introduce new algorithm for asymmetric encryption by utilizing two mathematical operators called Pentors and Ultra Pentors. The public and private key in this algorithm represent a quadruple of parameters which are directly dependent from the above mentioned operators. The strength of the algorithm resides in the inability to find the respective Pentor and Ultra Pentor operator from the mentioned parameters.

## 1. Introduction

The introduction of public-key cryptography is often attributed to Diffie and Hellman, presented in "new directions in cryptography" (Diffie & Hellman, 1998), where they described the usage of one way functions, and notions of trapdoor permutations in cryptography to which group belongs the public-key cryptosystem as well where there is a hidden trapdoor which enables the decryption to the legitimate party (Vaudenay, 2006).

A cryptosystem which is consisted of set of enciphering transformations  $\{E_e\}$  and of deciphering transformations  $\{D_d\}$  is called a public-key cryptosystem or an asymmetric cryptosystem if for each particular key pair  $(e; d)$ , the enciphering key  $e$  is publicly available called the public key, whilst the deciphering key  $d$ , called the private key, is being kept secret. The mentioned cryptosystem must satisfy the fundamental property of infeasibility to compute  $d$  from  $e$  (Mollin, 2007).

In (Luma & Raufi, 2009) and (Luma & Raufi, 2010) we have introduced two new operators as mathematical models that can be used in cryptography

and in many other ideas as well. The contribution of this paper is that through these mathematical operators we are capable of creating and implementing powerful asymmetric encryption/decryption algorithm that can be utilized in many security systems such as banking systems, database security etc. We coin these two operators as Pentor and Ultra Pentor accordingly.

### 1.1. Pentor Operator

We can introduce the Pentor of an integer number  $n$  with base  $B$ . For every integer number  $n$  there exists one Pentor for the given base  $B$ . For representing this operator mathematically, we are going to start from modular equation for Pentor of an integer number  $n$  with base  $B$  that fulfills the condition  $\gcd(n, B) = 1$ .

Considering the above mentioned conditions we could have:

$$B^m \cdot P(n) \equiv 1 \pmod{n} \quad (1)$$

Where  $B$  is the base of the integer number  $n$ ,  $P(n)$  is the Pentor for the integer number  $n$  and  $m$  represents the order of the Pentor  $P(n)$  for the integer number  $n$ . The modular expression (1) can be also transformed to the equality expressions of the form:

$$B^m \cdot P(n) = 1 + n \cdot k \quad (2)$$

$$P(n) = \frac{1 + n \cdot k}{B^m} \quad (3)$$

where  $k$  is an integer number that fulfills the condition for the fraction to remain an integer number. For example if we want to find the Pentor of the first order than,  $m = 1$  the Pentor of the second order  $m = 2$  and so on.

### 1.2. Ultra Pentor Operator

The definition of Ultra Pentor of a number  $n$  with base  $B$  is that for every natural number  $n$  there exist an Ultra Pentor operator for the given base  $B$ . The mathematical definition of an Ultra Pentor operator begins from modular equation of Ultra Pentor of integer number  $n$  with base  $B$  that satisfies the condition  $gcd(n, B) = 1$ . Considering the above mentioned conditions, the modular equation of Ultra Pentor is given as (Luma & Raufi, 2009):

$$B^m \equiv 1(mod n) \tag{4}$$

where  $m$  is an integer number. From the modular expression 4, a transformation to equality expression is possible by applying logarithmic operations on both sides and finding the Ultra Pentor given in the form as:

$$B^m \equiv 1 + n \cdot l \mid \cdot \log_B \tag{5}$$

$$\log_B B^m = \log_B(1 + n \cdot l) \tag{6}$$

$$m \cdot \log_B B = \log_B(1 + n \cdot l) \tag{7}$$

where we will have :

$$m = \log_B(1 + n \cdot l) \tag{8}$$

If  $m = UP(n)$ , then Ultra Pentor of integer number  $n$  with base  $B$  can be written as:

$$UP(n) = \log_B(1 + n \cdot l) \tag{9}$$

In the above mentioned equation,  $l$  is an integer number that fulfils the condition for  $(1 + n \cdot l)$  to be written as  $B^a$ , where  $a$  is also an integer number. The rest of the work is organized as follows: In section 2 a mathematical outline of the new asymmetric encryption algorithm is being outlined. In section 3, a case study of the functioning of the proposed algorithm with an example is depicted and finally, section 4 concludes this paper with some future directions and proposals.

### 2. New Asymmetric Encryption/Decryption Algorithm

Let us chose at the beginning a natural number  $n$ , from which we generate the Pentor and Ultra Pentor by using equations 3 and 9. Now, a prime number  $p$  is chosen from which we find its primitive root and name it as  $\alpha$ .

Let us define a function  $\gamma$  written as:

$$\gamma = n \cdot p \cdot UP(n) \tag{10}$$

The resulted value from the function  $\gamma$  is being checked by the number of digits it has and its digits are chopped” by the value of Ultra Pentor. All the ”chopped pieces” are summed between each other and if the sequence is again longer than the value of Ultra Pentor the process is repeated until the sequence’s length is less or equal to the value of Ultra Pentor. The digits of the produced sequence are right shifted by one place, resulting in non-repeating combination of sequences out of which we generate a block with length no greater than that of the value of Ultra Pentor.

Let us choose a value  $a$  which represents one of the sequences taken from the above mentioned block. Now, we define a function  $\beta$  written as:

$$\beta \equiv \alpha^a(mod p) \tag{11}$$

After the above mentioned apparatus we define the public key as quadruples  $(p, \alpha, \beta, P(n))$  while the secret key as  $(n, UP(n), \gamma, a)$ .

The overall process of communication through a secure line with above proposed approach goes as follows:

- 1) Adam sends to Eve the public key with quadruples  $(p, \alpha, \beta, P(n))$ .
- 2) Eve calculates a parameter:

$$r \equiv \alpha^{P(n)}(mod p)$$

- 3) Eve also calculates the ciphertext:

$$t \equiv \beta^{P(n)}m(mod p)$$

where  $m$  is the message.

- 4) Now, Eve sends a pair  $(r, t)$  to Adam.
- 5) Adam, after receives the pair  $(r, t)$  by using its secret key finds the message as:

$$m \equiv t \cdot r^{-a} \pmod{p}$$

Proof:

$$\begin{aligned} t \cdot r^{-a} &\equiv \beta^{P(n)} \cdot m \cdot (\alpha^{P(n)})^{-a} \equiv \\ &\equiv (\alpha^a)^{P(n)} \cdot m \cdot (\alpha^{-a})^{P(n)} \equiv \\ &\equiv \alpha^{a \cdot P(n)} \cdot m \cdot \alpha^{-a \cdot P(n)} \equiv m \pmod{p} \end{aligned}$$

### 3. A Case Study

Let us illustrate the above stated algorithm through a real life example. Initially, let us adopt the value of  $n = 13$ . We find the value of  $P(n)$  and  $UP(n)$  as stated in equations 3 and 9 as follows:

$$\begin{aligned} P(13) &= \frac{1 + 13 \cdot 3}{10} = 4 \\ UP(13) &= \log_{10}(1 + 13 \cdot 76923) = 6 \end{aligned}$$

Now, if we adopt a prime number  $p = 22621$  and by finding the primitive root of  $p$  to be  $\alpha = 2$ , the  $\gamma$  function, as seen from equation 10, can be calculated as:

$$\gamma = n \cdot p \cdot UP(n) = 13 \cdot 22621 \cdot 6 = 1764438$$

By taking the value of function  $\gamma$  and by "chopping" its digits from the right side by the value of  $UP(n)$  which in our case is 6.

$$1 \mid 764438$$

After we perform addition of these two blocks we get:

$$1 + 764438 = 764439$$

The non-repeating combination of the above presented value by doing a right shift as given in the algorithm above, results in a block as given below:

$$\begin{pmatrix} 7 & 6 & 4 & 4 & 3 & 9 \\ 6 & 4 & 4 & 3 & 9 & 7 \\ 4 & 4 & 3 & 9 & 7 & 6 \\ 4 & 3 & 9 & 7 & 6 & 4 \\ 3 & 9 & 7 & 6 & 4 & 4 \\ 9 & 7 & 6 & 4 & 4 & 3 \end{pmatrix}$$

By taking one of these combination and assigning to  $a$ , in a concrete case  $a = 397644$  and calculating the function  $\beta$  as given in equation 11 we will have:

$$\beta \equiv \alpha^a \equiv 2^{397644} \equiv 17011 \pmod{22621}$$

If we return to the above elaborated steps of encryption/decryption with calculated values here, for a simple message like "art", which has been converted to numbers based on letters from English alphabet (Luma & Zeqiri, 2008) the process will go as follows:

- 1) Adam sends to Eve the public key through quadruple (22621, 2, 17011, 4).
- 2) Eve calculates a parameter:

$$r \equiv 2^4 \equiv 16 \pmod{22621}$$

- 3) Eve also calculates the ciphertext:

$$17011^4 \cdot 11820 \equiv 588 \pmod{22621},$$

where  $m = 11820$  is the message.

- 4) Now, Eve sends a pair (16, 588) to Adam.
- 5) Adam, after receives the pair (16, 588) by using its secret key finds the message as:

$$m \equiv 588 \cdot 16^{397644} \equiv 11820 \pmod{22621}$$

The strength of this algorithm consists in the secret key because of the parameter  $a$  which is dependent from the function  $\gamma$ , while function  $\gamma$  is dependent from the Ultra Pentor itself. If an intruder intersects the encrypted line, he does not possess the parameter  $a$  which in our case, as explained in step 5 of our algorithm is a private key which only Eve possesses.

#### 4. Conclusion and Future Work

In this paper we have introduced new algorithm for asymmetric encryption / decryption by utilizing two mathematical operators called Pentors and Ultra Pentors. The strength of the proposed algorithm lies in the quadruples of parameters used as public as well as private keys.

Future work and development would involve the creation of electronic certificate which can be used in many aspects of everyday life such as: e-commerce, banking transactions, electronic signatures etc.

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# AUTOMATIZATION OF PHARMACY INVENTORY MANAGEMENT

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## ABSTRACT

Pharmacy inventory management (PIM) comprises business activities which are connected with the size and placement of stocked drugs. To manage minimal and maximal drugs stock, orders dynamics etc., pharmacies must track expiration dates of each drug in stock. Outdated drugs can't be counted as stock and produce lot of costs, especially for their disposal. The most number of pharmacies in Bosnia use European Article Numbering (EAN13) barcode by which is impossible to define drug expiration dates. Radio Frequency Identification (RFID) enables full automatization of PIM, but it is still not in use, mostly because of high costs of implementation of this system.

In our research we have observed 52 Bosnian pharmacies and presented another approach to barcode technology which can be used in automatization of PIM. As the base we have used existing EAN13 code, adding 6 digits for expiration dates. We have successfully created and tested program for extraction of EAN13 and expiration dates from that barcode using separate files in database to keep inputs, outputs and stocks of each item by expiration dates.

**Key Words:** Pharmacy Inventory Management, Automatization, Barcode Technology, Radio Frequency Identification (RFID), Clarion Programming Language

## INTRODUCTION

Inventory management is the systems and processes of maintaining the appropriate level of stock in a warehouse. The activities of inventory management involves in identifying inventory requirements, setting targets, providing replenishment techniques and options, monitoring item usages, reconciling the inventory balances, and reporting inventory status (Sysoptima, 2005). The main activities (amongst the others) are: inventory planning and demand forecasting, inventory monitoring and balance reconciliation and inventory reporting. There is different types of costs that take part in inventory cost structures: ordering (or setup) cost, carrying (or holding) cost (cost of capital, cost of storage, cost of obsolescence, deterioration, and loss), stock out cost, item costs, shipping costs and other cost subject to volume discounts.

To have a successful pharmacy inventory management, it is very important (especially for drugs) to track and control of the expiration dates. As researches show (Charlotte A. S., 2002) (McCarthy G., 2005): Much of the pharmaceutical waste occurring at a pharmacy was due to expired pharmaceuticals. The development of reverse distribution companies has enabled pharmacies to ship all outdated drugs as products back through these firms for the purpose of returning them to the manufacturer for credit. Any outdated items that do not meet the manufacturers' return policy become waste at the reverse distributor which becomes the waste generator, since this is where the decision to discard the item is made.

The most number of pharmacies in Bosnia (in the Europe also) use EAN13 barcode as the standard by which is impossible to define expiration dates. Pharmacies in Bosnia mostly follow expiration dates manually. Employees walk around from shelf to shelf and write down quantity with separate expiration dates of each lot (or item) and send this, paper based reports to the managers. They enter the data into computers (mostly in Excel), analyze them and make appropriate decisions connected with orders, prices, sales etc. This approach to the pharmacy inventory management is less successful.

## 1. THE ROLE OF INFORMATION TECHNOLOGY

### 1.1. Barcode Technology

There are two main types of barcodes which are used in enterprises: linear (1D) and two-dimensional (2D). The usage of first one is much cheaper and simple but it can present smaller number of human readable codes. Linear barcodes are used widely and there is a lot of types of them like: UPC, CodaBar, Code 25, 39, 128, Pharmacode, European Article Numbering -EAN, etc. There is a lot areas for use of barcode technology like: inventory management, stock control, manufacturing, patient identification, drug identification, purchased items scanning, work orders scanning, equipment tracking, document

management, entertainment (tickets with barcode) etc. (Šabanović Z., Osmanbegović E., 2010). EAN13 barcode is used as a standard in most European countries.

## 1.2. Radio Frequency Identification (RFID)

The purpose of an RFID system is to enable data to be transmitted by a portable device (using radio frequency), called a tag, which is read by an RFID reader and processed according to the needs of a particular application. The data transmitted by the tag may provide identification or location information, or specifics about the product tagged, such as price, color, date of purchase, etc. RFID technology has been used by thousands of companies for a decade or more. RFID quickly gained attention because of its ability to track moving objects. There are a lot of current and potential uses of this technology (Association for Automatic Identification and Mobility, 2010) like: asset tracking, manufacturing, supply chain management, retailing, payment systems, security and access control.

## 2. MATERIAL AND METHODS

In September 2011. we have observed 52 small and middle size pharmacies in North Eastern of Bosnia and Herzegovina. Tracking of drug expiration dates is very important for all of them. For simulation and testing purpose we have generated extended barcode which includes EAN13 barcode and 6 digits for expiration date (with point as delimiter) (Picture 1, Picture 2). Through experiments, as the most appropriate we have found Codabar which can accept up to 30 numeric digits. We have printed barcodes in 600\*600 dpi in various sizes (width from 10cm to 2cm) using Datamax I-4604 thermal printer which is used for label printing applications that demand high-resolution graphics, two-dimensional barcodes or very small labels. For barcode scanning we have used two types of barcode scanners: Metrologic mk9590-61a38 (lower resolution reader) and 3800g Linear & PDF Image Reader (2dimensional and high resolution reader).

In Clarion programming language we have created form for extended barcode scanning and routine for EAN13 and expiration date extraction from it (Šabanović, Z., Osmanbegović, E., 2010). Separate files (tables) were added to the relational database to keep expiration dates and quantity for each item (with different expiration date).

Picture 1. Samples of smallest extended barcodes (Codabar) that can be decoded



Picture 2. Sample of drug with extended barcode (front side) and EAN13 (top side)



### 3. RESULTS

By analyzing of data from 52 observed pharmacies we have found that 100% of observed pharmacies use barcode technology for point of sale purposes, 17,3% generates and prints barcodes (EAN13 only 11,5% of pharmacies), 88,5% of pharmacies track expiration dates manually (Table1). In observed pharmacies there is no any specific Decision Support Systems – DSS, built to help and automate pharmacy inventory management. There is no usage of RFID technology in pharmacies inventory management

Table 1. Usage of barcode technology (52 observed pharmacies)

Description	Number of pharmacies	Percentage
Point of Sale (POS) usage of barcode technology	52	100,0%
Other uses of Barcode (inventory management)	7	13,5%
Barcode generate and print	9	17,3%
EAN13 generate and print	6	11,5%
Manual tracking of drugs expiration dates	46	88,5%
Usage of RFID	0	0,0%
Computer generated drugs orders	11	21,2%
Usage of specific DSS in pharmacy inventory management	0	0,0%
Usage of Excel in pharmacy inventory management	36	69,2%

Picture 3. Form for extended barcode scanning

During testing of form and program routine made in Clarion (Sofvelocity Inc., 2011) (Picture 3, Picture 4) we didn't find any errors in drugs expiration dates extraction and storing them in the database. Barcode can be printed in a minimal size 2,8cm of width (Picture 1). Smaller barcode pictures cannot be scanned and decoded. Files/tables which keep expiration dates have been successfully added in existing relational database Sofvelocity Inc., 2011) (Diagram 1)

Picture 4. Routine for EAN13 and drugs expiration date extraction

```

Extract_EAN_ExpiryDate  ROUTINE

  IF barcode = '' then exit.

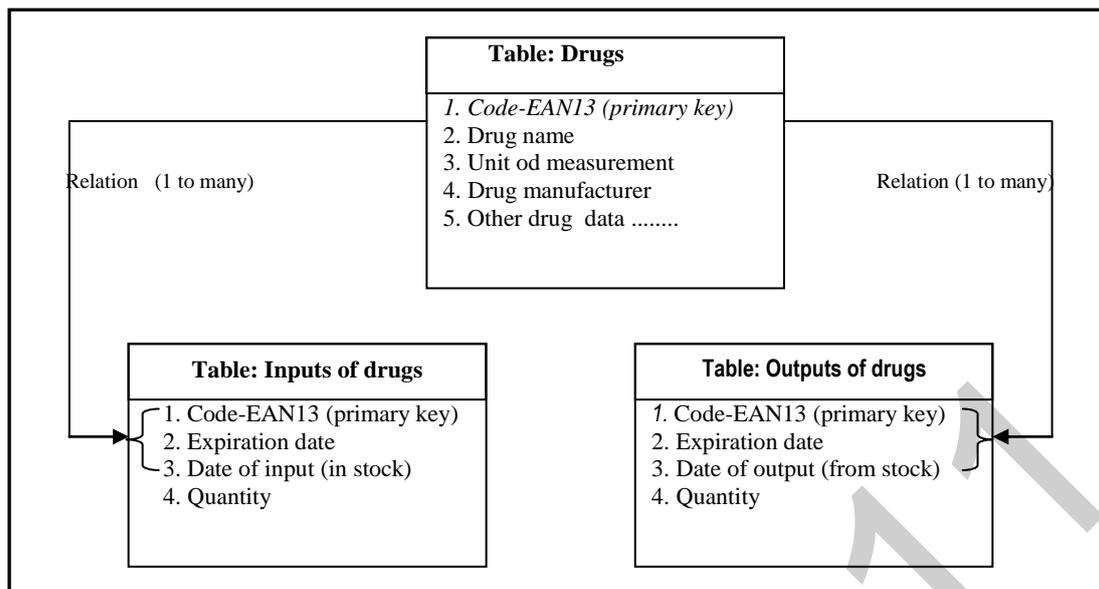
  extract_date# = 0; EAN13 = ''; exp_date = 0; Day'' = ''
  Month'' = ''; Year'' = ''

  LOOP x# = 1 TO LEN(CLIP(barcode))

    IF SUB(barcode,x#,1) = '.' ? Delimiter (here point)
      extract_date# = 1
      CYCLE
    -
    IF extract_date# <> 1 ? EAN13 extraction
      EAN13[x#] = SUB(barcode,x#,1)
    ELSE ? Expiry Date Extraction
      Day'' = sub(barcode,x#,2)
      Month'' = sub(barcode,x#+2,2)
      Year'' = sub(barcode,x#+4,2)
      BREAK
    -
    Date'' = clip(Day'') & '.' & clip(Month'') & '.' & clip(Year'')
    exp_date = DEFORMAT( Date'', @d5.)

  DISPLAY
  
```

Diagram 1. A part of database created to store drug expiration dates of inputs and outputs



#### 4. CONCLUSIONS

Based on our research we can conclude that barcode technology is used regularly in most Bosnian pharmacies but they cannot track expiration dates automatically. Extended barcode (which shouldn't be printed on the same side with existing EAN13) is cheap and very successful solution for drugs expiration dates tracking. This barcode can be even smaller since many drugs has only month and year as expiration date (for ex. 12.2012), so for coding is necessary additional 4 digits. Even with full expiration date we can make barcode smaller using ordinal numbers of days in year (3 digits) and one digit for year (for example 0042 - extracted drug expiration date is 04.01.2012).

On the drugs manufacturers side extended barcode should be printed on the package of each item (for point of sale purposes). In the hospital, wholesale and community pharmacies with smaller changes in their pharmacy information systems (software and databases) they should be able to track drugs expiration dates (with single barcode scan of drugs inputs and outputs) increasing level of automatization of pharmacies inventory management (planning of drugs stock, determining of drugs prices, generating drugs orders automatically and decision making process).

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# AZ91 MAGNEZYUM ALAŞIMININ İŞLENEBİLİRLİĞİ

## MACHINABILITY OF AZ91 MAGNESIUM ALLOY

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### Özet

Çevre kirliliğinin artması ve doğal enerji kaynaklarının azalması hem ekonomik hem de ekolojik-çevreci tasarımların ve ürünlerin önemini artırmıştır. Bu nedenle, günümüzde otomotiv endüstrisinde daha düşük yakıt tüketimine olan ihtiyacı karşılamak önemli bir faktör olmuştur. Bunu sağlamanın önemli bir yolu da araçların ağırlığını azalmaktır. Bu özelliği ile Magnezyum ve magnezyum alaşımları, araçlarda %35 oranında ağırlık azaltma imkanı sağlayan, en düşük yoğunlukta olması ile (yaklaşık 1.7 g/cm<sup>3</sup>) konstrüksiyonlarda kullanılan önemli bir yapı malzemesi olmuştur. Magnezyum alaşımları Alüminyum ile karşılaştırıldığında Alüminyumdan % 33, çelik ile karşılaştırıldığında ise %77 oranında daha düşük yoğunluğa sahiptir. Bu nedenle, yapısal uygulamalarda, taşıma, otomotiv, havacılık ve uzay endüstrisinde ve taşınabilir iletişim ve mikroelektronik parçaları da dâhil olmak üzere çok geniş bir kullanım alanına sahiptir.

Bu çalışmada, yaygın olarak kullanılan AZ serisi magnezyum alaşımlarından AZ91 magnezyum alaşımının işleme parametrelerinin kesme kuvvetleri ve yüzey pürüzlülüğü ve talaş oluşumuna etkisi incelenmiştir. Yapılan deneysel çalışmada AZ91 işlenmesinde işleme parametrelerinden devir sayısı ve talaş derinliğinin elde edilen talaş tipleri ile yüzey pürüzlülük değerleri arasında yakın bir ilişkinin olduğu görülmüştür.

### Abstract

The increase in environmental pollution and the decrease of energy resources attached importance to both ecological and environmental designs. Therefore, today, meeting the requirements of less fuel consumption in the automotive industry has been an important factor. One of the important ways to meet those requirements is to reduce the weight of the vehicles. With such a feature Magnesium and magnesium alloys make it possible to reduce the weight of the vehicles at a rate of %35 and since the density of magnesium is about 1.7 g/cm<sup>3</sup>, the magnesium has been a fundamental construction material. Magnesium alloys have % 33 less density when compared with aluminum and %77 when compared with steel. Therefore, Magnesium and magnesium alloys are used in a wide variety of structural applications including portable microelectronics and telecommunication, automotive, materials-handling and aerospace industries due to their low density.

In this study, AZ-series magnesium alloys AZ91 magnesium alloy is widely used, machining parameters, cutting forces and chip formation and surface roughness were investigated. In the experimental study, AZ91 chip cutting speed and cutting depth parameters with surface roughness values obtained from the types of chips were a close relationship.

### 1.Giriş

Günümüzde Magnezyum ve Magnezyum Alaşımlarının çok geniş alanlarda kullanılması sahip olduğu özellikler ile yakından ilgilidir. Bu bağlamda, magnezyum ve magnezyum alaşımlarının kullanım alanlarının giderek artması, en önemli işleme yöntemlerinden birisi olan talaşlı işleme yöntemlerinde karşılaşılan sorunların çözülmesi önemlidir.

Magnezyum ve magnezyum alaşımlarının, bilinen bütün metalik yapı elemanları içerisinde en düşük yoğunluğa sahip olması, yüksek özgül mukavemeti, dökülebilirliğinin iyi olması ve yüksek basınçlı kalıp döküm mümkün olması, yüksek hızlarda talaşlı işlenebilirliği ve doğada kolay bulunabilir özellikleri magnezyum ve magnezyum alaşımlarının önemini artırmaktadır (Friedrich ve Mordike, 2006; Friemuth ve Winkler, 1999). Magnezyum ve magnezyum alaşımları, düşük yoğunluğa sahip olmalarının yanı sıra, iyi süneklik, dayanım ve iyi korozyon direncine sahip demir dışı metaldir. Ancak, kristal yapısının hegzagonal sıkı paket (HSP) olmasından kaynaklanan şekillenebilirlik ve talaşlı işleme sırasında tutuşma ve yanma gibi sorunlar yüzünden üzerinde Alüminyum (Al) kadar çalışmalar yapılamamıştır. Ancak ekolojik denge, yakıt tasarrufu vb. konular son yıllarda gündeme geldiğinden, magnezyum ve magnezyum alaşımlarının kullanımı üzerinde daha fazla yoğunlaşma olduğu göze çarpmaktadır. Alaşımlandırma veya farklı döküm yöntemleri kullanılarak göreceli olarak

şekillenebilirlik geliştirilebilmektedir. Magnezyum ve alaşımlarından en yaygın olarak kullanılanlar AZ serisi (Al-Zn), AM serisi (Al-Mn) ve AS serisi (Al-Si) alaşımlardır. Bu alaşım serilerinde de görüldüğü gibi magnezyum içinde bulunan en yaygın ikincil element olarak alüminyum önde gelmektedir (Denkena ve diğ., 2004). Bunlardan en yaygın kullanılanlardan birisi AZ91 magnezyum alaşımıdır (Candan ve diğ., 2011).

Magnezyum ve magnezyum alaşımlarından elde edilen parçaların en önemli üretim yöntemi dökümdür. Magnezyum ve magnezyum alaşımları yaygın olarak kullanılan diğer metallerle karşılaştırıldığında daha yüksek işlenebilirlik özelliğine sahiptir (Friedrich ve Mordike, 2006; Mordike ve Ebert, 2001).

Talaşlı imalat yöntemleri kullanılarak yapılan makine parçalarının yüzey kalitesi birçok değişkene bağlı olarak değişmektedir. İşlenmiş bir yüzeyin yapısı, kalite açısından en önemli kriterlerden biridir. Tornalama operasyonlarında ideal talaş kaldırma işlemi, kesici uç yüzeyinde düşük mekanik ve termal yüklerin olduğu, düşük kesme kuvvetleri ile elde edilen yüksek yüzey kalitesi ve kolay kırılarak kesici ve iş parçası üzerinden uzaklaşan talaşlar olarak tanımlanmaktadır (Denkena ve diğ., 2005). Tornalama işlemlerinde kesme hızı (Cutting Speed), talaş derinliği (Depth of Cut) ve ilerleme miktarı (Feed Rate) önemli parametrelerdir.

Magnezyum ve magnezyum alaşımlarını talaşlı işleme operasyonlarında yüksek kesme hızlarında işlemek mümkündür. Ancak, kesme hızını artırdıkça işleme esnasında iş parçası ile kesici ucun talaş yüzeyi arasında sürtünmeden kaynaklanan sıcaklık artışı ile talaşların kesici yüzeyine yapışması sonucunda kesici yüzeyinde talaş yığılması (Flank Build Up - FBU) meydana gelir ve bunun sonucunda magnezyum talaşlarının tutuşması ve yanması ihtimali yükselir (Tönshoff ve diğ., 2006; Friemuth ve Winkler, 1999).

Magnezyum alaşımlarının talaşlı işleme operasyonlarında yüksek kesme hızlarında talaş kaldırma sırasında yüksek mekanik ve termal gerilmelerin oluşmasına bağlı olarak işleme sırasında kesicinin ucunda yüksek sıcaklıkların ortaya çıkmasına yol açmaktadır (Hou ve diğ., 2010). Kesicinin uç kısmında sıcaklık artışına bağlı olarak kesici talaş açısı ile kesici yan kesme yüzeylerinde aşınma meydana gelir. Ayrıca, yüksek kesme hızlarında tornalama operasyonlarında açığa çıkan yüksek sıcaklıklar kesicinin sertliğinin azalmasına ve işlenen yüzeylerin yumuşayarak çıkan talaşların kesici uca yapışması ile kesici ucun aşınması daha da hızlanmaktadır (Weinert ve Lange, 2001; Tönsoff ve Winkler, 1997). İşlenen makina parçalarında titreşim ve termal genleşmelerin artışına sebep olur ve bunun yanı sıra toleransların ve yüzey kalitelerinin bozulmasına neden olur.

Talaşlı işlemede operasyonlarında soğutma sıvısı kullanılarak yapılan işlemlere ıslak işleme (Wet machining), soğutma sıvısı kullanılmadan yapılan talaşlı işleme operasyonlarına kuru işleme (Dry Machining) denilmektedir (Groover, 2010). Talaşlı işleme operasyonlarında özellikle kesicinin ısınmasını önlemek amacıyla soğutma sıvısı kullanılmaktadır. Magnezyum parçaları, kuru ya da ıslak işlemek mümkündür. Ancak, talaşlı işleme operasyonlarında özellikle yüksek kesme hızlarında kuru işleme sırasında magnezyum talaşlarının kolayca tutuşması ve yanması en büyük olumsuz özelliğidir (Ruzi ve diğ., 2009).

Tönsoff ve Winkler (1997) tarafından AZ91 magnezyum alaşımı üzerinde kuru işleme koşullarında 900 m/dk kesme hızında tornalama işlemleri yaparak magnezyumun talaşlarının iş parçası ile kesici uç arasında sürtünmeden dolayı talaşların yığıldığı (FBU) ve kesici üzerine yapıştığı rapor etmişlerdir. Friemuth ve Winkler (1999) magnezyum alaşımlarının kuru işleme koşullarında kesme kuvvetlerini azaltarak ve elmas kesici uç (Polycrystalline Diamond-PCD) kullanarak tornalama sırasında talaş sıcaklığını düşürerek talaşın yanma tehlikesini azaltabileceğini rapor etmişlerdir.

Fang ve arkadaşları (2005) tarafından yapılan bir çalışmada ise, magnezyum alaşımlarının freze tezgâhında kuru işleme koşullarında yüksek kesme hızlarında ortalama sıcaklıklarda kesici yan yüzeyinde yanmanın meydana geldiği sıcaklık değerlerini belirlemeye çalışmışlardır. Ozsváth ve arkadaşları (2008), AZ91 magnezyum malzemenin, yeni görüntü inceleme metodu ile freze çakısının dönmesi ile oluşan talaşın sıcaklıklarını incelemişlerdir.

Soğutma sıvısı kullanılarak yapılan tornalama işlemlerinde özellikle yağ esaslı soğutucuların kullanılmasında da bazı olumsuzluklar söz konusudur. Yüksek kesme hızlarında yağ esaslı soğutma sıvılarının yanma tehlikesi bulunmaktadır (Tikal ve diğ., 2000). Su esaslı soğutma sıvılarında ise talaşlı işleme sırasında talaşların biriktiği ortamda hidrojen birikmeye başlar. Hidrojenin düşük tutuşma noktasına sahip olduğu dikkate alındığında ortamda biriken hidrojenin ne kadar tehlikeli olabileceği unutulmamalıdır. Eğer ortamda bulunan bir ateş magnezyum talaşlarına ulaşırsa, magnezyum suyla doğrudan reaksiyona girerek daha güçlü yanacaktır. Bu ekonomik ve ekolojik açıdan dikkate alınması gereken bir konu olduğu gibi çalışanların ve çalışma ortamının güvenliği açısından oldukça önemlidir. Ayrıca, tornalama işlemlerinde soğutma sıvısı kullanılması durumunda ise çıkan talaşların geri dönüşümünde kayıplara ve çevre kirliliğine neden olmaktadır (Hanko ve diğ., 2000).

Arai ve arkadaşları (1996), AZ91 magnezyum alaşımlarının işlenmesinde talaşın kırılmasını incelemişler ve helisel olarak oluşan boru biçimindeki talaşların yanmasının kolay olmadığını ve katmanlar biçiminde talaş kaldırmanın uygun olduğunu belirtmişlerdir.

Hou ve arkadaşları tarafından (2010) yapılan çalışmada, AM50 ve AZ91 magnezyum alaşımlarının düzlem yüzey frezeleme operasyonunda, talaş derinliği ve kesme hızının etkileri araştırılmıştır. Bu çalışmada, farklı kesme parametrelerinde elde edilen talaşların şekli ile talaşın tutuşması arasındaki ilişki incelenmiş ve AZ91 ve AM50 magnezyum alaşımlarında kesme hızına, ilerleme hızına ve talaş derinliklerine bağlı olarak talaşların tutuşması ve yanmanın nasıl olduğu araştırmada rapor edilmiştir. AZ91 alaşımında tutuşma ve yanmanın AM50 alaşımına göre daha çabuk olduğu araştırmaların önemli bulguları arasındadır. Bu araştırmalardan, magnezyum alaşımlarının bileşen özellikleri ile yanma ve tutuşmanın kesme hızı, talaş derinliği gibi işleme parametreleri ile ilişkili olduğu tezinin doğru olabileceğini göstermektedir.

Friemuth ve Winkler (1999) tarafından yapılan araştırmada ise, Sementit karbid kesici kullanarak AZ91D magnezyum alaşımının kesme uzunluğuna ve kesme kuvvetine bağlı olarak kesici ucunda meydana gelen talaş yığılmasının oluşumunu (FBU) araştırmışlardır. Tönsoff ve Winkler (1997), yaptıkları çalışmalar ile AZ91 alaşımının işlenmesinde en uygun kesici özellikleri üzerinde araştırmalar yapmışlar ve en iyi sonuçların Polycrystalline diamond (PCD) kesici uçlar ile elde edildiğini ve bu kesicilerin talaş yığılmasını (FBU oluşumunu) en aza indirdiğini rapor etmişlerdir. Bu araştırmalar, kesici ucunda talaş yığılmasının kesme kuvvetleri ile ilişkili olduğunu ve kesme kuvvetlerinin talaş yığılmasını artırdığı, bunun sonucunda kesici ucunda sıcaklık artışına bağlı olarak tutuşma ve yanma meydana geldiği tezini ortaya çıkarmaktadır.

Bu çalışmada talaşlı imalatta, AZ91 magnezyum alaşımında, kesme hızı, devir sayısı, talaş derinliği ve ilerleme miktarına bağlı olarak yüzey işleme parametrelerinin kesme kuvvetleri ve yüzey pürüzlülüğü ve talaş oluşumuna etkisi incelenmiştir.

## 2. Deneyel Çalışmalar

Mg, Al ve Zn külçeler (%99.9 saflıkta) Sakarya Metal Ltd.'den temin edilmiştir. Hazırlanan ön alaşımlardan ikinci bir ergitme ile deney numunelerinin dökümü yapılmıştır. Tablo 1.'de AZ91 magnezyum alaşımının kimyasal bileşimi verilmiştir. AZ 91 alaşımının üretim yöntemi ve proses parametrelerinin detayları Ünal (2008) ve Koç (2008) tarafından daha önce rapor edilmiştir. Kısaca, ergiyik Mg alaşımı 720 °C de 30 mm çap ve 170 mm boyunda çubuklar halinde kokil kalıba SF<sub>6</sub> gazı altında dökülerek elde edilmiştir. Mikroyapı incelemeleri optik mikroskop ile yapılmıştır. Metalografik inceleme için numunelerin yüzeyleri sırasıyla 400, 600, 1000 mesh'lik zımparalar ile saf su kullanılarak zımparalanıp ve 1µm alumina pasta kullanılarak parlatılmıştır. Sonra numune dağlanarak mikroyapı inceleri Nikon Epiphot 200 marka optik mikroskopta gerçekleştirilmiştir.

**Tablo 1. AZ91 Magnezyum Alaşımının Kimyasal Bileşimi**

AZ91 Magnezyum Alaşımı	%Al	%Mn	%Zn	%Si	%Fe	%Mg
	9.41	0.11	0.96	0.12	0.022	Kalan

Numunelere talaşlı işleme operasyonlarından tornalama işlemi yapılmıştır. Talaşlı işleme operasyonlarında Boxford 250 CNC torna tezgâhı kullanılmıştır. İşleme parametreleri olarak devir sayısı, talaş derinliği ve ilerleme hızı ele alınmıştır. Deney çalışmasında ön temizlik talaşı alınarak numuneler çapı 20 mm indirilmiştir (Şekil 1). Çalışmada üç farklı devir sayısında (1000, 2000 ve 3000 dev/dk), beş farklı talaş derinliklerinde (0.1, 0.25, 0.5, 1.0, 2.0 mm) ve sabit ilerleme hızında (f: 0.102 mm/dev) işlenmesi ile veriler elde edilmiştir. Kuru işleme koşullarında işleme gerçekleştirilmiştir. Kesici takım malzemesi olarak Taegutec CCGT 120408 FL K10 kesici uçlar kullanılmıştır.

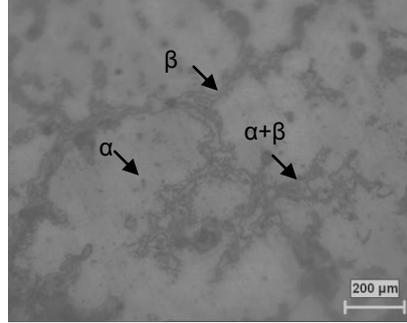


**Şekil 1. AZ91 Magnezyum alaşımı işlenen deney numuneleri**

Belirlenen parametrelerde işlenen numunelerinin yüzey pürüzlülükleri Time TR200 yüzey pürüzlülük cihazı ile elde edilmiştir. Yüksek çözünürlüklü fotoğraf makinası ile numunelerin devir sayısı ve talaş derinliğine bağlı oluşan talaş tiplerinin görüntüleri elde edilmiştir.

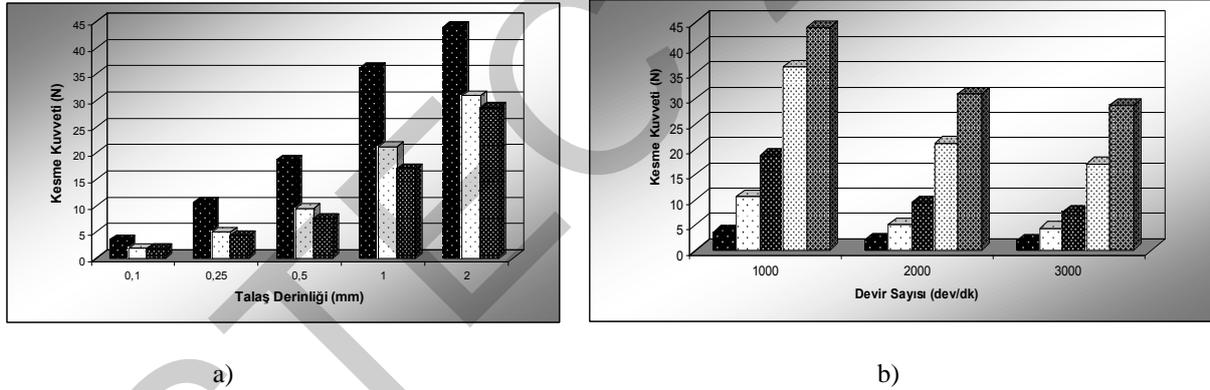
### 3. DeneySEL SonuÇlar ve Deęerlendirme:

AZ91 alařımının mikroyapısı Őekil 2’de verilmiřtir. Mikroyapı incelendięinde, yapıda Mg matris ( $\alpha$ ) fazının yanı sıra,  $Mg_{17}Al_{12}$  ( $\beta$ ) ve  $\alpha+\beta$  ötektięinin tane sınırları boyunca daęıldığı grlmektedir. Literatrde (Cizek ve dię., 2007) AZ91 alařımında  $\alpha$ -Mg matrisin yanı sıra  $\beta$  intermetaliki ve  $\alpha+\beta$  ötektięi oluřtuęu rapor edilmektedir ki bu alıřma ile uyumludur.  $\beta$  intermetalik fazı tane sınırları boyunca aę Őeklinde ince bir faz olarak grnrken  $\alpha+\beta$  ötektięi Chinese Script (in yazısı) Őeklinde grlmektedir.



Őekil 2. AZ91 Magnezyum alařımının mikroyapısı

AZ91 magnezyum alařımının tornalama iřlemlerinde, devir sayılarına baęlı olarak (1000, 2000 ve 3000 rpm) farklı talař derinliklerinde (0.1, 0.25, 0.5, 1.0 ve 2.0 mm) talař derinlięi verilerek elde edilen kesme kuvvetlerine iliřkin grafik Őekil 3’te verilmiřtir. Devir sayılarındaki artıř ile birim devirdeki kesme yzey alanının sabit tutulabilmesi iin ilerleme hızları F:102, 204 ve 306 mm/dk olarak belirlenmiřtir. AZ91 magnezyum alařımına ait tornalama iřleminde oluřan kesme kuvvet eęrileri strain-gage yardımıyla bir dzenek oluřturularak elde edilmiřtir.

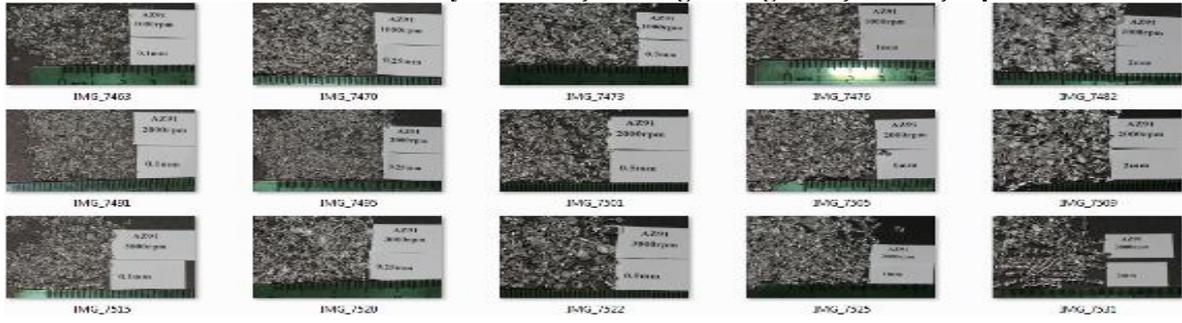


Őekil 3. (a-b) AZ91 Magnezyum alařımının Devir Sayısı-Talař Derinlięi-Kesme Kuvveti iliřkisi (İlerleme hızı sırasıyla F:102, 204 ve 306 mm/dk).

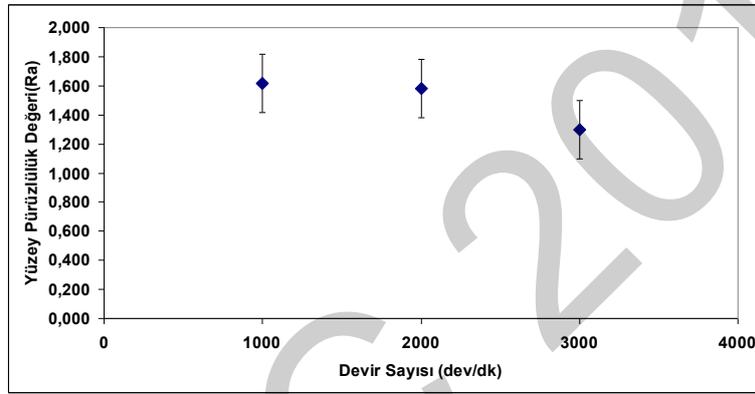
DeneySEL alıřmada AZ91 Magnezyum alařımının devir sayısına ve talař derinlięine baęlı olarak oluřan kesme kuvvetlerine iliřkin grafik Őekil 3. te grlmektedir. Grafiklerden anlařıldıęı gibi talař derinlięi arttıka kesme kuvvetinde bir artıřın olduęu gzlenmiřtir. Devir sayısının artması ile kesme kuvvetinin azaldıęı benzer Őekilde elde edilen grafiklerden anlařılmaktadır. Kesme kuvvetinin talař derinlięi ile artması malzemenin kesme sırasında meydana gelen talař kesit alanındaki artıř nedeniyle meydana gelmektedir.

Devir sayısı ve talař derinlięine baęlı oluřan talař tipleri Resim 1’de verilmiřtir. Talař oluřumu incelendięinde 1000, 2000 ve 3000 dev/dk ve 0.1 mm talař derinlięinde elde edilen talařların toz talař olarak oluřtuęu grlmřtir. Dřk devir sayısında (1000 dev/dk) talař derinlięinin artması ile talařların ok fazla uzamadan kırıldıęı grlmektedir. Devir sayısının 3000 dev/dk ıkarılması ile talařların belirgin bir Őekilde helisel biimde uzayarak ve kıvrılarak oluřtuęu gzlenmiřtir.

Resim 1. Devir Sayısı ve Talaş Derinliğine Bağlı Oluşan Talaş Tipleri



AZ91 magnezyum alaşımının Şekil 4’de devir sayısı-yüzey pürüzlülük değerleri görülmektedir. Devir sayısı arttıkça yüzey kalitesi iyileşmektedir. Yüzey kalitesinin devir sayısı ile artışı kesme sırasında arayüzeyde kırılmanın hızlı kesme ile dislokasyon yığılması ve buna bağlı gevrek kırılma nedeni ile meydana geldiği düşünülmektedir. Düşük talaş derinliklerinde talaşın toz olarak meydana gelmesi ve derin talaşlarda helisel ve uzun olması talaş yüzeyinde sünek davranışın olduğunun bir göstergesidir. Bu noktadan, devir sayısı ile kesme kuvvetlerindeki düşüşün talaş/kesme kalemi arayüzeyinde dislokasyon yığılması ve buna bağlı gevrek kırılmanın meydana gelmesi olarak açıklanabilir.



Şekil 4: Devir Sayısı-Yüzey Pürüzlülük Değer (Talaş Derinliği 1 mm, f:0.102mm/dev)

#### 4.Sonuçlar

Deneysel sonuçlar;

- AZ91 alaşımlarında talaş derinliği arttıkça kesme kuvvetinde artışın olduğu,
- Devir sayısının artması ile kesme kuvvetinin azaldığı,
- Düşük talaş derinliklerinde ve tüm devir sayılarında talaş oluşumunun toz olarak oluştuğu,
- Talaş derinliğinin artması ile 2000 dev/dk’da talaşların çok fazla uzamadan kırıldığı,
- Devir sayısının 3000 dev/dk çıkarılması ve talaş derinliğinin artışı ile helisel biçimde uzayarak ve kıvrılarak oluştuğu,
- Devir sayısı artışı ile yüzey pürüzlülük değerinin düştüğünü göstermiştir.

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# BIODEGRADATION OF PESTICIDE: BROMUCONAZOL BY MICROBIAL CONSORTIUM IN BIPHASIC SYSTEM

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## Abstract

The bromuconazol is a fungicide which is toxic for the environment. This present study was led with the aim of testing, in vitro, its biodegradation.

The bromuconazol was thus used in the presence of a microbial consortium resulting from a treated soil. A biphasic system MBS / oil of silicone was used during all the period of acclimatization. The fermentation was followed by measure of the optical density, the determination of the dry weight, the emulsifying power as well as the hydrophobicity of the selected consortium.

The results obtained after one year revealed a strong adaptation of this one to the bromuconazol. The use of the biphasic system allowed a better assimilation of the pesticide. The microbiological study allowed identifying a single bacterial strain capable of using the fungicide as unique source of carbon. It is about *Aeromonas hydrophila*. This strain shows a strong hydrophobicity as well as an emulsifying power lived in saw some pesticide.

**Keywords:** fungicide, Biodegradation, Bromuconazol, biphasic system, Batches, microbial Consortium. *Aeromonas hydrophila*

## INTRODUCTION

The intensification of agriculture has been accompanied by an extensive use of pesticides that generated a contamination of soil and water, major environmental problem of current. This situation is particularly worrying that the use of pesticides should be repeated periodically. This repetition in the long term, necessarily leads to an accumulation of pesticides and their residues in our natural environment, endangering the entire population by their multifaceted toxicity (Bouziani, 2007). The most frequent studies concern the presence of these molecules in the soil (Senesi, 1993), water contamination, biotic and abiotic degradation of these products (Muller et al. 1978; Bollag, 1982), and finally the identification of residues that apparently seem to have a relationship with them (Calderbank, 1989).

The pesticide to which we are interested in this study is bromuconazol, a fungicide widely used around the world. It is a systemic fungicide activity. It belongs to the family of triazoles which are inhibitors of sterol biosynthesis. It is intended to protect cereal crops against fungal diseases. Its target is a cytochrome P450 enzyme encoded by the gene CYP51 (Robbertsee and al., 2001). Bromuconazol is an environmental contaminant. Moreover, it is toxic to humans. Repeated exposure can cause health problems, adverse effects on the liver resulting in tissue lesions and impaired functions (anonymous 4, 2008)

The main objective of this study is in this context and aims to study the ability of a microbial consortium obtained from different biotopes, to degrade this fungicide

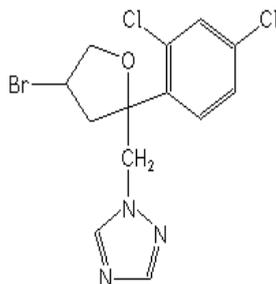
## 1. MATERIAL AND METHODS

### 1.1. Origin of the microbial consortium:

The first sample was taken from a ground agricultural nature located in the region of North- eastern Algeria. This soil is intended for crops of vineyards and has been extensively treated by bromuconazol. The second sample was collected from basins of biological treatment of wastewater also situated in North -eastern Algeria.

### 1.2. Bromuconazol:

This fungicide comes from Bayer (Rhône-Poulenc Agro- France). It is imported and widely marketed in Algeria as the Vectra. His brute formula is:  $C_{13}H_{12}BrCl_2N_3O$  and chemical structure is presented in the following figure.



**Fig.1. Chemical structure of the herbicide used: bromuconazol**

### 1.3. Selection and acclimatization of microbial consortium:

The acclimatization and selection of the microbial consortium was conducted in biphasic system MBS / silicone oil (batch culture). Thus, at 40 ml of medium basic salin MBS (aqueous phase) are added 10 ml of silicone oil (organic phase). bromuconazol is added in the organic phase at 50 $\mu$ g/ml. The aqueous phase was inoculated with 10 ml of microbial inoculum (biomass). After incubation at 30 $^{\circ}$ C and stirring at 190 rpm, cultures were centrifuged for 20 min at 5000 rpm. The culot obtained were washed with phosphate buffer and again centrifuged. Biomass collected will be used as inoculum for the next fermentation.

### 1.4. Biodegradation tests of bromuconazol in batch culture:

#### 1.4.1. Biodegradation of bromuconazol in biphasic batch:

After several months of acclimatization of microbial consortium in presence of bromuconazol, biodegradation is followed in biphasic system (medium MBS / silicone oil). At flasks containing a culture medium composed of 40 ml MBS and 10 ml of silicone oil are added 10 ml of the consortium previously acclimated to bromuconazol. The latter is added at a concentration of 50 $\mu$ g/ml. After incubation for one week at 30 $^{\circ}$ C with stirring of 200 rpm, fermentation was monitored by measuring the optical density, the determination of dry weight and changes in the pH of the medium. The emulsifying power and the hydrophobicity of the consortium were also studied.

#### 1.4.2. Biodegradation of bromuconazol in monophasic batch:

After acclimatization of the microbial consortium in presence of xenobiotic, biodegradation is also followed in the same way in monophasic system, in the absence of the organic phase (MBS without silicone oil).

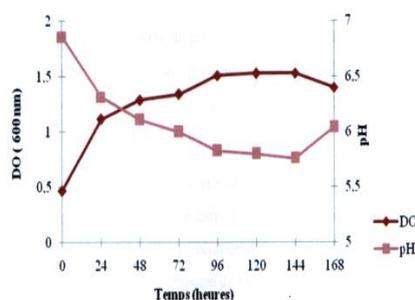
#### 1.4.3. Biodegradation of bromuconazol in pure culture:

Biodegradation tests of bromuconazol in pure culture were performed in monophasic system. bromuconazol is added at 50 $\mu$ g/ml. The samples are incubated for one week at 30 $^{\circ}$ C, with stirring at 190 rpm. The disappearance of the herbicide in the culture medium was performed using the technique of LC- MS -MS.

## 2. RESULTS AND DISCUSSION

### 2.1. Acclimatization of microbial consortium in batch culture:

After 4 weeks of acclimatization of the consortium in the presence of bromuconazol, the results obtained from different batch in biphasic system are shown in the following figure.



**Fig.2. Growth of the microbial consortium in biphasic system (MBS/silicone oil) in the presence of bromuconazol at 50 $\mu$ g/ml**

2.2. Study of the performance of biphasic system (MBS / silicone oil):

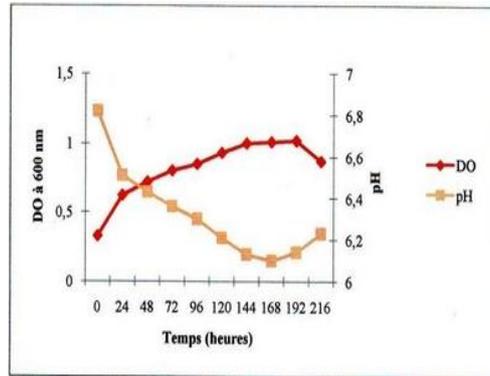


Fig. 3. Growth of the microbial consortium acclimated in batch monophasic

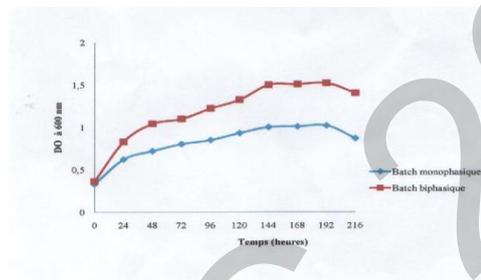


Fig.4. Evolution of the optical density of biomass in batch culture

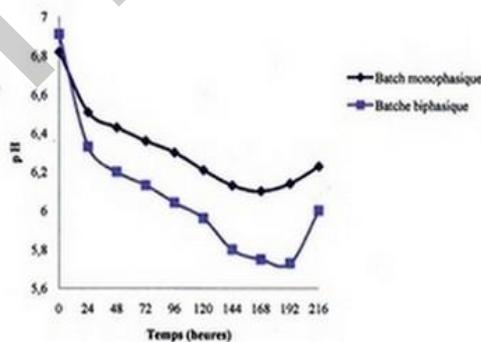


Fig.5. Evolution of pH in batch culture in the presence of bromuconazol

After about five months for the selection and acclimatization of the consortium implicated in the biodegradation of bromuconazol, the study of the biodegradation in batch monophasic (MBS only) was also studied. The aim of this comparative study between the two systems is to determine the usefulness and effectiveness of the organic phase (silicone oil) not only in the degradation process but also with regard to the viability of the consortium involved in the process. The results of test in monophasic system show clearly the complete absence of inhibitory effect of bromuconazol on the growth of microbial consortium previously

acclimated. In fact, a typically growth is thus obtained with an increase in the D.O of the culture and acidification of the medium. The maximum growth is obtained after 192 h of incubation at 30°C. The microbial consortium previously acclimated seems able to grow in the presence of bromuconazol as unique source of carbon and energy in monophasic system.

Comparing the curves obtained in monophasic and biphasic system show that the viability of the consortium is maintained in the two types of batch in the presence of bromuconazol. Although the same concentration of substrate (50µg/ml) was added, it does not appear to have the same effect on microbial activity. In the absence of silicone oil, the optical density of the medium reached an average maximum estimated at 1.02, whereas in the presence of the organic phase, the D.O recorded is 1.52. These observations were also found for pH.

### 2.3. Determination of emulsifying activity of the consortium:

After acclimatization in the presence of the herbicide, the study of the emulsifying activity of the consortium shows that it evolves in a similar way to the cell growth for reaching a maximum production after 144 h of incubation. So, the shape of the curve (Fig.6) shows clearly, a strong emulsifying power exhibited by the microbial culture in the presence of bromuconazol.

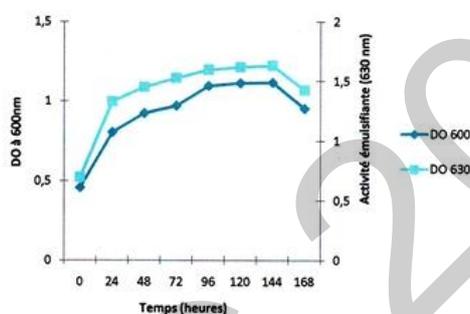


Fig.6. Emulsifying activity of the consortium acclimated to bromuconazol



Fig.7. The emulsifying power of the consortium in the presence of bromuconazol

### 2.4. Study of the hydrophobicity of the microbial consortium:

The study of the hydrophobicity performed according to the protocol BATH (bacterial adhesion to hydrocarbons) (Rosenberg, 1984) revealed that 55.67 % of the cells are hydrophobic. The hydrophobicity is a key factor in the selection of microorganisms for degradation of xenobiotics, demonstrating the strong adaptation of the culture of the consortium.

### 2.5. Identification of microorganisms in the consortium degrading bromuconazol:

After a period of acclimatization and adaptation after more than one year in the presence of bromuconazol used as the sole source of carbon and energy, the results obtained after tests of isolation and purification revealed the presence of a single type of colony. After the macroscopic and microscopic examination, the biochemical tests API 20 E and API 20 NE have identified the bacterium implicated in the biodegradation of bromuconazol. It is the species *Aeromonas hydrophila*

### 2.6. Results of the biodegradation of bromuconazol by *Aeromonas hydrophila*:

Different concentrations of bromuconazol shown in Fig.9 are those obtained after a series of dilutions performed on the initial sample for reasons of handling required by the technique used for the determination of the compound. The form of the curve indicating a gradual disappearance of the herbicide in the culture medium and an increase in the biomass of *Aeromonas hydrophila*, confirming the ability that has this species in the elimination of bromuconazol. The maximum growth, estimated by dry weight is reached after 144 h. The maximum degradation of bromuconazol seems occur during these first 72h.

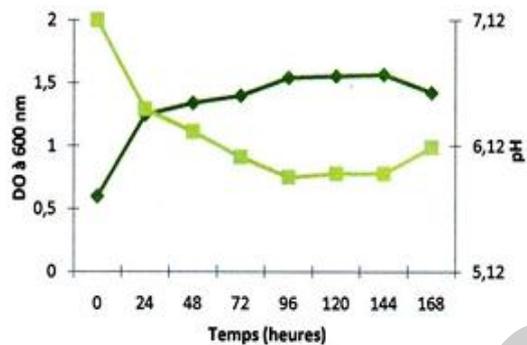


Fig.8. Growth of *Aeromonas hydrophila* in batch monophasic in the presence of bromuconazol

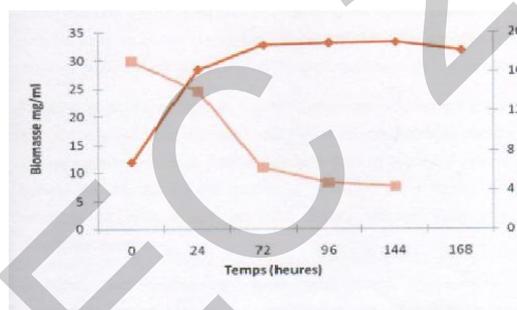


Fig.9. bromuconazol biodegradation by *Aeromonas hydrophila* in monophasic system

### CONCLUSION

The use of system biphasic has not only lifted the inhibition due to the substrate, but also allowed better pesticide assimilation compared to that obtained in monophasic system (mineral medium).

After one year of adaptation and acclimatization, the bacterium *Aeromonas hydrophila* has been isolated from a consortium initially inoculated in the MBS culture medium in the presence of bromuconazol.

The disappearance of bromuconazol in the medium culture confirms a real use of herbicide as unique source of carbon and energy by *Aeromonas hydrophila* and the ability possessed by this bacterial species to acclimatize and metabolize the herbicide. This ability is largely due to the presence of the organic phase (silicone oil).

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# BULANIK ÇOK KRİTERLİ KARAR VERME METODU İLE YAPIM İŞLERİNDE EN AVANTAJLI TEKLİFİN SEÇİMİ

## SELECTION OF MOST ADVANTAGEOUS PROPOSAL USING FUZZY MULTI-CRITERIA DECISION-MAKING METHOD IN CONSTRUCTION WORKS

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### Özet

Ülkemizde şu an uygulanmakta olan 4734 Sayılı Kamu İhale Kanunu kapsamında yapılan ihalelere ilişkin 2011 yılının ilk altı aylık istatistik raporları [1] incelendiğinde, toplam 32.166.939.000 TL'lik sözleşme imzalandığı görülmektedir. Bu toplam sözleşme bedelinin 12.654.533 TL'lik kısmını yapım işleri oluşturmaktadır. Kamu alımları içerisinde yapım işlerinin yaklaşık olarak %40 gibi en büyük paya sahip olması kamu kaynaklarının kısıtlı olduğu gerçeğiyle birlikte değerlendirildiğinde yapım işlerinin önemini ortaya koymaktadır. Yapım işi projelerinin belirlenen sürede öngörülen bütçe sınırları içerisinde kalınarak istenen kalitede gerçekleştirilebilmesi, belirtilen kriterlerin göz önünde bulundurularak, bu bilince sahip yüklenici seçimiyle mümkün olmaktadır. Bu doğrultuda, ihale karar verme sistematığı incelendiğinde, karar verme sürecinde etkin rol oynayan en önemli unsur, Ekonomik Açından En Avantajlı Teklifin belirlenmesidir. Bu çalışma kapsamında, insan düşünce sistematığına en yakın model olan ve sözel ifadelerin modellenbildiği Bulanık Mantık ile en uygun teklifin belirlenmesi hedeflenmiştir.

**Anahtar kelimeler :** 4734, En Avantajlı Teklif, Bulanık Mantık

### Abstract

In our country, is currently being implemented in contracts made under the Public Procurement Law No. 4734 on the statistical reports of the first six months of 2011 [1] is examined, contract total of TL 32.166.939.000 were signed. These works are part of the total contract amount of TL 12.654.533. Public procurement in the construction works have the largest share of approximately 40%, constrained by the fact that public resources are evaluated together, reveals the importance of construction works. Construction work projects, the realization of the required quality by keeping within the budget provided for a specified period, the specified criteria in mind, this consciousness, it is possible to have the choice of contractor. Accordingly, the procurement decision-making systematic analysis of the most important factor is playing an active role in decision-making process, the proposal to determine Most economically advantageous. Scope of this study, the closest model of human thinking system and verbal expressions that are modeled with fuzzy logic is aimed to determine the most appropriate proposal.

**Keywords:** 4734, Most advantageous proposal, Fuzzy logic

### Giriş

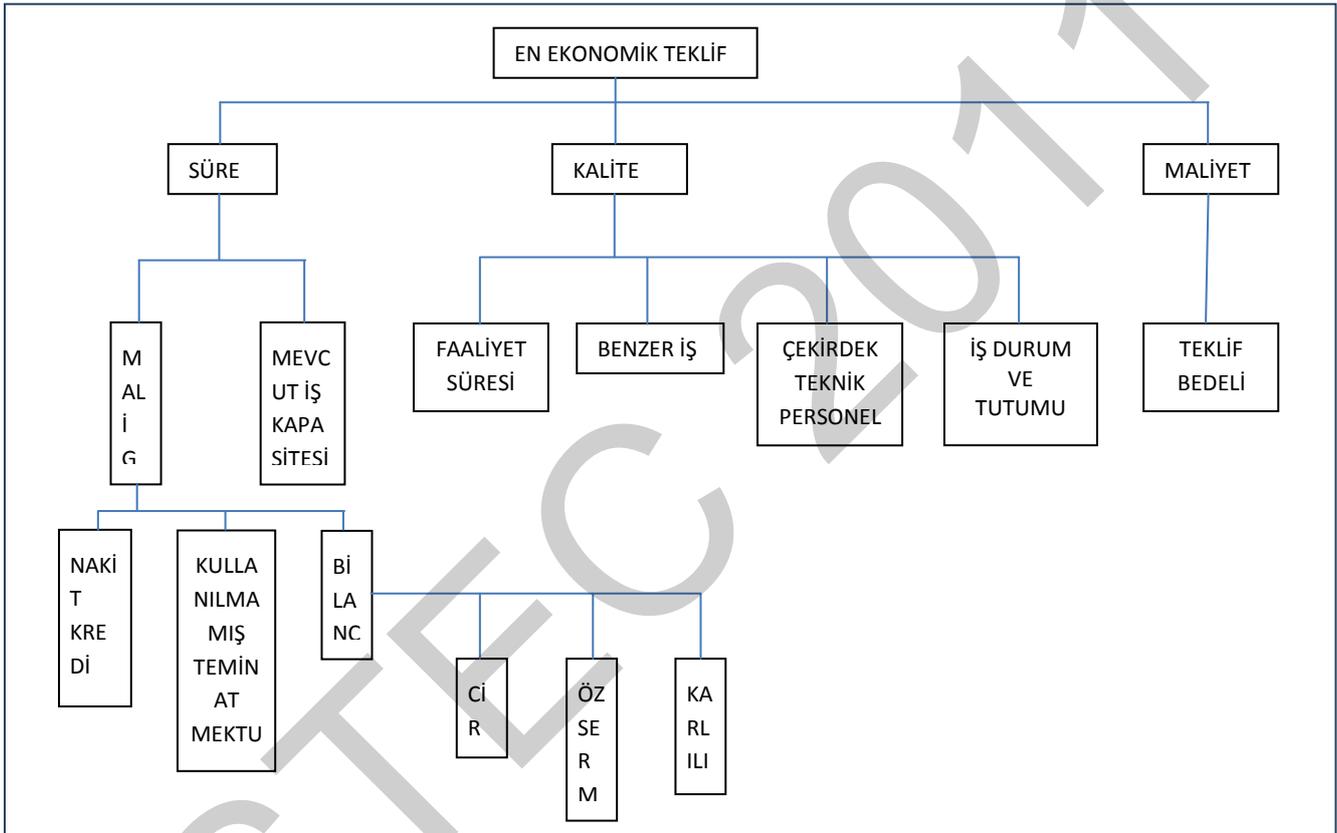
İnşaat sektörü, 100'den fazla yan sektörü doğrudan etkilemesi ve ekonomi içerisinde özel bir işlev üstlenmesinden dolayı, ülke ekonomisine yön veren lokomotif sektör olma özelliğine sahiptir. Özelde ve kamuda gerçekleştirilen tüm inşaat projelerinde amaç; projeyi kalite, maliyet ve süre üçgeni içerisindeki en optimum çözüm noktasında tamamlayabilmektir. Maalesef ülkemizde kamu sektörü Devlet İhale Kanunu'ndaki Uygun Bedelin Tercihinde Kullanılacak Kriterler Hakkında 2002 yılı Tebliği'ne göre "geçerli tekliflerin içinden en yüksek indirimli ihtiva eden teklif uygun bedeldir" tanımından yola çıkarak en düşük teklif veren firmalara ihaleyi vermek zorunda kalmaktadır. Bu durum, %50-60'lara varan tenzilatlarla iş alan yüklenicilerin, kaliteden büyük ödünler vermeleri sonucunu getirmiştir. Ülkemizde son zamanlarda meydana gelen depremlerde özellikle kamu binalarının en çok hasarı görmesi ve can kayıplarının bu tür binalarda yoğunlaşması gözleri

kamuya iş yapan müteahhitlere dolayısıyla ihale kanununun çarpıklığına çevirmiştir. Gerek yukarıda sayılan eksiklikler gerekse Avrupa birliğine giriş sürecinde artık bir zorunluluk haline geldiğinden 1.1.1984 yılında yürürlüğe giren 2886 sayılı Devlet İhale Yasası yerini 1.1.2003 tarihinden itibaren 4734 sayılı Kamu İhale Yasasına bırakmıştır. Yüksek ihale indirimleri hiçbir zaman en ekonomik teklif ve maliyet olmamaktadır. 4734 sayılı ihale kanunu asgari yeterlilik değerlerine sahip en düşük teklifin ekonomik açıdan en avantajlı teklif olmasını öngörmektedir. Bu durumda uygulamada kalite açısından problemleri beraberinde getirecektir. Aşırı düşük tekliflerin değerlendirme dışı kalması, objektif bir kriter olmaktan uzaktır. Bunun yerine süre ve kalite açısından çeşitli kriterleri yerine getirmeyen teklifler dikkate alınmamalıdır.

### En Avantajlı Teklifin Seçimi

İnşaat projelerinin gerçekleştirilmesinde süre, kalite ve maliyet üçgeni Tablo 1’de görülmektedir. [2]

**Tablo 1.** En Ekonomik Teklifin Seçiminde Kriterlerin Hiyerarşik Yapısı



Bir inşaat projesinin istenen sürede bitirilmesinde, yüklenicilerin mali bakımdan güçlü olması önemli bir faktördür. Bir yüklenicinin mali gücü yüksek ve taahhüdündeki iş miktarı kapasitesinden az ise yüklenici işine konsantre olabilir ve bunun sonucu işi süresinde bitirebilir. Mali gücün yüksek olması ise banka nezdinde ki profili ve bilanço ile ölçülebilir. Kullanılmamış nakit kredisi ve kullanılmamış teminat mektubu kredisi banka nezdinde aranacak alt kriterleri oluşturur. Bilançoya bakılacak olursak son beş yılda yapılan cironun yüksek olması, öz sermayenin fazlalığı ve karlılık oranının maksimum olması da yüklenicinin mali gücünün yüksek olduğunun bir göstergesidir. Taahhüdündeki iş miktarı, kapasitesinin altında ise işi süresinde bitirme olasılığı yüksektir [3].

### Bulanık Çok Ölçütlü Karar Verme Yöntemleri

Bulanık çok ölçütlü karar verme konusunda bir çok yöntem mevcuttur. Bu çalışma kapsamında Yager ve Chen'in yöntemleri incelenecektir.

## Yager'in Yöntemi

Bulanık ortamda karar mekanizması; Bellman ve Zadeh tarafından, amaçların ve belirsizliklerin doğada bulanık olduğu bir karar süreci olarak belirlenmiştir. Bu demektir ki amaç ve belirsizlikler, sınırları net olmayan alternatif grupları oluşturmaktadır. Bellman ve Zadeh, karar mekanizmasının konvensiyonel yaklaşımındaki genel faktörleri ve karar sürecine dahil olan kavramları onaylamıştır [4].

Bunlar;

- Alternatif kümesi
- Çeşitli alternatifler arasındaki seçimin belirsizlik kümesi
- Alternatifin seçimi sonucunda oluşan kazanç veya kayıpla ilişkilendirilen bir performans fonksiyonu

Bulanık bir ortamda performans fonksiyonunun yerini "bulanık amaç" alabilmektedir. Bulanık amaç, bulanık bir küme olarak  $\{\chi, \mu_G(\chi) \mid \chi \in U\}$  şeklinde gösterilebilir. Burada "U" bulanık küme (G)'nin evrenidir.  $\mu_G(\chi)$  bulanık amacın dahil olma fonksiyonudur ve değerleri [0,1] arasındadır [5].

Bulanık ortam içindeki, amaç ve belirsizlikler, bir karar mekanizmasının formülasyonunda bulanık amaç ve bulanık belirsizlik olarak aynı şekilde ele alınabilmektedir. Geleneksel karar mekanizması yaklaşımında kullanılan Lagrange çarpanları ve ceza fonksiyonları performans fonksiyonları ve belirsizlikler arasında bir ilişki/benzerlik olduğunu açıkça gösterir.

Bulanık karar; amaç ve belirsizliklerin kesişerek oluşturduğu, bulanık küme;  $D$  şeklinde ifade edilebilir.  $G_i, i = 1, 2, \dots, m$  şeklinde verilmiş bulanık amaçlar ve  $C_j, j = 1, 2, \dots, n$  şeklinde verilmiş bulanık belirsizlikler ile çözüm  $D$  aşağıdaki ifade kullanılarak bulunur [6].

$$D = G_1(x) \cap G_2(X) \cap \dots \cap G_m(X) \cap C_1(X) \cap C_2(X) \cap \dots \cap C_n(X)$$

$D(x), x \in X$  alternatifleri kapsamında tanımlanmış bulanık kümedir. Karar mekanizmasında  $D$  içerisinde en fazla bulanık olma özelliğine sahip  $x^*$ , optimum karar mekanizması için alternatif olarak seçilmelidir. Çünkü  $x^*$ 'in amaç kümesine ve belirsizliklere uygunluğu en iyi düzeydedir.

Bunun matematiksel ifadesi;

$$x^* = \arg \{ \max D(x) \}$$

$D(x)$  en büyük değerini aldığı anda  $x^*$  argüman veya indeks değerini almış olur.

## Yager'in Yaklaşımı

Bu yaklaşım, karar verici için amaçlar ve belirsizlikler aynı önemde olmadığı durumlarda kullanılır. Yager, her kritere karar verici için önemini gösteren bir rakam atanması fikrine dayalı bir metod geliştirmiştir. Bir üstel ağırlıklandırma metodu Saaty tarafından geliştirilen ikili karşılaştırmaların yöntemini kullanarak elde edilen ağırlıklandırma ve karar bileşenlerini önemlerinin ağırlıklandırması için kullanmıştır. Bu ağırlıklandırma şekli bulanık karar sürecinin gerçek dünya ihtiyaçlarına yanıt vermesini daha kolay hale getirmiştir.

Bulanık karar göz önüne alındığında, tüm alternatifler için bütün kriterleri altındaki performans verileri uygun üsse yükseltilmiştir ve alternatif aşağıdaki koşulu sağlar [5].

$$\text{MaxMin} \left[ G_1^\alpha(X), G_2^\alpha(X), \dots, G_m^\alpha(x), C_{m+1}^\alpha(x), C_{m+2}^\alpha(x), \dots, C_{m+n}^\alpha(x) \right]$$

Bu yaklaşım bir ikili karşılaştırma matrisinin maksimum özdeğerine atanmış özvektör kullanılmasına dayalıdır. Daha önce etkileri keşfedilmiş olan bulanık kümenin skalar üsse yükseltilmesiyle eğer  $\alpha$ 'ya (belirli bir amaç veya kısıtım karar verici için bağlı önemi) uygun bir değer atamak için bir yöntem bulunursa bütün karar üzerindeki arzulanan etkilerde elde edilebilir.

Eğer her amaca bir  $\alpha > 0$  atanırsa (amaç veya kısıt önemli oldukça  $\alpha$  büyür) ve ağırlıklandırılmış karar fonksiyonumuz;

$$D(X) = \left[ G_1^\alpha(X) \cap G_2^\alpha(X) \cap \dots \cap G_m^\alpha(x) \cap C_{m+1}^\alpha(x) \cap C_{m+2}^\alpha(x) \cap \dots \cap C_{m+n}^\alpha(x) \right]$$

$$D(X) = \min [G_{1\ 1}^\alpha(X), G_{2\ 2}^\alpha(X), \dots, G_{m\ m}^\alpha(x), C_{m+1\ m+1}^\alpha(x), C_{m+2\ m+2}^\alpha(x), \dots, C_{m+n\ m+n}^\alpha(x)]$$

olur. Böylece her amaç kriterini ve kısıtını sağlamak için her alternatifin önce yeteneğine göre oranlandığı ve her amaç kriteri yada kısıtım üstel ağırlıklandırma ile karar vericiye göre gerçek önemini yansıtmak için modifiye edildiği, karar verme için hiyerarşik sistem elde edilir.

Eldeki bir  $p$  amaçlar kümesi için, amaçların birbirlerine göre oranlama ölçeği oluşturmak istenirse; amaçlar,  $p = m+n$  durumunda karar problemini karakterize eden amaç kriteri ve/veya kısıtlar olabilir,  $i$  ve  $j$  amacını karşılaştırırken karar vericiden ilk önce hangi amacın daha önemli olduğu ikili karar vermesi istenir. Bu karar verildiğinde önem derecesine göre 1' den 9' a kadar değer atanması istenir.

Eğer  $i$  amacı  $j$  amacından üstünse atanan değer  $a_{ij}$  şeklinde olacaktır. İkili karşılaştırma matrisi;

$$a_{ij} = \frac{1}{a_{ji}}$$

olup bu denklem  $p \times p$  boyutundaki  $R$  ikili karşılaştırma matrisinin kolayca oluşturulmasını sağlar.

$$r_{ij} = 1, r_{ij} = a_{ij} \text{ ve } r_{ji} = 1/r_{ij}, i \neq j \text{ için}$$

Saaty;  $R$  ile gösterilen ve maksimum özdeğere karşılık gelen özvektörün karşılaştırılmasında sayısal oran ölçeği olduğunu göstermiştir. Yager normalize edilmiş özvektör ile sistemin mertebesini, karardaki bulanık kriterin ağırlıklandırması için çarpmıştır. Bu üstlerin değerini eğer faktörler eşit ise bir yapar.

Yager'in yaklaşımına göre aşağıdaki adımlar uygulanmalıdır [6].

1. Her kriter için bağıl önem hesaplanır. Ağırlıkları hesaplamak için Saaty'nin yöntemi kullanılır.
2. Ağırlıklaştırılmış karar matrisi elde edilir.
3. En iyi alternatif seçilir. Amaç en yüksek üyeliğe sahip alternatifin seçilmesidir.

### Chen'in Yöntemi

Chen yöntemi, Çok Ölçütlü Karar Verme (MADM) problemlerini, bulanık mantık çevresinde, hızlı ve etkili bir şekilde çözen, hesapsal zorlukların olmadığı yeni bir yaklaşımdır.

Bu yöntem, problemleri iki aşamada çözer. İlk aşamada, bulanık veri, sayısal puanlara dönüştürülür. Bulanık veri, sözel terimlerden, bulanık küme veya bulanık sayılardan oluşmuş olabilir. Eğer bulanık sayılar sözel terimlerden oluşmuşsa, ilk olarak bulanık sayılara dönüştürülür. Sonra, tüm bulanık sayılar (veya bulanık kümeler) sayısal skorlara atanır. Böylece ilk aşama sonucunda, sayısal verilerden oluşan bir karar matrisi elde edilmiş olur. İkinci aşamada, klasik MADM yöntemleri, alternatifler arasında bir sıralama yapmak için kullanılır. Genellikle, matematiksel hesaplamalar minimum düzeyde tutulur. Chen' in yaklaşımının kolay anlaşılır ve uygulanabilir olması özellikle yönetim ve sistem analistliğinde tercih edilmesini sağlar [7].

### Sözel Terimlerin Bulanık Sayılara Dönüştürülmesi

Sistemik olarak sayısal terimleri, onlara karşılık gelen bulanık sayılara dönüştürmek için, sekiz dönüşüm ölçeğinden oluşan bir sayısal tahmin sistemi uygulanır. Baas ve Kwakernaak, Bonissone, Efstathiou ve Rajkovic, Efstathiou ve Tong, Kerre, ve Wenstop' da bu dönüşüm ölçeğini sentezleyerek ve değiştirerek yöntemlerinde kullanmıştır. Kullanılan sözel terimler arasında çok az fark olabilmekte ve sözel terimler farklı ölçeklerde farklı şekillerde ifade edilebilmektedir. Bu durum, sözel terimlerin farklı durumlarda farklı anlamlara sahip olması ile ifade edilebilmektedir [8].

### Modelin Oluşturulması ve Örnek Uygulama

Bir inşaat projesinin istenen kalitede gerçekleştirilebilmesinde iş deneyimi en önemli kriterdir. İş deneyimi de yüklenicinin yapmış olduğu benzer işlerin büyüklüğüne, geçici ve kesin kabullerin sorunsuz bir şekilde yapıp teminatların çözülmesine, çalıştırdığı çekirdek deneyimli teknik kadroya ve feshedilmiş veya başkasına devredilmiş işi olup olmadığına bağlıdır.

Projenin gerçekleştirilmesinde en önemli faktör maliyettir. Maliyeti belirleyen kriter ise teklif bedelidir. En ekonomik teklif projenin istenen süre ve kalitede gerçekleştiren en düşük tekliftir. Bu doğrultuda Tablo 2'deki 10 kriteri baz alan ve 10 firmanın katıldığı bir ihale için örnek model aşağıdaki gibi olacaktır.

İsteklilerin kriterlere göre performans değerleri sözel ifadelerle değerlendirildikten sonra bu ifadeler bulanık sayılara dönüştürülecektir. En ekonomik teklifin seçiminde kriterlerin göreceli üstünlükleri hesaplanır. Bu değerler 1-9 arasındaki tek sayılardan oluşan önem skalası değerleridir. Önem skalasında yer almayan 2, 4, 6, 8 gibi değerler ara değerlerdir. Örneğin karar verici 1 ve 3 arasında kalırsa 2 değerini kullanabilir [9].

**Tablo 2.** Önem Skalası Değerleri

Sayısal Değer	Tanım
1	Öğeler eşit önemde
3	1. öğe 2.'ye göre biraz daha önemli
5	1. öğe 2.'ye göre fazla önemli
7	1. öğe 2.'ye göre çok fazla önemli
9	1. öğe 2.'ye göre aşırı derecede önemli

### Yager Yöntemi ile Çözüm

Bu yöntemle çözümde yukarıda tabloda verilen kriterlerden faydalanılacaktır. Alternatiflerin ve kriterlerin gösterimi aşağıdaki gibidir.  $\chi_1 = A$  firması,  $\chi_2 = B$  firması,  $\chi_3 = C$  firması,  $\chi_4 = D$  firması,  $\chi_6 = F$  firması,  $\chi_7 = G$  firması,  $x_8 = H$  firması,  $x_9 = I$  firması,  $\chi_{10} = J$  firması olmak üzere, alternatifler kümesi;

$X = \{ x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8, x_9, x_{10} \}$  olacaktır.

Kriterler aşağıdaki şekilde ifade edilebilir.

$\tilde{G}_1 =$  Kullanılmamış nakit kredisi,  $\tilde{G}_2 =$  Kullanılmamış teminat kredisi,  $\tilde{G}_3 =$  Ciro,  $\tilde{G}_4 =$  Öz sermaye,  $\tilde{G}_5 =$  Karlılık,  $\tilde{G}_6 =$  Taahhüdündeki iş miktarı,  $\tilde{G}_7 =$  Faaliyet süresi,  $\tilde{G}_8 =$  Benzer iş,  $\tilde{G}_9 =$  Çekirdek teknik personel,  $\tilde{G}_{10} =$  İş durumu ve tutumu şeklinde gösterilebilir.

Öz vektör diğer bir ifadeyle kriterlerin ağırlıkları uzman görüşlerine göre expertchoice programında hesaplanmış ve aşağıda verilmiştir :

$$w = \{ w_1, w_2, w_3, w_4, w_5, w_6, w_7, w_8, w_9, w_{10} \}$$

$$w = \{ 0.096, 0.066, 0.055, 0.055, 0.028, 0.10, 0.05, 0.448, 0.06, 0.042 \}$$

İsteklileri verilen kriterlere göre değerlendirmek için, Tablo 3'teki sözel ölçekten faydalanılacaktır.

**Tablo 3.** Sözel Ölçek [8]

Sözel İfade	Bulanık Sayı Karşılığı
En iyi	0.9
Çok iyi	0.75
İyi	0.50
Orta	0.25
Kötü	0

### Örnek Uygulama

Tablo 4'te görülen verilere göre uygulama yapılacak olursa;

**Tablo 4. İsteklilerin Kriterlere Göre Performans Değerleri**

İSTEK.	KULLANILMAMIŞ NAKİT KREDİSİ	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ	CİRO	ÖZSERMAYE	KARLILIK	HALEN TAAHÜDÜNDEKİ İŞ MİKTARI	FAALİYET SÜRESİ	BENZER İŞ	ÇEKİRDEK TEKNİK PERSONEL	İŞ DURUM VE TUTUMU	TEKLİF BEDELİ
	%	%	Tek. Bedel %	Tek Bedel. %	Tek. Bedel %	%	Yıl	%			Milyon TL
A	10	30	30	3	3	0	6	30	Var	1	1.80
B	20	20	30	3	3	50	10	60	Var	1	1.90
C	30	20	30	3	3	100	10	90	Var	1	1.75
D	8	10	40	4	4	150	15	90	Var	0.5	1.68
E	20	30	40	4	4	200	8	60	Var	0.5	1.69
F	30	20	20	3	3	300	9	100	Var	1	1.67
G	30	5	10	5	5	80	7	100	2 ad.	1	1.75
H	20	30	10	6	6	0	6	100	2 ad.	1	1.72
I	20	20	20	6	6	200	16	90	Var	1	1.70
J	10	10	20	3	3	320	4	90	Var	1	1.72

Objektif kriterlere dayandırılan alt kriterlerin seçenekleri aşağıda gösterilmiştir :

*Kullanılmamış nakit kredi*

- Teklif bedelinin %10'undan küçük ise orta
- Teklif bedelinin %10'u ise iyi
- Teklif bedelinin %20' si ise çok iyi
- Teklif bedelinin %30'u veya fazlası için en iyi

*Kullanılmamış Teminat mektubu kredisi*

- Teklif bedelinin % 10'undan küçük ise orta
- Teklif bedelinin %10'u ise iyi
- Teklif bedelinin %20'si ise çok iyi
- Teklif bedelinin %30'u veya fazlası için en iyi

*Ciro*

- Teklif bedelinin %10'u veya daha küçük ise Orta
- Teklif Bedelinin %20'si ise iyi
- Teklif bedelinin %30'u ise çok iyi
- Teklif bedelinin %40'ı veya daha büyük ise en iyi

*Öz sermaye*

- Teklif bedelinin %3'ü veya daha fazla küçük ise orta
- Teklif bedelinin %4'ü ise iyi
- Teklif bedelinin %5'i ise çok iyi
- Teklif bedelinin %6'sı veya daha fazla ise en iyi

*Karlılık oranı*

- Teklif bedelinin %3' ü veya daha fazla küçük ise orta
- Teklif bedelinin %4'ü ise iyi
- Teklif bedelinin %5'i ise çok iyi
- Teklif bedelinin %6'sı veya daha fazla ise en iyi

*Taahhüdündeki iş miktarı*

- Elinde iş yok veya teklif bedelinin altında ise en iyi
- Teklif bedelinin %100'ü ile %200'ü arasında ise çok iyi
- Teklif bedelinin %200'ü ile %300'ü arasında ise iyi
- Teklif bedelinin %300'ü veya daha fazla ise orta

*Faaliyet süresi*

- 0-5 yıl ise iyi
- 5-10 yıl (dahil) arası ise çok iyi
- 10 yıldan fazla ise en iyi

*Benzer iş*

- Bitirilen iş yoksa veya %30'unun altında ise kötü
- Bitirilen işin keşif bedeli teklif bedelinin %30'u ile %60'ı arasında ise orta
- Bitirilen işin keşif bedeli teklif bedelinin %60'u ile %90'ı arasında ise iyi
- Bitirilen işin keşif bedeli teklif bedelinin %90'ı ile %100'ü arasında ise çok iyi
- Bitirilen işin keşif bedeli teklif bedelinin %100 veya fazlası için en iyi

*Çekirdek teknik personel*

- İsteklinin merkez teşkilatında hiç teknik personel yoksa kötü
- İsteklinin merkez teşkilatında en az 1 senedir çalışan en az 5 yıl deneyimli 2 adet mimar veya mühendis olması durumunda orta
- İsteklinin merkez teşkilatında en az 1 senedir çalışan en az 5 yıl deneyimli 3 adet mimar veya mühendis olması durumunda iyi

*İş durumu ve tutumu*

- Son beş yıl içerisinde sözleşmesi feshedilmişse veya son iki sene içerisinde birden fazla iş devretmişse kötü
- Son iki yıl içerisinde bir iş devretmişse orta
- Son iki yıl içerisinde hiç iş devretmemişse iyi

Kriterlere göre sözel ölççeğin ışığı altında alternatifleri Tablo 5-15'te değerlendirilmiştir.

**Tablo 5.** Kullanılmamış Nakit Kredisine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	KULLANILMAMIŞ NAKİT KREDİSİ (%)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	10	İyi	0.50
B	20	Çok İyi	0.75
C	30	En İyi	0.90
D	8	Orta	0.25
E	20	Çok İyi	0.75
F	30	En İyi	0.90
G	30	En İyi	0.90
H	20	Çok İyi	0.75
I	20	Çok İyi	0.75
J	10	İyi	0.50

**Tablo 6.** Kullanılmamış Teminat Mektubu Kredisine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ (%)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	30	En İyi	0.90
B	20	Çok İyi	0.75
C	20	Çok İyi	0.75
D	10	Orta	0.25
E	30	En İyi	0.90

F	20	Çok İyi	0.75
G	5	Çok İyi	0.25
H	30	En İyi	0.90
I	20	En İyi	0.75
J	10	İyi	0.50

**Tablo 7.** Ciro Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	CİRO (Teklif bedeli %)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	30	Çok İyi	0.75
B	30	Çok İyi	0.75
C	30	Çok İyi	0.75
D	40	En İyi	0.90
E	40	En İyi	0.90
F	20	İyi	0.50
G	10	Orta	0.25
H	10	Orta	0.25
I	20	İyi	0.50
J	20	İyi	0.50

**Tablo 8.** Özsermaye Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	ÖZSERMAYE (Teklif Bedeli %)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	3	Orta	0.25
B	3	Orta	0.25
C	3	Orta	0.25
D	4	İyi	0.50
E	4	İyi	0.50
F	3	Orta	0.25
G	5	Çok İyi	0.75
H	6	En İyi	0.90
I	6	En İyi	0.90
J	3	Orta	0.25

**Tablo 9.** Karlılık Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	KARLILIK (Teklif Bedeli %)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	3	Orta	0.25
B	3	Orta	0.25
C	3	Orta	0.25
D	4	İyi	0.50
E	4	İyi	0.50

F	3	Orta	0.25
G	5	Çok İyi	0.75
H	6	En İyi	0.90
I	6	En İyi	0.90
J	3	Orta	0.25

**Tablo 10.** Taahhüdündeki İş Miktarı Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	TAAHÜDÜNDEKİ İŞ MİKTARI (%)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	0	En İyi	0.90
B	50	En İyi	0.90
C	100	Çok İyi	0.75
D	150	Çok İyi	0.75
E	200	İyi	0.50
F	300	Orta	0.25
G	80	En İyi	0.90
H	0	En İyi	0.90
I	200	İyi	0.50
J	320	Orta	0.25

**Tablo 11.** Faaliyet Süresi Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	FAALİYET SÜRESİ (Yıl)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	6	Çok İyi	0.75
B	10	Çok İyi	0.75
C	10	Çok İyi	0.75
D	15	En İyi	0.90
E	18	En İyi	0.90
F	9	Çok İyi	0.75
G	7	Çok İyi	0.75
H	6	Çok İyi	0.75
I	16	En İyi	0.90
J	14	En İyi	0.90

**Tablo 12.** Benzer İş Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	BENZER İŞ (%)	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	30	Orta	0.25
B	60	İyi	0.50
C	90	Çok İyi	0.75
D	90	Çok İyi	0.75
E	60	İyi	0.50

F	100	En İyi	0.90
G	100	En İyi	0.90
H	100	En İyi	0.90
I	90	Çok İyi	0.75
J	90	Çok İyi	0.75

**Tablo 13.** Çekirdek Teknik Personel Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	ÇEKİRDEK TEKNİK PERSONEL	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	Var	İyi	0.50
B	Var	İyi	0.50
C	Var	İyi	0.50
D	Var	İyi	0.50
E	Var	İyi	0.50
F	Var	İyi	0.50
G	2 ad.	Orta	0.25
H	2 ad.	Orta	0.25
I	Var	İyi	0.50
J	Var	İyi	0.50

**Tablo 14.** İş Durum ve Tutumu Kriterine Göre Sözel İfadeler ve Bulanık Sayı Karşılıkları

İSTEKLİLER (Firmalar)	İŞ DURUM VE TUTUMU	SÖZEL İFADE	BULANIK SAYI KARŞILIĞI
A	1	İyi	0.75
B	1	İyi	0.75
C	1	İyi	0.75
D	0.5	İyi	0.25
E	0.5	İyi	0.25
F	1	İyi	0.75
G	1	Orta	0.75
H	1	Orta	0.75
I	1	İyi	0.75
J	1	İyi	0.75

**Tablo 15.** İsteklilerin kriterlere göre değerlendirilmesi

	Firmalar									
	A	B	C	D	E	F	G	H	I	J
Kullanılmamış nakit kredi	0.5	0.75	0.9	0.25	0.75	0.9	0.9	0.75	0.75	0.5
Kullanılmamış teminat mektubu kredisi	0.9	0.75	0.75	0.25	0.9	0.75	0.25	0.9	0.75	0.5
Ciro	0.75	0.75	0.75	0.9	0.9	0.5	0.25	0.25	0.5	0.5

Öz sermaye	0.25	0.25	0.25	0.5	0.5	0.25	0.75	0.9	0.9	0.25
Karlılık oranı	0.25	0.25	0.25	0.5	0.5	0.25	0.75	0.9	0.9	0.25
Taahhüdündeki iş miktarı	0.9	0.9	0.75	0.75	0.5	0.25	0.9	0.9	0.5	0.25
Faaliyet süresi	0.75	0.75	0.75	0.9	0.9	0.75	0.75	0.75	0.9	0.9
Benzer iş	0.25	0.5	0.75	0.75	0.5	0.9	0.9	0.9	0.75	0.75
Çekirdek teknik personel	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.25	0.5	0.5
İş durum ve tutumu	0.75	0.75	0.75	0.25	0.25	0.75	0.75	0.75	0.75	0.75

Alternatiflerin (istekliler) kriterlere göre üyelik dereceleri aşağıdaki şekilde ifade edilebilir.

$$\tilde{G}_1(x_i) = \{(x_1, 0.5), (x_2, 0.75), (x_3, 0.9), (x_4, 0.25), (x_5, 0.75), (x_6, 0.9), (x_7, 0.9), (x_8, 0.75), (x_9, 0.75), (x_{10}, 0.5)\}$$

$$\tilde{G}_2(x_i) = \{(x_1, 0.9), (x_2, 0.75), (x_3, 0.75), (x_4, 0.25), (x_5, 0.9), (x_6, 0.75), (x_7, 0.25), (x_8, 0.9), (x_9, 0.75), (x_{10}, 0.5)\}$$

$$\tilde{G}_3(x_i) = \{(x_1, 0.75), (x_2, 0.75), (x_3, 0.75), (x_4, 0.9), (x_5, 0.9), (x_6, 0.5), (x_7, 0.25), (x_8, 0.25), (x_9, 0.5), (x_{10}, 0.5)\}$$

$$\tilde{G}_4(x_i) = \{(x_1, 0.25), (x_2, 0.25), (x_3, 0.25), (x_4, 0.5), (x_5, 0.5), (x_6, 0.25), (x_7, 0.75), (x_8, 0.9), (x_9, 0.9), (x_{10}, 0.25)\}$$

$$\tilde{G}_5(x_i) = \{(x_1, 0.25), (x_2, 0.25), (x_3, 0.25), (x_4, 0.5), (x_5, 0.5), (x_6, 0.25), (x_7, 0.75), (x_8, 0.9), (x_9, 0.9), (x_{10}, 0.25)\}$$

$$\tilde{G}_6(x_i) = \{(x_1, 0.9), (x_2, 0.9), (x_3, 0.75), (x_4, 0.75), (x_5, 0.5), (x_6, 0.25), (x_7, 0.9), (x_8, 0.9), (x_9, 0.5), (x_{10}, 0.25)\}$$

$$\tilde{G}_7(x_i) = \{(x_1, 0.75), (x_2, 0.75), (x_3, 0.75), (x_4, 0.9), (x_5, 0.9), (x_6, 0.75), (x_7, 0.75), (x_8, 0.75), (x_9, 0.9), (x_{10}, 0.9)\}$$

$$\tilde{G}_8(x_i) = \{(x_1, 0.25), (x_2, 0.5), (x_3, 0.75), (x_4, 0.75), (x_5, 0.5), (x_6, 0.9), (x_7, 0.9), (x_8, 0.9), (x_9, 0.75), (x_{10}, 0.75)\}$$

$$\tilde{G}_9(x_i) = \{(x_1, 0.5), (x_2, 0.5), (x_3, 0.5), (x_4, 0.5), (x_5, 0.5), (x_6, 0.5), (x_7, 0.25), (x_8, 0.25), (x_9, 0.5), (x_{10}, 0.5)\}$$

$$\tilde{G}_{10}(x_i) = \{(x_1, 0.75), (x_2, 0.75), (x_3, 0.75), (x_4, 0.25), (x_5, 0.25), (x_6, 0.75), (x_7, 0.75), (x_8, 0.75), (x_9, 0.75), (x_{10}, 0.75)\}$$

Bu aşamada kriterlerin üssel ağırlıkları aşağıdaki gibi hesaplanmıştır.

$$\tilde{G}_1(x_i)^{0.096} = \{(x_1, 0.9356), (x_2, 0.9728), (x_3, 0.9899), (x_4, 0.8754), (x_5, 0.9727), (x_6, 0.9899), (x_7, 0.9899), (x_8, 0.9728), (x_9, 0.9728), (x_{10}, 0.9356)\}$$

$$\tilde{G}_2(x_i)^{0.066} = \{(x_1, 0.9931), (x_2, 0.9812), (x_3, 0.9812), (x_4, 0.9126), (x_5, 0.9931), (x_6, 0.9812), (x_7, 0.9126), (x_8, 0.9931), (x_9, 0.9812), (x_{10}, 0.9553)\}$$

$$\tilde{G}_3(x_i)^{0.055} = \{(x_1, 0.9843), (x_2, 0.9843), (x_3, 0.9843), (x_4, 0.9942), (x_5, 0.9942), (x_6, 0.9626), (x_7, 0.9266), (x_8, 0.9266), (x_9, 0.9626), (x_{10}, 0.9626)\}$$

$$\tilde{G}_4(x_i)^{0.055} = \{(x_1, 0.9266), (x_2, 0.9266), (x_3, 0.9266), (x_4, 0.9626), (x_5, 0.9626), (x_6, 0.9266), (x_7, 0.9843), (x_8, 0.9942), (x_9, 0.9942), (x_{10}, 0.9266)\}$$

$$\tilde{G}_5(x_i)^{0.028} = \{(x_1, 0.9619), (x_2, 0.9619), (x_3, 0.9619), (x_4, 0.9808), (x_5, 0.9808), (x_6, 0.9619), (x_7, 0.992), (x_8, 0.9971), (x_9, 0.9971), (x_{10}, 0.9619)\}$$

$$\tilde{G}_6(x_i)^{0.1} = \{(x_1, 0.9895), (x_2, 0.9895), (x_3, 0.9716), (x_4, 0.9716), (x_5, 0.933), (x_6, 0.8706), (x_7, 0.9895), (x_8, 0.9895), (x_9, 0.9330), (x_{10}, 0.8705)\}$$

$$\tilde{G}_7(x_i)^{0.05} = \{(x_1, 0.9857), (x_2, 0.9857), (x_3, 0.9857), (x_4, 0.9948), (x_5, 0.9948), (x_6, 0.9857), (x_7, 0.9857), (x_8, 0.9857), (x_9, 0.9948), (x_{10}, 0.9948)\}$$

$$\tilde{G}_8(x_i)^{0.448} = \{(x_1, 0.5773), (x_2, 0.7331), (x_3, 0.8791), (x_4, 0.8791), (x_5, 0.7331), (x_6, 0.9539), (x_7, 0.9539), (x_8, 0.9539), (x_9, 0.8791), (x_{10}, 0.8791)\}$$

$$\tilde{G}_9(x_i)^{0.06} = \{(x_1, 0.9593), (x_2, 0.9593), (x_3, 0.9593), (x_4, 0.9593), (x_5, 0.9593), (x_6, 0.9593), (x_7, 0.9202), (x_8, 0.9202), (x_9, 0.9593), (x_{10}, 0.9593)\}$$

$$\tilde{G}_{10}(x_i)^{0.042} = \{(x_1, 0.9880), (x_2, 0.9880), (x_3, 0.9880), (x_4, 0.9434), (x_5, 0.9434), (x_6, 0.9880), (x_7, 0.9880), (x_8, 0.9880), (x_9, 0.9880), (x_{10}, 0.9880)\}$$

Yukarıda yapılan işlemler neticesinde, her bir alternatifin aldığı en küçük değerlerden oluşan bulanık çözüm kümesi, D aşağıdaki gibi oluşturulur.

$$\tilde{D} = \{(x_1, 0.5374), (x_2, 0.7331), (x_3, 0.8791), (x_4, 0.8754), (x_5, 0.7331), (x_6, 0.8705), (x_7, 0.9126), (x_8, 0.9202), (x_9, 0.8910), (x_{10}, 0.8705)\}$$

Bu çözüm kümesi içerisindeki en yüksek değere sahip istekli süre ve kalite açısından en iyi alternatifi oluşturmaktadır. Bu duruma göre H, G ve I firmaları sırasıyla süre ve kalite açısından en iyi üç alternatifi oluşturmaktadır.

Süre ve kalite açısından en iyi üç alternatif olan H, G ve I firmalarından, daha düşük bedel teklif eden I firması en iyi alternatif olarak belirlenmiştir (Tablo 16).

**Tablo 16.** Tekliflerin değerlendirilmesi

İSTEKLİLER (Firmalar)	SÜRE ve KALİTE AÇISINDAN ALINAN DEĞERLER	TEKLİF BEDELİ (milyar TL)
A	0.5374	1.80
B	0.7331	1.90
C	0.8791	1.75
D	0.8754	1.68
E	0.7331	1.69
F	0.8705	1.67
G	0.9126	1.75
H	0.9202	1.72
I	0.8910	1.70
J	0.8705	1.72

### Değerlendirme ve Sonuç

Kamu Alımlarının Gayri Safi Milli Hasılanın %13-14'ünü oluşturduğu kalkınmakta olan ülkemizde kaynakların etkin verimli olarak kullanılması oldukça önemlidir. Hizmet, Mal ve Yapım İşlerini oluşturan kamu alımları içerisinde en büyük pay yapım işleri için harcanmaktadır. Yapım işlerinde en uygun teklifin belirlenmesi dolayısıyla yüklenici seçimi en önemli unsur olarak ön plana çıkmaktadır.

Bu çalışma kapsamında, en uygun teklifin seçiminde süre ve kalitenin değerlendirilmesinde objektif kriterler ortaya konmuş ve bu kriterlere bağlı olarak bulanık karar verme metodu yardımıyla ve Yager'in yaklaşımıyla problem çözülmeye çalışılmıştır. İnşaat projelerinde en ekonomik teklifin en düşük teklif bedeli olmadığı gerçeğinden hareketle teklif bedelinin yanı sıra kalite ve süre gibi parametrelerinde karar verme aşamasında göz önüne alınması gerektiği vurgulanmıştır. Gerçekleştirilen uygulamanın geliştirilip bilgisayar ortamında programlanması halinde, özellikle kamu ihalelerinde başarıyla uygulanabileceği görülmüştür.

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## CHANGE IN RELATIVE WATER CONTENT, CELLULAR INTEGRITY, ACCUMULATED BIOMASS AND EFFICIENCY OF WATER USE VARIETIES OF DURUM WHEAT (*TRITICUM DURUM*.DESF) CONDUCTED UNDER WATER STRESS

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### INTRODUCTION

Cereal cultivation is the predominant speculation Algerian agriculture. It covers nearly six million hectares in a system which is the dominant two-year fallow / cereal. Most of the acreage is located on the high plains characterized by the altitude, cold winters, an insufficient and irregular rainfall, frequent spring frosts and the onset of Sirocco end of the cycle (Annichiarico et al., 2002). Cereal production in rainfed dry remains low and irregular in space and time. The search for a better adaptation to environmental change has become a necessity to stabilize yields in these regions (Benmahammed et al., 2005). Lack of water is, however, the most limiting factor faced by the Rainfed cereals, followed by negative effects caused by low winter temperatures and spring (Annichiarico et al. 2002; Annichiarico et al. 2005; Bahlouli and al. 2005; Mekhlouf et al., 2007). This makes the improvement of production techniques is centered, increasingly, around the efficiency of water use (Chenaffi et al., 2006).

This paper aims to characterize a set of varieties of wheat (*Triticum durum* Desf.) Pots of plants tested under different conditions of water stress, the expression for the surface of the sheet, the relative water content, cellular integrity, biomass, and efficiency of water use.

### Materials and methods

The experiments conducted during the 2006/07 season, includes the establishment of a test under plastic cover in order to control the water factor. Five durum wheat varieties whose seeds are courtesy of station (CETO) Setif, were tested. Water treatments studied have a witness to the capacity of irrigated pot (100% CP), a treatment representing a moderate water stress in 70% of the capacity of the pot (70% CP) and a third treatment simulating severe stress by 40% the capacity of the pot (40% CP).

#### Plant material:

Five varieties were used as plant material, it is Mohamed Ben Bachir, Waha, Korifla, Oum rabia and Boussalam

#### Measurements carried out:

The average area of the last fully developed leaf was estimated by the product  $SF \text{ (cm}^2\text{)} = [0.607 \text{ (L x I)}]$

Specific leaf weight was calculated by the ratio of the weight of the dry matter of leaf area standard

$$PSF \text{ (mg / cm}^2\text{)} = PS \text{ (mg)} / SF \text{ (cm}^2\text{)}$$

$$ERR \text{ (\%)} = 100 \text{ (PF-PS)} / \text{(PT-SP)},$$

with TRE is the leaf relative water content, PF, PT and PS are respectively the weight (mg) fresh, turgid and dry leaf samples.

The percentage of cells damaged by water stress was estimated as described by Bajja et al, (2001), as follows:  $IC \text{ (\%)} = 100 \text{ (EC1/EC2)}$

The number of grains per ear (NGE) is derived by calculating it using the following formula:  $NGE = (1000 \times \text{RTD}) / (\text{x PMG NE})$ .

### Results and Discussion

The yield is a complex, low heritability and more subject to genotype x environment interactions (Annichiarico et al., 2006). The selection is made, in addition to grain yield, based on physiological characteristics to balance yield potential and tolerance of environmental stresses (Brin, 1995; Benmahammed et al. 2001; Passioura et al., 2002). A better understanding of morpho-physiological mechanisms involved in resistance to water stress is therefore essential for the selection of resistant genotypes (Zhang et al. 1999).

Three climatic factors interact to allow the externalization or inhibition potential of a given genotype. These factors are the low temperatures, the accumulated degree-days and cumulative rainfall (Kabouche et al. 2001; Mekhlouf et al., 2001). If the response of genotypes to the variation of climatic factors is predictable, the advent of these constraints is the realm of the unpredictable, so the selection of a given genotype to express that this genotype is potentially productive, but also he has the ability to absorb changes in settings that will suffer, once adopted (Bouzerzour et al., 2001).

The objective of this study is to determine the effects of water stress on morphological and physiological characteristics of contrasting genotypes of durum wheat. The results indicate that water stress significantly reduced virtually all the variables measured. In the absence of water stress, and MBB Waha present rates of accumulation of biomass highest. Korifla hand with a capital of DM significantly

higher at the beginning of the cycle, while Boussalam and MBB earn relatively less biomass in beginning of the cycle, with low temperatures. Waha and MBB adopt a growth rate higher end of the cycle. Water stress, moderate, significantly reduces the average speed of accumulation of biomass of about 45.0% of all varieties.

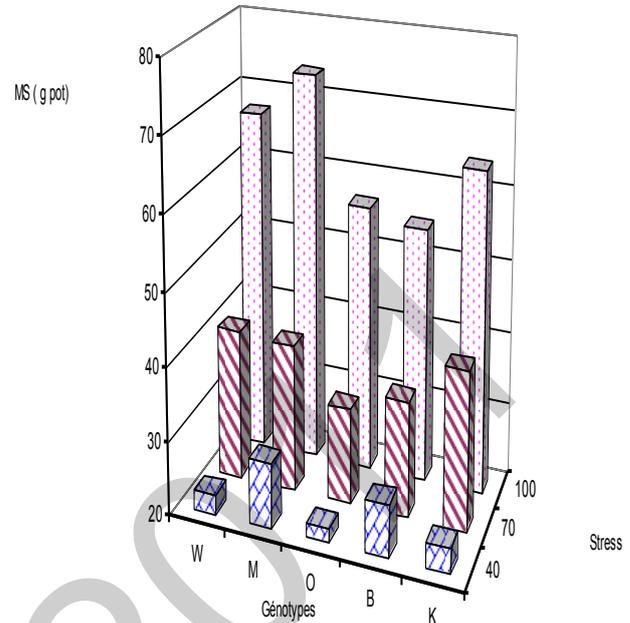


Figure 1. Change in amounts of dry air produced by different genotypes evaluated in the absence and under water stress

MBB and Waha are less sensitive to lack of water. Under severe water stress, and MBB Boussalam manage to do better yields of dry matter in the end of the experiment, while Waha, and MRB5 Korifla are most affected.

The results indicate the presence of genotypes that accumulate more biomass in the absence as in presence of water stress and in the case of MBB. Genotypes that accumulate more biomass in the absence of water stress and under moderate water stress, in the case of Waha and Korifla. Genotypes that accumulate more biomass under severe stress and it is only the case of Boussalam. MBB develops slowly in the beginning of the cycle and accelerates its growth at the end of cycle. By cons Korifla is growing faster at the beginning of the cycle and slowing growth at the end of cycle. The best genotype for semi-arid environments is the type Korifla.

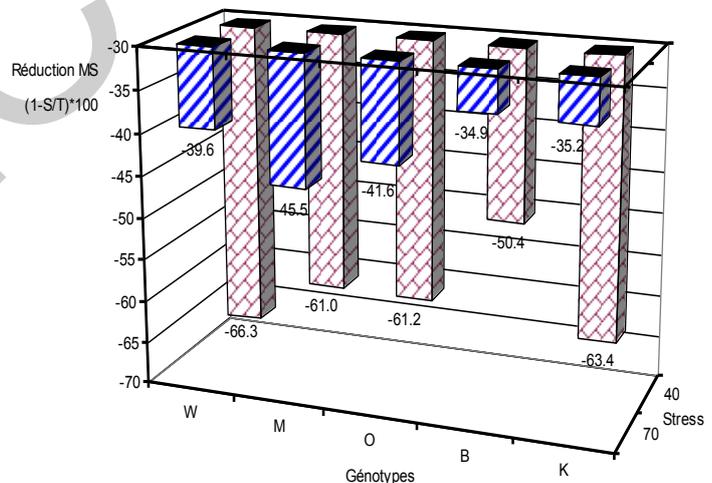
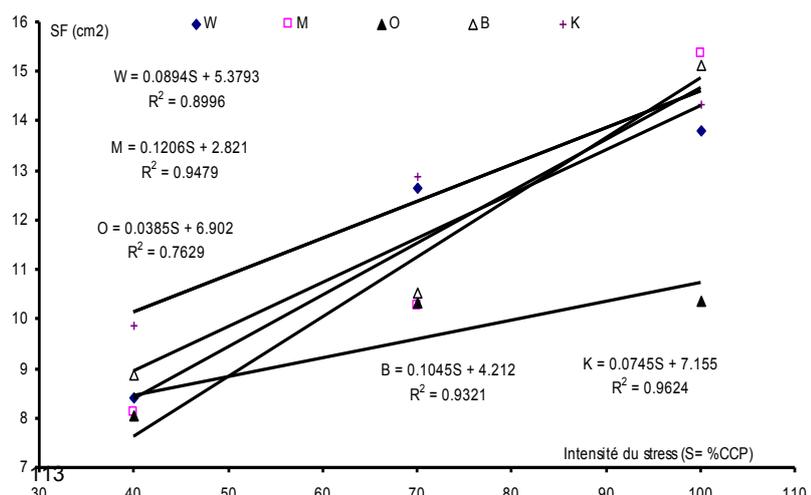


Figure :2 Influence of water stress intensity of moderate and severe reduction of the dry air produced by different genotypes relative to the control non-stressed

The effect of water stress is marked on the surface, the weight specific and leaf water status, but it is not noticeable on cellular integrity.

Korifla develops a large leaf surface that is relatively less reduced under the effect of water stress. Waha, MBB and Boussalam development of broad leaves whose surface is greatly reduced as a result of water stress. MRB5 produced a sheet of small area, which is slightly reduced due to the effects of water stress

Figure 3 Influence of water stress on the development of the middle surface of the sheet of different genotypes



Reductions in specific leaf weight, under severe stress, are 26.2%, 19.1%, 29.6%, 14.7% and 30.6% respectively for Waha, MBB, Boussalam, and MRB5 Korifla. Genotypic differences for the TRE are relatively more important under severe water stress. Korifla reduced its relative content more significantly, by cons MRB5 shows some stability for the leaf water status. In relative reduction in relative water content of 4.1, 5.3, 2.3, 8.5 and 11.4% respectively for Waha, MBB, MRB5, and Boussalam Korifla.

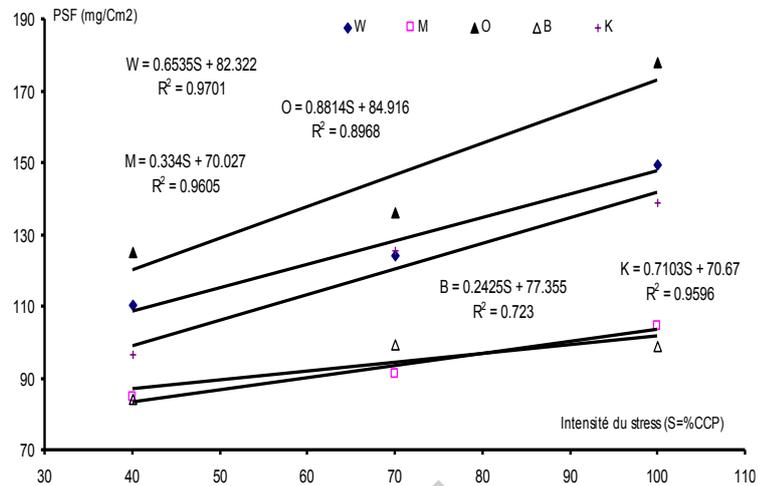


Figure 4. Influence of water stress on the development of specific leaf weight in different genotypes

For the cellular integrity genotypes rise significantly different. Waha genotype is less damaged compared to Boussalam which shows the highest percentage of cell damage. Damage to the cell membrane are less obvious in moderate stress for four of the five genotypes studied, but they become consistent in severe stress Boussalam which expresses the most damage while Mohamed Ben Bachir and Korifla are the most tolerant to this feature . In relative terms, moderate water stress reduces yield and yield components of 13.5%, 4.1%, 21.3% and 0.0% for grain yield, number of ears, number of grains per ear and weight of 1000 grains. Severe water stress affects the same variables in the proportions 49.5%, 17.5%, 37.9% and 3.4%.

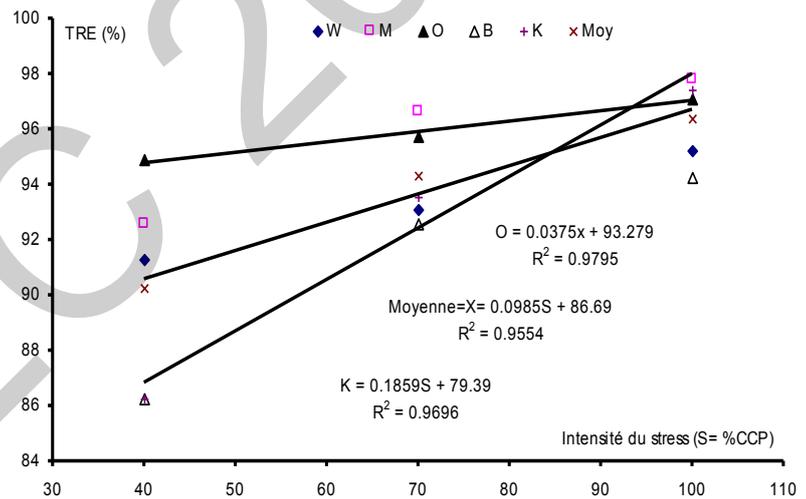


Figure 5. Influence of water stress on leaf water status of different genotypes

In the absence of water stress MBB has a low yield, while the other four genotypes have significantly higher yields and equal. Under moderate water stress, the yield is greatly reduced MBB followed Boussalam. Waha, and MRB5 Korifla minimize, for cons, the reduction of moderate performance stress. Under severe stress, Waha, and MBB Boussalam are very sensitive to water stress, while MRB5 and Korifla to show relatively more tolerant. In terms of selection of genotypes for specific adaptation in the absence of coercion,

MBB excluding the other genotypes give yields Similar grain.

Under moderate water stress, the choice is Waha, and Korifla MRB5 that are relatively more tolerant this degree of water stress.

Severe water stress, and Korifla MRB5 maintain a relatively high yield.

For a general adjustment, the choice of genotype is on Korifla, MRB5 and to a lesser extent Boussalam. These genotypes have the ability to minimize the reduction of grain yield under water stress.

The values taken by the number of grains per ear, in the absence of water stress varied from 22.2 (index 100) at MBB in 19.5 (87.8%) in Korifla. Under moderate stress, they drop to 90.5% for Waha and 55.0% of the maximum value for MBB. Under severe stress, they drop to 34.2% for Waha, and remain at a level similar to that observed under moderate stress and Boussalam Korifla be 70.7 and 77.5% of the maximum value.

The accumulated biomass at maturity passes 63.1g/pot, average 5 genotypes and in the absence of stress, to 24.7 g / pot under severe stress. Stubble height is reduced by 96.9 to 80.8 cm, a lowering of 16.6%. The ratio of the weight of the ears on the ground biomass measured at maturity, falling 38.3% to 34.4%. The average harvest index increases, against, as a result of water stress, it goes from 17 to 21%.

The efficiency of water use of biomass is not significantly affected by the performance against the increases under the effect of water stress of 1.45 to 1.95 mg / ml water per pot. Under water stress the biomass and the ratio of the weight of the ears of the biomass, the higher are rated at MBB, Waha and Korofla. MRB5 Korifla and express the best harvest index, while MBB Boussalam and are distinguished by the greater efficiency of water use for the production of dry matter and Waha, Korifla MRB5 and for that to produce grain.

The grain yield was positively correlated with grains per ear, weight of ears at the above-ground biomass measured at maturity, the ratio of the weight of the ears on the ground biomass to leaf area, specific leaf weight, content in chlorophyll a and b. These correlations indicate that the genotype happens to be a good grain yield in the absence of coercion, such as water stress, must have values greater than the average for the variables listed above and are positively related to grain yield. In other words, the genotype that minimizes the reduction of the average value of these variables, as a result of water stress, at the same time minimizes the drop in performance because it is tolerant.

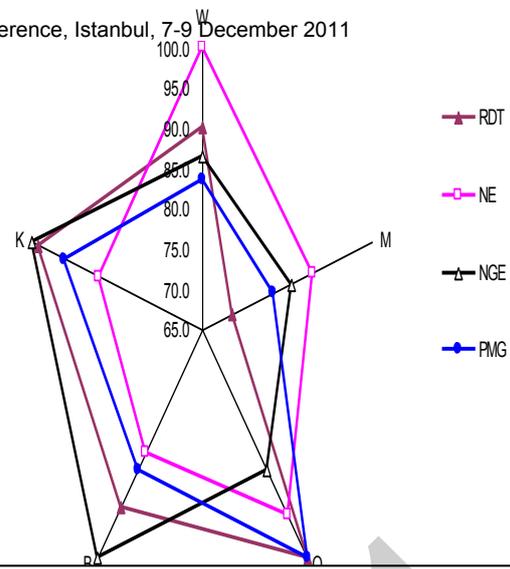


Figure 6. The yield and its components, the different genotypes, expressed in% of the maximum value

According Villages et al., (2001) grain yield in

rain-fed cereal lines is determined by the accumulated biomass and harvest index. Under water stress genotypes that are able to support the accumulation of dry matter often minimizes the effect of stress on the expression of performance gains. The accumulation of high biomass at maturity stage is due to a relative high growth rate.

Khanna-Chopra et al., (1991) indicate that water stress reduced the number of grains per ear and number of ears produced per unit area. The effect of the reduction of these two components of grain yield, however, is variable depending on the genotypes, in some genotypes, it is reducing the number of grains per ear which is decisive, whereas in other genotypes it is the effect of the number of ears which is crucial in reducing the grain yield.

This variation of the effect of the components and characteristics related to performance on the reduction of grain yield suggests that the expression of grain yield under stress and in the absence of stress is not necessarily maximized by the same alleles. This suggests that under favorable environment must aim at the selection of genotypes with high yield potential regardless of their stress response while in unfavorable environments should mainly reflect the response vis-à-vis the stress that is factor in the expression of grain yield.

Kirnak et al., (2001) indicate that water stress induced a significant decrease in chlorophyll content, the relative water content of the foliage of vegetative growth and increased leakage of the electrolyte. The severe water stress reduced 46%, the total accumulated dry air of 43% and leaf elongation of 75%. These reductions are the result of reducing the rate of elongation and leaf transpiration.

The ratio of root dry matter on the dry air increases under stress by a factor of 2.1, suggesting a diversion of newly produced assimilates to the roots as much to the aerial part, to improve accessibility to more soil moisture.

Bajja et al., (2001) indicate that water stress induces an increase in the concentration of soluble sugars and proline, but to varying degrees depending on the response genotype. Water stress also affects the number of leaves developed which contribute to a reduction in transpiring surface stress, but at the same time reduced image synthesizing capacity of the plant under stress.

Retention under water stress, high mean values of characters such as leaf weight, nitrogen content and chlorophyll content of the leaf is considered a good indicator of the stability of photosynthetic tissues. The chloroplasts are under stress when the absorbed energy is far superior to the usability of photosystems, which leads to the photo inhibition of photosynthesis that occurs when the rate of transfer of excitation energy in the center of the antennas photochemical reaction exceeds the rate of transit of the electrons, causing damage to the thylakoids.

According Pooter and Farquhar (1994) genotypes that are characterized by slow growth early in the cycle, have the advantage not to use a luxury available resources of the environment, saving for the end of the cycle that is often more stressful. Nageswara Rao et al., (1995) mention the significant correlation between the isotope discrimination ( $\Delta$ ) and specific leaf weight, whereas Wright et al., (1993) report a significant positive correlation between specific leaf weight and photosynthetic capacity. Stomatal closure is related to the loss of turgor of stomatal guard cells. Martin et al., (1996) reported that genotypes that tolerate water stress maintain a TRE high under conditions of moderate stress and severe compared to susceptible genotypes. Similarly Rekik et al., 1998 note that maintaining a TRE Waha high water stress by osmotic adjustment capacity. Merah et al., (2001) report that Waha is characterized by the values of  $\Delta$  and grain of the paper high. The genotypes that have a high capacity to adjust, under water stress, manage to maintain a TRE high under

these conditions, by controlling stomata gas exchange. The genotypes that maintain a high  $g_s$  sweat more, have a value  $\Delta$  and high ash content (Voltas et al., 2002). It is well known that stomatal closure leads to an increase in leaf temperature, which induces increased sweating and reduced the activity of CO<sub>2</sub> fixation by Rubisco (Van den Boogaard et al., 1996). When grain yield was positively correlated with  $g_s$ , this effect is associated with the cooling of leaves by transpiration permitted by a high stomata conductance, which often allows the maintenance of photosynthetic activity (Lu et al., 1998). Thus the depression of the temperature of the canopy relative to that of the ambient air is most often associated with grain  $\Delta$  and yield under stress conditions hydriques. participation of assimilates formed before heading can often be significant under stressful conditions. This contribution increases relatively in terms of limiting water, as the photosynthetic activity is reduced by the effect of stress that accelerate leaf senescence. In this context, the straw genotypes have a high storage capacity of assimilates most important, which is located in the neck of the ear and between the penultimate node (Rebetzke et al., 2007). The ratio of the length of the neck of the spike on the stubble height is an indicator of the ability of assimilates stored and transferred to the grain (Rekik et al., 1998).

## CONCLUSION

The search for indicators of capacity for better use of water by the plant such as leaf water status, net assimilation and relative growth under stress is a necessary prerequisite to hope to make progress in matters of improvement of production under water stress. The results of this paper indicate that water stress significantly reduced all variables measured. Among the genotypes evaluated MBB accumulate more biomass in the absence as in presence of water stress by Korifla against Waha and accumulate more biomass in the absence of water stress and water stress in moderate Boussalam while accumulating more biomass in Only severe stress. MBB develops slowly in the beginning of the cycle and accelerates its growth at the end of cycle. By cons Korifla is growing faster at the beginning of the cycle and slowing growth at the end of cycle.

The effect of water stress is very pronounced on the surface, the weight and leaf water status. Korifla develops a large leaf surface that is relatively less reduced under the effect of water stress. Waha, MBB and Boussalam develop large leaves whose surface is greatly reduced as a result of water stress. MRB5 produced a sheet of small area, which is slightly reduced due to the effects of water stress. Genotypic differences in the relative water content and cellular integrity are relatively more important under severe water stress. Korifla reduced its relative water content to a greater extent, by cons MRB5 shows some stability for the leaf water status. Damage to the cell membrane are less obvious in moderate stress, but they become consistent in severe stress Boussalam which expresses the most damage while Mohamed Ben Bachir and Korifla are the most tolerant to this feature.

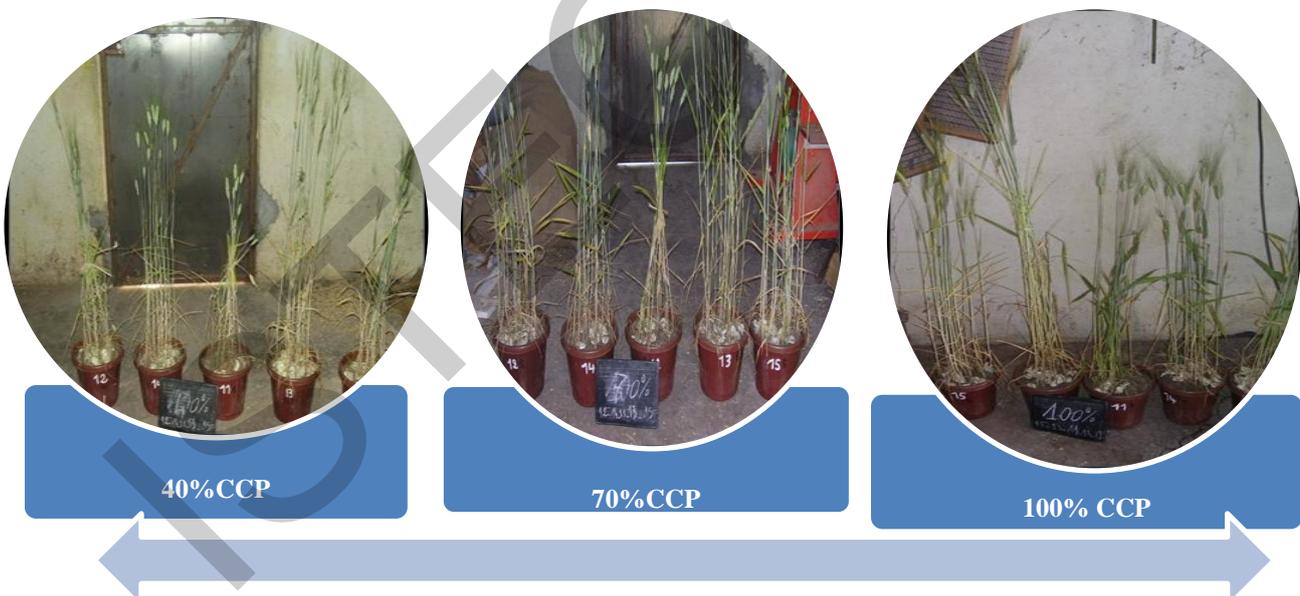
Under moderate water stress, the choice is Waha, and Korifla MRB5 that are relatively more tolerant to the degree of water stress. Severe water stress, and Korifla MRB5 maintain a relatively high yield. For a general adjustment, the choice of genotype is on Korifla, MRB5 and to a lesser extent Boussalam. These genotypes have the ability to minimize the reduction of grain yield under water stress. The accumulated biomass at maturity increased from 63.1g/pot, average of 5 genotypes and in the absence of stress, to 24.7 g / pot under severe stress. Stubble height is reduced by 96.9 to 80.8 cm, a lowering of 16.6%. The ratio of the weight of the ears on the ground biomass measured at maturity, falling 38.3% to 34.4%. The average harvest index increases as a result of water stress from 17 to 21%. In terms of selection of genotypes for specific adaptation in the absence of constraint, except MBB, other genotypes gave similar grain yield. Under moderate water stress, the choice is Waha, and Korifla MRB5 that are relatively more tolerant to the degree of water stress. Severe water stress, and Korifla MRB5 maintain a relatively high yield.

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# CHARACTER LEVEL AUTHORSHIP ATTRIBUTION FOR TURKISH TEXT DOCUMENTS

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## ABSTRACT

Individuals have their own style of speaking and writing. Style of a text can be used as a distinctive feature to recognize its author. In recent years, practical applications for authorship attribution have grown in areas such as criminal law, civil law and computer security. Recent research has used techniques from machine learning, information retrieval and natural language processing in authorship attribution. In this paper, Statistical Language Modeling is utilized in Authorship Attribution. Each author is represented with feature statistics. Letters, punctuations and special characters which build up the feature set are utilized to calculate the profiles of the authors.

**Keywords:** Authorship Attribution, Character Level Method, Centroid Values, Centroid Vector, Document Vector

## 1. INTRODUCTION

The topic of the article is authorship attribution and this study aims to recognize authors of Turkish texts automatically. In addition, it can be utilized in different areas such as spam filtering, determining plagiarism cases, identifying author of program code and in forensic analysis. The output of this study will be classification of texts based on the authors, determining the authors with similar styles in writing and classification of authors depending on their styles. Similarity in the authors' styles is related to their cultural or geographical backgrounds. This situation makes us able to reach interesting information about the authors.

In authorship attribution studies researches have experienced different features such as function words, content words, character n-gram, word and punctuation marks profile etc. Their performances are changeable. While some of these methods give best results, some of them don't give because of preferred dataset. Stylistic and statistical methods can be utilized for authorship attribution. This study deals with the statistical methods in authorship attribution. Recognizing the author by statistical methods necessitates accurate expressions of numerical data.

In the proposed method; letters, punctuation marks and some special characters are added to the feature set individually. Feature set of this method is considerably small compared with the feature sets of other methods. In the character level authorship attribution, including the punctuation marks and special characters such as "space" and "enter", all characters that form the text are all members of the feature set. For this reason, no preprocessing step is required and we are able to work with raw data. And we can easily acquire this type of information. With the proposed character level method, we profit from the costly preprocessing steps. Proposed method uses centroid based classification algorithm which is a very successful algorithm in text classification as well as Bayesian text classification (Han & Karypis, 2000).

The rest of the paper is organized as follows. Next, in Section 2, we give briefly related works. Section 3 describes the character level authorship attribution. After that, Section 4 gives information about experiments and results, and finally Section 5 includes our conclusion that we have been able to achieve so far.

## 2. RELATED WORKS

The authorship attribution system is an application which aims to recognize the author of a text and it is in relation with different areas such as speech recognition, spam filtering and copyright. The studies on authorship attribution have been continuing since 19th century. In 1887 Mendenhall made first known study about authorship attribution and he used words as feature (Mendenhall, 1887). Zipf and Yule used statistical method for authorship attribution respectively 1932 and 1938 (Statamatos, 2008). In 1964 Mosteller and Wallace used Bayesian Analysis of 90 functional words to find authorship of "The Federalist Papers" (Mosteller & Wallace, 1964). This study is accepted milestone of authorship attribution. After Mosteller and Wallace study, functional words were started to use in many studies (Koppel, Scheler & Argamon, 2008).

In 1990s, researchers started to use linguistic style for authorship attribution (Statamatos, 2008). Using linguistic style for text is called stylometry. Stylometry originates with the suggestion of Augustus de Morgan in 1851 that "it might be possible to identify authors because one might deal in longer words" (Morgan & Elizabeth, 1882).

In 2001 Grant and Baker described an approach known as Principal Component Analysis. This approach identifies which marker or combinations of markers are effective in discriminating the author of a text (Grant & Baker, 2001). In Baayen and his

colleagues' study they proved that authors have 'textual fingerprints'. Statistical methods were used in their study and according to the results discriminant analysis is a more powerful technique than principal component analysis. Using punctuation marks with function words and content words increase the classification accuracy (Baayen, Halteren, Neijt & Tweedie, 2002).

Vocabulary richness and repetition; word type frequencies and distributions; word, sentence clause and paragraph lengths and distributions; syntactic analysis, co-occurrence and collocations; and content analysis are the other valid criteria in authorship attribution. Diri and Amasyalı used these criteria to identify authors of Turkish texts and developed a new classification technique. In their study 22 of style markers figured out for each 18 authors and %84 success rate has been reached in average (Diri & Amasyalı, 2003). In 2007 Taş and Görür developed a new classification technique to identify author for Turkish texts. For identifying the authors, 35 of style markers have been figured out. Their experimental group consists of 20 authors and with the developed method they obtained a success rate of %80 in average (Taş & Görür, 2007). Grieve used thirty nine different types of textual measurements in attribution studies in 2007, with word and punctuation mark profile they reached best results, also 2-gram and 3-gram profiles give best results (10-author limit) (Grieve, 2007).

### 3. CHARACTER LEVEL AUTHORSHIP ATTRIBUTION

Character level authorship attribution is an author recognition method which deals with individual characters that compose the text. Characters can also be utilized by the other author recognition methods. But in those methods characters are generally taken into consideration as combinations of characters not individually. In the proposed system, each character individually is a member of the feature set. Besides characters such as "enter" and "space" which can provide vital information about the author's style are also added to the feature set. Character level method is very effective technique for author attribution. Characters were also used in identification of languages and best results were acquired. Language identification studies with characters using centroid based model gave best results. Therefore, in this study character level features and centroid based model were used.

Feature selection which determines the feature set is a very important process. Dimension of the feature set is another important aspect for studies in author recognition. In some methods, such as n-grams and functional words, large feature set decrease the effectiveness of the authorship attribution system. For example, in order to recognize the author of a Turkish text by using the functional words method, all the frequently used words (adjectives, pronouns, adverbs, conjunctions...) are required to be added to the feature set. On the other hand, the feature set of character level model is quite smaller than other methods. Despite the small size of the feature set, features are very successful at representing the text. The other approach in authorship attribution is word level analysis has also some problems. While using word level analysis, morphological features is not important and when studying with some Asian languages which have no explicit boundaries researchers face with problems (Keselj, Peng, Cercone & Thomas, 2003), character level method avoids such problems.

By using individual characters instead of n-grams or functional words, the feature set would be limited with the letters and punctuation marks that are included in the alphabet. For the authorship attribution in Turkish text documents, it is possible to make a feature set consisting of 29 letters of Turkish alphabet and the punctuation marks that are most frequently used in the language. So, individual characters can be used in authorship attribution for real time applications where effectiveness has a vital importance.

When we examine texts from different authors, we find out that different texts of an author have similar character frequencies. Therefore, character frequencies can be utilized to find out the author of a text. Texts written by the same author as well as texts written by different authors have distinct character frequencies. But, while character frequencies of texts written by the same author are very similar to one another, the frequency of texts written by different authors has quite different character frequencies. This case constitutes the basis of the character level model. Hypothesis of our study is "Characters are discriminative markers for authors and texts can be classified due to the frequencies of characters that it includes. Owing to this, each text can be designated to the related group of its author."

Author's style can be used to identify it. This is the second basis of authorship attribution. For example; while some authors hardly ever use exclamation mark, some authors use the exclamation mark quite often, some authors use comma frequently because they like long sentences while some authors use dot more frequently by using short sentences in their writings. These kinds of details in the text have vital importance in authorship attribution.

A model is a simplified prototype of a system. When the character level authorship attribution is considered as a classification problem, the model of the system will consist of training and test phases. Character level model can be stated as follows.

$d_i$	$i^{th}$ document in the corpus
$fr_{ip}$	the frequency of $p^{th}$ character in document $i$
$d_{ip}$	the relative frequency or n normalized value of $fr_{ip}$
$\hat{y}_i$	Represents authors of document (training phase)
$x_i$	Represents authors of document (test phase)
$C_j$	centroid value for $j^{th}$ author
$A_k$	represents the average character frequency for $k^{th}$ author
$a_{(T)p}$	represents the total usage frequencies of $p^{th}$ character
$c_{jp}$	represents the centroid value for $p^{th}$ character in texts of $j^{th}$ author
$m$	Number of features

Table 1: Parameters

Each document has at least one author. The relation between the documents and their authors (authors are defined with numbers) is stated as follows.

$$D \rightarrow \{1,2,\dots,k\}$$

In this study, characters are used as features of the documents, and feature values are the frequencies of these characters in the documents. Values of the determined features are generally presented by vector space model.  $d_i$  is represented with a document letter vector as below.

$$\vec{d}_i = (d_{i1}, d_{i2}, \dots, d_{im})$$

Relative frequency ( $d_{ip}$ ) is calculated in order to prevent errors caused by the length of the document. The relation between  $fr_{ip}$  and  $d_{ip}$  is as follows.

$$d_{ip} = \frac{fr_{ip}}{\sum_{p=1}^m fr_{ip}}$$

$d_{ip}$  is the  $p^{th}$  dimension of vector  $d_i$ . Each dimension of document vector represents frequency value of a character. The documents whose authors are unknown are represented by  $X$  and the document  $i$  is represented by the statement  $x_i$ .  $\hat{y}_i$  is different from  $y_i$  because  $\hat{y}_i$  is an estimated value, not an accurate value. It is inevitable to make clear the relation between  $\hat{y}_i$  and  $x_i$  in order to find the author of a document. The equation :

$$\hat{y}_i = \underset{j=1 \dots k}{\operatorname{argmax}} (\operatorname{Sim}(\vec{x}_i, \vec{C}_j))$$

can be used to show this relationship.  $C_j$  value is required for authorship attribution. Before centroid values, average character frequencies for each author have to be calculated. This process aims to find the average character frequencies of the samples. For example, after getting the character frequencies of 100 sample 1KB documents, we can obtain average frequency value for each author by calculating the average value of these frequencies. Average character frequency calculation is as below.

$$\vec{A}_j = \frac{1}{n} \sum_{i=1}^n \vec{d}_{ji}$$

Character frequencies for each author can be stated as  $A=(a_1, a_2, \dots, a_m)$ . For the author with indice  $j$ , presentation of average frequency values by means of features is as follows.

$$A_j = (a_{j1}, a_{j2}, \dots, a_{jm})$$

Following equations can be written where  $a_{(T)p}$  represents the total usage frequencies of  $p^{th}$  character for all the authors and  $c_{jp}$  represents the centroid value for  $p^{th}$  character in texts of  $j^{th}$  author.

$$a_{(T)p} = \sum_{i=1}^k a_{jp}$$

$$c_{jp} = \log(a_{jp} * 100 / a_{(T)p})$$

A function called Sim is used for finding similarity. This function is cosine similarity function. Function is stated in 3.9. When the denominator of this equation is removed, we can obtain text scores.

$$\operatorname{Sim}(\vec{x}_i, \vec{C}_j) = \frac{\sum_{p=1}^m x_{ip} \cdot c_{jp}}{\sqrt{\sum_{p=1}^m (x_{ip})^2} \cdot \sqrt{\sum_{p=1}^m (c_{jp})^2}}$$

#### 4. EXPERIMENTS AND RESULTS

Data set, that was required for training and test phases of the character level author attribution system, was formed from the articles of a daily newspaper SABAH (www.sabah.com.tr). Articles of the authors who write about different topics such as politics, magazine and medical were preferred. Training set consists of 10 different texts written by 10 different authors and the test set consists of 10 sample texts for each author. The feature set initially consisting of 29 letters of the Turkish alphabet, has been extended to 42 features by adding punctuation marks and some special characters in progress.

Texts have to be presented by numerical data because classification algorithm is used in authorship attribution. For this reason, the frequencies of letters and punctuation marks in the texts are calculated. Characters are counted simply in order to find the frequencies of characters. As the raw data about the character frequencies can't help much, relative frequencies also have to be calculated. After reaching the relative character frequencies for documents, each document is represented by a document vector in document character space.

It is possible to consider the centroids as vectors that present the authors' characteristics. While centroid vectors represent authors, document character vectors represent the documents. Centroid values are obtained from the frequencies of characters which are used by each author. After getting the centroid vectors, similarities between test document and centroid vectors are examined in order to perform authorship attribution process. By applying test scoring method for similarity, it is possible to find the authors' scores of the test document from the dot product of document character vector and centroid vector. After the author scores for the test document are examined, the test document is classified.

Each author has its own style of writing and this is the main idea of character level authorship attribution. In this respect, each author expresses his taught and ideas with different words and different styles of sentences. An author's style makes us possible to recognize the author of a text. Character frequencies being able to let us recognize the author of a text will be the proof of character level method. High success ratio for the authorship attribution has been aimed. For this reason, different experiments have been held in order to find an optimum success ratio. These experiments aim to show that which numerical values should be used to represent the data and which similarity methods should be used.

It is possible to use average frequency and centroid values of texts for recognizing the author. But these experiments show that using centroid values more successful than using average frequency. The most important difference between centroid values and average character frequencies is the logarithm transformation. So, owing to the logarithm transformation high success ratio can be obtained with the centroid values.

Functional words method used besides character based method in respect of correct identification and performance. Accuracy rates are shown in the table below.

ID	Author	Functional words	Characters
1	Author1	%60	%90
2	Author2	%40	%90
3	Author3	%50	%60
4	Author4	%70	%100
5	Author5	%50	%90
6	Author6	%20	%60
7	Author7	%40	%80
8	Author8	%10	%100
9	Author9	%100	%90
10	Author10	%90	%100
Average Success Rate		%53	%86

Table 2: Accuracy Rates

It is examined from the results of the experiments made with the same dataset that character based method is more successful than functional words method. In this study 67 functional words were used. While the success ratio for the functional words method is 53%, this ratio is 86% for character based method. While character based method not required preprocessing step, functional words method requires this step. Preprocessing step which is a process applied to each article in the dataset necessitates a lot of time. Besides, small feature set of the character based method makes it superior to the other methods with large feature set.

#### 5. CONCLUSION

With this study, an authorship attribution system has been developed with a character level method and it has been compared to the preceding systems with functional words method. Each author in the character level authorship attribution system has been represented by centroid vectors. The author of a test document is identified after examining the similarities between the document character vector of the document and the centroid vectors of the authors. Cosine method has been used to find similarities.

Character based authorship attribution is superior to other methods in respect of performance and effectiveness. Small feature set, studying with raw data makes this method effective. In respect of correct identification and performance, character based method is the most appropriate and successful method for daily articles. For this reason, it is suitable for cases where performance is important. Character based method can be used in spam filtering or plagiarism detection because these processes are also performed by examining the characteristic features of a text.

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# CHARACTERISTICS AND ACCEPTANCE OF YOGURT CONTAINING POWDER OF POMGRANATE (*PUNICA GRANATUM*) PEEL

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## Abstract

Yogurt was prepared by adding pomegranate peel powder (PPP) to cultured milk. The aim of this study was to investigate the influence of pomegranate peel on chemical and microbiological characteristics (pH, titratable acidity, total solids, fat and lactic flora), sensory, texture quality and acceptability of yogurt thus obtained. So, the PPP is used at different concentrations (0.5, 1 and 1.5%) in yogurt as a natural diet ingredient. Also, the addition of PPP in yogurt provides product with conform physicochemical and microbiological standard parameters. Concerning textural properties, the yoghurt with 0.5% PPP (Y0.5g) showed a firmer texture compared to other yogurts (nature and those with 1 and 1.5% PPP). On the other hand, the sensorial analysis has revealed that the yogurt (Y0.5g) presents the most appreciated taste in comparison with the ones.

**Keywords:** Yogurt, powder, pomegranate peel, chemical and microbiological characteristics, texture, taste.

## 1. Introduction

Recent years have seen a significant operating of plants, including fruits. Latters aroused a strong interest among both consumers and nutritionists. They are also used as component of high energy food like yogurt, flour baby, jams...

The fruit studied in our present work is the pomegranate tree (*Punica granatum*). The seeds, bark and flowers of the pomegranate have been used for thousands of years for their medicinal properties in the Middle East, Asia and Latin America, regions where this shrub is native. The fruit used historically to treat gastrointestinal diseases and parasitic diseases. This work is part of the recovery of pomegranate peel, used since antiquity as bitter and astringent infused invaluable for most people to cure some diarrhea (Afak, 2005).

It's given all these considerations we thought of incorporating pomegranate peel rind powder form at different concentrations in the preparation of a yogurt. This experiment aims to develop a food of high nutritious quality. Yogurt is one of the dairy products, which should continue to increase in sales due to the diversification in the range of yogurt-like products, including reduced fat content yogurts, probiotics yogurts, yogurts shaks, drinkable yogurts, yogurt mousse, yogurt ice cream, etc (Fisman et al, 1999). The key to market growth is continuous evaluation and modification of the product to match consumer expectations.

For a long time, yogurt, by itself has been recognised as a healthy food, due to the beneficial action of its viable bacteria that compete with pathogenic bacteria for nutrients and space. Yogurt is an important nutritional source (Tamine & Robinson, 1985; Dello Staffolo et al, 2004).

The objective of this work is the characterization and optimization of pomegranate peel, by formulating a yogurt powder added thereto, as produced for the yogurt date by Amellal (2008).

To this effect, a physico-chemical powder pomegranate peel is performed to its addition during the process of making yogurt. The texture, viscosity, pH, total solids, ash, fat, protein levels, electrical conductivity, microbiological and sensory analysis were investigated.

## 2. Materials and methods

### 2.1 Materials

#### 2.1.1 Plant Material

The fruit used in this study is the fresh pomegranate variety. The fruit is picked kindly on September 2008 in BOUIRA region, Algeria. Once at the laboratory, the fruit is cleaned and separated from its peel. These are dried in air and ground into a powder using a mortar (Photo 1).



Photo1: Peel and pomegranate peel powder

### 2.1. 2 The milk used for the manufacture of yoghurt

The milk used is commercial full cream powdered milk (Mark NESPRAY/French).

### 2.1. 3 The lactic ferments

The lactic ferments used are represented by *Streptococcus thermophilus* and *Lactobacillus bulgaricus* at a freeze-dried state.

## 2.2 Methods of Analysis

### 2.2.1 pH Determination (NF V 05-108, 1970)

The pH of the yogurt samples were measured directly using a pHmeter (Hanna instruments, Italy). The pH meter was standardized with pH 4.0, 7.0 and 9.0 buffer solutions.

### 2.2.2 Titratable Acidity (NF V 05-101, 1974)

Titratable Acidity was determined as Lactic Acid by titrating with 0.1 N NaOH using phenolphthalein as an indicator.

### 2.2.3 Total Solids

Dry matter content (Total Solids) was calculated after evaporation of the water present in the samples placed in an oven (102°C) for 48 h (until constant mass was obtained).

### 2.2.4 Total Fat

It is based on the separation of fat milk and yogurt in a centrifuge butyrometer after dissolution of proteins by sulfuric acid. The separation of fat is enhanced by the addition of a small amount of iso-amyl alcohol. Butyrometer is calibrated to allow direct reading of fat content.

### 2.2.5 Total protein (method Kjeldhal)

The principle of the method is based on the transformation of organic nitrogen into ammonium sulfate by the action of sulfuric acid in the presence of a catalyst, and measured after displacement in alkali and distillation in the form of ammonium.

### 2.2.6 Ash (NF V05-113, 1972)

The yogurt samples were calcined at 550 ° C in a muffle furnace until a white ash of constant weight.

### 2.2.7 Electrical Conductivity

The electrical conductivity of water is the conductance of the water column between two metal electrodes of 1 cm<sup>2</sup> of surface and separated from each other by 1 cm (Rodier, 1996). The electrode meter (Model JUNUAY) is immersed in a solution of 20% solids. The value is directly read by the display meter.

### 2.2.8 Serum Separation (Syneresis)

Samples were placed into 50 ml graduated cylinders, stored at 4°C for 15 days and the serum separation was measured as a volume of separated serum at the top on day 15 as described by Koksoy and Kilic, (2004); measurements were performed in duplicate.

### 2.2.9 Texture Analysis (Penetration tests)

Texture is measured on the finished product, 24 hours after formulation (Carrieu & Luquet, 2005).

Tests were performed with a TA plus Texture Analyser (LLYOD Instruments) on the sample without removing them from their jars. The plunger used was cylindrical, with a flat base 12.7 mm in diameter, moving at a speed of 1 mm s<sup>-1</sup>. The following parameters were recorded: the force of breaking (N), defined as the first significant discontinuity produced in the curve as the plunger penetrated the gel during a total displacement of 20 mm and the distance at which the breaking took place (mm). In those cases in which the samples did not break, the penetration at a displacement of 15 mm (N) was recorded as the firmness value (Fizman et al, 1999).

### 2.2.10 Viscosity

Apparent viscosity was determined at 5°C using a rotational viscometer (Brook Field ROV) equipped with a cylindrical spindle (number 3) at 30 rpm. Measurements were made at intervals of 30 s over a total period of 30 min, and results were expressed in Pas.

**2.2.11 Statistical Analysis**

All the analyses were performed in three replicates. Values of different parameters were expressed as the mean ±standard deviation. Statistical analysis was performed using the Excel-XLSTAT logiciel. The Duncan test was performed to evaluate the significance of differences between mean values at the level of  $P < 0.05$ .

**2.2.13 Sensory Evaluation**

Sensory analysis aims to describe the sensory characteristics of products: appearance (aspect), texture (texture with a spoon and texture in the mouth), flavour and aroma (Carrieu & Luquet, 2005). The methodology followed for this analysis is that described by Beal and Sodini (2003) with minor modifications.

Briefly, yoghurts were served in four glass containers, coded with random three-digit numbers. Hedonic evaluation was carried out by an untrained panel of 17 subjects (10 females and 7 males, aged 22 to 50 years). These panelists were students and staff members of the technology food laboratory (Boumerdes University, Algeria). They were asked to evaluate the yoghurts for odor, taste, appearance and texture. Samples were evaluated based on a four-point hedonic scale, from 0 to 3

**2.2.14 Yogurt preparation**

Yogurt samples were prepared in the laboratory scale according the processing standard diagram, with the addition of different concentrations of powdered pomegranate peel (table 2) chosen after preliminary taste test.

Table 2: Recipe of standard yogurt and Yoghurt with pomegranate peel powder (100g).

Recipe	Milk powder (g)	Sugar (g)	pomegranate peel powder (g)	Water (ml)	Lactic Ferment (%)
Standard Yogurt	13	10	0	100	0.03
Yogurt with pomegranate peel powder	13	10	0.5	100	0.03
			1		
			1.5		

**3. Results and discussion**

**3.1 Physico-chemical properties of yoghurts prepared**

The results of physico-chemical analysis of the four yogurts prepared are reported in Table 4. According to this results, the four yogurts prepared show higher contents of ash. The value recorded for the yogurt with 1.5 g PPP (Y1.5) showed the higher value compared to the other ones. These results are correlated to the electrical conductivity values.

The titratable acidity values were different for the four yogurts. The highest levels were observed in the (Y0.5) and (YS) samples. The difference observed in the results is due to the presence of the PPP in fact. Nevertheless, our results meet those required by international standard FIL (1988), who recommend values between (80-90).

For pH values, they are almost identical for the various yoghurts and they agree those (4.5 and 4.6) required by the IDF (1988).

Table 3: Results of physico-chemical parameters of the four recipes.

Yaourts	Paramètres	pH	Acidity (°D)	Fat (%)	TS (%)	Ash (%)	C.E (mss.cm <sup>-1</sup> )	TP (g/l)	VIS (cp/p)
Y 0,5		4.44 <sup>b</sup>	82 <sup>a</sup>	3.15 <sup>a</sup>	20.69 <sup>a</sup>	0.66 <sup>b</sup>	3.5 <sup>b</sup>	5.81 <sup>a</sup>	17756.33 <sup>b</sup>
		± 0.03	± 0.01	± 0.70	± 0.42	± 0.11	± 0.2	± 0.01	± 6653.15
Y 1		4.4 <sup>b</sup>	74 <sup>c</sup>	3.1 <sup>a</sup>	20.55 <sup>a</sup>	0.70 <sup>a</sup>	4.16 <sup>a</sup>	5.77 <sup>a</sup>	2877.6 <sup>c</sup>
		± 0.04	± 0.01	± 1.41	± 0.06	± 0.07	± 0.15	± 0.1	± 906.62
Y 1,5		4.62 <sup>a</sup>	74 <sup>c</sup>	3.15 <sup>a</sup>	20.65 <sup>a</sup>	0.72 <sup>a</sup>	3.96 <sup>ab</sup>	5.85 <sup>a</sup>	2261.56 <sup>c</sup>
		± 0.11	± 0.02	± 0.70	± 0.25	± 0.014	± 0.3	± 0.03	± 985.01
YS		4.82 <sup>a</sup>	80 <sup>b</sup>	3 <sup>a</sup>	15 <sup>b</sup>	0.6 <sup>c</sup>	2.1 <sup>c</sup>	5.70 <sup>a</sup>	14650 <sup>a</sup>
		± 0.05	± 0.01	± 0.70	± 0.01	± 0.01	± 0.1	± 0.04	± 969.79

\*Mean values of duplicate measurements±standard deviation.

\*Means having the same letters in the same column are not significantly different  
 TS: Total Solids, EC: Electric Conductivity, TP: Total Proteins, Vis: Viscosity

Concerning the total solid (TS), results found was considerably higher for the entire yoghurt sample prepared but there were no difference between yogurts with PPP. At the same time, significant difference was observed between the last samples and YS. It is clear that the incorporation of powdered peel of pomegranate in yogurt increases the total solids approximately 40%.

In contrast, the protein and fat content (TP) were virtually identical for the four yogurts. These results suggest clearly that the peel of pomegranate is low in both protein and fat. Results related to fats are consistent with those given by the IDF (1988), who requires values of 0.5 - 3%.

Viscosity is an important component of sensory characteristics and therefore the texture of product. From Table 4, it can be noted that the Y0.5 has a higher viscosity compared to the other yoghurts, followed by YS, Y1 and Y1.5. So, the Y0.5 prepared has a good strength compared to the other yogurts and therefore a good texture.

**3.2 Texture Analysis of four yoghurts obtained**

Data related to the mechanical behaviour (penetration test) of the different yogurt are given in Table 5.

Globally, the addition of PPP seems to increase the gel firmness. However, the (Y0.5) together with YS show the highest gel force. This observation suggest a negative effect of certain soluble materials on the gel structure. In fact, it is well know that the texture of yogurt is associated to its composition in total solids, presence of stabilizers and fruit (Shaker et al, 2000). Also, it must be recalled that the structure of fruit yoghurt can be enhanced by using texturing agents such as sucrose, gelatin and pectin. These ingredients improve equally the aspect of the texture, the effect in the mouth and the delay in syneresis (Jawalker et al, 1993 and). Always concerning the physical stability, the serum separation commonly named syneresis in dairy product result of the aggregation and sedimentation of casein particles during storage. It the reason for which the use of stabilizers is necessary to prevent syneresis (Towler, 1984 and Vignola, 2002).

In our case, there is unexpected significant syneresis in yoghurt Y1 and Y1.5 regarding their high PPP content, in contrast to Y0.5g which is virtually identical to the standard yogurt value. This anomaly can be explained essentially by the heat treatment and insufficient homogenization. In this context, Luquet (1985) has already reported about the important role of these parameters in the formulation of the gel.

Table 4: Settings penetrations of the four yogurts containing powdered pomegranate peel.

Echantillons	Force of gel (N)	Breaking distance (mm)	Force at 15 mm	syneresis ml/100ml
Y 0,5	0.175 <sup>a</sup> ± 0,03	3 ± 0.3	0.155 <sup>a</sup> ± 0.007	1 <sup>a</sup> ± 0.01
Y 1	0.11 <sup>bc</sup> ± 0.02	3 ± 0.32	0.12 <sup>a</sup> ± 0.002	4.5 <sup>a</sup> ± 0.77
Y 1,5	0.08 <sup>c</sup> ± 0.01	3 ± 0.3	0.07 <sup>b</sup> ± 0.001	5 <sup>b</sup> ± 1.41
YS	0.155 <sup>ab</sup> ± 0.03	3 ± 0.31	0.16 <sup>a</sup> ± 0.006	1.2 <sup>b</sup> ± 0.02

\*Means having the same letters in the same column are not significantly different  
 \*Mean values of duplicate measurements±standard deviation.

**3.4 Sensory analysis**

The diagrams presented in figure 2 allow interpreting easily the results of sensory analysis parameters (taste, odor, appearance and texture).

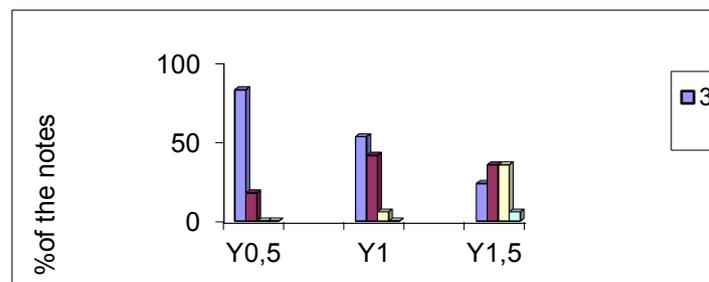


Fig .2: Results of sensory analysis of « taste »

Generally and according to the histograms, the Y0.5 is the most appreciated by the panelists for all the descriptors adopted in this study.

### 3. Conclusion

Indeed, three formulations of yogurt were prepared (Y0.5, Y1 and Y1.5). These are fortified with minerals (high ash rate of 0.66, 0.72 and 0.74 for Y0.5, Y1 and Y1.5 respectively) and total solids (20.65, 20.55 and 20.69 for Y0.5, Y1 and Y1.5 respectively). Yogurt (Y0.5) has a higher gel strength (0.174N) compared to the standard yogurt and the other yogurt formulation. The taste test showed that the yoghurt (Y0.5) is pleased in comparison to the two other yogurts (Y1 and Y1.5). The results obtained in the present work showed that this type of valorization appears to be very interesting, since it permits to produce a yogurt-type biologic. Taking into account the therapeutic power of the PPP, the yogurt elaborated should have functional and dietetic properties for consumers.

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# CHEMICAL MODIFICATION OF WATER HYACINTH FOR THE REMOVAL OF DYESTUFFS

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## ABSTRACT

Water Hyacinth (WH), an aquatic weed, is a good heavy metal adsorbent. Their adsorbing capacity and binding selectivity can be increased by converting the WH's hydroxyl functional group into the desired ones. In this report, the chemical modifications of WH by cyanoethylation (WH-CE), amidoximation (WH-AO) were carried out. The chemical testing and the FTIR spectrums of the WH, WH-CE and WH-AO indicated that higher nitrogen content of the modified WH than that of WH was found with the existing of nitrile and amine functional group on WH-CE and WH-AO, respectively. The adsorption of Acid Blue 25 and Basic Blue 9 by WH and WH-AO were studied. Based on Freundlich adsorption isotherm, WH-AO has a much higher dye-adsorption capacity than does WH. The adsorption capacity of WH for BB9 was higher than AB25. For WH-AO, the adsorption capacity of AB25 was higher than WH.

**Keywords:** dyestuffs; water hyacinth powder; chemical modification of water hyacinth; adsorption

## INTRODUCTION

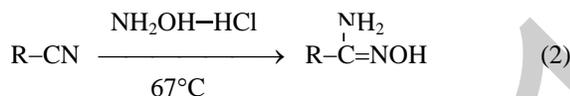
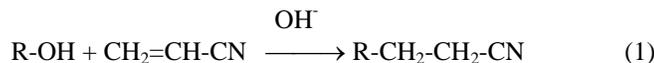
Water hyacinth (*Eichhornia crassipes*) is a perennial, freshwater, aquatic vascular plant with rounded, upright, shiny green leaves. The petioles of the plant are spongy with many air spaces which contribute to the buoyancy of the hyacinth plant. Water hyacinth (WH) is ranked eighth among the world's top 10 in growth rate and is found abundantly throughout Thailand. It is composed of 43-44% cellulose and 12-13% lignin (Strelpapatkul, 1989). Somboon et al. (1990) has reported that water hyacinth powder (WH) has a very high adsorption capacity for heavy metals (Cr, Cu, Ni, Pb and Zn). Like cotton, WH has the tendency to form a strong bond with direct dyes, reactive dyes, and basic dyes.

Color contamination from textile-dyeing effluents has been the target of great concern in the last few years, mainly due to its unsightliness but also due to its toxicity. The de-colorization of textile wastewater is a worldwide problem to which successful treatment technologies have been applied, including coagulation, adsorption, oxidation, and biological treatment. Coagulation can be used effectively to remove certain types of dyes. Generally, this process is most efficient when dealing with pigment-type materials or dispersed dyes. The process is least efficient when dealing with true water soluble dyes. The oxidation methods are effective only in wastewater having a very low concentration of organic color. The adsorption process by activated carbon and polymer resin is expensive, and it is difficult to regenerate the adsorbent (Bousher, Shen & Edyvean, 1997). These conventional methods are costly and require some skill to operate and to maintain. Consequently, the wastewater has been discharged untreated. There is a need for a more practical technology that is more effective and more selective to organic dyestuffs. In this report, the chemical modification of WH powder into two new products with different functional group was studied.

The main functional group of the natural cellulose (cotton) is the hydroxyl group (OH). The hydroxyl group could bond to the positive charges of the adsorbates such as heavy metal ions or cationic dyes. In case of silk, it is the amino group (negative charge) instead of the hydroxyl group. Thus, silk has the affinity for the anionic dyes. The conversion of the hydroxyl group of the cellulose to the amino group could be performed directly through the carbamoylation

reaction. The conversion could be achieved by converting the hydroxyl group of WH to the nitrile group (CN) by cyanoethylation reaction with basic catalysts (Parker, 1993). A chemical reaction, to introduce the  $\beta$ -cyanoethyl group ( $\text{CH}_2\text{CH}_2\text{CN}$ ), involves the addition of acrylonitrile ( $\text{CH}_2=\text{CH}-\text{CN}$ ) to a compound carrying a reactive hydrogen (reaction 1).

Yields in cyanoethylation are generally high. The reaction is strongly exothermic and is usually carried out at moderate temperature in solvent such as dioxane or t-butanol. The cyanoethylated product can be subjected further to the usual nitrile reactions such as hydration, hydrolysis and reduction. Morita, Higuchi & Sakata (1987) converted the cyanoethylated wood to the amidoximated wood by reacting with methanol saturated with hydroxylamine hydrochloride at  $60^\circ\text{C}$ . The reaction is shown in reaction (2).



## MATERIALS

### Water Hyacinth Powder

WH stalk was washed with tap water and cut into pieces of 0.20 cm or less in length. The cut WH pieces were dried overnight at room temperature before being ground and sieved to a size between 0.15 and 0.85 mm (20 - 100 mesh). The ground powder was oven-dried overnight at  $103^\circ\text{C}$  prior to use.

### Dyestuffs

Dyestuffs selected for study and associated information are indicated in Table 1. The chemical structure of each dye is presented in Fig. 1. Dyestuffs are used as received without any purification. They are dried at  $60^\circ\text{C}$  for 3 hours prior to use.

Table 1. Dyestuffs selected for the studies.

Name of dyestuffs	Abbreviation	Type of Dye	CI No.
Acid blue 25	AB25	Acid	62055
Basic blue 9	BB9	Basic	52015

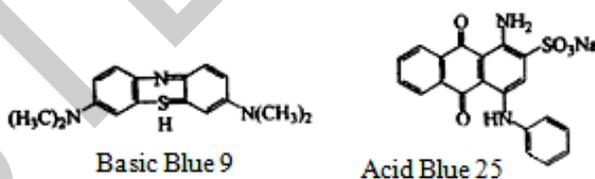


Figure 1. Chemical structure of dyes.

## METHODS

### Chemical Modification of WH

The hydroxyl functional group (OH) of WH is chemically converted into the amine group ( $\text{NH}_2$ ) by indirect conversion to the nitrile group (CN) via the cyanoethylation reaction and then converting into the amino group via the amidoximation.

Cyanoethylation of WH: Place WH into 4.0% NaOH saturated with NaI for 30 min. The mixture is pressed to a wet pickup of 150% with a piece of cloth. The damped WH is quickly placed in a three-necked round-bottomed flask and equips the flask with a reflux condenser. Heat the mixture to a constant temperature of  $60^\circ\text{C}$  after adding acrylonitrile. After 12 hours, allow the flask to cool and neutralizes the mixture with 0.1 M acetic acid. Wash the product in the Buchner funnel, using DI water, until a constant pH of the rinsed water is observed. The product (WH-CE) is dried in a vacuum oven at  $70^\circ\text{C}$ .

Amidoximation of WH: Place WH-CE into methanol saturated with hydroxylamine hydrochloride in a round bottom flask and refluxed the mixture 67°C for 15 hours. The product was washed in the Buchner funnel with deionized water until a constant pH of the rinsed water is observed, then washed the product with methanol and dried in a vacuum oven at 70°C. This product is called WH-AO.

#### Determination of Wavelength at Maximum Adsorption

The dye adsorption spectrum of each dye is determined by dissolving dye in deionized water. The dye solutions were scanned with a UV-VIS Spectrophotometer. The wavelength at the maximum adsorption ( $\lambda_{\max}$ ) was determined from the spectrum.

#### Adsorption Isotherm Study

The adsorption isotherms were determined by shaking fixed weights of WH or WH-AO with known volume of dye solutions having concentrations ranging from 50 to 550 mg-dye/l, at room temperature.

## RESULTS AND DISCUSSION

#### Some Physical Properties of WH Powder

The surface area of WH powder (0.15 - 0.85 mm) is 1.01 m<sup>2</sup>/g, indicating a non-porous solid. The  $\text{pH}_{\text{zpc}}$  was determined by the method described by Huang & Ostovic (1987). The  $\text{pH}_{\text{zpc}}$  of WH is about 6.3, indicating that WH has a weakly acidic surface which is of the cationic type.

WH is a weak cationic ion exchanger, the total cation exchange capacity was found to be 1.0 meq/g. The total exchange capacities for a number of commercial resins ranged from 2.5 to 4.9 meq/g of resin on a dry basis. The total exchange capacity of WH is low because of its low surface area.

#### Chemical Properties of WH and the Modified WH

Solubility tests are performed on WH, WH-CE and WH-AO. The solubility test in acid or a basic solvents can reveal whether the compound in a base (amine), an acid, or a neutral substance. WH, WH-CE and WH-AO are all soluble in sulfuric acid (Table 2). The solubility of WH-CE, but not WH, in pyridine indicates that some of the OH groups of WH are converted into the nitrile groups, as revealed by the IR spectrum. Aromatic amine (amide) is soluble in pyridine. WH-CE and WH-AO are soluble in pyridine, while only WH-AO is soluble in benzaldehyde. The solubility tests and along with the IR-spectra of WH-AO show that it is quite possible that WH-AO contains the amine functional groups.

Table 2. Some chemical testing of WH and modified WH

Type of WH	Solubility Test			Amide Test		Amine Test		Nitrogen Content, %
	H <sub>2</sub> SO <sub>4</sub>	Pyridine	Benzaldehyde	Ammonia smell	Color of Litmus paper	Nitrous acid test	Hinsberg's test	
WH	Y	N	N	N	Red	No bubble	N	0.28
WH-CE	Y	Y	N	Y	Blue	No bubble	N	7.81
WH-AO	Y	Y	Y	Y	Blue	Bubble at 4°C	N	7.73

Note: Y = positive test and N = negative test

The smell of ammonia resulting from the WH-CE and WH-AO tests confirms the presence of the CN group on WH-CE, and the presence of either the CN group or the amide group on WH-AO. If most of the CN functional groups on WH-CE are converted, then the smell of ammonia will indicate the presence of the amide groups on WH-AO. The positive nitrous acid test on WH-AO indicates the presence of the primary amine. The differing results from the nitrous acid test indicate that WH-AO contains the amino group. The ammonia smell from the nitrous acid test comes from the presence of the amide group, not the CN group. The Hinsberg's reagents do not dissolve the WH and all of the modified WH and thus no reaction occurred. The Hinsberg's test cannot differentiate the modified WH, and thus the presence of the amine group cannot be determined.

The nitrogen (N) content of WH and the modified WH was determined by the Total Kjeldahl Method (TKN). The fact that the N content of WH-CN (about 7.81%) is higher than that of WH (about 0.28%) confirms the conversion of the OH group of WH into the CN group of WH-CE. The N content of WH-AO is not twice as much as that of WH-CE could be because of the N content of C=N cannot be determined by the Kjeldahl method.

Thin layer chromatography can be performed on WH-CE and WH-AO only because of their ability to be dissolved in pyridine. The retardation factor ( $R_f$ ) value of WH-CE and WH-AO are 0.88 and 0.63, respectively. It is clearly shown by the  $R_f$  values that the CN functional groups of WH-CN are consumed, and the new products (WH-AO) have different functional groups.

### The Spectrum of WH and the Modified WH

WH is a natural fiber, which is primarily composed of cellulose, lignin, and wax. The IR-spectrum of WH would therefore contain many bands at the different absorption regions. The WH IR-spectrum cannot be accurately interpreted to identify its functional groups. It can, however, be used as one of the tools to differentiate the modified WH. In the infrared spectrum of WH (Fig. 2), the broad band between 2,800 and 3,000  $\text{cm}^{-1}$  results from C-H stretching vibrations. The band at 665.59  $\text{cm}^{-1}$  is from the rocking of the  $\text{CH}_3$  and  $\text{CH}_2$  groups.

The spectrum of WH-CN is shown in Fig. 3. The OH functional group of WH (or WH-OH) is converted into the nitrile group by cyanoethylation (reaction 2). The strong band at 2,252.51  $\text{cm}^{-1}$  result from  $\text{C}\equiv\text{N}$  stretching. The broad band of O-H stretching centered at 3,476.39  $\text{cm}^{-1}$  is still apparent. The adsorption bands in the range of 2,850 to 2,950  $\text{cm}^{-1}$ , and at 1,677.05  $\text{cm}^{-1}$  and 1,104.38  $\text{cm}^{-1}$ , indicate the stretching frequencies of C-H, C=C, and C-O-C, respectively.

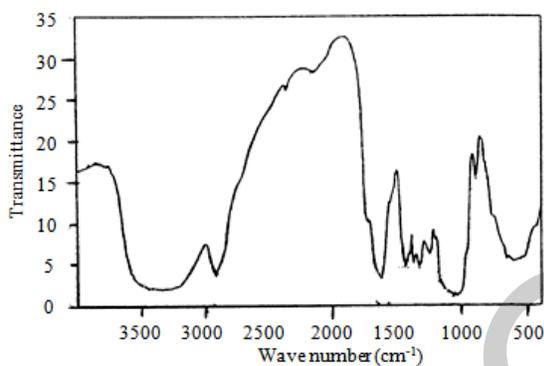


Figure 2. FTIR-Spectrum of WH

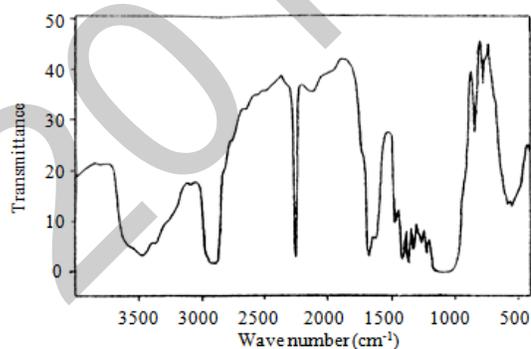


Figure 3. FTIR-Spectrum of WH-CE

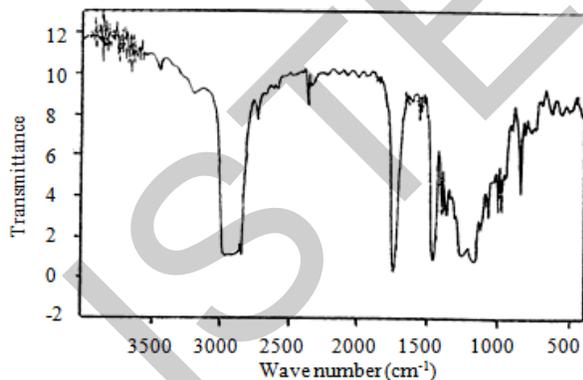


Figure 4. FTIR-Spectrum of WH-AO

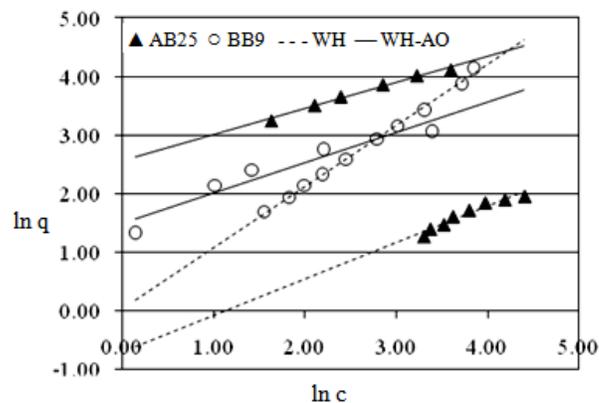


Figure 5. Freundlich adsorption isotherm.

The spectrum of WH-AO is shown in Fig. 4. The fact that there is no broad absorption band around 3,500  $\text{cm}^{-1}$  indicates that most of the hydroxyl groups are largely consumed. The intensity of the  $\text{C}=\text{N}$  vibration (1,630 - 1,680  $\text{cm}^{-1}$ ) lies between that of the  $\text{C}=\text{O}$  vibration (1,600 - 1,950  $\text{cm}^{-1}$ ) and the  $\text{C}=\text{C}$  vibration (1,560 - 1,680  $\text{cm}^{-1}$ ). In the spectrum of WH-CN there is, however, no band in the range of 1,680 to 1,950  $\text{cm}^{-1}$  as indicated in Fig. 3. It is possible that the strong band at 1,742.68  $\text{cm}^{-1}$  (Fig. 4) is the vibration of  $\text{C}=\text{N}$  and not that of  $\text{C}=\text{O}$  or  $\text{C}=\text{C}$ . There is a weak absorption at around 3,440  $\text{cm}^{-1}$  which is most likely the stretching vibration of either the primary amines or the secondary amines. Most of the primary amines show two spikes in the N-H stretching. The secondary amines generally show one N-H spike in the absorption range of 3,400

to  $3,530\text{ cm}^{-1}$ . If the band at  $3,440\text{ cm}^{-1}$  is one of the stretching vibrations of the OH group, then it should be a broad band. There are two bands at  $1,180$  and  $1,280\text{ cm}^{-1}$  that could be the stretching vibrations of the C-N (aromatic) group. The band at  $1,280\text{ cm}^{-1}$  also could be, however, the C-O-C stretching vibration.

### Adsorption Isotherm

Adsorption isotherm data were fitted to the linear form of the Freundlich model. The plots of  $\ln q$  against  $\ln C$ , for the adsorption of dyes by WH and WH-AO gave a straight line indicates that the adsorption process conforms to Freundlich adsorption isotherms. The values of  $K$ ,  $n$  and the corresponding correlation coefficients ( $r$ ), are presented in Table 3.

Table 3. Freundlich adsorption constants.

Adsorbent	Dyestuffs	K	n	r
WH	AB25	0.5034	1.62	0.938
WH	BB9	1.0500	0.96	0.998
WH-AO	AB25	12.8726	2.22	0.988
WH-AO	BB9	4.4817	1.96	0.916

The adsorptions of AB25 and BB9 by WH and WH-AO are shown in Fig. 5. The OH functional group of WH is first converted to the CN group and then to the  $\text{NH}_2$  group. The WH-AO should, however, contain some OH, CN, and  $\text{NH}_2$  groups. The OH group is a negatively charged group, while both CN and  $\text{NH}_2$  are positively charged groups. The adsorption of AB25, an anionic dye, by WH-AO is much higher than that by WH, indicating the net positive charge of WH-AO. The positive charges of both CN and  $\text{NH}_2$  on WH-AO can form hydrogen bonding with  $=\text{O}$  groups of AB25 molecules. At a high equilibrium dye concentration, the adsorption of BB9 by WH-AO is lower than that by WH, due to the repellency between the positive charge of dye and the positive charge of WH-AO.

### CONCLUSION

The hydroxyl functional groups of WH are chemically converted to the nitrile group by cyanoethylation reaction. Some part of these nitrile groups are converted to the amine group by amidoximation reaction. AB25, an anionic dye, has a net negatively charge while that of BB9, a cationic dye, has a net positively charge. WH-AO has a higher positive charge comparing to WH and therefore can adsorption AB25 much more than BB9. The lower adsorption of BB9 by WH-AO is due to the higher repellence force between the positive charge of BB9 and the positive charge of WH-AO.

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# CHEMICAL, BACTERICIDAL AND TOXICOLOGICAL ANALYSIS OF SOME COMPONENTS EXTRACTED FROM *URGINEA MARITIMA* GROWING IN THE NORTH OF ALGERIA

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## Abstract

The dried powder from the Scilla (*Urginea Maritima*) (Algeria (Kabylia)) had been characterized and submitted to toxicological and bactericidal analysis.

solvents: water; mixture EtOH-water (80 : 20v/v)], MeOH-water (80 : 20v/v), EtOH (8 spots), MeOH (10 spots), acetone (10 spots) had been choosen.

For the TLC, we used Silicagel 60 F<sub>254+366</sub> Merck plates, chloroform/ methanol/dimethylformamide as mobile phase and Carr-Price reagent under 366 nm. The HPLC conditions: JASCO PU 1580 with JASCO UV-1570 (UV/VIS Detector); Discovery C<sub>18</sub> (250mmX4.6mm, 5µm column); acetonitrile / water (30 :70, v/v). λ= 280 nm.

Calculation of LD50 by the method of Miller and Tainter allowed to find that :

$$DL_{50} = 213 \pm 22 \text{ mg/Kg.}$$

## EXPERIMENTAL

### Plant Material and Chromatographic Analyses.

We used plant material from *Urginea Maritima* (Scilla) that was collected in Kabylia (Algeria) and dried in air. Dry raw (onion) material was separated into peaces and stems and ground to particle size 0.5-1.0 mm. The ground raw material was stored in a hermetically sealed container under Ar until used in the experiment. The moisture content of ground leaves and stems was 2.0 and 3.0%, respectively.

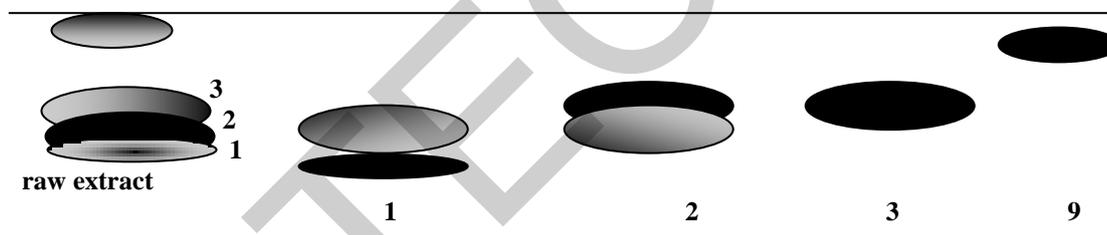
The choice of solvent had led to the following mixtures: water; mixture EtOH-water (80 : 20v/v)], MeOH-water (80 : 20v/v), EtOH (8 spots), MeOH (10 spots), acetone (10 spots).

For the TLC, we used Silicagel 60 F<sub>254+366</sub> Merck plates, chloroform/ methanol/dimethylformamide (80 :19 :1, v/v/v) as mobile phase and Carr-Price reagent under 366 nm .

*Standard solution for analysis :*

Inject 40 µl of each extracted solution .

The results obtained are shown on the **Fig.1.** (using Carr-Price solution)



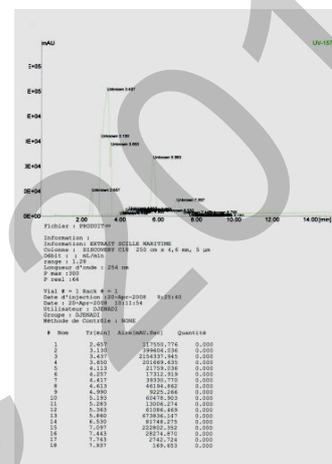
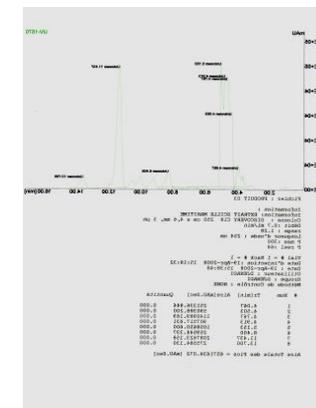
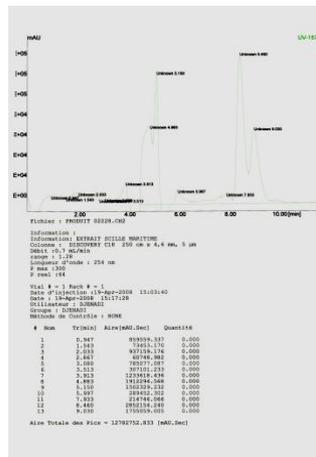
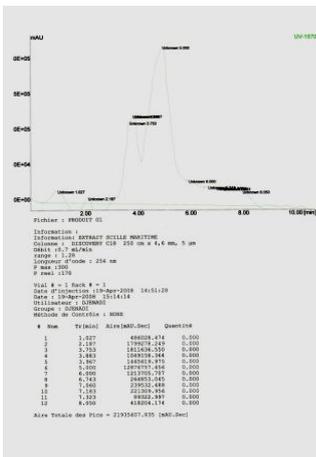
**Fig .1. Thin Layer Chromatography of extracted components**

**1, 2, 3, 9 : Main components.**

### HPLC analysis

We used for this aim a JASCO PU chromatograph using a Discovery C<sub>18</sub> (250mmX4.6mm, 5µm).column packed with acetonitrile / water (30 :70, v/v) reversed phase thermostated at 35°C. The eluent was a linear gradient from CF3COOH (0.1%) to methanol (100%). The elution rate was 0,7 ml/min for the components 1, 2, 3and and 1 ml/min for the component 9.

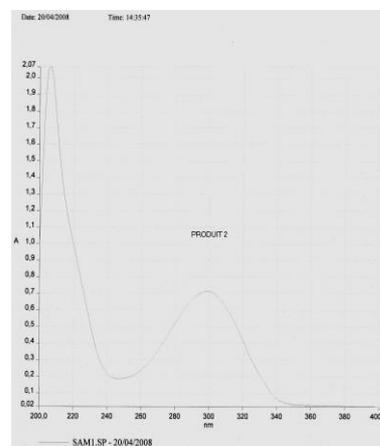
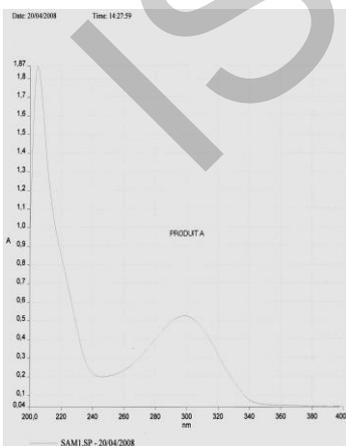
Multi-wavelength JASCO UV-1570 (UV/VIS Detector) was used. Scanning used wavelengths 260, 280, 300, 320, and 360 nm. The resulting chromatograms were processed as shown on the **Fig. N° 2, 3, 4 et 5.**

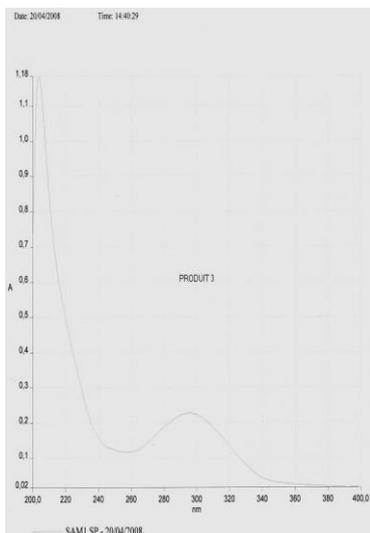


**UV-Vis analysis :**

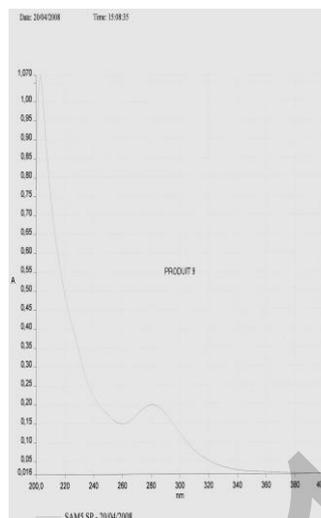
It had been carried on UV/VIS PERKIN-ELMER. Λ 25.

The cardiac glycosides bufadienolides type is generally characterized by an absorption maximum at 298 nm, which is due to the presence of a doubly unsaturated lactone rings. It was conducted a sweep from 200 to 400 nm for four separate products (Fig. 6, 7, and 8). The spectra obtained show the presence of a doubly unsaturated lactone rings in the chemical structure of products 1, 2 and 3.





**Fig 8. UV Spectra of component N°3**



**Fig 8. UV Spectra of component N°9**

**Study of the antiviral and antifungal activity:**

These studies are to determine the action of drugs on plant pathogenic microorganisms (bacteria, ungi) In this work, the antibacterial and antifungal activity was limited to a preliminary study on aqueous and alcoholic extracts.

*Preparation of extracts:*

Prepare three samples to 25 and 50% of the powder Scilla, by soaking in solvents: water, EtOH, MeOH.

*Experimental Protocol:*

The method chosen for testing antibacterial and antifungal is by diffusion in solid.

The product to be tested is placed on a nutrient agar, inoculated with bacteria or yeast and selected cast into petri dishes. Antibiotic substances circulate around the various points of the deposits.

The activity of the antimicrobial is assessed by measuring zones of inhibition.

*Pathogens:*

- Bacteria: Escherichia coli
- Yeast: Candida albicans

*Culture media and products:*

- Medium A agar: Maconcky (composition, see Annex).
- Medium B agar: Sabouraud (composition, see Annex).
- NaCl.
- Purified water.

*Test performance:* Prepared from a 24 h culture of the bacteria studied, a bacterial suspension in saline solution (0.9% NaCl) and a 48 h culture of yeast studied, a suspension of yeast, also in solution saline. Introduce 0.4 ml of the prepared suspension (equivalent to 8 drops per pipette) in 200 ml of agar medium for the bacterial suspension and the agar medium B for yeast. Pour immediately into uniform layer of 2 mm to 5 mm thick in the middle inoculated Petri dishes. Using a tweezers, put on the surface of water; disks impregnated with the extract solution to consider. Leave broadcast solution at room temperature for 1h to 4h. Bring to the incubation at 20 ° C for 48 h boxes antifungal test and at 35 ° C for 18 h to 24 boxes of the antibacterial test. After incubation, the inhibitory activity of extracts is around discs with circular clear zones on the opaque background of culture. Measure the diameter of the zones of inhibition with accuracy of 0.1 mm.

inhibition Areas diameters (mm)

Extract	Concentrations (%)	<i>Candida albican</i>				<i>Escherichia coli</i>
		d <sub>1</sub>	d <sub>2</sub>	d <sub>3</sub>	M	
		Aqueous	25	31,84	29,85	
Methanolic	25	25,61	24,50	24,96	25,02	-
	50	27,18	27,93	28,27	27,79	-
Ethanolic	25	-	-	-	-	-
	50	-	-	-	-	-

The results show that:

- The Maritime Scilla has antifungal activity against the growth of *Candida albicans*.
- The fungicidal effect is greater in the aqueous extract than in the methanolic extract. It is zero in the ethanolic extract.

**Determination of Lethalis Dosis 50**

Test results of acute toxicity are shown in the table and in the figure

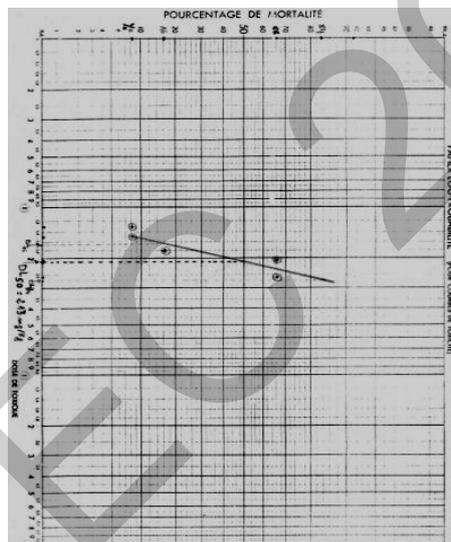
acute toxicity

Dosis mg/Kg	Number of deaths				Symptoms
	24 h	48 h	72h	amount	
125.3	0	0	0	0	<i>No phenomena of intoxication</i>
150.4	0	0	0	0	Weakness
180.4	0	0	1	1	Convulsions
216.5	2	0	1	4	Tono-clonic convulsions, ataxia.
260	3	0	1	4	tremors

Calculation of LD50 by the method of Miller and Tainter allowed to find that :

$$DL_{50} = 213 \pm 22 \text{ mg/Kg}$$

This result showed the effect of the rat poison dry



**Fig.10.** dose- mortality relation of the dried extract

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# COMMON SPORTS-RELATED INJURIES AND THE EFFECTIVENESS OF REHABILITATION IN THE PREVENTION OF REOCCURRENCE

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## ABSTRACT

Injuries among student athletes are a major concern, especially when the prevalence of injury is high among load-bearing sports (e.g. basketball, volleyball, football, soccer). The purpose of this study was to determine the most common injuries among college-aged individuals that participated in load-bearing sports, to determine the most common method of treatment/rehab for these injuries, and the prevalence of reoccurrence. We hypothesized that ankle and knee injuries would be the most prevalent type of injury with electric stimulation and bracing as the most common form of treatment. Also, we precluded that higher reoccurrence in ankle injuries would predominate over other reoccurrence injuries.

Data collected through a survey showed that the most common injuries were to the lower extremities, which accounted for 21% of our findings with ankle injuries (ankle sprains) being the most common. However, 41% of athletes still had reoccurrence injury to the ankle following treatment. We conclude that while ankle injuries are among the most prevalent injuries among college-aged athletes, further studies are warranted to determine an effective treatment for these injuries in the prevention of injury reoccurrence.

## INTRODUCTION

In recent years, more focus has been given to sport-related injuries, particularly in lower extremities, which can be attributed to the types of movement, frequency of participation, and intensity of the sport (Agel et al., 2007; Sharpe et al., 1997).

According to the National Collegiate Athletic Association (NCAA), injury surveillance data for women's basketball indicated the most common sports-related injuries were to the lower extremities. Specifically, more than 60% of all game and practice injuries were to the lower extremity including ankle, knee, and upper leg muscle injuries (Agel et al., 2007). In addition, studies pertaining to female soccer players reported that ankle injuries (i.e. ankle sprains) were among the most common impairments at the collegiate level (Sharpe et al., 1997; Elkstrand and Tropp, 1990; Garrick and Requa, 1973; Knapik et al., 1991). Based on previous studies, individuals that experience ankle sprains are more likely to endure reoccurrence (Elkstrand and Tropp, 1990; Garrick and Requa, 1973; Jones et al., 1993; Milgrom et al., 1991).

## PURPOSE AND HYPOTHESIS

The purpose of this study is to: i) determine the most prevalent sports-related injuries and the most common form of treatment for these injuries and ii) determine the most common modality of treatment and its effectiveness in preventing re-injury.

Based on previous studies, we hypothesized that ankle and knee injuries would be the most frequent type of injury with electric stimulation and bracing as the most common form of treatment. In addition, we hypothesized that ankle injuries lead to a higher rate of reoccurrence compared to other injuries.

## METHODS

### Experimental Protocol

84 student athletes of the Ohio Dominican University male and female basketball and soccer teams were asked to participate in a survey questionnaire regarding past injuries.

### Experimental Measurement and Data Collection

Each team was given a survey questionnaire proctored by a co-investigator involved in the study.

The purpose of the study, the details of the survey, and information of the right to refuse participation was explained to each subject.

Those who chose to participate signed a form of consent and all data was kept in a locked cabinet accessible only to the co-investigators of the study. The study was approved by the Ohio Dominican University Institutional Review Board and complied with the regulations and rules set forth by the Declaration of Helsinki.

Each survey included information regarding: type of sport, position of the athlete, years of participation at the collegiate level, past injuries (upper and lower extremity), treatment for those injuries, and any record of reoccurrence based on modality of treatment and/or rehab.

## RESULTS

**Table 1 – Survey response of all reported sports injuries and applied methods of treatment.**

Treatment	Injuries						Total # of Athletes
	Ankle Sprain	Hamstring	Groin	Shin Splits	Knee	Concussion	
Surgery	0	0	0	0	4	0	4
Cast	2	0	0	0	0	0	2
Brace	7	0	0	0	4	0	11
Sling	0	0	0	0	0	0	0
Rehab	1	2	0	0	5	0	8
Chiropractor	0	0	0	0	1	0	1
Ultrasound	3	4	1	1	4	0	13
Electric Stimulation	9	4	1	1	4	0	19
Rest	6	2	1	1	4	0	14
Functional Bracing	3	0	0	0	3	0	6
Cortisone Shots	0	0	0	0	1	0	1
Anti-inflammatory	2	1	0	1	3	0	7
Pain medication	1	1	0	1	3	0	6
Ice	2	1	1	0	1	0	5
Muscle Relaxants	0	2	3	1	0	0	6
None	1	0	0	0	0	0	1

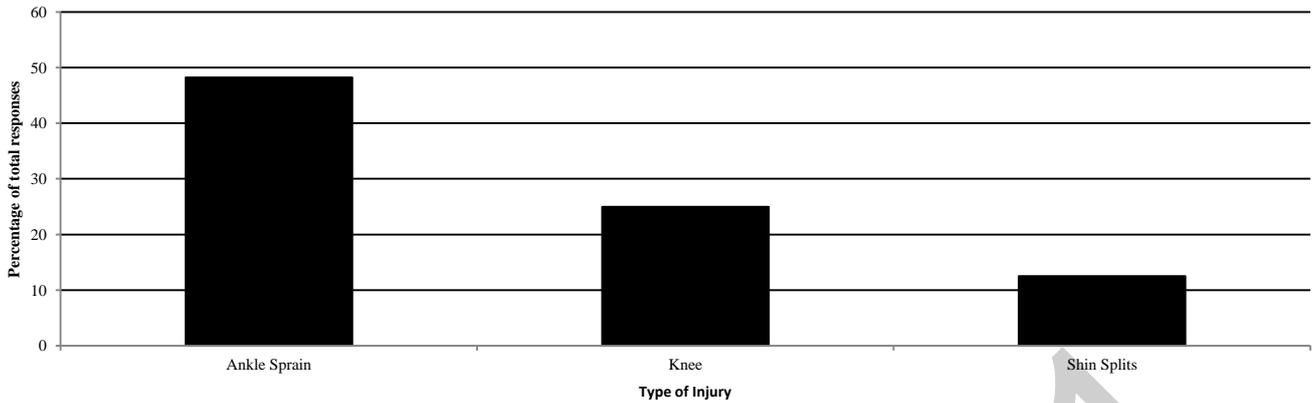
**Table 2 – Most common reported injuries and prevalence for each sport.**

	Men's Soccer	Men's Basketball	Women's Soccer	Women's Basketball
Ankle Sprain	7	9	8	3
Hamstring	1	3	3	0
Groin	3	1	1	0
Shin Splits	1	0	5	1
Knee	4	3	4	3
Concussion	4	0	2	2

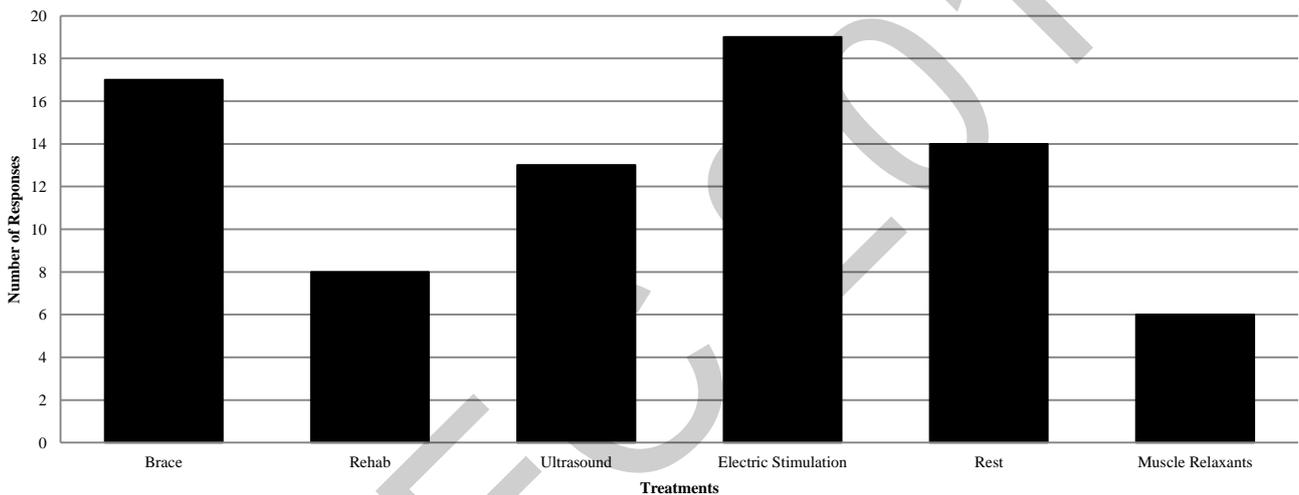
**Table 3 – Number of post-rehabilitation reoccurrence injuries for each sport.**

	Men's Soccer	Men's Basketball	Women's Soccer	Women's Basketball
Ankle Sprain	4	3	4	0
Hamstring	1	0	0	0
Groin	0	0	0	0
Shin Splits	0	0	1	0
Knee	1	0	0	0
Concussion	2	0	0	1

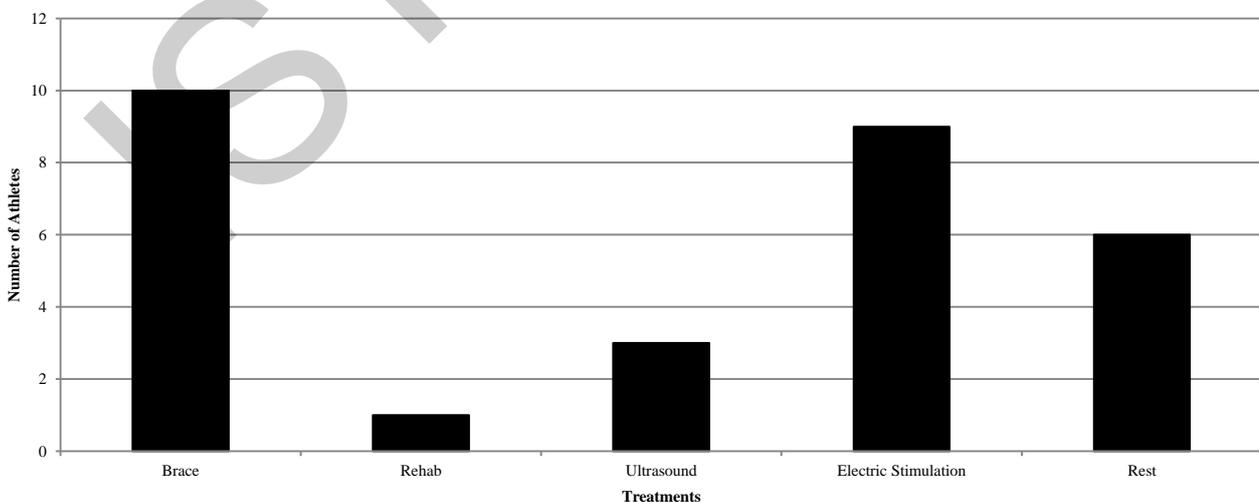
**Figure 1 – Most prevalent load-bearing sport-related injuries among college-aged women’s and men’s basketball and soccer teams.**



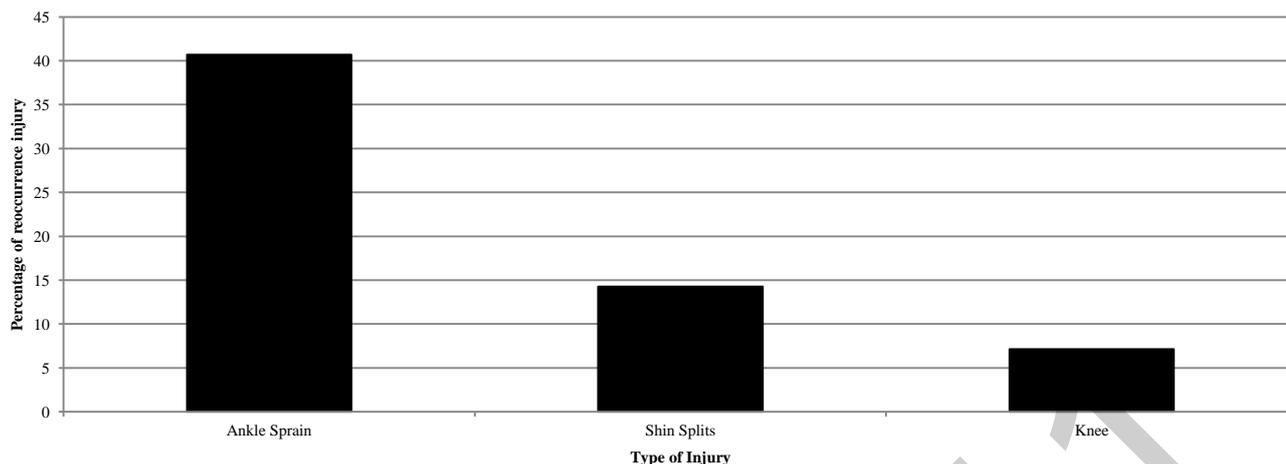
**Figure 2 – Most common methods of treatment for all injuries among college-aged women’s and men’s basketball and soccer teams.**



**Figure 3 – Most common methods of treatment for ankle sprains among college-aged women’s and men’s basketball and soccer teams.**



**Figure 4 – Most prevalent post-rehabilitation reoccurrence injuries among college-aged women’s and men’s basketball and soccer teams.**



### SUMMARY OF RESULTS

The most common sports-related injuries, by percentage, were ankle sprains, knee injuries, and shin splits. The most common injuries were to the lower extremities, which accounted for 21% of our findings. In particular, ankle injuries (ankle sprains) were the most common type of injury. Bracing, electric stimulation, rest, and ultrasound were among the most common forms of treatment. 41% of the athletes still had reoccurrence injury to the ankle following treatment.

### CONCLUSIONS

Based on the present study, ankle injuries are among the most prevalent injuries among college-aged athletes participating in load-bearing sports. Electric stimulation is the least effective treatment in rehabilitation of ankle sprains in preventing reoccurrence.

### LIMITATIONS

Data obtained from subjects that did not fill out the survey in accordance to the directions were excluded from the study. While we understand this is a survey, all subjects were informed that all responses had to be completed to the best of their knowledge. While the data was collected from ODU women’s and men’s basketball and soccer teams, a larger pool of athletes would ensure more definitive findings as to injuries and treatments.

### FUTURE STUDIES

Future studies would include surveying a larger pool of athletes over a wide range of sports. One possible study would be to survey NCAA athletes preceding their season. Additional studies could focus on discrepancies between gender-related injuries. Other research can focus on the effects of various playing surfaces on sports-related injuries.

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# COMPARISON OF THE FPGA-BASED IMPLEMENTATION AND MATLAB/SIMULINK SIMULATION TORQUE CONTROLLER OF A PMSM MACHINE DRIVE

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**Abstract**— This paper starts with an overview of *FPGA* technology development, followed by a presentation of design methodologies, development tools and relevant *CAD* environments, including the use of portable hardware description languages and system level programming/design tools. In this paper, a new contribution for the *FPGA*-Based implementation of controls electrical. This approach is based on concept modularity and reusability. A detailed description of the structure of direct torque control for PMSM drive, and the simulation performed on *Matlab & Simulink* highlight their advantages and disadvantages. A bench test was realized by a prototyping platform, the experimental results obtained show the effectiveness and the benefit of our contribution and the different stages of implementation for the control *FPGA*.

**Keywords**— Permanent Magnet Synchronous Machine, *FPGA*, Direct Torque Control, reusability, *UART*, *ADC*.

## I. INTRODUCTION

The Permanent magnet synchronous Motor is an electric actuator very robust and has a low moment of inertia compared to a DC machine. This characteristic confers to him a dynamics characterized by weak constants of times what makes it possible to design controls in torque, of speed and in position with a better precision and very satisfactory dynamic performances[1, 2, 3].

Currently, two of the best techniques for controlling electrical machines have high performance for the Control of PMSM, namely the Direct Torque Control and the Space Vector Modulation Control. Invented by twentieth century, its operating principles are totally different but the goals are the same. its main objectives and control of torque and current to force the target to follow instructions given by the user with high accuracy and stability, but regardless of the variation of machine parameters and disturbances submitted by outside [4].

However, specific hardware technologies such as field programmable gate arrays (*FPGAs*) can also be considered as an appropriate solution in order to boost the performance of controllers. Indeed, these generic components combine low cost development (owing to their reprogrammability), use of convenient software tools, and more and more significant integration density [5-8]. *FPGA* technology is now considered by an increasing number of designers in various fields of application such as wired and wireless telecommunications [9], and image and signal processing [10, 11], where the always more demanding data throughputs take advantage of the ever increasing density of the chips. Still, more recently, other application fields are in growing demand, such as medical equipment [12], robotics [13]–[15], automotive [16], and space and aircraft embedded control systems [17]. For these embedded applications, reduction of the power consumption, thermal management and packaging, reliability, and protection against solar radiation are of prime importance and electrical control systems. This last domain, i.e. the studies of control of electrical machines, will be presented in this paper.

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column for. Please refer the next section for detail.

The principal advantages of the digital solutions are as follows:

- High flexibility of changing structures of control;
- Immunity against disturbances;
- No problems of variations of control parameters.

This paper presents the simulation (*Matlab & Simulink*) and realization of a platform for *DTC* control of *PMSM* using *FPGA* based controller. This realization is especially aimed for future high performance applications. In this approach, not only the architecture corresponding to the control algorithm is studied, but also architecture and the *ADC* interface and *RS232 UART* architecture.

Considering the complexity of the diversity of the electric control devices of the machines, it is difficult to define with universal manner a general structure for such systems. However, by having a reflexion compared to the elements most commonly encountered in these systems, it is possible to define a general structure of an electric control device of machines which is show in *Fig.1*:

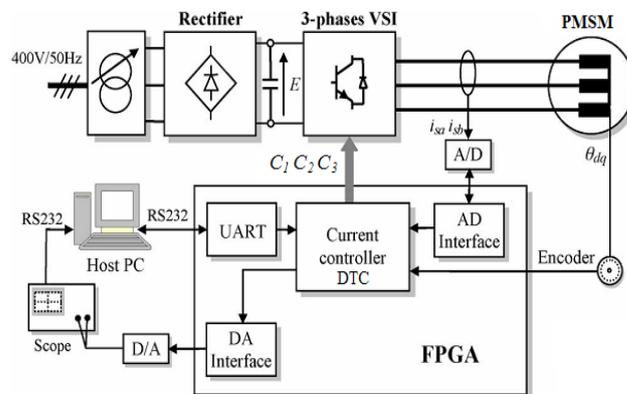


Fig.1. Architecture *DTC* Control

The concept of implementation is defined as being the introduction of a functionality given on a physical support. Within the framework of control of electric machines, the functionality to be introduced constitutes the algorithm of control, whose objective is to control the development state

of mechanical or electric variables of the electric machine (flux, power, torque, speed...). As for the physical support, it constitutes the target of implementation. The latter can be of analogical or numerical nature.

According to the application, consider several algorithms of control can be used such as the current control algorithms, of active or reactive power, speed, position...etc. the structure of the these control algorithms generally comprises an internal loop of regulation of the current. Finally it is often the most difficult to implement because it generally constitutes the most complex part of the control algorithm. The other control loops are relatively much simpler to implement. This is why, within the framework of this work, one will particularly be interested in the current control technique implementation of the electric machines "Direct Torque Control (DTC)".

## II. DIRECT TORQUE CONTROL STRUCTURE

### A. Structure

In the middle of 1980's Depenbrock and Isao Takahashi proposed Direct Torque Control for electrical machines [9, 11], more than one decade later. Idea the DTC basic for electrical motor is slip control. In the 1990's, DTC for PMSM was developed [7, 12, and 13]. The DTC control a magnet synchronous motor Standing is based on the direct determination of sequence of commands applied to switches a voltage inverter. This strategy is based generally on the use of comparators hysteresis whose role is to control the amplitudes stator flux and electromagnetic torque. The Fig.2 is a typical DTC system. It includes estimators flux and torque electromagnetic, flux and torque hysteresis controllers and a switching table.

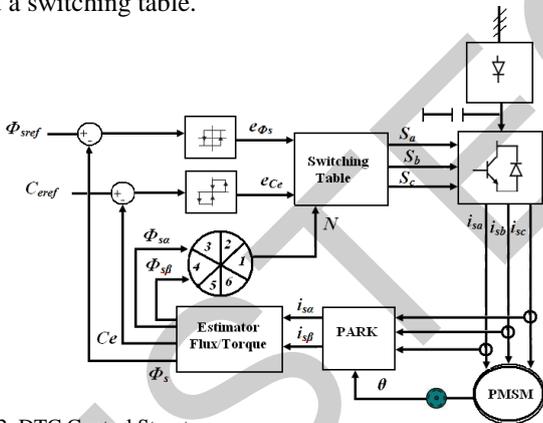


Fig.2. DTC Control Structure

The Fig.2 presented the chosen control. The characteristics memorized for an optimal torque control strategy generates the  $d-q$  component of the vector stator current. Then, an  $abc$ -to- $\alpha\beta$  transformation generates the flux and torque electromagnetic. Finally, these generated parameters are compared to the references and hysteresis controllers to allow the determination of the switching table status  $S_a$ ,  $S_b$  and  $S_c$  of the voltage inverter.

In this paper, we apply the command on a machine type PMSM (Permanent Magnet Synchronous Motor), which consists of three stator windings and a rotor magnet. This motor is described by the following equation (Voltage, Flux, Torque...) [2],

$$u_{sd} = r_s \cdot i_{sd} + \frac{d\Phi_{sd}}{dt} - \omega \cdot \Phi_{sq} \quad (1)$$

$$u_{sq} = r_s \cdot i_{sq} + \frac{d\Phi_{sq}}{dt} - \omega \cdot \Phi_{sd} \quad (2)$$

$$\Phi_{sd} = L_d \cdot i_{sd} + \Phi_f \quad (3)$$

$$\Phi_{sq} = L_q \cdot i_{sq} \quad (4)$$

$$C_e = \frac{3}{2} p [\phi_f \cdot I_q + (L_d - L_q) \cdot I_d \cdot I_q] \quad (5)$$

$$C_e - C_r = J \cdot \frac{d\Omega}{dt} + f \cdot \Omega \quad (6)$$

Where  $\Omega$  is the rotation's speed,  $p$  the Number of pairs of poles,  $J$  the moment of inertia,  $f$  the Coefficient of viscous friction,  $C_r$  the resistive torque,  $\Phi_f$  the flux produced by the permanent magnet,  $L_{sd}$  and  $L_{sq}$  the  $d-q$  axis stator inductance,  $V_{sd}$  and  $V_{sq}$  the  $d-q$  axis stator voltage,  $r_s$  the stator winding resistance and  $C_e$  the electromagnetic torque.

### B. Principle

#### 1) Stator flux control

The stator electric equations of the PMSM, in the reference mark ( $\alpha-\beta$ ) are given by:

$$\begin{cases} V_{s\alpha} = r_s \cdot i_{s\alpha} + \frac{d\Phi_{s\alpha}}{dt} \\ V_{s\beta} = r_s \cdot i_{s\beta} + \frac{d\Phi_{s\beta}}{dt} \end{cases} \quad (8)$$

Then,

$$\begin{cases} \hat{\Phi}_{s\alpha} = \int_0^t (V_{s\alpha} - r_s \cdot i_{s\alpha}) \cdot dt \\ \hat{\Phi}_{s\beta} = \int_0^t (V_{s\beta} - r_s \cdot i_{s\beta}) \cdot dt \\ \hat{\Phi}_s = \hat{\Phi}_{s\alpha} + j \cdot \hat{\Phi}_{s\beta} \end{cases} \quad (9)$$

Or

$$\begin{cases} \Phi_s = \sqrt{\Phi_{s\alpha}^2 + \Phi_{s\beta}^2} \\ \delta = \text{Arc tan} \left( \frac{\Phi_{s\beta}}{\Phi_{s\alpha}} \right) \end{cases} \quad (10)$$

#### 2) Electromagnetic torque control

The electromagnetic torque is:

$$C_e = \frac{3p}{2} (\Phi_{s\alpha} \cdot i_{s\beta} - \Phi_{s\beta} \cdot i_{s\alpha}) \quad (11)$$

$p$ : Number of pairs of poles

Knowing the real sizes ( $i_{s\alpha}, i_{s\beta}$ ) the estimated sizes ( $\hat{\Phi}_{s\alpha}, \hat{\Phi}_{s\beta}$ ), the estimated torque can be given by:

$$\hat{C}_e = \frac{3p}{2} (\hat{\Phi}_{s\alpha} \cdot i_{s\beta} - \hat{\Phi}_{s\beta} \cdot i_{s\alpha}) \quad (12)$$

#### 3) Switching Table

The control table is built according to the state of variables  $e_\phi$  and  $e_{Ce}$  and to the  $i$  zone and  $\Phi_s$  position, and so, it is shaped as presented in the table 1.

TABLE I  
Table that allows choosing the adequate vector

Sector	$e_\phi$	$e_{Ce}$	1	2	3	4	5	6
			$\delta \in [-\pi/6, \pi/6]$	$\delta \in [\pi/6, 3\pi/6]$	$\delta \in [3\pi/6, 5\pi/6]$	$\delta \in [5\pi/6, 7\pi/6]$	$\delta \in [7\pi/6, 9\pi/6]$	$\delta \in [9\pi/6, 11\pi/6]$
1	1	$V_3$	$V_4$	$V_5$	$V_6$	$V_7$	$V_2$	
	0	$V_1$	$V_8$	$V_1$	$V_8$	$V_1$	$V_8$	
	-1	$V_7$	$V_2$	$V_3$	$V_4$	$V_5$	$V_6$	
0	1	$V_4$	$V_5$	$V_6$	$V_7$	$V_2$	$V_3$	
	0	$V_8$	$V_1$	$V_8$	$V_1$	$V_8$	$V_1$	
	-1	$V_6$	$V_7$	$V_2$	$V_3$	$V_4$	$V_5$	

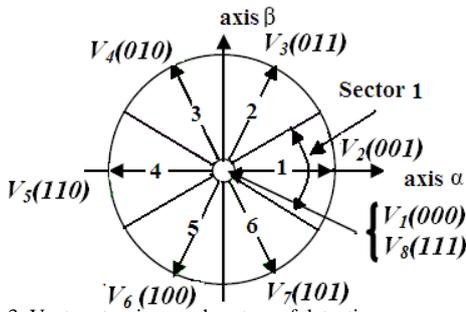


Fig.3. Vectors tensions and sectors of detection

**C. Results of simulations**

The Fig.4 shows the general structure of the Direct Torque Control DTC of the PMSM in the reference mark dq.

The currents  $i_{sd}$ ,  $i_{sq}$ ,  $V_{sd}$  and  $V_{sq}$  are subjected to the transformation of Clark in order to obtain the components  $i_{sa}$ ,  $i_{sb}$ ,  $V_{sa}$  and  $V_{sb}$ .

Its applied components have a block of estimator of torque and flux as well as the detector of sector.

These values estimated thereafter are compared with values of reference to be included in correctors of hysteresis to 2 and has 3 levels, to introduce its errors into a table of commutation which functions by report sector to generate the impulses of the inverter.

This will generate the tension three-phase current thereafter which will be transformed into coordinates dq, the output voltages  $V_{sd}$  and  $V_{sq}$  are applied in average values at the boundaries of the phases stator of the PMSM.

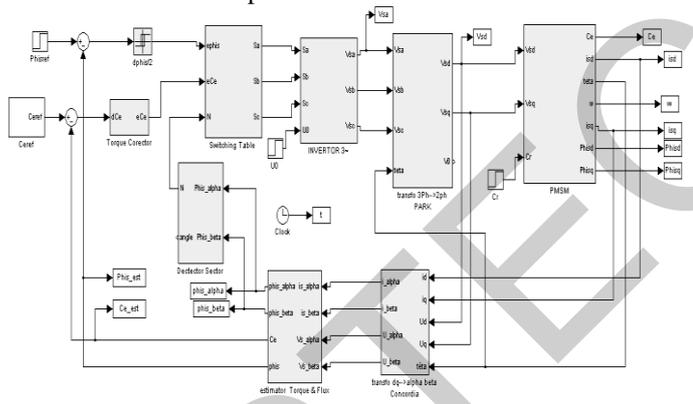


Fig.4. Blocks for the simulation of the DTC under Matlab/Simulink

By applying a set level ( $\Phi_{sref} = 0.13wb$ ) to the reference flux and a set square to the reference electromagnetic torque (Fig.8: +8 Nm, -8 Nm, 10Nm).

Changing system parameters is:

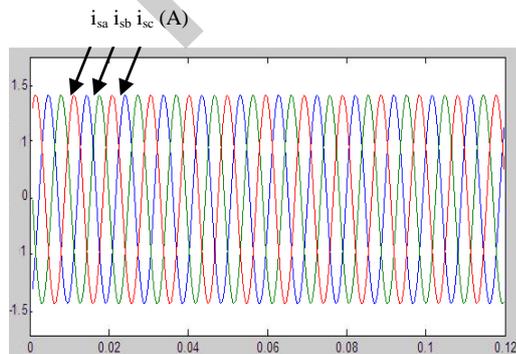


Fig.5. Stator current (A)

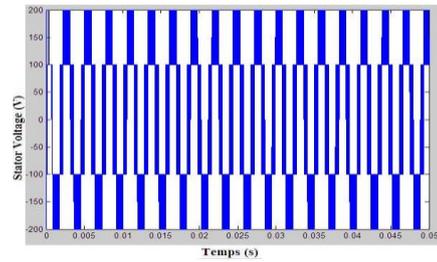


Fig.6. Stator voltage ( $V_{sd}$ )

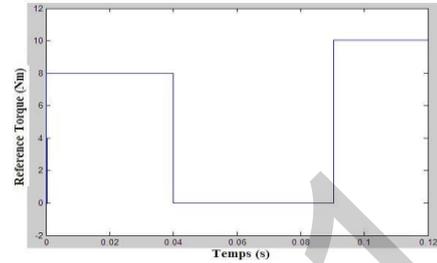


Fig.7. Reference Torque ( $C_{eref}$ ) (Nm)

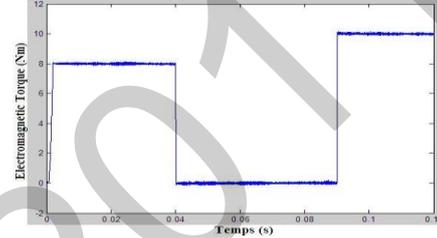


Fig.8. Electromagnetic Torque ( $C_e$ ) (Nm)

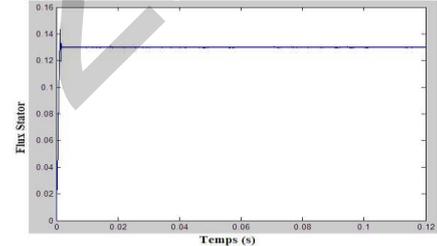


Fig.9. Evolution of the Amplitude of  $\Phi_s$

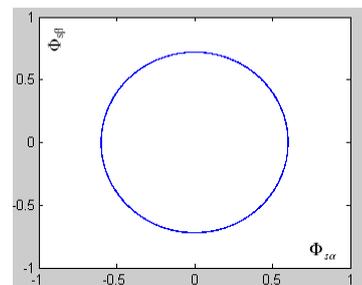


Fig.10. Trajectory of flux ( $\Phi_{s\alpha}$ ,  $\Phi_{s\beta}$ )

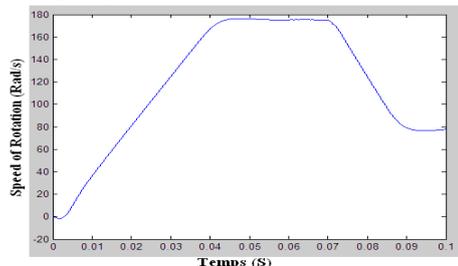


Fig.11. Rotor Speed ( $\omega$ )

In the performed simulation, certain stator flux and torque references are compared to the values calculated in the driver and errors are sending to the hysteresis comparators.

The Fig.5 and Fig.6 show the variation of the stator voltage and current phase of the PMSM, which shows the great performance of the inverter voltage due to the switching table.

The evolution of the electromagnetic torque (*Fig.7*) follows a very specific set the reference, its amplitude is very low, giving high accuracy and stability to the permanent magnet synchronous machine by report further work.

The *Fig.9* shows the evolution known stator flux follows obviously the reference set by cons we see a small excess at the beginning because of the start of the electrical machine, the change in amplitude and well done periodically.

The outputs of the flux and torque comparators are used in order to determine the appropriate voltage vector and stator flux space vector. Vector locations are shown in *Fig.10*.

From all results it is clear that the system is faster, a simulation with a time of 0.12 gives us the best results concerning the speed, stability and accuracy.

### III. DEVELOPMENT OF THE IMPLEMENTATION

#### A. FPGA Generic Architecture Description

FPGAs belong to the wide family of programmable logic components [4–8]. An FPGA is defined as a matrix of configurable logic blocks (CLBs) (combinatorial and/or sequential), linked to each other by an interconnection network which is entirely reprogrammable. The memory cells control the logic blocks as well as the connections so that the component can fulfil the required application specifications. Several configurable technologies exist. Among them, only those that are reprogrammable (Flash, EPROM, SRAM) are of interest since they allow the same flexibility as that of a microprocessor. Therefore, the rest of this paper will discuss only the SRAM-based FPGA.

#### B. FPGA devises

There are several manufacturers of FPGA components such: Actel, Xilinx and Altera...etc. These manufacturers use different technologies for the implementation of FPGAs. These technologies are attractive because they provide reconfigurable structure that is the most interesting because they allow great flexibility in design.

Nowadays, FPGAs offer the possibility to use dedicated blocks such as RAMs, multipliers wired interfaces PCI and CPU cores.

The architecture designing was done using with CAD tools. The description is made graphically or via a hardware description language high level, also called HDL (Hardware Description Language). Is commonly used language VHDL and Verilog. These two languages are standardized and provide the description with different levels, and especially the advantage of being portable and compatible with all FPGA technologies previously introduced.

The *Fig.12* summarizes the different steps of programming an FPGA. The synthesizer generated with CAD tools first one *Netlist* which describes the connectivity of the architecture. Then the placement-routing optimally place components and performs all the routing between different logic. These two steps are used to generate a configuration file to be downloaded into the memory of the FPGA. This file is called *bitstream*. It can be directly loaded into FPGA from a host computer.

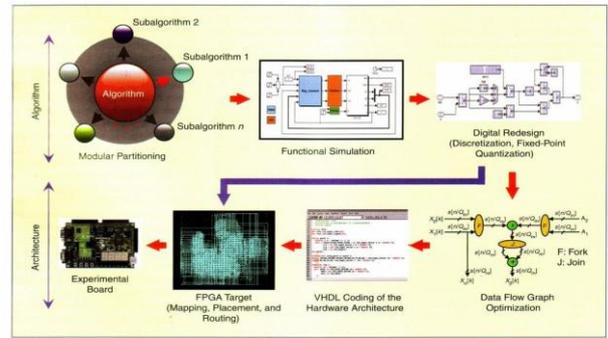


Fig.12. Programming FPGA devisee

#### C. Simulation Procedure

The simulation procedure begins by verifying the functionality of the control algorithm by trailding a functional model using Simulink’s System Generator for Xilinx blocks. For this application, the functional model consists in a Simulink times discredited model of the DTC algorithm associated with a voltage inverter and PMSM model. The *Fig.13* gives a global view of the functional model.

The *Fig.13* shows in detail the programming of the control shown in *Fig.2* (DTC Control) in the SYSTEM GENERATOR environment from Xilinx; we will implement it later in the memory of the FPGA for the simulation of PMSM.

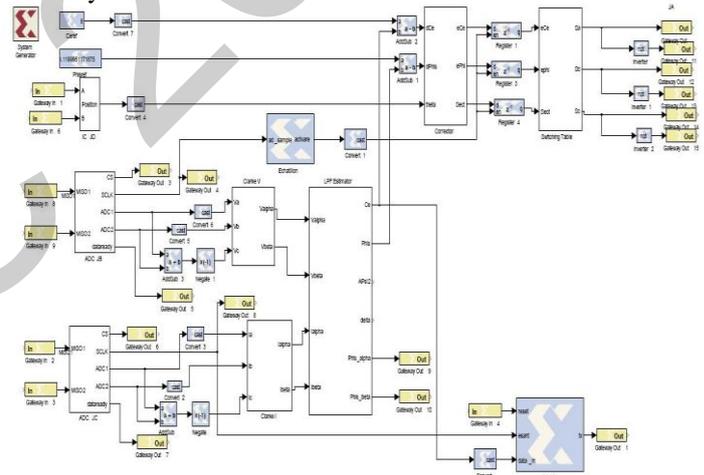


Fig.13. Functional Model DTC from SYSTEM GENERATOR

The description of the different modules is detailed below.

- Two blocks of coordinates transformation: the Clark transformation ( $abc\text{-}to\text{-}a\beta$ );
- The block switching table is the most important, because it can provide control pulses to the IGBT voltage inverter in the power section from well-regulated voltages.
- The block estimator torque and flux, corrector hysteresis and detector sector.
- The block encoder interface IC allows the adaptation between the FPGA and the acquisition board to iniquity the rotor position of the PMSM;
- The ADC interface allows the connection between the FPGA and the analog-digital converter (ADCS7476MSPS 12-bit A / D) that will be bound by the following two Hall Effect transducers for the acquisition of the stator currents machine;
- Block "Timing" which controls the beginning and the end of each block, which allows the refresh in the voltages reference  $V_{10}$ ,  $V_{20}$  and  $V_{30}$  at the

beginning of each sampling period;

- The RS232 block allows signal timing and recovery of signals viewed, created by another program on Matlab & Simulink to visualize the desired output signal.

The second step of the simulation is the determination of the suitable sampling period and fixed point format. The Fig.14 gives the specification model of the  $abc$ -to- $\alpha\beta$  (Clark) transformation.

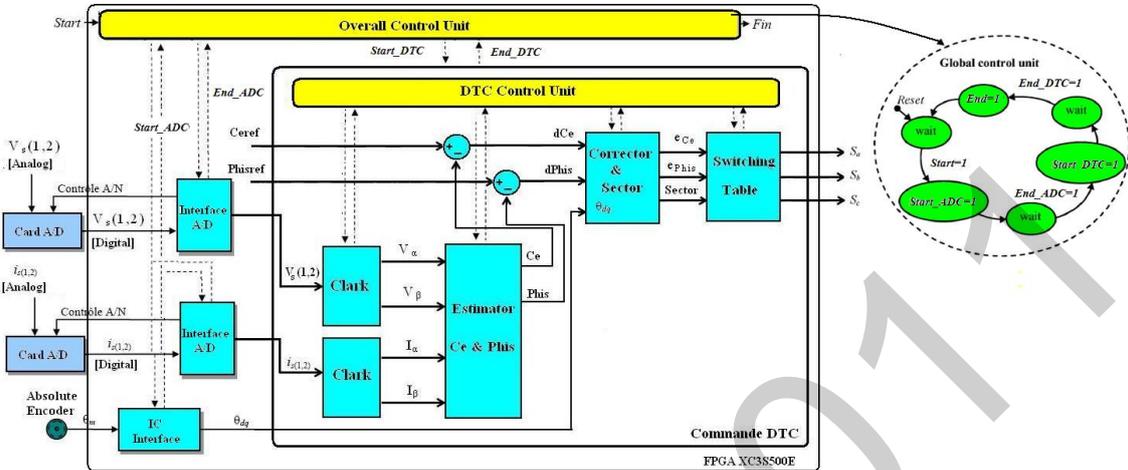


Fig.14. FPGA based hardware DTC

The control unit for architecture ensures implanted control module of the ADC interface, the encoder interface and the command encoder DTC. The Fig.14 shows the timing diagram for the mode of operation of these four modules. At the beginning of each sampling period, the A/D interface module and encoder interface are activated simultaneously. Then, after a delay conversion from analog to digital  $t_{AD}$ , the control module DTC is activated. This is driven by its own control unit and allows you to refresh the reference torque and flux after a computation time equal to  $t_{cr}$ . Once activated, the control unit control module DTC activates the first two modules of the transformation of Clark ( $123$ - $\alpha\beta$ ) that will calculate the components  $i_{sa}$  and  $i_{s\beta}$  stator current vector and the components  $V_{sa}$  and  $V_{s\beta}$  stator voltage vector. The computation time of this transformation is equal to  $t_c$ . When the modules of this transformation indicate the end of the calculation, the estimator module flow and electromagnetic torque is activated. It has the same computation time equal to test and calculates the flux and torque estimated.

Subsequently, when the estimator module indicates the end of the calculation, the correction module of hysteresis and the detector area is activated to calculate the error of the torque and stator flux and the area  $N$ . This module is characterized by a computation time equal to  $t_{cr}$ . Finally, when the errors of flux and torque and sector  $N$  are calculated, the module of the switching table is activated. The latter has a running time equal to  $t_{table}$  and generates the control signals  $S_a$ ,  $S_b$  and  $S_c$  for controlling the switches of the voltage inverter.

The following table shows the performance of computing time and resource consumption, obtained during the implementation of the control DTC architecture. The resources consumed are obtained for a fixed point format  $20/Q18$ . The total computing time of  $t_{DTC}$ , in the DTC squeal module is equal to  $0.95\mu s$ . By

IV. EXPERIMENTAL SET-UP

For this work, the used FPGA target is a XC3S500E Spartan3E the firm Xilinx, the FPGA based hardware control system includes the DTC, an ADC interface and IC interface in one FPGA chip. Fig.14 presents the corresponding implemented architecture.

adding the analog to digital conversion time  $t_{AD}$ , total time  $T_{ex}$  architecture equals  $3.39\mu s$ .

TABLE II  
FPGA PERFORMANCES

Module	Latency	Time Calculation
Interface A/D	120	$t_{AD}=2.2 \mu s$
IC Interface	2	$t_{cod}=0.04 \mu s$
123- $\alpha\beta$	18	$t_c = 0.34 \mu s$
Estimator Flux & Torque	12	$t_{Est} = 0.23$
Corrector & Sector	14	$t_{cr} = 0.2$
Switching Table	8	$t_{table} = 0.18 \mu s$
$t_{DTC} = t_c + t_{Est} + t_{cr} + t_{table}$		$t_{DTC} = 0.95 \mu s$
Run time $T_{ex} = t_{AD} + t_{DTC}$		$t_{ex} = 3.39 \mu s$
Resources Consumed	Number of Slices	1850 de 5376 (34%)
	Wired Multipliers	12 de 16 (65%)
	Memory RAM	6%

To test the FPGA based controller, a prototyping platform for the control of a Permanent magnet Synchronous Machine was assembled.

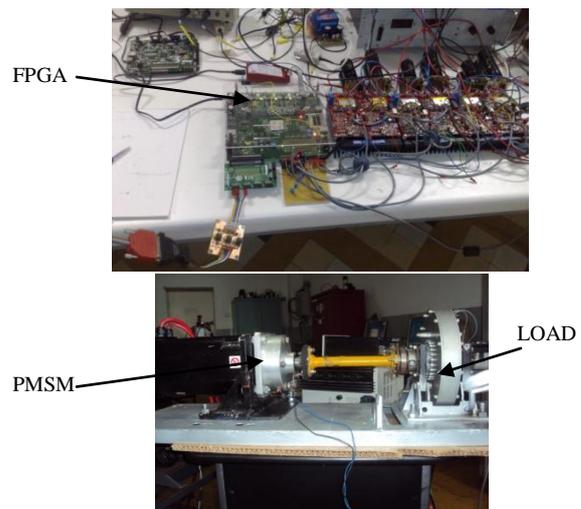


Fig.15. Prototyping platform control

At the hardware level, the execution time of the control architecture is of the order of several microseconds, which allows a better control of current, including a THD lower.

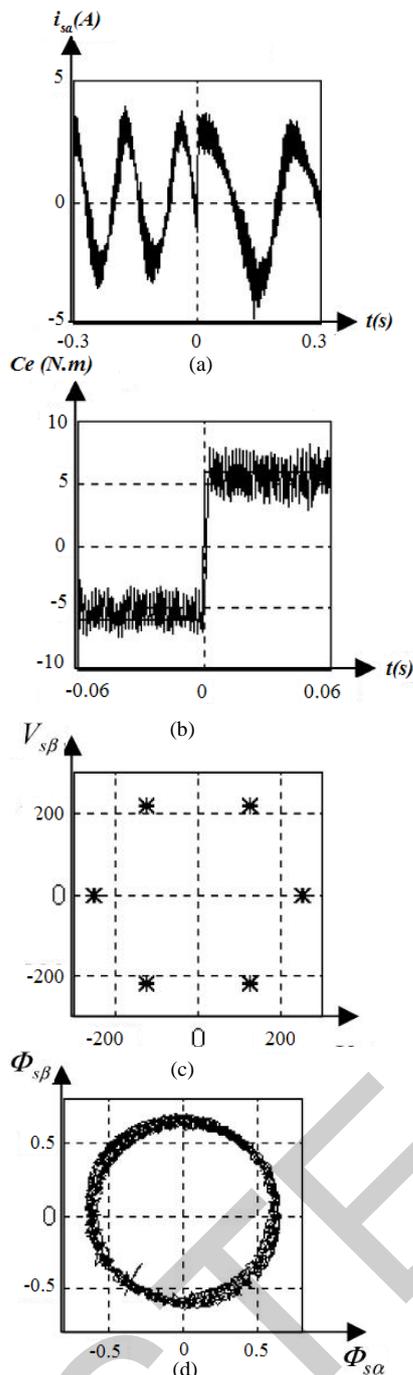


Fig.16. (a) the  $\alpha$ -axis current, (b) the torque  $C_e$  in the PMSM, (c) the  $\alpha$ -axis and  $\beta$ -axis voltage stator, (d) the stator flux locus for DTC PMSM.

In Fig.16 the experimental results *DTC* of *PMSM* with the *FPGA* platform are shown. Clearly the constant set values for stator flux linkage magnitude and torque result, because of the hysteresis controllers in the *DTC* scheme, in *d*-axis and *q*-axis current components that are bounded within hysteresis limits. The hysteresis control is visible in the stator flux locus plot as well. Update frequency for this implementation is 20 kHz. All results were extracted from the *FPGA* by the ChipScope tool of Xilinx. The  $\alpha$ -axis and  $\beta$ -axis current and voltage are measured.

The Fig.14 and Fig.15 show that control system satisfy the basic requirements of the control strategy and validate therefore the good functionality of the system. In fact, it can be noted that:

- The switching frequency is limited to the sampling frequency of the control algorithm to guarantee safe operation of the semiconductor power devices.
- The switching frequency increases weakly when the

stator current vector magnitude decreases.

- Implementing the *DTC* control in *FPGA* has the drawbacks:
- The switching frequency is variable. It is limited to half the sampling frequency of the control algorithm and maximum at very low speed.
- The zero voltage vectors are not applied.

## V. CONCLUSION

In this work, we presented the *FPGA* implementation of Direct Torque Control architecture for permanent magnet synchronous machine (*PMSM*). The results obtained show the benefits of an appropriate methodology that allows the creation of a library of reusable modules optimized. This work provides a new benefit to our laboratory work and a new route for the development and implementation of other control architectures.

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# COMPARISON STUDY ON NP-HARD PROBLEM BASED DIGITAL SIGNATURE SCHEMES

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**Abstract**—This paper shows the development in public-key digital signature schemes which are actually based on non deterministic polynomial mathematical hard problems (NP-Hard). In general, most of the currently used digital signature cryptosystems are computationally expensive with relatively lengthy key requirement due to the dependency on the number theory. Therefore, it's important to study the performance of the most used digital signature schemes which are based on different mathematical hard problems that are, in some sense, difficult to solve. In the surveyed schemes, we present the powerful and practical of some public-key schemes depending on its security level and execution time.

**Keywords**—Cryptography, Digital Signature, Hard Problem, and Public-key.

## I. INTRODUCTION

Digital signature is a verification mechanism based on the public-key scheme (refer to Figures 1 and 2) that is focused on message authenticity. The output of the signature process is called the digital signature [1] [2]. Digital signatures are then used to provide authentication of the associated input, which is called a message [3] (refer to Figure 2). In digital signature public-key algorithms, the private key is used to sign a message, while the public key is used to verify the authenticity of the message. Moreover, digital signatures scheme used to provide the following [4]:

- Data integrity (the assurance that data has not been changed by an unauthorized party).
- Message authentication (the assurance that the source of data is as claimed).
- Non-repudiation (the assurance that an entity cannot deny commitments).

Generally, every public-key digital signature schemes is based on a mathematical problem. This problem is known as NP (Non-deterministic polynomial) hard problem. The problem is considered to be an NP hard mathematical problem if the validity of a proposed solution can be checked only in polynomial time [5].

Basically, public-key digital signature schemes are successfully classified into many major types depending on the NP mathematical hard problem. These problems are the integer factorization problem (IFP), the discrete logarithm problem (DLP), the Elliptic Curve discrete logarithm problem (ECDLP), the chaotic hard problem, etc. This study will help us to identify the strength of the used public-key digital signature schemes according to their mathematical hard problem.

Furthermore, cryptography algorithms can be classified into two board categories, secret key (symmetric) algorithms and public key (asymmetric) algorithms (refer to Figure 1). In general, digital signature scheme is categorized under public-key cryptosystem as shown by Figure 1 [1] [6]. Public-key digital signature on the other hand, works in a very different way, since there are two keys; both belong to one party, either the recipient or the sender. One key is used to accomplish half of the task (e.g. signing) while the other key will be used to complete the rest of the task (e.g. verifying).

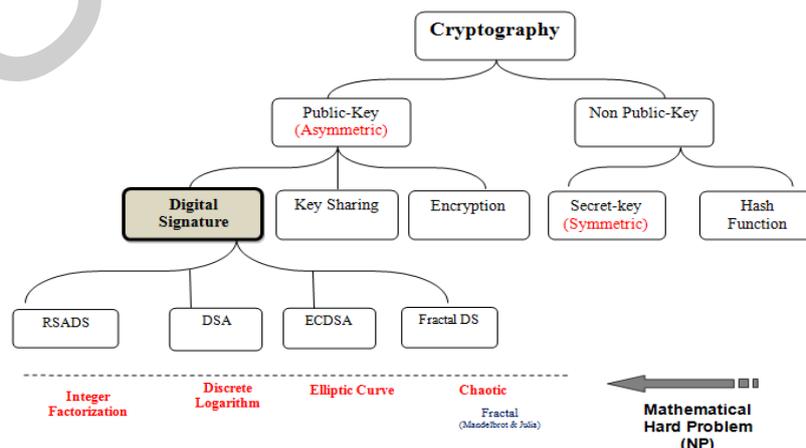


Fig. 1: Main branches of public-key scheme

This paper summarizes the development in public-key digital signature schemes that based on different mathematical NP hard problems. The paper shows a new development on public-key digital signature schemes which include RSADS [7], DSA [8], ECDSA [9], and Fractal digital signature [10].

**II. PUBLIC-KEY DIGITAL SIGNATURE SCHEMES**

In 1976, the first notion of a digital signature scheme was given by Whitfield Diffie and Martin Hellman, although at that time they only conjectured the existence of such scheme [11]. Soon after that, in 1978, Rivest, Shamir, and Adleman invented the first digital signature scheme which is called RSA digital signature algorithm [7]. Subsequently, there were a few more proposed digital signature algorithms such as ElGamal signature scheme [12], Undeniable signature [13] and others.

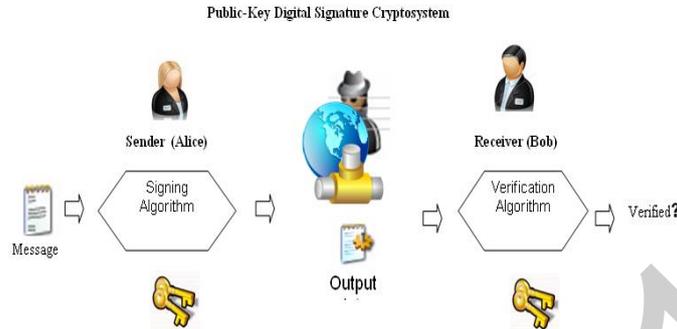


Fig. 2: Digital signature scheme

**III. DIGITAL SIGNATURE BASED ON INTEGER FACTORIZATION: RSA DIGITAL SIGNATURE SCHEME**

In the RSA digital signature algorithm (refer to Figure 3), the private key is used to sign the message. The signed message will be sent to the receiver with the sender’s electronic signature. Figure 3 shows the steps of the RSA digital signature algorithm. To verify the contents of digitally signed data, the recipient generates a new verification key from the signed message that was received, by using his public key, and compares the verified value with the original message value. If the two values match, then the message is verified and authenticated.

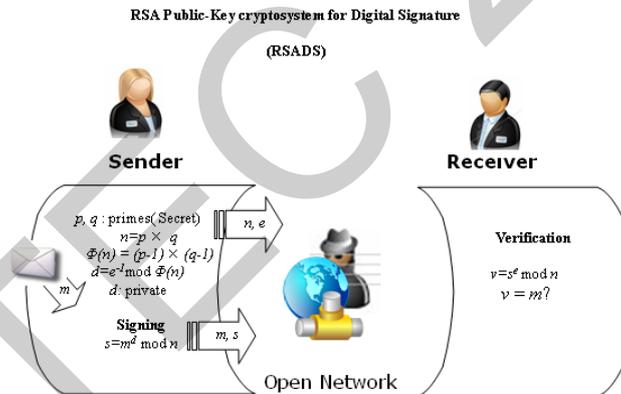


Fig. 3: RSA digital signature scheme

**III-1- The RSA Digital Signature Algorithms:**

Key generation algorithm (generated by receiver, Bob)

Alice must do the following ( Figure 3):

1. Choose two prime numbers ( $p, q$ ) randomly, secretly, and roughly of the same size.
2. Compute the modulus  $n$  as follows:  $n = p \times q$ .
3. Compute the  $\Phi(n)$ , as follows:  $\Phi(n) = (p-1) \times (q-1)$ .
4. Choose the key  $e$ , such that  $1 < e < \Phi(n)$ , and  $GCD(e, \Phi(n)) = 1$ .
5. Compute the private key  $d$ , such as  $d = e^{-1} \text{ mod } \Phi(n)$ .
- Send the public ( $n, e$ ) to Bob.

Signature and verification algorithms

Signature (sender - Alice)

Alice must do the following (Figure 3):

6. Determine the message  $m$  to be signed such that  $0 < m < n$ .
7. Sign the message as follows:  $s = m^d \text{ mod } n$ .
8. Send the signature  $s$  with the message  $m$  to Bob (receiver).

Verification (receiver - Bob)

Bob must do the following (Figure 3):

9. Obtain the keys  $(d, n)$ .
10. Obtain  $s, m$  from Alice.
11. Compute  $u$  as follows:  $u = s^e \text{ mod } n$ .
12. Verify the message  $m$  as follows: is  $m = u^{-1}$ ?

II-2- The Security of RSA Digital Signature Scheme:

Similar to RSA encryption scheme [7], the security of RSA digital signature is based on the integer factorization problem and the large key size which is typically 1024-2048 bit is used [14].

IV. DIGITAL SIGNATURE BASED ON DISCRETE LOGARITHM: THE DIGITAL SIGNATURE ALGORITHM (DSA)

In 1991, the U.S. National Institute of Standards and Technology (NIST) proposed the digital signature algorithm (DSA) and was specified in a U.S. Government Federal Information Processing Standard [8]. The algorithm is called Digital Signature Standard (DSS). Figure 4 illustrates the steps in the DSA digital signature algorithm. The DSA can be viewed as a variant of the ElGamal signature scheme[12]. Both signature schemes are based on the same mathematical problem - discrete logarithm problem. DSA bases its security on the complexity of the discrete logarithm problem in the field of  $Z_p$ , where  $p$  is a prime [9].

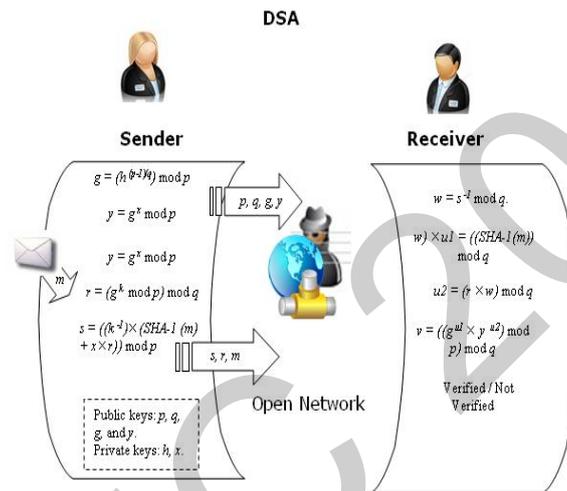


Fig. 4: DSA scheme

IV-1- The DSA Algorithms:

Key generation algorithm (generated by receiver, Alice)

Alice must do the following (Figure 4):

1. Choose a prime number  $(p)$ , where  $2^{L-1} < p < 2^L$  for  $512 \leq L \leq 1024$  and  $L$  a multiple of 64.
2. Choose a prime numbers  $(q)$ , where  $q$  divisor of  $(p - 1)$ , and  $2^{159} < q < 2^{160}$ .
3. Compute  $g$  as follows:  $g = (h^{(p-1)/q}) \text{ mod } p$ , where  $1 < h < (p - 1)$ , and  $g > 1$ .
4. Choose a random integer  $x$ , with  $0 < x < q$ .
5. Compute  $y$  as follows:  $y = g^x \text{ mod } p$ .
6. Send  $(p, q, g,$  and  $y)$  to Bob (verifier).

Signing and verifying algorithms

Signing (sender - Alice)

Alice must do the following (Figure 4):

7. Determine the message  $m$  to be signed such that:  $0 < m < p$ .
  8. Choose a random integer  $k$ , with  $0 < k < q$ .
  9. Compute  $r$  as follows  $r = (g^k \text{ mod } p) \text{ mod } q$ .
  10. Compute  $s$  as follows:  $s = ((k^{-1}) \times (\text{SHA-1}(m) + x \times r)) \text{ mod } q$ .
  11. The signature is  $(r, s)$ .
- Send the signature  $(r, s)$  and the message to the receiver.
  - $k^{-1}$  is a multiplicative inverse of  $k$  in  $Z_q$ .

Verifying (receiver - Bob)

Bob must do the following (Figure 4):

12. Obtain the keys  $(p, q, g,$  and  $y)$ .
  13.  $w = s^{-1} \text{ mod } q$ .
  14.  $u1 = ((\text{SHA-1}(m)) \times w) \text{ mod } q$ .
  15.  $u2 = (r \times w) \text{ mod } q$ .
  16.  $v = ((g^{u1} \times y^{u2}) \text{ mod } p) \text{ mod } q$ .
- Verify the message  $m$  as follows: is  $v = r$ ?

IV-2- The Security of DSA:

The discrete logarithm problem ensures the security of the digital signature algorithm (DSA) (Figure 1). The security of a digital signature system relies on maintaining the confidentiality of the user private key [8]. However, the key space in DSA depends on the key large prime numbers (refer to Figure 4) [14]. The 128-bit DSA key space is limited the number of primes existing in the finite field of  $Z_p$ , where  $p$  is the largest prime that can be represented by a 128-bit value. Hence, DSA keys size space is typically 1024 bit long [3].

V. DIGITAL SIGNATURE BASED ON ELLIPTIC CURVE: ELLIPTIC CURVE DIGITAL SIGNATURE ALGORITHM (ECDSA)

In 1992, Elliptic Curve DSA (ECDSA) was proposed by Scott Vanstone requesting for the National Institute of Standards and Technology comments on their first proposal for DSS. ECDSA is the Elliptic Curve analogue of the DSA (refer to Figure 5). Elliptic Curve digital signature was accepted in three stages: ISO (International Standards Organization), ANSI (American National Standards Institute), and IEEE (Institute of Electrical and Electronics Engineers) in 1998, 1999 and 2000, respectively.

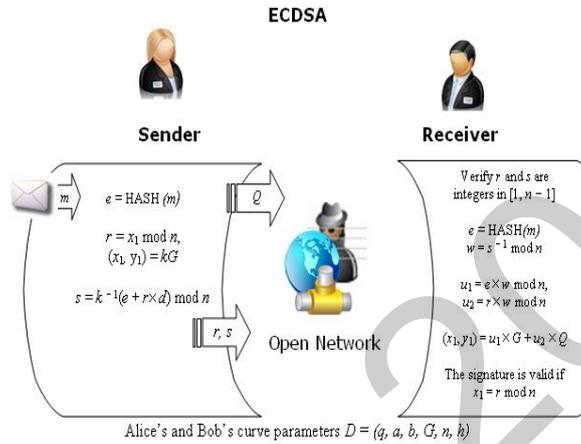


Fig. 5 ECDSA scheme

The operations in the ECDSA are different from the operations in DSA because the ECDSA operations are based on the Elliptic Curve’s mathematical operations (refer to Figure 5). Supposedly the ECDSA uses smaller key size for similar security levels compared with DSA. For example, the DSA with 1024-bit  $p$  and 160-bit  $q$  and ECDSA with the 160-bit prime field both produce 320-bits signatures in less time [9].

V-1- The ECDSA Algorithms:

Alice and Bob must agree with the curve parameters  $D = (q, a, b, G, n, h)$ .

Algorithm for Signature generation algorithm (Sender - Alice)

Alice must do the following (Figure 5):

1. Choose the associated keys suitable for Elliptic Curve Cryptography ( $d, Q$ ) (where  $d$  is a randomly selected integer in the interval  $[1, n - 1]$ ) and  $Q$  is a public key (where  $Q = d \times G$ ).
2. Calculate  $e = \text{HASH}(m)$ , where HASH is a Cryptographic Hash function, such as SHA-1.
3. Choose a random integer  $k$ , with  $1 < k < n$ .
4. Calculate  $r = x_1 \text{ mod } n$ , where  $(x_1, y_1) = kG$ . If  $r = 0$ , go back to step 2.
5. Calculate  $s = k^{-1}(e + r \times d) \text{ mod } n$ . If  $s = 0$ , go back to step 2.
6. Note that the signature is the pair  $(r, s)$ .

Algorithms for Signature verification (Receiver – Bob)

Bob must do the following (Figure 5):

7. Obtain Alice’s public keys ( $Q$ ).
8. Obtain Alice’s signature  $(r, s)$ .
9. Verify  $r$  and  $s$  are integers in  $[1, n - 1]$ . If not, the signature is invalid.
10. Calculate  $e = \text{HASH}(m)$ , where HASH is the same function used in the signature generation.
11. Calculate  $w = s^{-1} \text{ mod } n$ .
12. Calculate  $u_1 = e \times w \text{ mod } n$  and  $u_2 = r \times w \text{ mod } n$ .
13. Calculate  $(x_1, y_1) = u_1 \times G + u_2 \times Q$ .
14. The signature is valid if  $x_1 = r \text{ mod } n$ .

V-2- The Security of Elliptic Curve Digital Signature Algorithm:

The security in the Elliptic Curve Digital Signature Algorithm is based on discrete logarithm problem. However, the Elliptic Curve discrete logarithm is considered more difficult than the discrete logarithm problem (refer to Fig. 1). In addition, the

ECDSA can use short key size comparing with the key size used in the other traditional discrete logarithm. The ECDSA keys are typically 128 bit [9] [15].

**VI. DIGITAL SIGNATURE BASED ON THE MANDELBROT AND JULIA FRACTAL SETS**

Mandelbrot and Julia Fractal shapes (refer to Figure 6) consist of complex number points, computed by the recursive functions [10]. In this Section, with the aid of Figure 7, we are going to explain in brief the idea of the Fractal digital signature scheme based on Fractal set.

The Fractal based digital signature uses a specific Mandelbrot function, *Mandelfn* and similarly, a specific Julia function, *Juliafn* (refer to Equation 1 and 2). Figure 7 shows an image which was generated from the *Mandelfn* and Julia function, *Juliafn*. However, the value which is generated by *Mandelfn* must belong to the Mandelbrot set, and likewise, the value generated by *Juliafn* must belong to the Julia set [16]. This scheme sets  $f()$  as shown by Equation 3 for *Mandelfn* function and Equation 4 for *Juliafn* function.

$$z_n = c \times f(z_{n-1}); z(0) = c; c, z \in \mathbf{C}; n \in \mathbf{Z} \quad (1)$$

$$z_k e = z_{k-1} \times c^2 \times e; z, c, e \in \mathbf{C}; k \in \mathbf{Z} \quad (4)$$

$$z_n = c \times f(z_{n-1}); z(0) = y; y, c, z \in \mathbf{C}; n \in \mathbf{Z} \quad (2)$$

$$s = c^{k-x} \times (z_n d)_k e \times m; s, c, e, d \in \mathbf{C}; n, x, k \in \mathbf{Z}; m \in \mathbf{R} \quad (5)$$

$$z_n d = z_{n-1} \times c^2 \times d; z, c, d \in \mathbf{C}; n \in \mathbf{Z} \quad (3)$$

$$v = c^{n-x} \times (z_k e)_n d \times m; v, c, e, d \in \mathbf{C}; n, x, k \in \mathbf{Z}; m \in \mathbf{R} \quad (6)$$

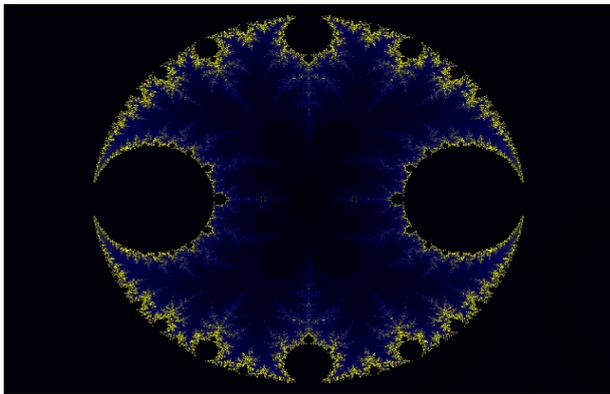


Fig. 6: Mandelfn image with the sine function (sin()) [17]

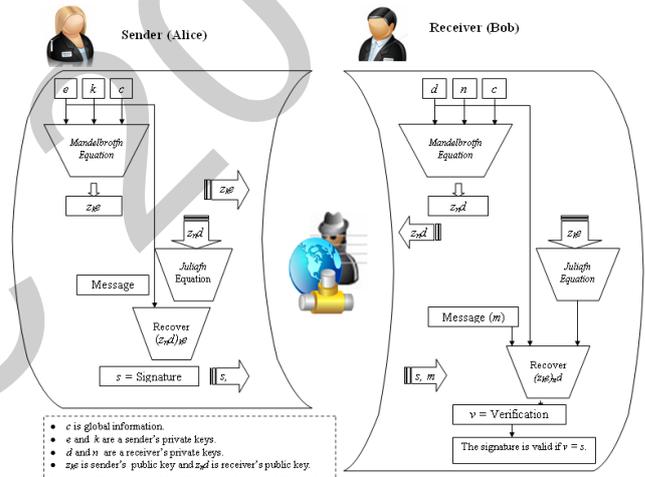


Fig. 7: Fractal digital signature algorithm

**VI-1- Fractal DS Algorithms:**

Algorithm for Signature generation algorithm:

Alice and Bob must do the following (Figure 7):

1. Sender and receiver must agree and use the public domain value,  $c$ .
2. The receiver, Bob, will generate  $e$  and  $k$  as the private keys.
3. The sender, Alice, generates  $n$  and  $d$  as her private keys.
4. Sender and receiver use their private values as well as the value  $c$  as inputs to the Mandelbrot function to produce the public keys  $z_n d$  and  $z_k e$ .
5. Then Bob and Alice must exchange their public keys.

Algorithm for Signature generation algorithm (Sender - Alice)

Alice must do the following (Figure 7):

6. Alice will obtain Bob's public key,  $z_n d$  and will use these values together with her private key and the plaintext, as inputs to the Julia function to produce the signature  $s$ , which will then be sent with the message to Bob (refer to Equation 5).

Algorithms for Signature verification (Receiver – Bob)

Bob must do the following (Figure 7):

7. Bob must obtain Alice's public key,  $z_k e$ , the signature  $s$  and the message  $m$  from Alice which will be used as input values together with his own private key to Julia function, to verify the message  $v$  (refer to Equation 6).

**VI-2- The Security of Fractal Digital Signature Scheme:**

The strength of the algorithm and the size of the key used, are key factors in the security of digital signature protocol. Nevertheless, Fractal digital signature algorithm is efficient since the algorithm uses small key size and executes faster than

other public key digital signature schemes. It is computationally impossible to attack the Fractal digital signature protocol. Since the system is based on the Chaos NP hard problem [18].

The Fractal digital signature is based on The Chaos hard problem, whereby, the chaotic nature of the Fractal equations ensures the security of this algorithm. However, the crucial key size in Fractal digital signature algorithm is chosen to prevent a brute force attack. The key space in Fractal digital signature depends on the size of the key [14]. The fractal based digital signature scheme provides high level of security at a much low cost, in term of key size and execution time.

## VII. CONCLUSION

This paper gives the reader basic concepts used throughout the rest of the study which are related to the concepts in digital signature cryptosystem. In addition, we studied some digital signature schemes (refer to Table 1) which are based on different mathematical hard problems as classified earlier. Those classifications help the reader to be familiar with the public-key digital signature cryptosystem. However, the security protection of the discussed digital signature schemes depend on the mathematical NP-hard problems and the randomness of the output generated.

TABLE I  
EXAMPLE OF DIGITAL SIGNATURE SCHEMES

Mathematical Hard Problem	Digital Signature Schemes	
	Efficiency	Typical Key Size for High Performance
Integer Factorization RSADS	The speed in RSADS is considered much slower than other symmetric cryptosystems	Large Prime Number (1024-bit)
Discrete Logarithm DSA	DSA is probabilistic, however, The security of a digital signature system relies on maintaining the confidentiality of the user private key	Large Prime Number (1024-bit)
Elliptic Curve ECDSA	The discrete logarithm problem on elliptic curve cryptosystem is more difficult than the other mathematical problem	Short Key (128-bit)
Chaos Fractal DS	The fractal based digital signature scheme provides high level of security at a much low cost, in term of key size and execution time.	Short Key (128-bit)

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# CONTRIBUTION TO THE STUDY OF CORROSION BY SRB IN INDUSTRIAL ENVIRONMENT. APPLICATION TO THE FIELD OF HASSI MESSAOU D ALGERIA

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## Abstract

In this work, we studied the mode of action of bactericides in particular on the sulphate-reducing bacteria which are the main responsible for corrosion phenomena in the absence of oxygen. They can act directly in contact with the metal by using the hydrogen formed on the surface or remotely by consuming the gaseous hydrogen. When we add an aldehyde, a biocide or a mixture in an environment of culture containing a bacterial population, it is important to understand at which level he acts on micro-organisms because after a time of contact of adaptation, substances are consumed and the process is not checked. The study is a contribution in the understanding of the corrosive action of bacteria and their hydrogenase activity in injected water and water contained in emulsion. Tests of evaluation of the efficiency of biocides were made as well as their mode of action. Different pH measures of the culture environment were performed at different time as well as the metallic pieces. Moreover, we present different plots of the SRB growth kinetic in various environments in the presence of biocides.

**Key-words:** Biocorrosion; Sulphate-reducing bacteria; Biocides; Activation energy; Emulsion.

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# CUBIC TRANSFORMATIONAL HIGH DIMENSIONAL MODEL REPRESENTATION

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**Abstract.** This work focuses on the development of a multivariate function approximating method by using cubic Transformational High Dimensional Model Representation (THDMR). The method uses the target function's image under a cubic transformation for High Dimensional Model Representation (HDMR) instead of the function's itself.

**Keywords:** Cubic Equation, Transformational High Dimensional Model Representation, Multivariate Functions, Approximation

## INTRODUCTION

When a natural event is analyzed, the number of factors affecting the event is higher than calculated. General way to overcome this is to eliminate or ignore some of factors which will be less effective. However as the investigated event complicates, the number of affecting factors increases. Nowadays computer technology cannot be suitable to the calculation limitations on this type of problems. High Dimensional Model Representation (HDMR) is perhaps the most fruitful solution to those multidimensional problems. Various HDMR versions were suggested in order to tackle with different problem types encountered. Factorized HDMR is one of them. The main problem with FHDHR is that unlike additivity measures of HDMR, multiplicativity measures of FHDHR is unfortunately not well ordered. This led to the Logarithmic HDMR. The main idea behind Logarithmic HDMR was to initially transform what is basically a function of multiplicative nature to one that is of additive nature. This would enable us to expand the transformed problem using plain HDMR and then transform back the individual terms. Previous works were focused on the HDMR constancy optimization under an affine transformation (Yaman, 2008 and Yaman, Demiralp, 2009), conic transformation (Gündoğar, Baykara, Demiralp, 2010 and Gündoğar, Baykara, Demiralp, 2011) and quartic transformation (Şen, 2011). We shall consider in this work a cubic transformation and attempt to find optimal parameters for such a transformation leading to a new approximation.

## TRANSFORMATIONAL HIGH DIMENSIONAL MODEL REPRESENTATION

Let us consider a function  $f(x_1, x_2, \dots, x_N)$  of  $N$  independent variables  $x_1, x_2, \dots, x_N$  which has a non-additive structure. A transformation  $T$  can be chosen which yields a new multivariate function  $\varphi(x_1, \dots, x_N)$

$$Tf(x_1, x_2, \dots, x_N) \equiv \varphi(x_1, x_2, \dots, x_N) \quad (1)$$

If we apply the HDMR expansion to  $\varphi$  we will get

$$\varphi(x_1, \dots, x_N) = \varphi_0 + \sum_{\beta=1}^N \varphi_{\beta}(x_{\beta}) + \dots + \varphi_{1\dots N}(x_1, \dots, x_N).$$

Additivity measures  $\sigma_i(\varphi)$ s can be defined for this expansion in the usual HDMR manner.

$$\sigma_0(\varphi) = \frac{\|\varphi_0\|^2}{\|\varphi\|^2}, \quad \sigma_1(\varphi) = \sigma_0(\varphi) + \sum_{\beta_1=1}^N \frac{\|\varphi_{\beta_1}\|^2}{\|\varphi\|^2}, \quad \sigma_2(\varphi) = \sigma_1(\varphi) + \sum_{\substack{\beta_1, \beta_2=1 \\ \beta_1 < \beta_2}}^N \frac{\|\varphi_{\beta_1 \beta_2}\|^2}{\|\varphi\|^2}, \dots \quad (2)$$

These measures will be different from those obtained by applying HDMR expansion to the original function  $f$ . Obviously the difference will be dependent on the specific choice of the transformation  $T$ . Since the basic philosophy of HDMR is to be able to represent the function with as few and as less variate terms as possible, we would prefer  $\sigma_0$  and  $\sigma_1$  to be as close to 1 as possible. In this study we choose to deal only with  $\sigma_0$  and attempt to maximize it.

**CUBIC TRANSFORMATIONAL HIGH DIMENSIONAL MODEL REPRESENTATION**

A polynomial can be used as THDMR’s operator for choosing the transformation suggested in (1). Here the degree of the polynomial will be taken to be three. The linear combination coefficients of the cubic will be assumed to vary with independent variables. They will be regarded as operators dependent on the algebraic operators each of which multiplies its operand with a different independent variable. This gives flexibility to the relevant transformation and they can be selected so as to approximate the HDMR expansion optimally.

$$Tf(x_1, \dots, x_N) = \varphi(x_1, \dots, x_N) = a_0(x_1, \dots, x_N) + a_1(x_1, \dots, x_N)f + a_2(x_1, \dots, x_N)f^2 + a_3(x_1, \dots, x_N)f^3.$$

Since only  $\sigma_0(\varphi)$  will be under consideration,  $\varphi$  will be approximated by the constant component  $\varphi_0$

$$\varphi = a_0 + a_1f + a_2f^2 + a_3f^3 \approx \varphi_0$$

which gives the approximate equality

$$\begin{aligned} f_1 &\approx \sqrt[3]{-A + \sqrt{A^2 + B^3}} + \sqrt[3]{-A - \sqrt{A^2 + B^3}} \\ f_2 &\approx \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)\sqrt[3]{-A + \sqrt{A^2 + B^3}} + \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)^2\sqrt[3]{-A - \sqrt{A^2 + B^3}} \\ f_3 &\approx \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)^2\sqrt[3]{-A + \sqrt{A^2 + B^3}} + \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)\sqrt[3]{-A - \sqrt{A^2 + B^3}}, \end{aligned} \tag{3}$$

where

$$i^2 = -1, \quad A = \frac{1}{2}\left(\frac{a_0 - \varphi_0}{a_3} - \frac{a_2a_1}{a_3^2} + \frac{2a_2^3}{27a_3^3}\right) \text{ and } B = \frac{1}{3}\left(\frac{a_1}{a_3} - \frac{a_2^2}{3a_3^2}\right).$$

In this work we will consider only  $f_1$ . The other roots may be considered analogically. The aim here is to find convenient forms for  $a_0, a_1, a_2$  and  $a_3$  that maximize  $\sigma_0$  in (2). To this end  $a_0, a_1, a_2$  and  $a_3$  will be taken in  $L_2$  class. Hence orthonormal basis of the Hilbert space  $H^{(N)}$  will be taken into consideration. Orthonormality will be defined in terms of the inner product as

$$(u_j, u_k) = \int_V dV W(x_1, \dots, x_N) u_j(x_1, \dots, x_N) u_k(x_1, \dots, x_N) = \delta_{jk}, \quad 1 \leq j, k \leq \infty$$

where  $V = [a_1, b_1] \times \dots \times [a_N, b_N]$  represents the hyperprism which is the HDMR construction domain and  $W(x_1, \dots, x_N)$  the multiplicative weight function used in HDMR. The individual weight functions will be chosen as constants, normalized over the corresponding domain and  $dV$  is the product of individual differentials  $dx_1 \dots dx_N$ .

$$W(x_1, \dots, x_N) = \prod_{\beta=1}^N W_{\beta}(x_{\beta}) = \prod_{\beta=1}^N \frac{1}{b_{\beta} - a_{\beta}}$$

Although the basis mentioned above has an infinite number of elements, in practice a finite number of elements will be taken into consideration.

$$a_0(x_1, \dots, x_N) = \sum_{j=2}^m a_j^{(0)} u_j, \quad a_1(x_1, \dots, x_N) = \sum_{k=1}^n a_k^{(1)} u_k, \quad a_2(x_1, \dots, x_N) = \sum_{l=1}^p a_l^{(2)} u_l, \quad a_3(x_1, \dots, x_N) = \sum_{s=1}^t a_s^{(3)} u_s. \tag{4}$$

With these expressions in hand, the constancy mesurer  $\sigma_0(\varphi)$  will be a function of the parameters  $a_j^{(0)}, a_k^{(1)}, a_l^{(2)}, a_s^{(3)}$  where

$$2 \leq j \leq m, 1 \leq k \leq n, 1 \leq l \leq p, 1 \leq s \leq t.$$

Thus

$$\sigma_0(\varphi) = \sigma_0\left(\varphi, a_2^{(0)}, \dots, a_m^{(0)}, a_1^{(1)}, \dots, a_n^{(1)}, a_1^{(2)}, \dots, a_p^{(2)}, a_1^{(3)}, \dots, a_t^{(3)}\right).$$

Using (4)  $\varphi$  can be expressed as

$$\varphi(x_1, \dots, x_N) = \sum_{j=2}^m a_j^{(0)} u_j + \left(\sum_{k=1}^n a_k^{(1)} u_k\right) f + \left(\sum_{l=1}^p a_l^{(2)} u_l\right) f^2 + \left(\sum_{s=1}^t a_s^{(3)} u_s\right) f^3 \tag{5}$$

To obtain the constant HDMR term  $\varphi_0$  both sides of (5) are to be integrated with respect to  $x_1, \dots, x_N$  over  $V$  under the weight function  $W$ .

$$\begin{aligned} \varphi_0 &= \sum_{j=2}^m a_j^{(0)} \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_j + \sum_{k=1}^n a_k^{(1)} \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_k f + \\ &\sum_{l=1}^p a_l^{(2)} \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_l f^2 + \sum_{s=1}^t a_s^{(3)} \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_s f^3 \end{aligned}$$

Defining vectors  $\eta$  and

$$\eta = \left(a_2^{(0)}, \dots, a_m^{(0)}, a_1^{(1)}, \dots, a_n^{(1)}, a_1^{(2)}, \dots, a_p^{(2)}, a_1^{(3)}, \dots, a_t^{(3)}\right), \tau = \left(\tau_2^{(0)}, \dots, \tau_m^{(0)}, \tau_1^{(1)}, \dots, \tau_n^{(1)}, \tau_1^{(2)}, \dots, \tau_p^{(2)}, \tau_1^{(3)}, \dots, \tau_t^{(3)}\right)^T$$

With the elements of vector  $\tau$  defined as

$$\begin{aligned} \tau_j^{(0)} &= \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_j = (u_j, h), \tau_k^{(1)} = \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_k f = (u_k, f), \\ \tau_l^{(2)} &= \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_l f^2 = (u_l, f^2), \tau_s^{(3)} = \int_V dV \left(\prod_{\beta=1}^N W_{\beta}(x_{\beta})\right) u_s f^3 = (u_s, f^3), \end{aligned} \tag{6}$$

where

$$2 \leq j \leq m, 1 \leq k \leq n, 1 \leq l \leq p, 1 \leq s \leq t.$$

$h(x_1, \dots, x_N)$  appearing in the first inner product in (6) is a function which has the constant value 1 for all  $x_{\beta}$  in the hyperprism domain  $[a_1, b_1] \times \dots \times [a_N, b_N]$ .  $\varphi_0$  can now be written as an inner product  $\varphi_0 = \eta \tau$ . Since  $\varphi_0$  has a constant value, the square of its norm will be equal to the square of the function  $\varphi_0$ .

$$\|\varphi_0\|^2 = (\eta \tau)(\eta \tau)^T = \eta \tau \tau^T \eta. \|\varphi\|^2$$

On the other hand can be expressed in terms of the above defined vector  $\eta$  and a square matrix  $C$  which can be expressed in terms of its blocks as

$$C = \begin{pmatrix} K & L & N & S \\ L^T & M & P & T \\ N^T & P^T & R & Y \\ S^T & T^T & Y^T & Z \end{pmatrix}$$

where

$$\begin{aligned} K_{jk} &= (u_j, u_k), 2 \leq j, k \leq m, L_{jk} = (u_j, f u_k), 2 \leq j \leq m, 1 \leq k \leq n, \\ M_{jk} &= (u_j, f^2 u_k), 1 \leq j, k \leq n, N_{jk} = (u_j, f^2 u_k), 2 \leq j \leq m, 1 \leq k \leq p, \\ R_{jk} &= (u_j, f^4 u_k), 1 \leq j, k \leq p, P_{jk} = (u_j, f^3 u_k), 1 \leq j \leq n, 1 \leq k \leq p, \\ S_{jk} &= (u_j, f^3 u_k), 2 \leq j \leq m, 1 \leq k \leq t, T_{jk} = (u_j, f^4 u_k), 1 \leq j \leq n, 1 \leq k \leq t, \\ Y_{jk} &= (u_j, f^5 u_k), 1 \leq j \leq p, 1 \leq k \leq t, Z_{jk} = (u_j, f^6 u_k), 1 \leq j, k \leq t. \end{aligned}$$

$C$  is a symmetric, positive definite matrix. Norm square of  $\varphi$  can be expressed in terms of  $C$  and  $\eta$  as

$$\|\varphi\|^2 = \eta C \eta^T.$$

So the constancy measurer  $\sigma_0$  becomes

$$\sigma_0 = \frac{\|\varphi_0\|^2}{\|\varphi\|^2} = \frac{\eta \mu \mu^T \eta^T}{\eta C \eta^T}. \tag{7}$$

Our aim is to maximize  $\sigma_0$  which can be written as a Rayleigh quotient as

$$\sigma_0 = \frac{y^T C^{-1/2} \tau \tau^T C^{-1/2} y}{y^T y}$$

where  $y = C^{1/2} \eta^T$ . However, a Rayleigh quotient takes its maximum value at the maximum eigenvalue of its kernel, in this case  $C^{-1/2} \tau \tau^T C^{-1/2}$ . Similarly  $y$  is the eigenvector corresponding to the maximum eigenvalue. An analysis of the kernel will give the maximum eigenvalue and the corresponding eigenvector of it. They are respectively,

$$\sigma_0 = \tau^T C^{-1} \tau, \quad y = C^{-1/2} \tau.$$

The equation for  $y$  gives us the vector  $\eta^T$  in (7) that maximizes  $\sigma_0$  as

$$\eta^T = C^{-1/2} y = C^{-1} \tau.$$

Utilizing these equalities we can construct a function for  $\varphi_0$ . To complete this we can express  $\varphi_0, a_0, a_1, a_2$  and  $a_3$  in terms of matrix algebraic entities.  $\varphi_0$  can be written in compact form as

$$\varphi_0 = \eta \tau = \tau^T C^{-1} \tau.$$

We define a vector  $\xi$  with  $(m+n+p+t-1)$  elements  $\xi = [\xi_2, \dots, \xi_m, \xi_1, \dots, \xi_n, \xi_1, \dots, \xi_p, \xi_1, \dots, \xi_t]^T$  and express  $a_0, a_1, a_2$  and  $a_3$  more compactly as

$$a_0 = \eta^{(0)} \xi^{(0)}, a_1 = \eta^{(1)} \xi^{(1)}, a_2 = \eta^{(2)} \xi^{(2)}, a_3 = \eta^{(3)} \xi^{(3)}.$$

Here the vectors  $\eta^{(0)}, \eta^{(1)}, \eta^{(2)}, \eta^{(3)}$  and  $\xi^{(0)}, \xi^{(1)}, \xi^{(2)}, \xi^{(3)}$  are explicitly defined as

$$\eta^{(0)} = [a_2^{(0)}, \dots, a_m^{(0)}], \eta^{(1)} = [a_1^{(1)}, \dots, a_n^{(1)}], \eta^{(2)} = [a_1^{(2)}, \dots, a_p^{(2)}], \eta^{(3)} = [a_1^{(3)}, \dots, a_t^{(3)}],$$

$$\xi^{(0)} = [\xi_2, \dots, \xi_m]^T, \xi^{(1)} = [\xi_1, \dots, \xi_n]^T, \xi^{(2)} = [\xi_1, \dots, \xi_p]^T, \xi^{(3)} = [\xi_1, \dots, \xi_t]^T.$$

To proceed we define  $(m+n+p+t-1) \times (m+n+p+t-1)$  projection matrices  $P_1, P_2$  and  $P_3$  as

$$P_1 = \sum_{\beta=1}^{m-1} e_\beta e_\beta^T, P_2 = \sum_{\beta=m}^{m+n-1} e_\beta e_\beta^T, P_3 = \sum_{\beta=m+n}^{m+n+p-1} e_\beta e_\beta^T$$

Where  $e_\beta$  is the unit vector in  $(m+n+p+t-1)$  dimensional space. Utilizing these projection operators  $a_0, a_1, a_2$  and  $a_3$  can be approximated as

$$a_0 = \eta P_1 \xi = \tau^T C^{-1} P_1 \xi, a_1 = \eta P_2 \xi = \tau^T C^{-1} P_2 \xi,$$

$$a_2 = \eta P_3 \xi = \tau^T C^{-1} P_3 \xi, a_3 = \eta (I - P_1 - P_2 - P_3) \xi = \tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi$$

where  $I$  identity matrix. If now these substitutions are introduced into (3) we obtain

$$\begin{aligned}
 f_1 \approx & \left[ \frac{\tau^T C^{-1} P_1 \xi - \tau^T C^{-1} \tau}{\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi} - \frac{\tau^T C^{-1} P_3 \xi \tau^T C^{-1} P_2 \xi}{[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^2} + \frac{2[\tau^T C^{-1} P_3 \xi]^3}{27[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^3} \right] + \\
 & \left[ \frac{\tau^T C^{-1} P_1 \xi - \tau^T C^{-1} \tau}{\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi} - \frac{\tau^T C^{-1} P_3 \xi \tau^T C^{-1} P_2 \xi}{[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^2} + \frac{2[\tau^T C^{-1} P_3 \xi]^3}{27[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^3} \right]^2 \\
 & + \frac{1}{27} \left[ \frac{\tau^T C^{-1} P_2 \xi}{\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi} - \frac{[\tau^T C^{-1} P_3 \xi]^2}{3[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^2} \right]^3 \\
 & + \left[ \frac{\tau^T C^{-1} P_1 \xi - \tau^T C^{-1} \tau}{\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi} - \frac{\tau^T C^{-1} P_3 \xi \tau^T C^{-1} P_2 \xi}{[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^2} + \frac{2[\tau^T C^{-1} P_3 \xi]^3}{27[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^3} \right] - \\
 & \left[ \frac{\tau^T C^{-1} P_2 \xi}{\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi} - \frac{[\tau^T C^{-1} P_3 \xi]^2}{3[\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi]^2} \right]^3 \\
 & - \frac{\tau^T C^{-1} P_3 \xi}{3\tau^T C^{-1} (I - P_1 - P_2 - P_3) \xi}
 \end{aligned}$$

To simplify this expression we can use a spectral decomposition of  $C^{-1}$  as

$$C^{-1} = \sum_{\beta=1}^{m+n+p+t-1} \frac{1}{\lambda_{\beta}} \varphi_{\beta} \varphi_{\beta}^T$$

where  $\lambda_{\beta}$  is an eigenvalue of  $C$  and  $\varphi_{\beta}$  is an eigenvector corresponding to the eigenvalue  $\lambda_{\beta}$ . A good approximation will be to use the minimal eigenpairs of  $C$  as  $C^{-1} = \lambda_{\min}^{-1} \varphi_{\min} \varphi_{\min}^T$ .

### CONCLUSION

In this study we inserted certain flexibilities into the approximation. Because we want to improve its quality. Hence we applied HDMR on the image of the original function under a third degree transformation. The coefficients of the transformation are chosen to make the error of HDMR approximation as small as possible and this increases the efficiency of the method.

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# DAĞITIK SİSTEMLER İÇİN GÖRÜNTÜ İŞLEME WEB SERVİS UYGULAMASI

## AN IMPLEMENTATION OF IMAGE PROCESSING WEB-SERVICES FOR DISTRIBUTED SYSTEMS

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### ÖZET

Bu makale, servis odaklı mimariye (SOA) dayalı dağıtık görüntü işleme sistemini ortaya koymaktadır. Amacımız, görüntü işleme programlarını web servis olarak paketleyip, son kullanıcılar ve diğer dağıtık sistemler tarafından uzaktan erişilebilir hale getirmektir. Önerilen SOA mimarisi; Java Teknolojileri, Netbeans Web Servis kütüphaneleri ve Matlab kullanarak oluşturulmuştur. Görüntü işleme fonksiyonları, (Kenar bulma gibi) Matlab tarafından sunulur ve ilgili fonksiyonlar web servisler olarak paketlenir. Ayrıca, önerilen görüntü işleme web servislerinin kolay ve etkileşimli biçimde kullanılabilmesi için GUI geliştirilmiştir. Sistem sadece arayüze sahip son kullanıcılar tarafından değil, aynı zamanda diğer servisler tarafından da kullanılabilir. Önerilen sistemin etkinliği bazı test senaryolarıyla değerlendirilmiştir.

**Anahtar Sözcükler:** Dağıtık Sistemler, SOA, Web-servisler, Görüntü İşleme

### ABSTRACT

This paper introduces a distributed image processing system based on service oriented architecture (SOA). Our aim is wrapping the image processing functionalities and programs as web-services and making them accessible by other distributed systems and end users. The proposed SOA architecture is built by using JAVA technologies, Axis2 Web-service libraries and MatLab. Matlab provides the image processing functions (such as edge detection) and these are wrapped as Web-services. We also develop an easy to use, interactive GUI to use the proposed image processing web services seamlessly. The system can be accessed not only by the end users having GUI but also by other inter-operable services. The efficiency of the proposed technique is evaluated by some test cases.

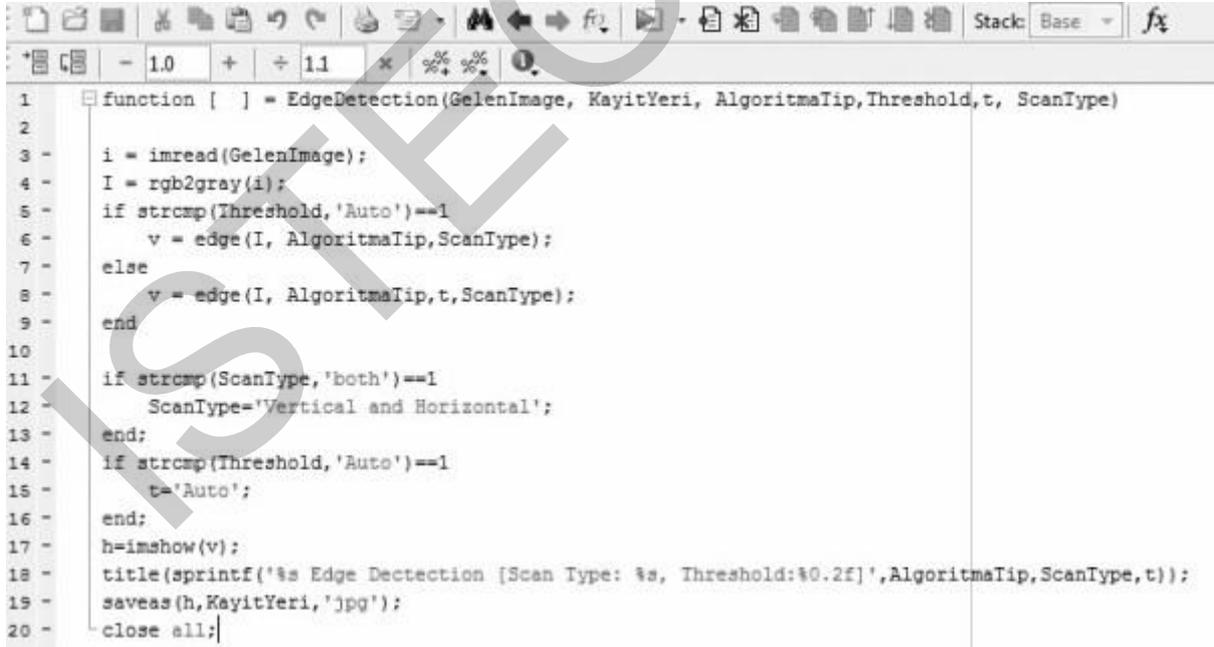
**Keywords:** Distributed Systems, SOA, Web-services, Image Processing

## 1. GİRİŞ

Sayısal bir görüntü bölgeler ve sınırlandıran kenarlardan oluşur. Görüntüdeki bir bölge genellikle aynı ya da benzer genlikleri paylaşan pikseller yığını olarak tanımlanabilen nesnelere gösterir. Kenar ise bir pikselden diğerine geçişteki piksellerin genliklerinde meydana gelen ani bir sıçrama olarak tanımlanır.(Güvenç ve Karagül, 2009). Başka bir ifadeyle, gri seviyeleri farklı iki bölge arasındaki geçiş veya sınır bölgesi kenar olarak belirlenir. Görüntülerden elde edilen kenar bilgileri sayısal görüntü işlemenin diğer analiz yöntemlerinde başarıyla uygulanmaktadır.(Güvenç,Karagül,2009)(Gonzalez, Woods,1993)

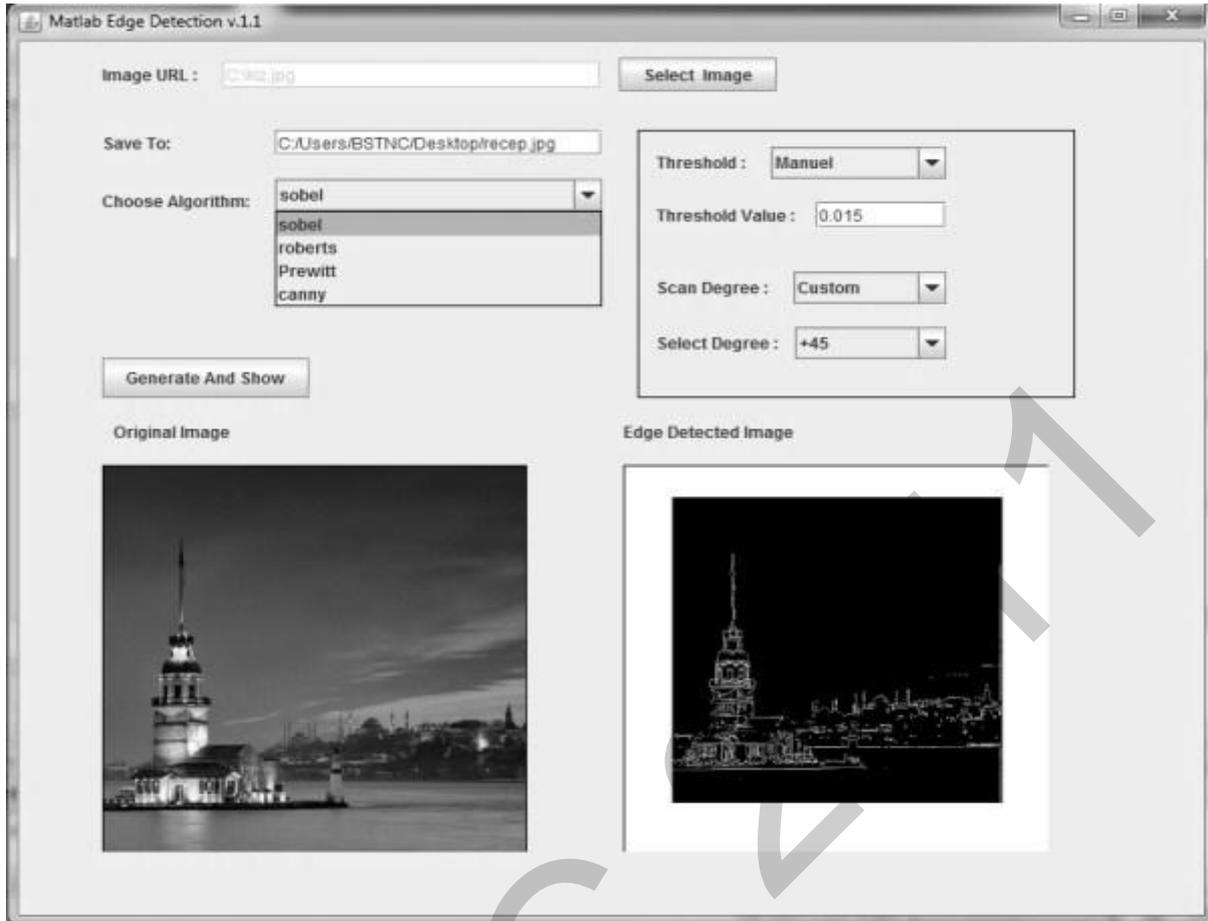
Görüntülerin kenarlarını belirlemek için araştırmacılar uzun bir süredir çalışmaktadır. Buna rağmen kesinleşmiş ve çok etkili bir kenar belirleme metodu bulunmamaktadır.(Albora ve Diğerleri,2007).Günümüzde kullanılan en popüler kenar belirleme yöntemleri Sobel, Prewitt, Robert ve Canny operatörleridir (Canny, 1986). Bu operatörler işlenecek olan pikselin yoğunluğu ile komşu piksellerin yoğunluklarının karşılaştırılması yöntemiyle çalışmaktadırlar. Ancak, bu operatörler görüntüdeki gürültüye çok duyarlı ve karmaşık matematiksel işlemler içermektedirler. Bu noktadaki karmaşıklığı azaltmak ve zamanı daha verimli kullanmak amacıyla Matlab vb. programlar kullanılmıştır ve bu sayede kenar belirleme ile diğer görüntü işleme operasyonlarını gerçekleştirmek oldukça kolaylaşmıştır.(McAndrew,2004)

Edge Detection (kenar bulma) algoritmaları görüntü işlemenin bir alanı olarak; plaka tanıma, yüz tanıma ve bulma, göz tanıma, harita ve uydu görüntüleme sistemlerinde aktif olarak kullanılmaktadır. Uygulamaya duyulan ihtiyaç göz önünde bulundurulduğunda hız, maliyet ve kalite de önemini artırmıştır. Matlab yazılımı kenar belirleme işlemini her ne kadar basit ve kısa bir komut setiyle uygulasa da, gerek hız gerekse maliyet açısından uygun olmayışı ve kullanıcıya daha basit bir arayüz sunmayı bizi bu konudaki yetersizlikleri karşılayacak bir uygulama geliştirmeye yönlendirmiştir. Sonuçta ortaya konan uygulama Matlab'ın yaptığı edge detection işlemine uzaktan erişimli bilgisayar mimarisi, kullanıcı etkileşimli ve hızlı işlem görebilen bir yapı ekleyerek, bu işleme kayda değer bir katkı sağlamıştır. Edge Detection işleminin iki uygulama tarafından nasıl gerçekleştirildiğini daha somut kavrayabilmek için Şekil-1 ve Şekil-2 incelenebilir.



```
1 function [ ] = EdgeDetection(GelenImage, KayitYeri, AlgoritmaTip,Threshold,t, ScanType)
2
3 i = imread(GelenImage);
4 I = rgb2gray(i);
5 if strcmp(Threshold,'Auto')==1
6 v = edge(I, AlgoritmaTip,ScanType);
7 else
8 v = edge(I, AlgoritmaTip,t,ScanType);
9 end
10
11 if strcmp(ScanType,'both')==1
12 ScanType='Vertical and Horizontal';
13 end;
14 if strcmp(Threshold,'Auto')==1
15 t='Auto';
16 end;
17 h=imshow(v);
18 title(sprintf('%s Edge Dectection [Scan Type: %s, Threshold:%0.2f]',AlgoritmaTip,ScanType,t));
19 saveas(h,KayitYeri,'jpg');
20 close all;
```

Şekil-1 Kenar belirleme için örnek bir Matlab uygulaması



Şekil-2 Kenar Belirleme için geliştirilen uygulama arayüzü

SOA, yani servis odaklı mimari, farklı platformların iletişiminin, entegrasyonunun sağlanması amacıyla bileşenlerin tek bir environment üzerinden tekrar kullanılabilen, standardize edilmiş ve birleştirilebilen servisler olarak diğer sistemlerin kullanımına açılmasıdır. Bir web servisi standardı olan SOA üzerinde, sözü edilen servisler tanımlanıp, konfigure edilerek dağıtık sistemlerin tek bir platform üzerinden, karşılıklı çalışabilir bir şekilde, birbirinden soyutlanmış olarak entegrasyonu sağlanır. Web servisleri, bağlantı ve iletişimle ilgili yöntemleri içerir. SOA ise tüm bir IT stratejisidir. Küçük projeler için uygun değildir, uygulamada başarısızlığa neden olabilir. Yapının geliştirilme amacı, büyük organizasyonların ihtiyacına cevap vermektir ( Computerworld Türkiye, 2010).

Web servisleri, SOA standardıyla çalışan uzaktan erişim mimari yöntemidir. Uygulamamız web servis client-server mantığında, ihtiyaç duyulan Matlab görüntü işleme metotlarını, belirlenen algoritmaları da kullanarak hizmete sunar. Kullanıcı, client host üzerinden istenilen paketi kullanarak, daha hızlı ve fonksiyonel olarak ihtiyacını giderebilir. Geliştirdiğimiz GUI, kullanım açısından basitliği ve etkileşimli yapısı ile kullanıcının herhangi bir kod yazmasına, bilgisayarına Matlab yazılımı kurmasına gerek kalmadan, işlemleri yürütmesini sağlar.

İlerleyen dönemde, web üzerinden ihtiyaca göre belirlenen başka paketler yayınlanabilir ya da yazılım geliştiricilerin uygulamalarında kullanabilmeleri için web servislerinin WSDL URL'leri yayınlanabilir.

## 2. TEMEL BİLGİLER

Web servisleri 2000 li yılların başlarında ortaya çıkan ve bir çok yazılım firması tarafından yoğun bir destek bulan bir modeldir. Web servisleri açık internet standartlarına dayanır. Henüz gelişme ve olgunlaşma aşamasında

olan bu modellerle ilgili olarak bu aşamada ortaya çıkan ve kullanılan çekirdek standartlar SOAP, WSDL ve UDDI'dir.

Web Servisler uygulama bileşenidir ve açık protokolleri(open protocols) kullanarak haberleşir. XML temeline dayanırlar. Web servisler bilgisayar ve telekomünikasyon sektöründe internette en büyük devrim olarak kabul edilir. Bu nedenle de büyük çaplı kurumlar bu konu üzerine yoğunlaşmış ve kendilerine uyarlamaya çalışmışlardır (Benslimane, Dustdar, Sheth, 2008).

Web servis mantığında, kullanıcı, diğer makinaya bir takım datalar gönderir ve geriye yine işlenmiş bir takım datalar alır. Diğer makinada gerçekleştirilen uygulamalar, kullanılan algoritmalar, fonksiyonlar hakkında hiçbir bilgisi yoktur. Web page mantığında ise, web sayfaları bir hostta yüklüdür. Kullanıcı, hostun çalışan dizinine bağlanır ve orada çalıştırılabilen sayfayı browser aracılığıyla görüntüler. Yani kullanıcı kendinde bir işlem gerçekleştirmez, her işlem host üzerindedir. Dolayısıyla güvenlik tehlikedir. Bu nedenle de web servisler daha hızlı, daha güvenli ve daha çok alanda etkileşimli olarak esnek kullanılabilir kabul edilir.

Uygulamamızdaki amaç da bu noktadan yola çıkarak, matematik dünyasını temel alan tüm mühendislik alanlarında, aktif olarak kullanılan Matlab yazılımının kullanımını, web sayfasından daha da etkileşimli kullanabilmeyi sağlamaktır.

Matlab programı da, command ekranından, farklı web sitelerinden verilen web servislerine erişip kullanabiliyor. Bunu *createClassFromWsd* fonksiyonu ya da SOAP fonksiyonlarını kullanarak yapıyor. *createClassFromWsd* arka planda yine SOAP kullanır. Uygulama geliştiricisinin SOAP protokollerini bilmesine gerek kalmaz. Eğer WSDL bağlantısı yoksa, SOAP fonksiyonları(*createSoapMessage, callSoapService, and parseSoapResponse*) kullanmak zorunda kalır (The MathWorks, 2011).

Kurduğumuz örnek mimari (edge detection) veya isteğe göre yayınlayabileceğimiz paket ya da WSDL linkleri, kullanıcıların ihtiyaçlarını karşılamaya yönelik olacaktır. Plaka tanıma, göz tanıma, yüz tanıma sistemlerinde, image ilk olarak web servisinde işlendikten sonra, elde edilen yeni görüntüyü kullanıcı kendi algoritmasına da uygulayabilir.

Uygulamanın Java teknolojileri ile geliştirilmesinin amacı, açık kaynağın vermiş olduğu güven, hız ve farklı platformlara entegrasyonunun kolay olmasıdır. Kullanıcı bu sayede ister Linux, ister Windows ister MacOS ortamından servislere bağlanma imkanı bulabilir, kendi uygulamalarına entegre edebilir.

### 3. UYGULAMA VE MİMARİ

Uygulama, Şekil 3 'te görüldüğü üzere, iki ana temel yapıdan oluşuyor. SOA Client(web service client) ve SOA Server (web service server). Veri akışı adım numaraları, transfer çizgileri üzerinde parantez içinde belirtilmiştir.

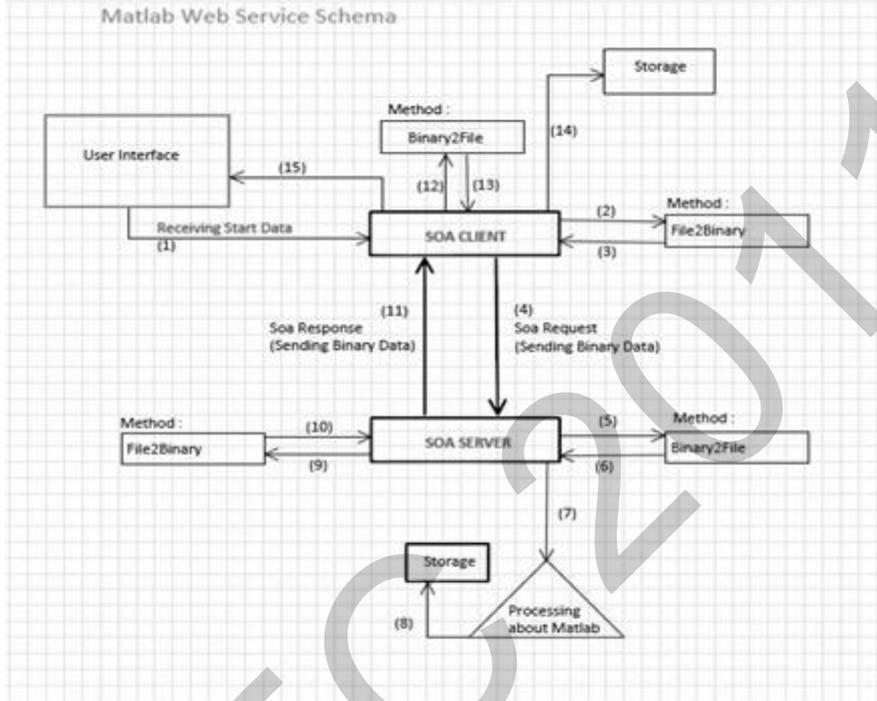
Kullanıcı kendisine sunulan paket aracılığıyla, GUI üzerinden, gerekli bilgileri girer, algoritma seçimini yapar ve Edge Detection uygulanacak olan resmi seçer. <Process> butonuna basıldığında, datalar işlenmek üzere, devamlı olarak erişilebilir ve run durumunda olan web service server'ına ulaşır. Server, gerekli işlemi kullanıcının seçimine göre yaptıktan sonra, geri döndürülecek image dosyasını client'a gönderir. Adım adım açıklaması ise;

*Adım 1.* Kullanıcıdan, GUI aracılığıyla bilgiler girmesi istenir. Bunlar kenar belirleme işlemi uygulanacak resim dosyasının seçilmesi, kullanılacak algoritmanın seçilmesi, üzerinde işlem uygulanan resmin hangi dizine hangi isimle kaydedileceği bilgileridir.

*Adım 2.* Seçilen resmin ağ üzerinden başka bir host'a gönderilebilmesi için binary array'e çevrilmesi gerekir. Bunun için metoda seçilen resmin URL'si gönderilir. Metod, resmi binary array'e çevirerek, diziyi *Adım 3* üzerinden tekrar main metoda gönderilir.

*Adım 4.* SOA Request olarak isimlendirilmiş adımdır. Web Service Server'a, kullanıcının GUI'de girdiği veriler ve seçilen resmin binary array'i gönderilir.

*Adım 5.* Ws-server, öncelikle binary array'i bir image file dönüştürmek için, gerekli metoda gönderir. Metod aldığı veriyi, server'da static olarak belirlenmiş bir dizine resim dosyası olarak kaydeder. *Adım 6* ile geriye resim dosyasının URL sini döndürür.



Şekil 3: Uygulamanın Genel Mimarisi

*Adım 7.* Matlab'ın Edge Detection işlemlerinin yapıldığı kütüphaneler daha öncesinden server uygulamasına dahil edilmiştir. Main metodumuz, kullanıcıdan aldığı işlenmemiş resmin static adresini, işlendikten sonra kaydedilecek resmin adresini ve kullanıcının tercih etmiş olduğu detection algoritmasını (sobel, roberts, prewitt), kendi yazdığımız library'den oluşturduğumuz sınıftaki metoda gönderir. Matlab bu noktada server makinasında arka planda çalışıyor durumdadır; ancak herhangi bir görsellik söz konusu değildir. Dolayısıyla herhangi bir yavaşlık, RAM üzerinde gereksiz alan işgali, CPU'yu gereksiz yere yorma gibi olumsuzluklar da söz konusu olmaz. "Matlab metodu" muz arka planda çalışıp, gerekli algoritmaya göre işlemleri yaptıktan sonra, yine developer tarafından önceden belirlenmiş static adrese kaydeder. (*Adım 8*) Bu işlenmiş resim dosyasının url'si main metod tarafından da biliniyordu.

*Adım 9.* Artık Server tarafında yapmamız gereken, işlenmiş olan resim dosyasını, client'a göndermektir. Bunun için yine binary array'e çevirme işlemine gerek duyuyoruz. File2Binary metodu geriye bir array döndürür. (*Adım 10*)

*Adım 11.* SOA-Response olarak adlandırdığımız adımdır. Kullanıcıya, işlenmiş resim dosyasının binary array'i gönderilir.

*Adım 12.* Ws-Client main metodu, server'dan aldığı binary array'i ve kullanıcıdan GUI aracılığıyla aldığı yeni işlenmiş resim adresini, Binary2File metoduna gönderir. Metod diziyi file'a çevirme ve kaydetme işlemlerini gerçekleştirir. *Adım 13, 14.*

*Adım 15.* İşlenmiş ve kaydetme işlemi başarıyla yapılmış resim, son olarak GUI ekranında, orijinal resmin yanında görüntülenir.

#### 4. SONUÇ VE YORUMLAR

Uygulamanın farklılık ve üstünlükleri şu şekilde sıralanabilir;

- 1-Matlab uygulamasına ihtiyacı olan kullanıcı, gerekli paketi bilgisayarına indirerek fonksiyonları kullanabilir.
- 2-Kenar belirleme işlemine ihtiyacı olan uygulama geliştiricisi, gerekli WSDL URL'yi kullanarak yazılımına entegre edebilir.
- 3-Uygulamamız Java tabanlı olması dolayısıyla, multiplatform çalışma imkanına sahiptir. Hem Unix/Linux hem de Windows kullanıcıları çalıştırabilir. Ayrıca .Net ortamına da kolayca entegre edilebilir bir yapısı vardır.
- 4-Web Servis mantığında bir mimariye sahip olduğu için, yine farklı uygulamaların birbiriyle daha hızlı ve güvenli haberleşmesini kolaylaştırır. Bir masaüstü uygulaması ile web uygulaması projelerinin, data transferini mümkün hale getirir.
- 5-Matlab'ın bir fonksiyonuna ihtiyacı olan kullanıcı, kod öğrenmek zorunda kalmaz. Bir Image Processing işlemi, kendi projesi için ara işlem ise, geliştirdiğimiz mimariyi kullanması ona hız ve kolaylık getirir.

Yapılan çalışma halen sürdürülmektedir ve ilerleyen zamanda daha da geliştirilecektir. Gelen isteklere ve ihtiyaçlara göre yeni servisler geliştirilip, WSDL'leri ve kullanıcı uygulama paketleri bir web sitesi üzerinden yayınlanabilir. Paketlerin, masaüstü uygulamaları olabileceği gibi projelere entegre edilebilen küçük Java kütüphanesi de olması mümkündür. Bu paketlerin kullanımına, kullanıcı adı ve şifreli kullanımlar, extra güvenlik eklentileri de konulabilir. Paketlerin WSDL linkleri, bağlanılan web service server'ların IP adresi dinamik değiştirilebilir yapılabilir.

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# DECENTRALIZED VERSUS CENTRALIZED EXECUTION OF SERVICE ORCHESTRATION

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## ABSTRACT

With the growth of distributed systems and the merge towards service oriented architectures. Naturally the need for service composition emerged and became an important software solution. Service composition is quite a large topic; it contains multiple steps, layers and components. In this paper we discuss the execution of service orchestration. We state both advantages and disadvantages of each one. Finally, we conclude that the choice of one versus the other depends on different criteria and constraints. In our service composition project, focused on e-learning web services [1]; we have chosen decentralized execution of the service orchestration. We have opted to use policies in order to prevent and solve some of the disadvantages and limitations caused by decentralized execution.

## 1. INTRODUCTION

Service Composition is such a big topic that has taken the attention and interest of researchers and developers both in academia and business spectrum. There are different approaches that have been used each with its own pros and cons. Service composition has been the best solution to run and execute services among business partners (buy an airline ticket, rent a car and book hotel stay at the same time). To run and manage network resources and mobile environments as well.

It has also been used to create services that do not exist by combining activities or operations from multiple existing basic services. Because service composition involves cross agency services and transactions, it is therefore a complex to build and run software solution; there are multiple layers from basic service description to execution of the composed service and may be even the reuse and reconfiguration of existing composed services. In the service composition solution that we have proposed in [1] we opted for service orchestration. Orchestration is the step that handles the interactions between the services chosen to create the composed service. The execution of the orchestration code can be distributed among basic service providers or centralized. In this paper we enlist both advantages and disadvantages of both approaches. We defend our choice of decentralized execution and illustrate how we use policies in order to solve some of the issues and limitation caused by decentralized execution of service orchestration. The rest of the paper is organized as follow: 2 orchestration for service composition, 3 centralized execution, 4 Decentralized execution, 4.1 Decentralized execution using policies.

## 2. ORCHESTRATION FOR SERVICE COMPOSITION

Orchestration is one approach to accomplish service composition in which there is a central server that controls and manages all the interactions between the participating services. The orchestration code is located in the central server. Once a user submits a request for a service that doesn't exist, the call to compose a service comes into play.

The central server searches for a set of services that match at least part of the user's request. Based on the set of basic services, the central server then must order and manage the execution as well as the interactions between the participating services; next from a set of possible combinations that meet the user's request, the orchestrator must select the best one then execute it so that the user can use it as a single composed service. The execution of the composed service requires retrieval and exchange of data and code with each basic service provider. This execution can be centralized or distributed among multiple servers. There are several existing tools and standards related to service orchestration such as BPEL business process language. Although a BPEL program invokes services distributed over several servers, the orchestration of these services is typically under centralized control [2]. To perform a decentralized orchestration using BPEL, the orchestration code must be divided among multiple servers. The BPEL program is partitioned into independent sub-programs that interact with each other without any centralized control [2]. There are also partitioning algorithms and programs like Zenflow and the one proposed in [2].

### 3. CENTRALIZED EXECUTION

Normally service orchestration is executed centrally. Typically, a composite web service specification is executed by a single coordinator node. It receives the client requests, makes the required data transformations and invokes the component web services as per the specification [2]. The coordinator node is responsible for coordination of all data and control flow between the components, and hence becomes a performance bottleneck. All data is transferred between the various components via the coordinator node instead of being transferred directly from the point of generation to the point of consumption. This leads to unnecessary traffic on the network. [2]. The general findings of the case studies concur with the literature that the centralized coordination Enhances optimization and decentralized coordination is more adaptive [9]. Also centralized orchestration makes responsibilities and dependencies clear and avoids duplications of activities; however, it not only needs a longer implementation period to realize its potential benefits but also requires additional communication and creation of new cross agency interfaces [3]. Figure 1a,b illustrate the typical architecture of centralized execution of service orchestration. In figure 1a Systems 1 through 8 are different systems in which participating services in the composition process reside. The central system contains the orchestration code and therefore handles its execution, the central system also communicates with all participating nodes and exchanges needed data to enable the execution of services provided by these systems. Communication and exchange of messaging between the central system and all the contributing service providers causes heavy network traffic. This limitation becomes more critical in mobile environments, in which some systems may become unavailable and the centralized system should resolve that by trying to update the list of service providers based on availability. A second limitation in the mobile environment is that once a composed service is generated it doesn't guarantee that it will be available each time the same request is submitted. For all these reasons we find that centralized execution is not the best choice for mobile environments. On the other hand, because the orchestration code is locally executed then trouble shouting running time issues and fault handling will easily be resolved. Moreover, the orchestrator handles monitoring and improving processes, making service level agreements and stores decision history in order to improve future decisions regarding cross business transactions. Security issues are resolved because the central system doesn't execute instructions in any of the participating nodes. Therefore it doesn't require permissions and relieves participating nodes from worrying about security breaches and cross business rejection or permission of execution requests. Thus, local control of the execution process ensures a secure execution and minimal risk of security cracks. Figure 1a illustrates how in centralized execution, the central system into which the orchestration code resides interacts with different service providers, such services do not have any knowledge of each other, although data and process between them is interchanged through the central system.

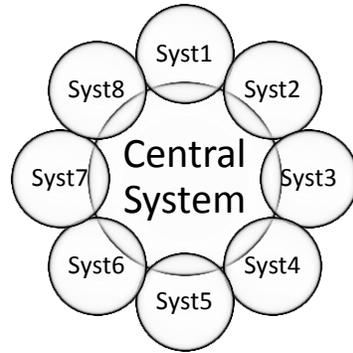


Figure 1a: Centralized execution of service orchestration

Figure 1b illustrates sample service providers, and the orchestrator request services from them, generate a workflow process and executes the composed service as one. The user sends a request to the central system who then handles communication, interactions and execution of the data and information collected from different service providers.



Figure 1b: Centralized execution of service orchestration

Studies have been done to evaluate the main advantages of centralized execution and the most suitable environments for it. The main advantages listed in [9] of centralized execution are: the full process is monitored and easily traced and tracked; reduce of duplication of tasks, and interfaces. The platform is more standard in terms of process, data and interfaces also dealing with information asymmetry and finally, Accountability for the complete process is clear and the users do not have to communicate with the service providers directly.

#### 4. DECENTRALIZED EXECUTION

The concept of decentralized execution is a natural evolving step in the merge of distributed systems, cloud computing, service oriented architectures and the growth of web services and standards supporting them and finally mobile environment. The main advantages of decentralized execution are, its relatively forward, easy to accomplish, short implementation time, Automating the current way of working, no redesign less resistance [9]. All of these have pushed the need for decentralized computing partially or completely. Execution is a major step in service composition because it involves services residing in different locations. Naturally it would be easier to think that having each service be executed by its provider will guarantee its proper execution as well as lessen communication and data transfer between different nodes (service providers). One way to do that is to partition the execution code among multiple servers or all the participating nodes. In figure2, each system presents a service provider; it has its own control manager that handles execution requirements for its services. The control manager contains the policies and aspects specific to the execution of services provided by that service provider. Therefore, a given service is executed within the service provider into which it resides. One or several service providers may receive a request directly from the user, and then the control manager handles communicating with other service providers to complete the user's request. The data and control dependences between the components can be analyzed and the code can be partitioned into smaller components that execute at distributed locations [2].

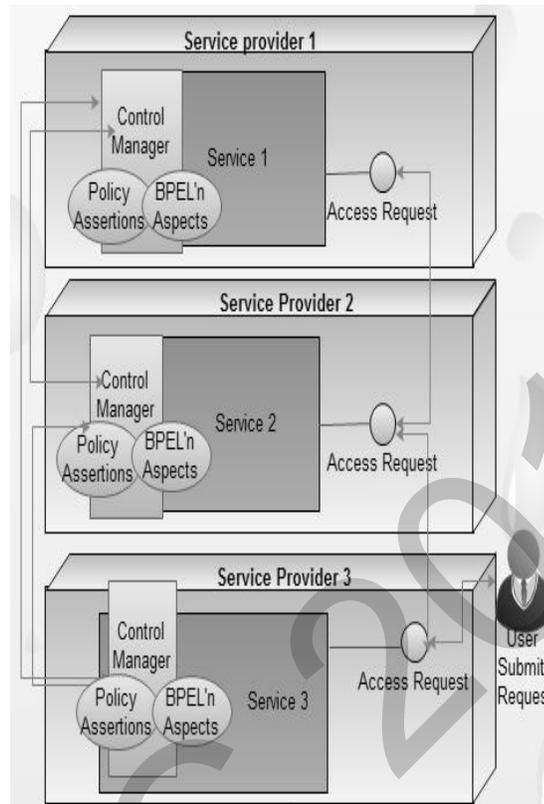


Figure2: Decentralized Execution of Service orchestration

From a technical stand point, decentralized execution in service composition is the best choice in mobile environment for several reasons; Firstly, because the resources are not always guaranteed to be available. Mobile environments cannot presuppose the existence of a centralized powerful machine. A centralized composition manager might not be able to access all the necessary services; secondly, a centralized composition manager might become unreachable from a device in a mobile environment [4]. On the other hand, the composition involves executing services which reside in distributed mobile devices, and using a single composition manager will result in an increase of response time with the increase of services involved in the composition process. One solution to this is to use multiple distributed composition managers. The service composition framework used in [4] had a single composition manager policy per request limitation. In mobile environments, mobility often changes the service topology. This along with other limitations like disconnections and network partition might make it impossible for the composition manager to compose the whole request after having completed a partial execution [4]. Again these limitations can also be solved by further distributing the management of the composition execution among all the participating systems in which the services reside. Furthermore, data security is widely recognized as a major barrier for widespread adoption of deploying data into open distributed systems[10], when the execution is distributed, it means that the data doesn't have to be outsourced to foreign systems. Overall we can say that decentralized orchestration takes a shorter lead time, and requires less structural and organizational transformation, however, is less transparent for user [3]. Finally, the evaluation study done in [9] further confirmed performance benefits that decentralization provides. Although there might be a tradeoff in terms of throughput and response time at very high loads.

With proper design, optimal partitioning and run time support for error handling and recovery, decentralized orchestration provides an attractive approach for execution of complex high performance composite services [2].

#### 4.1. Decentralized Orchestration using Policies:

We have opted for decentralized execution of the service composition orchestration proposition in [1]. This choice is in order to benefit from all the advantages listed in the previous section. However as we have stated, multiple issues arise in decentralized execution; Such as security and privacy concerns among others stated in previous sections. Our goal is to solve these issues using policies. Policies have been widely used in software development and especially in web services. There are several existing languages and standards to support the creation and the execution of policies such as WS-Policy. A composition policy is a set of policy rules specifying how a given set of elementary collaborations can be composed to obtain a given set of composite services [5]. Policies declaratively specify the behavior of these generated automatically. Policies allow the service composition to be adaptive without losing the benefit of enhanced optimization. One challenge is to ensure that fault handlers preserve their semantics regardless of the node (server) that is executing it. If the fault handler includes sending a message to some other component in the composite web service (which now executes on a different node due to decentralization), changes have to be made accordingly [2].

Policies are selection rules in which we can specify which action should take place given one or more conditions. WS-Policy a known standard defines a base set of constructs that can be used and extended by other Web services to express and advertise their policies. WS-policy for instance defines a set of assertions; each one specifies different requirements from authentication and messaging protocol to privacy policy, Quality of service characteristics. Having stated some of the issues caused by decentralized execution of the orchestration, we now see how policies provide a solution to control the flow and execution of each participating web service in the service composition process, also it delivers a very flexible environment to set all types of restrictions to assure total security and to solve the problem of fault handlers. Business process language BPEL offers BPEL 'n' Aspects which is a non-intrusive mechanism for adaptation of control flow of BPEL processes. It relies on Web service standards to weave process activities in terms of aspects into BPEL processes [7].

BPEL 'n' Aspects relies on existing technologies and standards. WS-Policy is used to specify aspects. Figure3 shows the structure of aspects as WS-Policy assertion. Association of aspects with BPEL processes is done with WSPolicyAttachment. This mechanism allows attaching aspects to processes at runtime without changing the target process definition [7].

Aspects allow us to specify where, when and what part of the code in which we should execute a specific instruction figure3. Pointcut specifies the methods in the code in which we would like to insert an instruction, in the before() part we specify when to execute, and in between the curly braces right after the before(), we specify the instruction that we would like to add. For example it could be an authentication request in case the user is not from the current staff list of a given organization.

```
public aspect AddUser{
pointcut CreateMethods(): call(public * *.bar(..)) ;
before() : CreateMethods()
{
System.out.println("adding an instruction" );
}
}
```

Figure3: Aspect sample in BPELnAspects

Integrating aspects into the execution of the base functionality is called *weaving*. In static AOP approaches, as e.g., in AspectJ, at compile-time/load-time pointcuts are mapped to places in the program code whose execution might yield a join point at runtime. The latter are instrumented to add calls to advice and eventually dynamic checks that the identified places in code do actually yield a join point at runtime [23]. To further allow a more dynamic interactions between services and less user interference, With aspect oriented programming languages, Aspects can be (un)deployed at application runtime, the behavior of which can thus be adapted dynamically [8].

## 5. CONCLUSION AND FUTURE WORK

In this paper we have addressed the problem of execution of orchestration for service composition. We have compared both decentralized execution verses centralized one. Then we have taken our project proposition in [1] as an example, in which we opted for distributed execution of service composition. Even though distributed execution has some disadvantages such as security and fault handling, we have listed how these can be overcome by the use of

policies. Policies are a powerful solution for several reasons, including existing standards supporting the creation, integration and implementation of policies for web services especially. Moreover, policies require minimal alteration to existing systems in which the services reside. They also allow adding restrictions and constraints to the execution of a given service without the need to change the specification, design or recreate any existing service. All this helps us enforce the security measures needed in terms of exchange of data between multiple service providers as well as express and execute fault handlers. We have shown that we have opted to use policies as part of a decentralized execution of service composition in order to benefit from the advantages of distributed execution and solve its limitations.

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# DEFORMATION EQUATIONS AND FLOW OF CRUDE OIL IN PIPELINES

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**Abstract:** Theory of deformation is used to set up equilibrium equation in terms of Lame's elastic constants. After subjecting proper boundary conditions, it yields analytical expressions for various stress and strain components in a cylindrical pipe. These are numerically solved to obtain the values of the stress components as a function of pressure for a given flow condition of crude oil.

## 1. INTRODUCTION

Transportation of crude oil or natural gas is one of the major concerns of the petroleum industry. This is basically achieved through pipelines which are found to be the most economical way for transportation. It is very important [Fessler and Lewin, 1956; Berlamont et al, 2003; Khodashenas and Paquier, 1999; Knight and Sterling, 2000] to determine the stress generated in pipelines in order to maintain their safety against external forces, and to do so by non destructive diagnosis for pipelines that are in service. Common methods involve the measurement of deformation through strain gauge or to use pipe deflection indicators to measure pipeline deformation and to enter deformation readings into an FEM( Finite Element Method) program to calculate the stress, but this is not a very precise method [Iimmura, 2004].

In the present work, we have applied the theory of deformation to compute the stress distribution inside the pipe. The deformation mechanism and the physical properties are closely related and depend in a complex way on stress, strain rate, pressure and temperature. Such studies are very helpful in the design and the selection of the material of the pipe. Theory of elastic deformation is used to setup the equilibrium equation which was further generalized for isotropic materials in terms of Lamé's elastic constants ( $\lambda$  and  $\mu$ ). The equilibrium equation forms the basis for establishing the connection between various thermo-elastic functions, which are solved to obtain the analytical expressions for various components of the stress, ( $\sigma_{rr}$ ,  $\sigma_{\phi\phi}$ , and  $\sigma_{zz}$ ). These are numerically solved to obtain the values of the stress components as a function of pressure for given flow conditions of crude oil.

## 2. DEFORMATIONS AND EQUILIBRIUM EQUATIONS

Elastic deformation is the action of forces when there is a net reversible movement. Stress and strain are used to quantify the elastic deformation. Stress is tension or compression - force acting per unit area - and strain is the response of the material to stress. The stress and strain orientation is significant in continuum mechanics [Fetter and Walecka, 1980] in expressing the interaction between one part of a material body and another. There are material actions and reactions across the surface contacting two bodies or two parts of the same material body. The material on the right exerts a force on the material to the left and vice versa.

### 2.1 Strain tensors for Finite Deformation:

Consider the infinitesimal line element  $dx$ , with reference to a fixed set of axes in space  $x$  and  $x + dx$ . After deformation due to a displacement field  $s(x)$ , the material element  $l(x)$  deforms to  $l(x + dx)$ ,

$$l(x) = x + s(x) \quad (1)$$

$$l(x + dx) = x + dx + s(x + dx) \quad (2)$$

In vector notation, the deformation,  $dl$ , can be expressed as

$$dl = l(x + dx) - l(x) = dx + s(x + dx) - s(x) \quad (3)$$

On making a Taylor expansion of  $s(x + dx)$  around  $x$  and confining our attention to a small enough region so that squares and products of  $dx_i$  can be neglected, we have for the components  $dl_i$  ( $i = 1, 2, 3$ ):

$$dl_i = \left( \delta_{ij} + \frac{\partial s_i}{\partial x_j} \right) dx_j \tag{4}$$

The components  $dl_i$  depend linearly on the components  $dx_i$  and on  $\partial s_i / \partial x_j$  evaluated at  $x$ . The nine quantities  $\partial s_i / \partial x_j$  determine the deformation and are components of a second-rank tensor. The components  $\partial s_i / \partial x_j$ , are called the deformation tensor. Hence we may write:

$$|dl|^2 = |dx|^2 + 2E_{ij}dx_i dx_j \tag{5}$$

where

$$E_{ij} = E_{ji} = \frac{1}{2} \left( \frac{\partial s_i}{\partial x_j} + \frac{\partial s_j}{\partial x_i} \right) + \frac{1}{2} \left( \frac{\partial s_k}{\partial x_i} \frac{\partial s_k}{\partial x_j} \right) \tag{6}$$

and where in writing (5) and (6) we have reverted to using the Einstein summation convention.  $E_{ij}$  is often referred to as the Lagrangian strain tensor. It is observed from equation (3-11) that if all  $E_{ij} = 0$ , then  $|dl| = |dx|$  for every line element  $dx$ . Hence  $E_{ij}$  specify the strain in the region around . For small deformations the second term in equation (6) can be neglected compared with the first and then.

$$E_{ij} = \varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial s_i}{\partial x_j} + \frac{\partial s_j}{\partial x_i} \right) \tag{7}$$

the strain tensor for infinitesimal deformations.

**2.2 Stress Tensor and the Associated Forces:**

Consider the forces acting on an element of volume due to the reaction of matter surrounding it. The force acting on a given face is proportional to the area. Let us denote the components of the force per unit area acting on a face perpendicular to the  $x_1$ -axis by,  $\sigma_{11}$ ,  $\sigma_{12}$  and  $\sigma_{13}$ . Similarly, for faces perpendicular to the  $x_2$ -axis and  $x_3$ -axis the components are,  $\sigma_{22}$ ,  $\sigma_{23}$ ,  $\sigma_{21}$ , and  $\sigma_{33}$ ,  $\sigma_{31}$ ,  $\sigma_{32}$  respectively. These components are known as the components of stress.  $\sigma_{ij}$  are called normal stress components and  $\sigma_{ij} (i \neq j)$  are called shear stress components all with the dimension of force per unit area. The  $i$  th component of the force per unit volume due to stress is

$$f_i^{(\sigma)} = \partial \sigma_{ji} / \partial x_j \tag{8}$$

**2.3 Equilibrium Equation:**

Every material point in an object is always under the influence of body forces. Denoting  $F_i$  as the components of the body forces acting per unit mass and  $\rho$  as the density of the material, the components of the body forces acting on the volume element  $dx_1 dx_2 dx_3$  are  $(F_i \rho) dx_1 dx_2 dx_3$ . The total force, which is the sum of the body forces  $(F_i \rho dx_1 dx_2 dx_3)$  and the stress forces  $(f_i^{(\sigma)} dx_1 dx_2 dx_3)$  is required to be zero for equilibrium

$$(F_i \rho + f_i^{(\sigma)}) dx_1 dx_2 dx_3 = 0 \tag{9}$$

Substituting  $f_i^{(\sigma)}$  from equation (8),

$$\partial \sigma_{ji} / \partial x_j + \rho F_i = 0 \tag{10}$$

This equation is one of the most general forms of the equilibrium equation.

**2.4 Generalization of Equilibrium Equation for Isotropic Bodies:**

The equilibrium equation (10) can be generalized to compute the stress distribution in a long cylindrical pipe. If a body is

acted upon by the body forces  $F_i$  and the stress distribution  $\sigma_{ij}$ , then the total force  $F^{(t)}$  acting per unit volume is

$$F_i^{(t)} = \frac{\partial \sigma_{ij}}{\partial x_j} + \rho F_i \quad i, j = 1, 2, 3. \quad (11)$$

Bhatia and Singh (1986) showed that for elastically isotropic system,  $\sigma_{ij}$  can be expressed in terms of Lamé's elastic constants ( $\lambda$  and  $\mu$ )

$$\sigma_{ij} = \lambda \Delta \delta_{ij} + 2\mu \varepsilon_{ij} \quad (12)$$

For homogenous deformation,  $\lambda$  and  $\mu$  can be expressed in terms of Young's modulus (E) and the Poisson ratio ( $\nu$ ), i.e.

$$\lambda = \frac{E\nu}{(1-2\nu)(1+\nu)} ; \quad \text{and} \quad \mu = \frac{E}{2(1+\nu)} \quad (13)$$

$\delta_{ij}$  are delta functions and  $\Delta$  stands for

$$\Delta = \sum_{i=1}^3 \varepsilon_{ii} \quad (14)$$

Substituting these equations and solving we get from eq (10)

$$F^{(t)} = (\lambda + \mu) \text{grad div } s + \mu \nabla^2 s + \rho F \quad (15)$$

Using the vector identity :  $\text{grad div } = \text{curl curl} + \nabla^2$ ; for equilibrium ( $F^{(t)} = 0$ ) we get,

$$(\lambda + 2\mu) \text{grad div } s - \mu \text{curl curl } s + \rho F = 0 \quad (16)$$

It may be noted that the last term,  $\rho F$ , represents the body forces which are the manifestations of gravitational forces. For elastic isotropic materials, the body force produces a negligibly small deformation and hence could be neglected. In that case the equilibrium equation becomes

$$(\lambda + 2\mu) \text{grad div } s - \mu \text{curl curl } s = 0 \quad (17)$$

The equilibrium equation together with the appropriate boundary conditions on  $\sigma_{ij}$  allows one to estimate the stress distribution in various structures.

### 3. STRESS COMPONENTS IN A LONG CYLINDRICAL PIPE

Let the internal and external radii of the pipe are  $R_1$  and  $R_2$  respectively. The boundary conditions are

$$\begin{aligned} \sigma_{rr} &= -p & \text{at } r &= R_1 \\ \sigma_{rr} &= 0 & \text{at } r &= R_2 \end{aligned} \quad (18)$$

from the symmetry of the problem, it is necessary that the displacement  $s$  must be a function of  $r$ , i.e.

$$s_r(r) \neq 0 \quad \text{but} \quad s_\phi = s_z = 0 \quad (19)$$

Following expressions in cylindrical polar coordinates one has,

$$\text{curl } s = 0 \quad \text{and} \quad \text{div } s = \Delta = \frac{1}{r} \frac{\partial}{\partial r} (s_r r), \quad (20)$$

therefore, the equilibrium equation (17) becomes

$$(\lambda + 2\mu) \text{ grad div } s = 0 \quad (21)$$

or, 
$$\text{div } s = \text{constant} \quad (22)$$

If we take  $\text{div } s = 2a$ , (where  $a$  is a constant), we can rewrite equation (22) as,

$$\frac{\partial(s_r r)}{\partial r} = 2ar \quad (23)$$

Integrating both sides, we get,

$$s_r = ar + br^{-1} \quad (24)$$

where  $b$  is another constant. The strain components thus become

$$\varepsilon_{rr} = \frac{\partial s_r}{\partial r} = a - \frac{b}{r^2} \quad (25)$$

$$\varepsilon_{\varphi\varphi} = \frac{s_r}{r} + \frac{1}{r} \frac{\partial s_\varphi}{\partial \varphi} = a + \frac{b}{r^2} \quad (26)$$

The stress-strain relation for isotropic materials in cylindrical coordinates can be written as

$$\sigma_{rr} = \lambda\Delta + 2\mu\varepsilon_{rr} = 2a(\lambda + \mu) - 2\mu br^{-2} \quad (27)$$

$$\sigma_{\varphi\varphi} = \lambda\Delta + 2\mu\varepsilon_{\varphi\varphi} = 2a(\lambda + \mu) + 2\mu br^{-2} \quad (28)$$

$$\sigma_{zz} = \lambda\Delta = 2a\lambda \quad (29)$$

where  $\lambda$  and  $\mu$  are Lamé's constants. Subjecting the boundary conditions in equations (27-29) one readily obtains

$$\frac{b}{a} = R_2^2 \left( \frac{\lambda + \mu}{\mu} \right) \quad (30)$$

and, 
$$-p = 2a(\lambda + \mu)(1 - R_2^2 R_1^{-2}) \quad (31)$$

Solving for  $a$  and  $b$  gives

$$a = \frac{p}{2} \frac{R_1^2}{(\lambda + \mu)(R_2^2 - R_1^2)} \quad (32)$$

$$b = \frac{p}{2} \frac{R_1^2 R_2^2}{\mu(R_2^2 - R_1^2)} \quad (33)$$

Making use of the constants in equations (25-26)

$$\varepsilon_{rr} = \frac{p}{2} \frac{R_1^2}{(\lambda + \mu)(R_2^2 - R_1^2)} \left[ 1 - \left( \frac{\lambda + \mu}{\mu} \right) \frac{R_2^2}{r^2} \right] \quad (34)$$

$$\varepsilon_{\varphi\varphi} = \frac{p}{2} \frac{R_1^2}{(\lambda + \mu)(R_2^2 - R_1^2)} \left[ 1 + \left( \frac{\lambda + \mu}{\mu} \right) \frac{R_2^2}{r^2} \right] \quad (35)$$

On substituting these values in equation (27-29), the following expressions for the stress components are obtained

$$\sigma_{rr} = \frac{pR_1^2}{(R_2^2 - R_1^2)} \left( 1 - \frac{R_2^2}{r^2} \right) \tag{36}$$

$$\sigma_{\phi\phi} = \frac{pR_1^2}{(R_2^2 - R_1^2)} \left( 1 + \frac{R_2^2}{r^2} \right) \tag{37}$$

$$\sigma_{zz} = \frac{p\lambda}{\lambda + \mu} \frac{R_1^2}{R_2^2 - R_1^2} = \frac{2p\nu R_1^2}{R_2^2 - R_1^2} \tag{38}$$

#### 4. COMPUTED VALUES OF STRESS IN A PIPELINE

Oil pipelines used for transportation of crude oil are normally vary in inner diameter from 10 cm to 120 cm which are buried at a typical depth of 1m - 2m. The oil is kept in motion by pump stations along the pipeline, and usually flows at a speed of 1 to 6 m/s. It has been a constant endeavour to increase the strength and the stability of the pipe which depends upon the materials which are used to construct these pipes. It is clear from the equations (36-38) that the shearing stress in the pipe depends upon the pressure and thickness of the pipe. It suggests, that the material of the pipe should be selected so that the shearing stress of the material of the pipe does not become greater than the critical value. In other words, knowing the critical shear stress of the material, one can choose the appropriate thickness ( $R_2 - R_1$ ) which should sustain the desired pressure p.

The equations (36-38) have been used to calculate the variation of stress components  $\sigma_{rr}$ ,  $\sigma_{\phi\phi}$ ,  $\sigma_{zz}$  as a function of the distance r from the central axis of the pipe at given pressures. For our calculations we have taken the typical values of the inner radius  $R_1 = 0.39\text{m}$  and outer radius  $R_2 = 0.41\text{m}$ . The computed values of the stress components ( $\sigma_{rr}$ ,  $\sigma_{\phi\phi}$ ,  $\sigma_{zz}$ ) are plotted in figures (1) to (3).

The variation of the radial stress  $\sigma_{rr}$  as a function of distance (r) from the central axis of the pipe at given pressures (p) is shown in figure (1).  $\sigma_{rr}$  decreases with increasing r. We observe that for a given r,  $\sigma_{rr}$  decreases with pressure. Also for,  $r \rightarrow R_2$ ,  $\sigma_{rr}$  becomes zero.

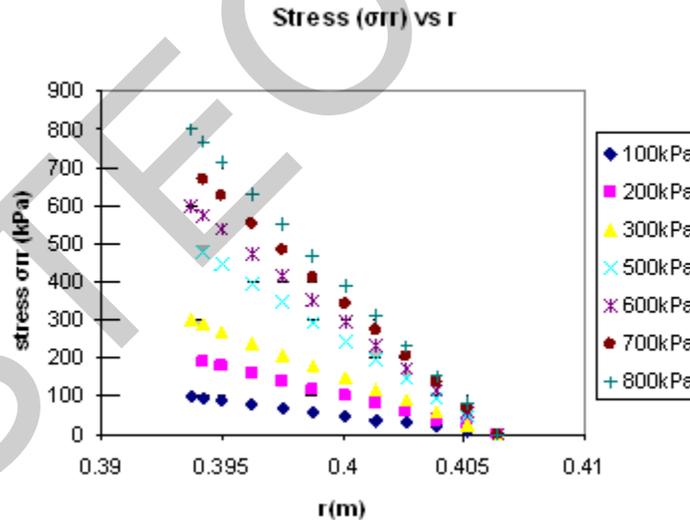


Figure 1: The variation of the radial stress ( $\sigma_{rr}$ ) as a function of the distance (r) from the central axis of the pipe calculated for various pressures (p) of the crude oil.

The computed values of stress component  $\sigma_{\phi\phi}$  are shown in figure (2). Unlike  $\sigma_{rr}$ ,  $\sigma_{\phi\phi}$  remains almost constant with r at a given pressure. At given r,  $\sigma_{\phi\phi}$  however decreases with decreasing pressure.

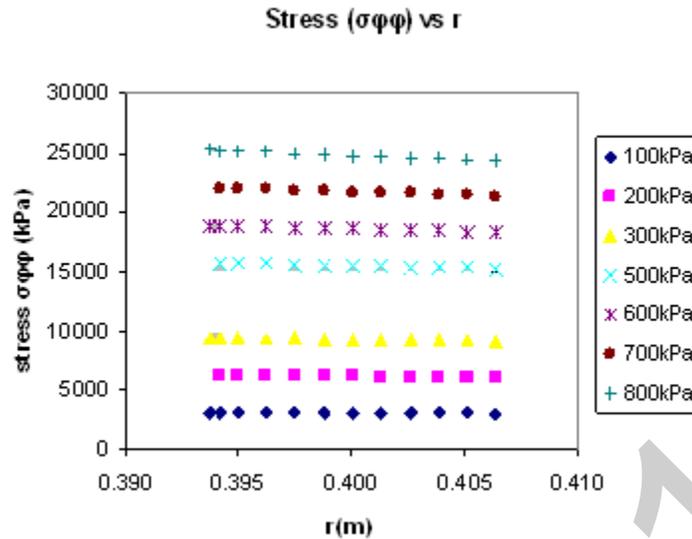


Figure 2: The variation of the stress component ( $\sigma_{\phi\phi}$ ) as a function of the distance (r) from the central axis of the pipe at different pressures.

The plot  $\sigma_{zz}$  with pressure is shown in figure (3). Results suggest that  $\sigma_{zz}$  increase linearly with increasing pressure. The distribution of stress components as shown in figures (1) to (3) at a given pressure can be used to select the material [Den Hartog, 1952] of the pipe so that the shearing stress remains less than the critical value of the breaking stress of the material used.

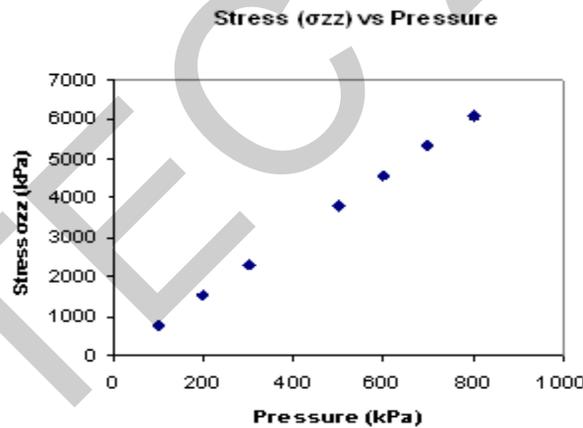


Figure 3: The variation of stress component  $\sigma_{zz}$  with pressure

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# DEMONSTRATION OF AN ELECTROSPRAY INJECTION SYSTEM

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## ABSTRACT

The use of liquid hydrocarbons as a chemical energy source is promising for the actualization of high energy density power sources in the near future. Electrospray injection method is a unique technique that provides equal droplet size distribution at very low flow rates. Therefore it is quite suited for the atomization of liquid hydrocarbon fuels in miniature energy conversion devices. This study reports the design and characterization of an electrospray system. First, the electrospray phenomenon is briefly discussed from an historical perspective. An experimental test rig is built and a proof-of-concept demonstration is provided. For the experiments methanol is used as the liquid fuel. Flow visualization is performed to identify the electrospray mode. Results suggest that a Taylor cone is cone formed when voltage is applied to the system. After a certain voltage threshold electrostatic forces overcome the surface tension forces and droplets begin to separate from the Taylor cone. For voltage values higher than 6 kV certain instabilities are observed. Starting voltage for the current configuration is measured to be 2.2 kV. This value is in close agreement the theoretical calculations which suggest that the starting voltage would be 2.5 kV. This 12% discrepancy can be attributed to experimental uncertainty. Flow rate from a single injector is found to be on the order of 2 ml/h. Therefore in order to utilize electrospray injection in practical power conversion devices manufacturing of high nozzle density multiplexed emitter arrays are needed.

## INTRODUCTION

Liquid hydrocarbons have a much higher energy density than conventional batteries. For example; a typical liquid hydrocarbon has an energy density around 42 MJ/kg, on the other hand a lithium battery can only store about 0.6 MJ/kg (Deng et al. 2007). For this very reason, batteries that work with liquid hydrocarbons can make a technological breakthrough in this field. Even if, these systems have low energy conversion efficiency (i.e. thermal to electric), they can produce much more electrical energy per unit battery weight. Thus, these devices would be quite suitable for military and aerospace applications due to their light weight and size.

In micro scale systems, fuel must be in liquid phase, to get the desirable energy density. Gaseous fuel is simply not an option. Liquid fuel must be atomized, be injected into the combustion chamber and mixed with air. Electrospray injection is a suitable method for liquid injection within micro scale devices.

Electrospray injection is a unique technique suited for very low flow rates, which can assure a uniform spray and droplet size distribution. This technique relies on the ionization of conductive liquids under strong electrostatic fields. Meniscus occurs on the conductive liquid's surface whenever the liquid is affected by the presence of an electric field. This in turn causes electrostatic pressure on the free surface of the liquid. The surface tension of the liquid manages to neutralize the effect of electrostatic pressure. For weak electric fields, meniscus effect on the liquid surface is not much pronounced, however when stronger fields are applied, the liquid surface assumes a conical form. Finally, when a sufficiently strong electric field is applied to the system, electrostatic forces overcome surface tension forces, as a consequence separation from tip of the cone occurs. This phenomenon is termed as electrospray ionization (Krpoun, 2009).

Electrospray can be described with two different phenomena. The first one is a phenomenon where an electric field is used to charge pneumatically or mechanically sprayed droplets. The second one results from the use of the electric field in order to generate a spray from the fluid surface. This latter phenomenon has been given the name "electro-hydrodynamic spraying" (Cloupeau and Prunet-Forch, 1994). This paper deals with electro-hydrodynamic spraying.

First observations of this electro-hydrodynamic spraying phenomenon were conducted by John Zeleny in 1914. His experiments were done in air and he used a single glass capillary for spraying. He used diluted hydrochloric acid, ethanol and glycerin as the conductive liquid.

Later on in the 1930's, Macky conducted research about behavior of water droplets in strong electric fields. In 1965, Taylor found the semi vertical angle of cone at the tip of capillary to be about 49°.

Zeleny's phenomenon was first fully described by Dole in 1968. Furthermore, in 1992, Fernandez de la Mora's solution explains the observed departure of the liquid cone angles from the spray-free value of 49° and predicts the droplet density as a function of position.

Practical applications are quite new. For example, in 1989 Fenn et al. used electrospray technique in mass spectrometry. This invention won the Nobel Prize for J. B. Fenn in 2002. Besides, electrospray technique is also used in aerospace applications, such as thrust and orbital control (Valesquez-Garcia, BGLF et al., 2008).

For many applications a single electrospray emitter cannot provide the required flow rate alone. Therefore it is often necessary to multiplex emitter arrays. Manufacturing of high density nozzle arrays is possible through state-of-the-art MEMS technology. For example, Kegi Tang et al. (2001) manufactured a multiplexed electrospray system with silicon micro fabrication and used it for mass spectrometry applications. Bocagnera et al. fabricated and tested an electrospray system with 115 source/cm<sup>2</sup> density using a conventional CNC drilling method in 2005. This study proves that, there is no difference of flow rates between a single electrospray and a nozzle of multiplexed electrosprays. 1024 emitters within an area of 0.64 cm<sup>2</sup> were manufactured and tested by Valesquez-Garcia for satellite thruster applications. Deng et al. (2007) manufactured a miniaturized ceramic combustor which has the same order of magnitude volumetric heat release rate with conventional gas turbines. This device is only 0.22 cm<sup>3</sup> in volume. In 2009, Deng et al. fabricated an electrospray system with 11,547 nozzles/cm<sup>2</sup> density. To date this value is highest nozzle density value reported in the open literature.

This paper is organized as follows; first the electrospray theory is briefly presented, and then a proof-of-concept demonstration is provided. Thereafter, the experimental results are compared against theoretical predictions. Finally, the paper concludes with a discussion section.

## MATHEMATICAL MODEL

Taylor explained the behavior of liquids issuing from the end of a thin tube due to electrostatic forces. He is the first to observe a conical form at the tip of the capillary needle when the charged liquid is attracted towards a ground electrode. This conical tip is named after him as the "Taylor cone". Taylor experimentally found that the cone half angle was 49.29° (Taylor, 1964). Later on he mathematically proves that, this angle is independent of fluid properties, applied voltage or the distance between the capillary and the ground electrode (Taylor, 1964).

Should a sufficiently strong electric field be applied to the system, electrostatic forces overcome the surface tension forces, as a consequence separation from tip of the Taylor cone occurs. The resulting flow is the so called cone jet. Starting voltage corresponding to this condition is provided in Eqn. (1).

$$V_{oc} = \sqrt{\frac{\gamma r_t}{\epsilon_0}} \ln \left( \frac{4d}{r_t} \right) \quad (1)$$

In the above expression (Eqn. 1),  $\gamma$  is the surface tension,  $r_t$  the radius at the tip of a hyperboloid needle and  $\epsilon_0$  is the permittivity of free space. Note that the free space permittivity constant is  $8,854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2}$ . Finally,  $d$  is the distance between tip of the capillary and the ground electrode. This mathematical relationship provides the minimum voltage needed to separate droplets from the tip of the Taylor Cone. When these droplets separate from the Taylor cone and fly towards the ground electrode the circuit is completed.

The minimum flow rate to start the electrospray operation is provided by Eqn. (2). Here  $\epsilon$  denotes the dielectric constant,  $K$  the conductivity and  $\rho$  the density of the liquid. This is the flow rate corresponding to the starting voltage.

$$Q_{\min} = \frac{\gamma \epsilon \epsilon_0}{\rho K} \quad (2)$$

The current of the system can be obtained with Eqn. (3). Inversely by measuring the electrospray current the flowrate can be obtained as well. Note that this relationship has been experimentally verified by Fernandez de la Mora (1994).

$$I = f(\epsilon) \sqrt{\frac{\gamma Q K}{\epsilon}} \quad (3)$$

The function  $f$  appearing in Eqn.3 is the derivative of the dimensionless spray current with respect to the dimensionless flow rate variable. It turns out that this derivative is only a function of the dielectric constant. Consequently, results from different liquids can all be collapsed into a single line. This result is quite important as it allows the indirect measurement of the electrospray flow rate via the current whose measurement is rather trivial. For further discussion reader is kindly referred to the extensive study of de la Mora (1994).

## EXPERIMENTAL SETUP

A photographic view of the experimental setup is provided in Figure 1. A glass capillary tube of 0.1 mm inner diameter was used for electrospray injection. A syringe pump is utilized for bringing the liquid towards the tip of the needle. 1/8" O.D.

tubing is used for connections between the capillary tube and the syringe pump. The liquid is positively charged by a high voltage DC power supply. The applied voltage is varied between 0-8 kV throughout the experiments. A ground electrode made of a conductive sheet metal is placed within a distance from the capillary needle.

Images of electrospray injection are recorded by a CCD camera. A far field microscope with a focal length of approximately 20 mm is mounted in front of the camera in order to increase the spatial resolution of the images. In this study, 10x and 20x magnification lenses are mounted onto the far field microscope. Also note that, the CCD camera was mounted onto a two axis traverse. Another traverse can be used for vertical adjustments (i.e. the distance between the capillary tube and the ground electrode). Therefore, the camera can move in all three directions for capturing desired images.

A digital multimeter is used to measure the electrospray current. A 10 k $\Omega$  control resistance is connected between the negative electrode and the ground (see Figure 2). Voltmeter is shunted to this resistance (see Figure 2). The electrospray current is inferred from the voltage drop across this control resistance. The experiments were carried out with methanol as the dielectric liquid. Physical properties of methanol are summarized in Table 1.

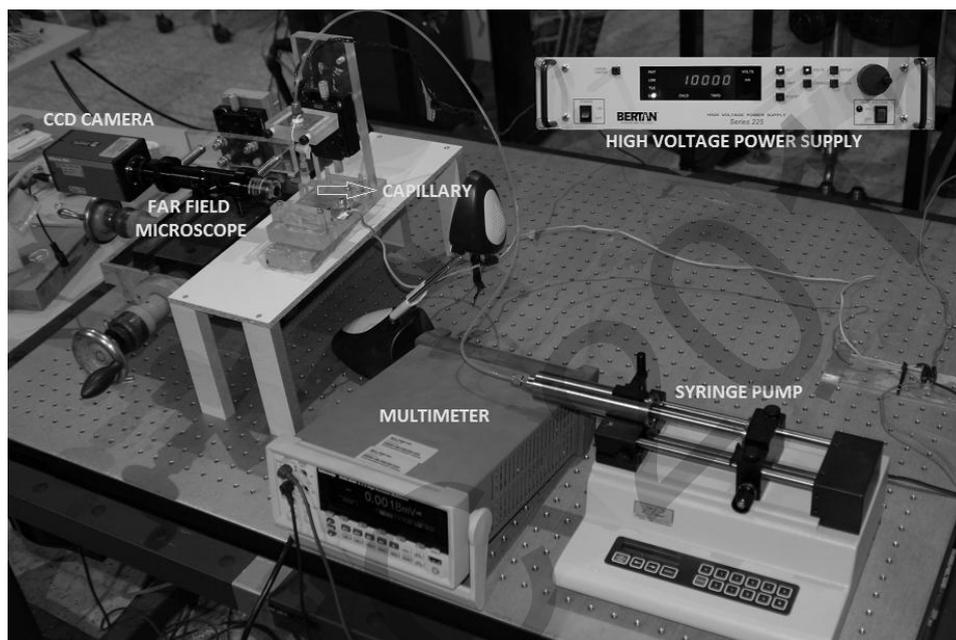


Figure 1 Experimental setup

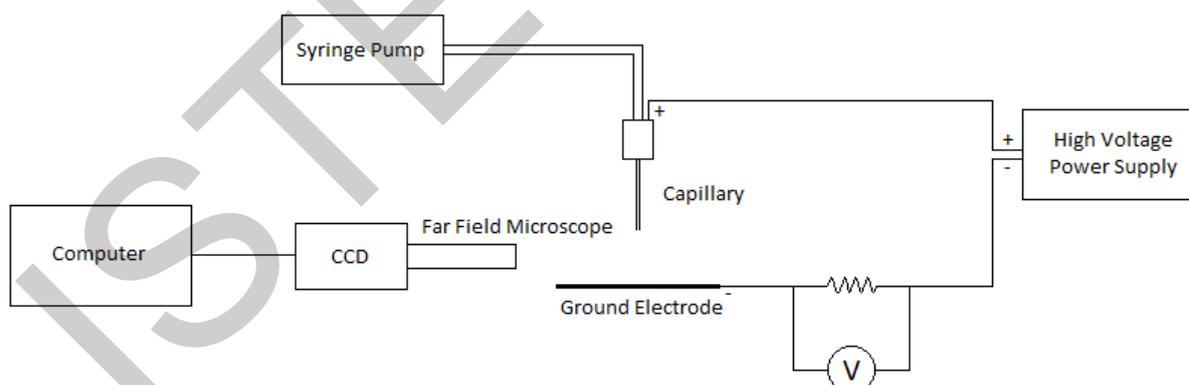


Figure 2 Schematic view of the experimental setup

Table 1. Physical properties of methanol

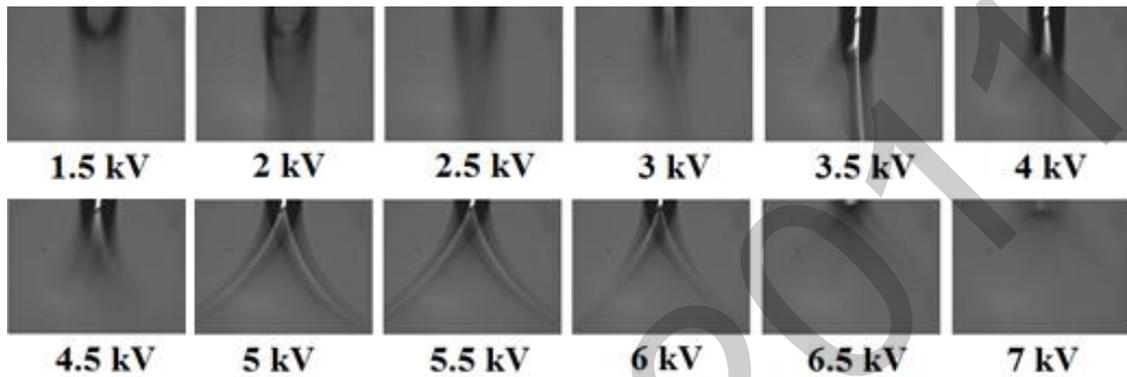
Density (kg/m <sup>3</sup> )	Surface Tension (N/m)	Relative Permittivity	Conductivity (S.m <sup>-1</sup> )
791.3	0.023	33.1	$2.1 \times 10^{-7}$

## RESULTS

Note that as mentioned previously the syringe pump in the test rig is only utilized to bring the liquid towards the tip of the capillary tube. Consequently, electrospray occurs without infusion from the syringe pump, only with the applied potential difference.

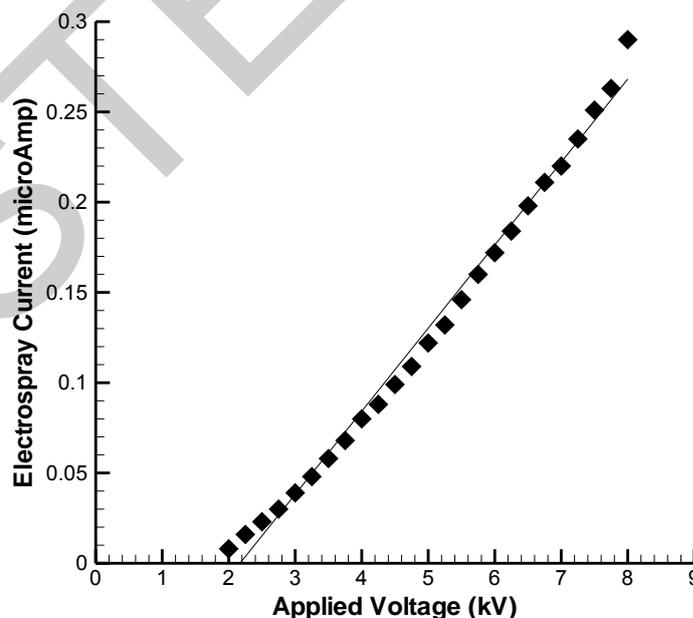
Theoretical starting voltage value is calculated via Eqn. 1 for 15 mm distance between the tip of the capillary tube and ground electrode and methanol as the dielectric liquid. The theoretical value for the current configuration is 2.5 kV.

Experiments were carried out with voltage values are applied between 0-6 kV at 0.5 kV intervals. Electro spray views in different voltages are provided in Figure 3. In this experiment syringe pump was adjusted to 1 ml/h flow rate and distance between tip of the capillary and ground electrode is 15 mm. Besides, methanol was used as a fuel. When 1.5 kV was applied to the system, droplets were separated from the Taylor Cone. If the applied voltage is increased, length of the tip of the Taylor Cone approaches to the ground electrode. In our system, Taylor Cone combines at 3.5 kV and flow of electro spray becomes stable. This stabilization can be seen between 3.5 kV and 6 kV in Figure 3. Two sided flow can be seen in 5, 5.5 and 6 kV. The reason is that the ground electrode is rather wider from the diameter of capillary and consequently the shape of the consisted magnetic field is affected. In the frames corresponding to 6.5 and 7 kV test cases the image resolution turns out to be somewhat poor, since the capillary tube which is secured to the test rig like a cantilever beam cannot stand the electrical forces and starts to vibrate.



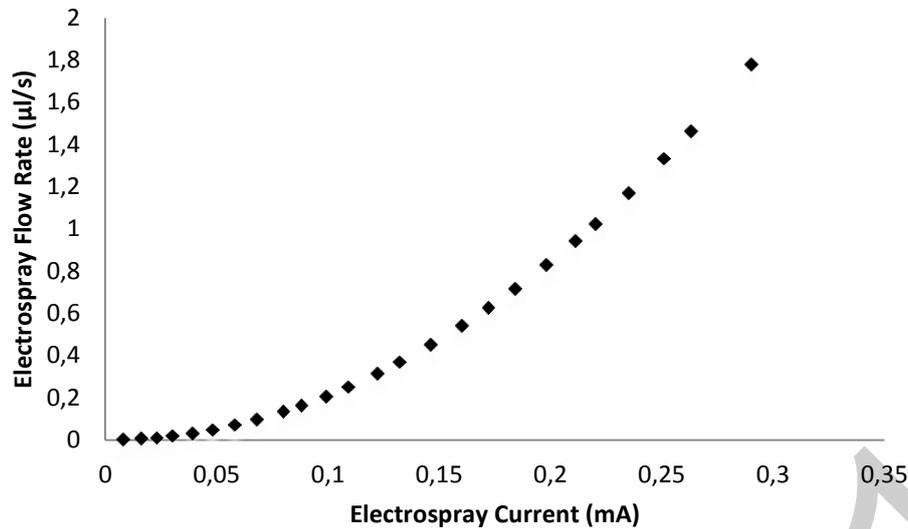
**Figure 3** Electro spray views for different electric field intensities

In Figure 4, the electro spray current is plotted as a function of potential difference between the charged liquid and the ground electrode. Results indicate a linear trend between the applied voltage and the electro spray current. A trend line is also plotted in Figure 4. The correlation coefficient of the line fit is  $R^2=0.99$ . The intersection point of curve fit and x-axis corresponds to the starting voltage of the system. As seen in the figure this value is about 2.2 kV. Note that when the electro spray initializes there is a sudden jump in the voltage drop across the shunt resistance. It is also possible to infer the starting voltage from this sudden jump.



**Figure 4** Electro spray Current versus Applied Voltage

Electro spray flow rate was calculated with Eqn. (3). In this equation, all values, except  $f(\epsilon)$  is known from Table 1.  $f(\epsilon)$  values vs.  $\epsilon$  for pure solvents is plotted by Fernandez de la Mora in 1994. Relative static permittivity for methanol is 33.1, and this value corresponds to  $f(\epsilon)=15$ . Thus, electro spray current vs. electro spray flow rate is plotted in Figure 5.



**Figure 5** Electro spray Current vs. Electro spray Flow Rate

### DISCUSSION

Starting voltage for methanol was found 2.5 kV theoretically and 2.2 kV experimentally. This 12% difference can be attributed to experimental uncertainty. Electro spray views in Figure 3 proves that the experimental system works properly and concludes the proof-of-concept demonstration of an electro spray injection system. Prospective studies shall focus on the manufacturing of dense electro spray emitter arrays. This experimental setup will be used and a similar set of experiments shall be performed for a compact multiplexed electro spray array manufactured with MEMS technology.

Flow rate from a single emitter is on the order of 2 ml/h. This barely corresponds to 17 W of thermal power for a typical liquid hydrocarbon fuel. Typical energy conversion efficiencies of thermoelectric generators are about 4% with the current state of the art. This would correspond to 0.67 W of electric power from a single emitter. For a 100 W electric power output, one would need about 150 emitters. Therefore it is imperative to use a multiplexed array of fuel emitters. Manufacture of high density nozzle arrays is possible with the utilization of MEMS technology. Ongoing efforts at the ITU-MEMS laboratory aims at manufacturing electro spray emitter arrays at a density of 1000 nozzle/cm<sup>2</sup>. This suggests that for one centimeter square area of the emitter array 17 kW of thermal power can be generated. This thermal power can then be converted to electric power via a thermoelectric energy conversion system.

### ACKNOWLEDGEMENT

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### NOMENCLATURE

- d Distance between tip of capillary and ground electrode [m]
- Q Volumetric flow rate [m<sup>3</sup>/s]
- K Conductivity [S/m]
- r<sub>t</sub> Radius at the tip of a hyperboloid needle [m]
- V Voltage [V]
- V<sub>oc</sub> Electro spray starting voltage [V]

### Greek Letters

- γ Surface tension [N/m]
- ε Dielectric constant
- ε<sub>o</sub> Permittivity of the free space [C<sup>2</sup>/Nm<sup>2</sup>]
- ρ Density [kg/m<sup>3</sup>]

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# DESIGN AND IMPLEMENTATION OF HARDWARE SYSTEM FOR DIGITAL IMAGE ENHANCEMENT BASED ON ATMEGA32 MICROCONTROLLER

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## ABSTRACT

In this paper a hardware system based on ATmega32 microcontroller has been designed and implemented to enhance edges and fine details of the digital images. Digital camera is connected to the ATmega32 microcontroller through an electronic system which provides serial communication between the camera and ATmega32 microcontroller. The latter is the host of the spatial filters algorithms that are used for the digital image processing. The developed hardware/software system has the ability to perform edge detection enhancement of the digital image by using sharpening spatial filters that are designed to detect and enhance the edge of the digital image. The developed system can enhance details that have been blurred in the noisy digital image. All the algorithms of the digital filters have been implemented using assembly language of ATmega32 microcontroller. The practical results were excellent and the system was able to detect the edges and enhance fine details of the digital image perfectly.

Keywords: ATmega32 microcontroller, Digital images, sharpening spatial filters.

## ATMEGA32 MICROCONTROLLER SYSTEM

A Microcontroller is a programmable digital processor with necessary peripherals. It can be thought of a microprocessor with inbuilt memory and peripherals. A microcontroller does not require much additional interfacing for operation and it functions as a standalone system. The microcontroller is used for multipurpose operations and its operation is controlled by a user written program interacting with the fixed hardware architecture resident within the microcontroller [2].

In this paper Atmel ATmega32 microcontroller is used for edge enhancement in the digital image. ATmega32 is register based architecture. It is equipped with 131 RISC type instructions most can be executed in a single clock cycle [1]. The ATmega32 is also equipped with additional hardware to allow for the multiplication operation in two clock cycles. Also ATmega32 is equipped with 32 general purpose 8-bit registers that are tightly coupled to the processor's arithmetic logic unit within the CPU. The processor is designed following the Harvard Architecture format. That is, it is equipped with separate, dedicated memories and buses for program and data information. The register based Harvard Architecture coupled with the RISC based instruction set allows for fast and efficient program execution and allows the processor to complete an assembly language instruction every clock cycle which makes it fast and suitable for the real time applications. ATmega32 is equipped with four 8-bit digital I/O ports which are used to interact with the external world. Each port has set of registers associated with it. Port pins are usually configured at the beginning of a program using the set of associated registers for either input or output, and their initial values are then set. These ports may be used as general purpose digital input/output (I/O) ports or they may be used for the alternate functions. The ports are interconnected with the ATmega32's CPU and internal subsystems via an internal bus. ATmega32 is equipped with three main memory sections which are 32Kbyte flash electrically erasable programmable read only memory (EEPROM), 1 Kbyte static random access memory (SRAM) and, 512 byte addressable EEPROM for data storage. Bulk programmable flash EEPROM is used to store programs. It can be erased and programmed as a single unit; it is in-system programmable. Flash EEPROM is nonvolatile and ATmega32 is equipped with 32K bytes of onboard reprogrammable flash memory [1].

There are different serial communication subsystems which are used by ATmega32 to communicate with the external systems; the most important one which is used in this paper is the Universal Synchronous and Asynchronous Serial Receiver and Transmitter (USART). It is used for full duplex communication between a receiver and transmitter. This is accomplished by equipping the ATmega16 with independent hardware for the transmitter and receiver. The USART is typically used for asynchronous communication. That is, there is not a common clock between the transmitter and receiver to keep them synchronized with one another. To maintain synchronization between the transmitter and receiver, framing start and stop bits are used at the beginning and end of each data byte in a transmission sequence. The ATmega16 USART is quite flexible. It has the capability to be set to a variety of Baud rates.

The hardware have been used in this work consists of the STK500 interface board. STK500 can actually be used with any of the microprocessors in the AVR family [2, 4]. STK500 interface the mounted microcontroller to different ports or headers that access to I/O (input and output) ports, two serial port connectors (one for programming the devices and one as a serial communication RS232 port), a power supply switch and connector, eight LEDs and eight switches for general use, and various jumpers for configuring the board. Figure (1) shows a top view of the STK500 interface board and the basic location of different components.

The final preparations for the STK500 boards are to check the default jumper settings and to connect the 6pin ISP ribbon cable for remote programming of the ATmega32. Typically, when the pins are connected, the jumper is considered to be in the ON

position. When setting a jumper in the OFF position, place the jumper on only one of the two pins. The jumper for OSCSEL is set so that it connects the two right most pins of the three. Thus set, it selects the on-board clock signal. ISP programming mode was used for communicating with and downloading programs to the ATmega32 microcontroller. As a result, the 6pin ISP ribbon cable from the ISP6PIN header on the STK500 should be connected to the 6pin header outlined in red above it as shown in Figure (2).

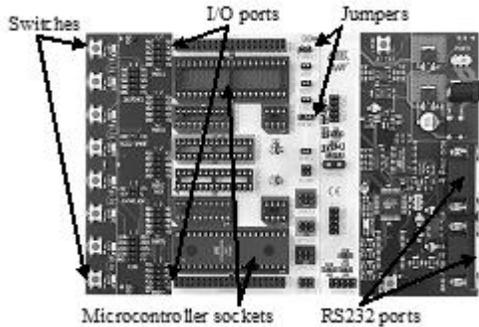


Figure (1): STK500 interface board

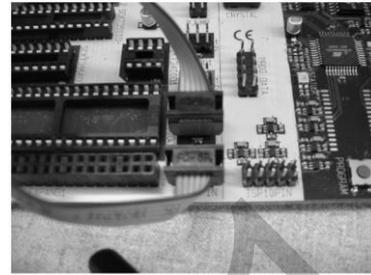


Figure (2): 6 pin ISP ribbon cable

**SPATIAL FILTER DESIGN AND IMPLEMENTAION**

Digital image processing is a subset of the electronic domain wherein the image is converted to an array of small integers, called pixels, representing a physical quantity such as scene radiance, stored in a digital memory, and processed by computer or other digital hardware such as microcontroller system as it was done in this work. The goal is to design, implement and then practical test of a spatial digital filter based on ATmega32 microcontroller that is used to sharp a soft digital image so that the fine details of the image appears better than that in the original image. Furthermore, digital image processing allows the use of much more complex algorithms for image processing, and hence can offer both more sophisticated performance at simple tasks, and the implementation of methods which would be impossible to be implemented by analog means [5, 6].

The main objective of the digital image sharpening filters is to shed light on sharpening the details in the image or to enhance the fine details to be clearer, whether in error or a natural result of the impact on the way of access to certain images. The sharpening can be achieved by spatial differentiation [3]. The clarity of the digital image in the spatial is scale of the average of pixels in the neighborhood. With an average similar to the merger, it is logical to conclude that the sharpening can be achieved by spatial differentiation. At the beginning and end of break (break step and ramp), and along the gray level ramps. These types of noise can be break points, lines and edges. Differentiation measures the rate of change of a function. A basic definition of the first order derivative of a one dimensional function f(x) is the difference. The formulas for the first and second derivatives of a function are given in equations (1) and (2) below.

$$\frac{\partial f(x)}{\partial x} = f(x + 1) - f(x) \dots \dots \dots (1)$$

$$\frac{\partial^2 f(x)}{\partial^2 x} = f(x + 1) + f(x - 1) - 2f(x) \dots \dots \dots (2)$$

A first derivative must be zero in flat segments (areas of constant gray level values); while the value of the derivative must be nonzero at the onset of a gray level step or ramp; and must be nonzero along ramps. It is just the difference between subsequent values and measures the rate of change of the function. It can be proved that first order derivative is nonzero along the entire ramp, while the second order derivative is nonzero only at the onset and end of the ramp in the digital image. Simply first derivative depends on the present and next value while the second derivative takes into account the values both before and after the current value. Thus second derivative is more useful for image enhancement than the first derivative because it has stronger response to fine detail than the first order derivative.

Laplacian operator is a second derivative method of enhancement. It is particularly good at finding the fine details in a digital image. Any feature with a sharp discontinuity like noise (unfortunately) will be enhanced by a Laplacian operator. Thus, one application of a Laplacian operator is to restore fine detail to an image which has been smoothed to remove noise such as output of the averaging filter that is used to remove the salt and pepper noise. The Laplacian is defined as shown in equation (3) below [3].

$$\nabla^2 f(x, y) = \frac{\partial^2 f(x, y)}{\partial^2 x} + \frac{\partial^2 f(x, y)}{\partial^2 y} \dots \dots \dots (3)$$

Where the partial first order derivative in the x and y directions are defined as shown in equations (4) and (5):

$$\frac{\partial^2 f(x, y)}{\partial^2 x} = f(x + 1, y) + f(x - 1, y) - 2f(x, y) \dots \dots \dots (4)$$

$$\frac{\partial^2 f(x,y)}{\partial^2 y} = f(x,y + 1) + f(x,y - 1) - 2f(x,y) \dots \dots \dots (5)$$

$$\therefore \nabla^2 f(x,y) = f(x + 1,y) + f(x - 1,y) + f(x,y + 1) + f(x,y - 1) - 4f(x,y) \dots \dots \dots (6)$$

A filter is a mathematical transformation (called a convolution product which will be performed in this work by ATmega32 microcontroller) which allows the value of a pixel to be modified according to the values of neighbouring pixels, with coefficients, for each pixel of the region to which it is applied. The filter is represented by a matrix which is characterized by its dimensions and its coefficients, whose centre corresponds to the pixel concerned. The matrix coefficients determine the properties of the filter. The matrix in Table (1) represents the 3×3 Laplacian filter given in equation (6).

**Table (1): Laplacian mask implementation of eq. (6)**

0	1	0
1	-4	1
0	1	0

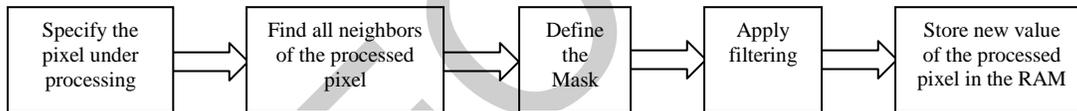
**Table (2): Laplacian filter implementation of eq (7)**

0	-1	0
-1	5	-1
0	-1	0

The entire enhancement of the digital image can be combined into a single filtering operation that is given in equation (7) below. Where g(x,y) is the new value of the gray level of the image pixel under processing.

$$g(x,y) = f(x,y) - \nabla^2 f = 5f(x,y) - [f(x + 1,y) + f(x - 1,y) + f(x,y + 1) + f(x,y - 1)] \dots \dots \dots (7)$$

Equation (7) has been implemented using ATmega32 microcontroller and it is used for edge enhancement in the digital image. The processing steps are shown in Figure (3). The gray level of the pixel under processing and its eight neighbours are defined, also the mask of the digital filter should be defined. The next step is filtering the digital image by using the pixel's gray level, its neighbours' gray levels and filters mask. The filtering is done by ATmega32 microcontroller which performs convolution product between the mask of the filter from the first side and the processed pixel with its neighbours from the second side. The new value of the gray level of the processed pixel is computed and stored in the RAM of the ATmega32 microcontroller. Then new pixel is fetched and the process continue to the last pixel in the image.



**Figure (3): Block diagram of computation the new (enhanced) gray level of the pixel under processing**

**RESULTS AND DISCUSSION**

The filter that is given in equation (7) is used to enhance the edges of the digital images. The coefficients of the filter which are given in table (2) are stored in the flash EPROM of the ATmega32 microcontroller. The input digital image that will be processed is supplied to the ATmega32 microcontroller through the serial port of the STK500 board from digital camera or from data file. The algorithm and program that is used to filter the digital image is stored in the flash EPROM of the ATmega32 microcontroller.

Several images are used to test the performance and ability of the filter in edge enhancement and clarity of the fine details in the digital image. The practical results show that filter performance is good in edge detection and clarity of the fine details of the digital image. The specifications on a histogram mapping pixels turning point in the form of a contribution in the processing so that the distribution has the same pixel values in some reference image. Histogram specification useful step prior to analysis aimed to compare the kind of input and reference.

Figures (4) to (6) show three digital images with the enhanced images and the histogram for both original and enhanced images. It is clear that fine details and edges of the enhanced image become better than that in the original image. In the three examples the histogram of the original image shows that the gray level of the pixels covers a narrow range compared with it in the enhanced image. The range of gray level of the first original image covers the range from 0 to 55, that means the gray levels of all pixels in the original lie between these two values and hence the edges in the image are not clear since there is no big change in the gray levels of the edges. Also there is not any gap between two adjacent gray levels in the histogram which means that there is no sharp edge in the image since there is no big change in the gray levels in the original image. The histogram of the enhance image spreads the range of the gray level to fill most of the available (possible) range of it (i.e. from 0 to 255). Now since there is big change in the gray level of the pixel then the edge and fine details in the enhanced image becomes clearer than the original image.

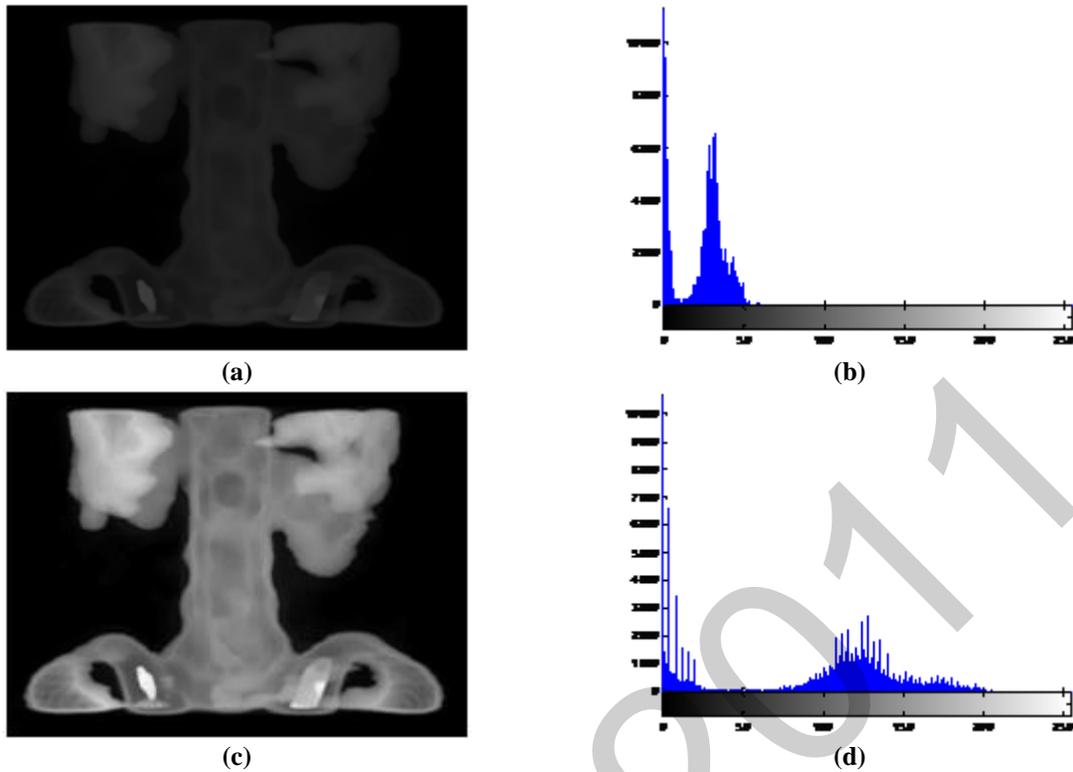


Figure (4): Edge and fine details Enhancement of medical digital image. (a) Original image, (b) Histogram of the original image, (c) Enhanced image, and (d) Histogram of the enhanced image.

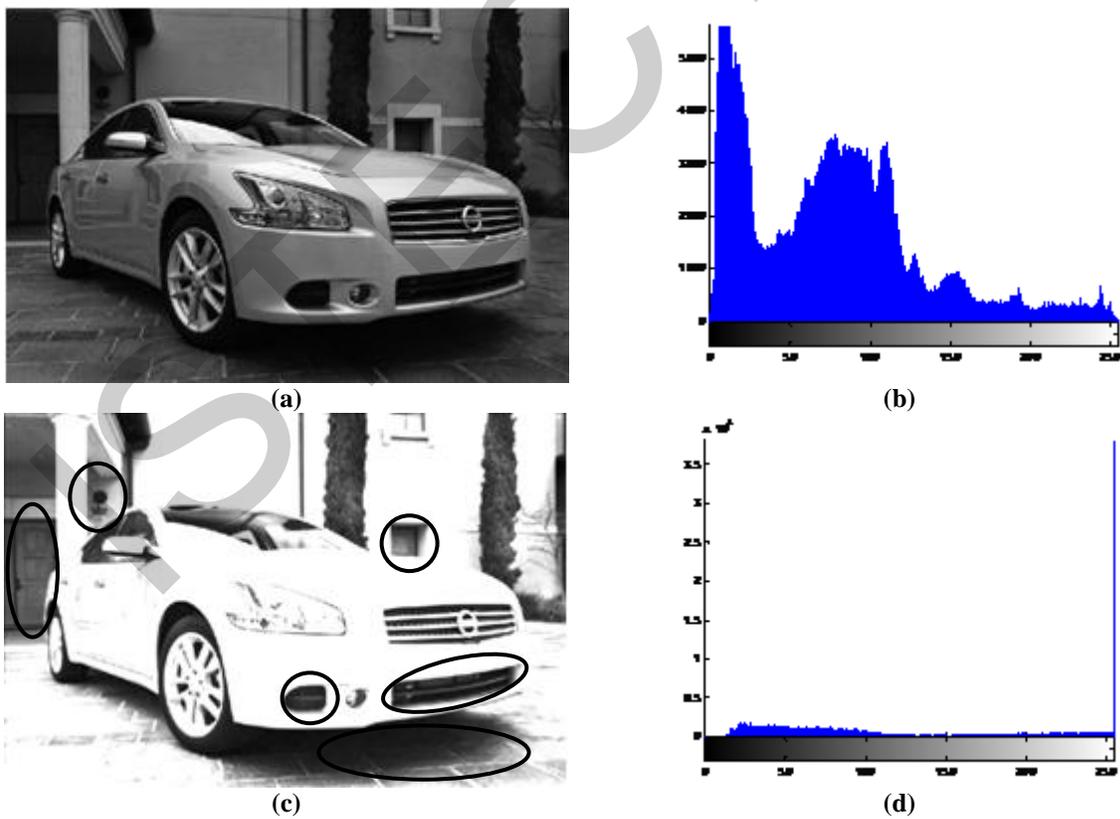
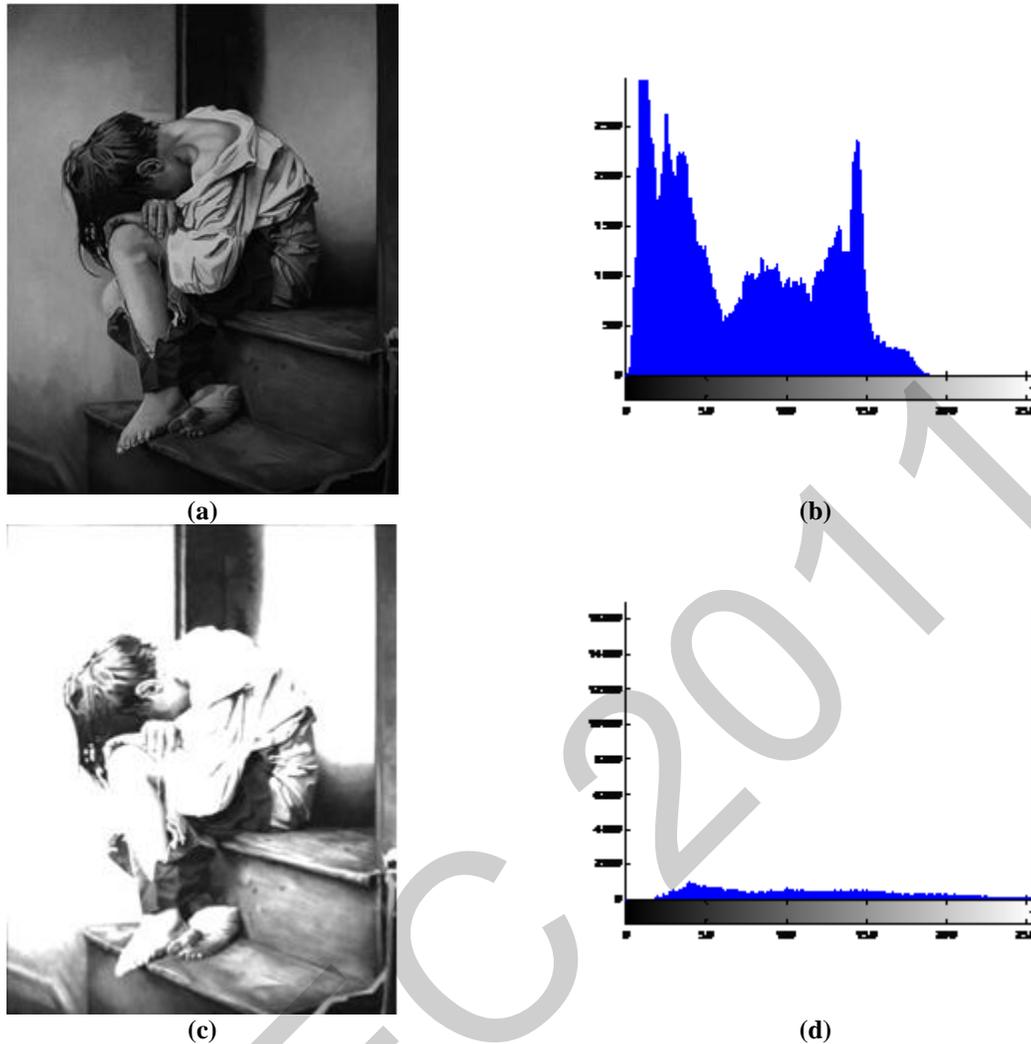


Figure (4): Edge and fine details Enhancement of digital image from digital camera. (a) Original image, (b) Histogram of the original image, (c) Enhanced image, and (d) Histogram of the enhanced image.



**Figure (6): Edge and fine details Enhancement of scanned digital image. (a) Original image, (b) Histogram of the original image, (c) Enhanced image, and (d) Histogram of the enhanced image.**

### CONCLUSIONS

It can be concluded that in most applications the second derivative is better suited than the first derivative for image enhancement because of the ability of the former to enhance fine detail. As Laplacian is a derivative operator, it has the good effects on the following features of the digital images:

- ✓ It highlights gray level discontinuities in the digital image.
- ✓ It deemphasizes regions with slowly varying gray levels.
- ✓ Background features be 'recovered'.
- ✓ Preserving the sharpening effect.

But it should be taken in the consideration that any feature with a sharp discontinuity like pepper and salt noise in the digital image can be enhanced by a Laplacian spatial filter. Thus, the proposed Laplacian filter should be used after smoothing filter which is used to remove the noise from the digital image but it decreases the sharpness of the image, then in the next stage the Laplacian filter enhances the sharpness of the digital image again.

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# DETERMINATION OF THE BOTTLENECKS OF A COMPANY THROUGH THEORY OF CONSTRAINTS AND SUPPLY CHAIN

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## ABSTRACT

In recent years it is seen that companies are adopting various management strategies in order to provide the firm's permanence. One of the best known of these strategies is Theory of Constraints (TOC). In fact there is not much innovation but it is reminded that the firms first aim is making money. The first thing to be considered is the bottlenecks of the company. Supply Chain Management (SCM) is the process of planning, implementing, and controlling the operations of the supply chain with the purpose to satisfy customer requirements as efficiently as possible. In both of the approaches it is assumed that the strength of the chain is determined by the weakest ring. In this study, the problems of a firm taking place in retail industry through supply chain is dealt with TOC and solution requests are presented.

**Keywords:** Theory of Constraints, Supply Chain Management, Inventory Management.

## 1. INTRODUCTION

Competitive marketplace forces the firms to renew oneself continuously. In the past, firms usually focused on reducing the cost, for this reason they used some methods. But this is not the real aim; in fact, all business' goal is to make money. So they have to do their useful activities. Some methods and strategies are improved for the real aim. One of the best known of these strategies is Theory of Constraints (TOC). SCM is a kind of management philosophy. SCM consider whole supply chain and focuses weakest ring in the chain. There is similarity in TOC and SCM as philosophy.

### 1.1. Theory of Constrains

TOC is a set of policies and practices originally developed in the early 1980's to manage factories (Goldratt, 1984). Eliyahu M. Goldratt wrote a book name of "The Goal: A Process of Ongoing Improvement", tells the main objectives of TOC. In this theory the first thing to be considered is the bottlenecks of the company. There are three measurements to define the success of firms' production. These are throughout, inventory and operational expense. The first measurement, throughout, would consist of what a product would be worth when sold at market value after deducting operational expense and inventory. Inventory could include the remains of their machines after being used toward the investment. Operational expense would include such items as depreciation of a machine, lubricating oil, scraps, etc (Goldratt, 1984). The objective of TOC is to increase throughout while decreasing inventory and operational expense. An other definition of TOC by Constraints Management Group; Theory of Constraints is a process to identify, exploit and manage a system through its leverage points and their interactions. Basic TOC processes are defined by [www.toc.co.uk](http://www.toc.co.uk) ; in first step identify the weak link or constraints of the system, secondly decide how to exploit the weak link or constraint of the system; tertiary subordinate everything else to the decision made in second step; fourth elevate the systems constraints; fifth if in previous step a constraint has been broken going back to the first step.

### 1.2. Supply Chain Management

There are many description of supply chain management in the literature. For example, Harland (1996) describes supply chain management as managing business activities and relationships (1) internally within an organization, (2) with immediate suppliers, (3) with first and second-tier suppliers and customers along the supply chain, and (4) with the entire supply chain (Tan, 2001). Figure 1 shows general structure of SCM.

Supply Chain Management's success is bounded to information and communication between supply chain rings; required information is right place and right time. To minimize information costs firms use technology. Information technologies provide reducing information cost, time and increasing truth. For this reason is an important key of SCM success.

Inventory is an important element in supply chain management as in Theory of Constraints. Because inventory cost is located a great area in general costs. Firms have to reduce this cost but simultaneously have enough inventory quantity. At this point there is a dilemma. In the applying this dilemma is considered in TOC and SCM.

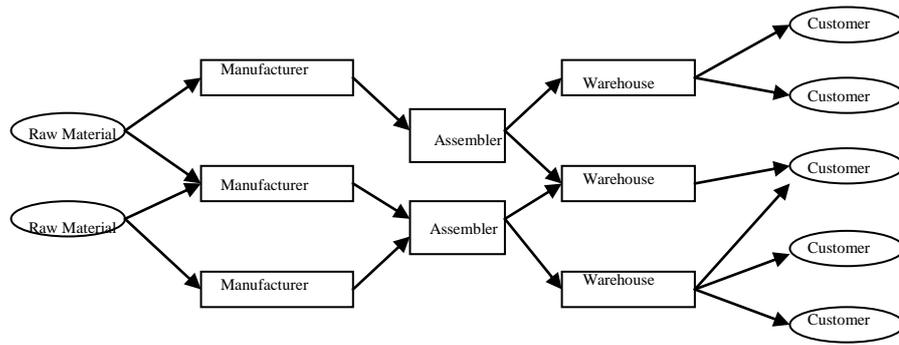


Figure 1. Structure of SCM  
(Thomas, Griffin 1996)

## 2. FIRM IDENTIFICATION

The firm is in Lüleburgaz and is takes place in retail selling sector. The store, which is on the most running street of Lüleburgaz called Istanbul Street, has 450 m2 entrance floor, 250 m2 mezzanine and a basement floor. If we look to population profile of Lüleburgaz totally 80.000 inhabitants live here and there are 20.00 families and 10.000 students in this population. This firm has approximately 10 staff (20 at special days) and sells around 3.000 different items.

### 2.1. Firm Serves in these following Departments

Table 1. Firm serves

Departments
Stationary
Gift Shop
Toy
Ironmonery
Home Appliances
Small Electrical Home Appliances
Cosmetics
Apparel

### 2.2. Purchase

The firm is permanently in relation with 30 suppliers because of serving 8 different departments. In some seasons especially in special days (Valentine day, Mother's day, Stationary Season) the firm is additionally in relation with 20 suppliers.

### 2.3. Competitors

The firm is in competition with two main competitors. Besides, it has 50 competitors in department level. Additionally the pressure of supermarkets is easily realized increasingly day by day. Lastly Lüleburgaz's closeness to city centers, especially to Istanbul, is an important disadvantage.

### 2.4. Supply types

The firm generally purchase from Istanbul Tahtakale and ISTOÇ markets.

Wholesaler  
Main wholesaler  
Main importer and distributor  
Main manufacturer

Goods are purchased from wholesaler by numbers, from main wholesaler by dozens and from main importers and distributors by gross.

### 2.5. Purchase Policy

The firm makes purchasing with its own vehicles in terms of 20 days. The budget which assigned for one term is 50.000 TL and department budgets are given in the following table.

Table 2.

FOR NORMAL SEASON

UNIT	ASSIGNED BUDGET	APP. PROFIT
Stationary	4 000	% 20
Gift Shop	8 000	% 30
Toy	5 500	% 30
Ironmongery	6 000	% 15
Home Appliances	10 000	% 15
S. Elect. Home Appliances	5 000	% 20
Cosmetics	7 500	% 20
Apparel	4 000	% 20

**3. ANALYSIS OF FIRM WITH TOC**

Firm was analyzed with TOC. Principles as below.

**3.1. Undesired Situations**

The firm’s outstanding basic problems are listed below.

1. Payments increase day by day.
2. Revenue decreases.
3. Demands can’t be answered properly. (Deficient inventory)
4. Deficient production variety.
5. Competition conditions get harder.
6. Productions are sold with high benefits but insufficient incomes.
7. In specific terms (special days) shop brims with customers.
8. Due to nonexistence of some main products in some terms other products’ sales decrease.
9. Firm needs more staff in special terms.

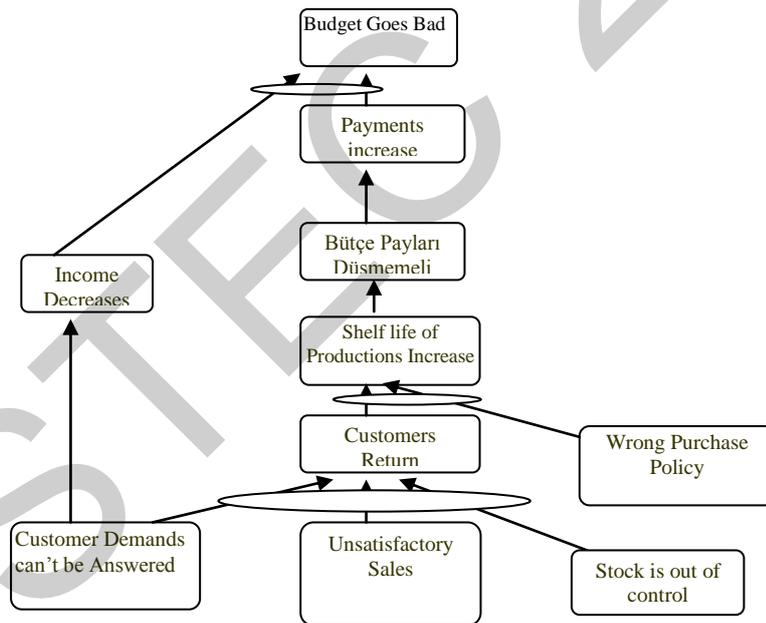


Figure 2.

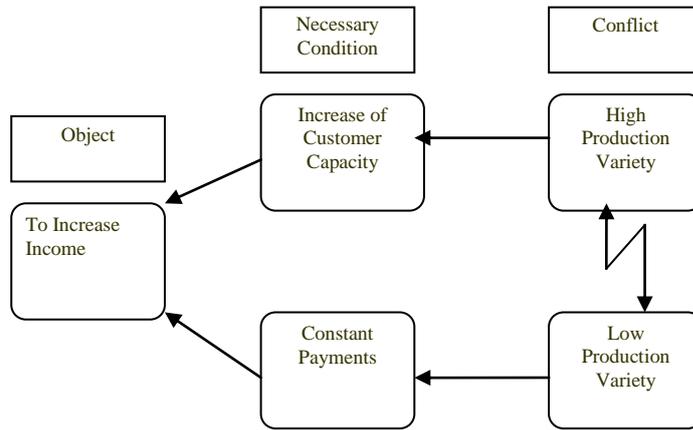


Figure 3.

**3.2. Problem Recognition**

The firm is a family firm, which has two partners and it can't be said they have professional management mentality. The firm doesn't use any software for inventory and storage management. Due to nonexistence of inventory files, demand predictions are made with experience. It is recognized that some products have been waiting on shelves for one year. It is known some products have positive effect for sales of other products but the relation of product groups cannot be recognized actually. Especially the lack of staff in cosmetic rayon affects rayon sales in bad way. There is a serious decrease in profits of firm and they try to decrease cost by making big purchases. Although purchasing large amounts it can be seen customer returns and required goods doesn't exist in stocks. Effect of competition and increased payments begin to be threats for company.

**3.3. Problem Diagnosis**

Source of problems, which is seen in firm is deficiency of professional management mentality and deficiency of inventory management software. Finally depending all on these factors, it is understood that wrong inventory kept in firm is the main problem.

**3.4. Application for Two Products**

Comparison made between hair paint and porcelain doll in following tables.

Table 3.

For Doll			
	Unit Cost	Unit	Sale Price
Wholesaler	10 TL	1	15 TL
Main Wholesaler	9 TL	12	15 TL
Main Importer	7,5 TL	144	15 TL

Table 4.

For Doll			
	Unit Cost	Unit	Sale Price
Wholesaler	10 TL	1	15 TL
Main Wholesaler	9 TL	12	15 TL
Main Importer	7,5 TL	144	15 TL

Table 5

Unit Profits		
	Doll	Hair Paint
Wholesaler	5	2,65
Main Wholesaler	6	
Main Importer	7,5	

**3.5. Demands for Two Products**

Demands for two products known with experience of stuff

Table 6

Doll	Hair Paint
1 unit in 2 days	10 unit in a day.

3.6. Profits

Table 7

Unit Profit			Day based Profit		
	Doll	Hair Paint		Doll	Hair Paint
Wholesaler	5	2,65	Wholesaler	2,5	26,5
Main Wholesaler	6		Main	3	
Main Importer	7,5		Main Importer	3,75	

Unit profits and daily profits compared for products above. In the following table its analyzed periodic sales relation of two products. In table 8 comparison made cost-based and in table 9 comparisons made sale cycle time-based.

Table 8

Product	Cost	Unit	Cycle Time	Cycle Day	Profit
Doll	1080 TL	144	1	288	1080 TL
H.Paint	1080 TL	216	1	21,6	572,4 TL

Table 9

Product	Cycle day	Cycle Time	Unit	Profit for a	Profit for a	Season
Doll	288	1	1080	1080 TL	100%	100%
H.Paint	288	13,33	2880	7630,1 TL	53%	706%

3.7. Stock Cost Relation

Table 10

	Season	Purchase Season	0-20	21-40	Mid Season	260-280	280-288
Purchase of 114 Dolls by Wholesale	Income	☐	150	150	☐	150	60
	Profit	☐	75	75	☐	75	30
	Cost	☐	75	75	☐	75	30
	First Investment	1080	1005	930	☐	30	0
	Total Profit	☐	75	150	☐	1050	1080
Purchase of Hair Paint	Income	☐	1530	1530	☐	1530	612
	Profit	☐	530	530	☐	530	212
	Cost	☐	1000	1000	☐	1000	400
	First Investment	1000	0	0	☐	0	0
	Total Profit	☐	530	1060	☐	7420	7932
Purchase of Dolls By unit	Income	☐	150	150	☐	150	60
	Profit	☐	50	50	☐	50	20
	Cost	☐	100	100	☐	100	40
	First Investment	100	0	0	☐	0	0
	Total Profit	☐	50	100	☐	700	720

Firms actual status can be seen on table 3. For increase of decreased profit, firm makes purchases by wholesales to decrease costs but calculations gave us different results. Wholesales were not useful for cash flow. As a result it's seen that unnecessary stock is too high.

4. RESULTS/RECOMMENDATIONS

It is understood that the firm's problem is the wrong management of stock levels. In order to increase profits the costs were decreased by increasing the amount of purchase. However the purchases have never contributed to the cash flow. Because of the cost of wrong stock level, the budget dedicated to other goods was decreased. So the product variety is reduced and for this reason some of the customers were returned. In addition the number of products sold in relation is reduced and customer dissatisfaction is occurred.

In order to increase the product variety the amount of buying is increased. But these buyings didn't reflect to the endorsement. For this reason the stock levels depts. And payments are increasing, but profits are decreasing gradually.

The wrong strategies affected the firm severely. In order to obtain inventory management, effective software is recommended. So the firm will be able to reach detailed sale information and make effective demand estimation. The firm will be able to find out which product is more profitable, as a result the firm will be able to use resources more efficiently.

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# DEVELOPMENT AND VALIDATION OF AN HPLC METHOD CHROMATOGRAPHIC ALTERNATIVE FOR QUANTIFICATION OF TRANS- RESVERATROL IN WINE

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## ABSTRACT

Resveratrol is a phytoalexin that presents mostly in grapes (*Vitis vinifera* L.) and their products. Its use is very important in the prevention of disease, maintenance of health and for incorporation with dermocosmetics. Therefore, its quantification in red wines is of interest and should be followed to the standards set by ANVISA for validation of analytical methods. The aim of this work was to propose and validate an alternative chromatographic method for the quantification of trans-resveratrol in red wines. The proposed method proved to be linear, exact, specific, precise and robust in the variation of column temperature to +5°C.

Keywords: resveratrol, validation, method, HPLC.

## INTRODUCTION

Resveratrol (3,5,4'-trihydroxytransstilbene) is present in approximately 72 plant species (distributed in 31 genera and 12 families), and is the most important dietary source of grapes (*Vitis vinifera* L.) and their products. Its synthesis occurs mainly in the skin of the fruit and is a biologically active secondary metabolite, found in both cis and trans forms with both isomers present in wines in varying quantities, especially in red wine (Delgado, González, Trujillo, & Montelongo, 2002; Fan, Zhang, Jiang, Yan, & Bai, 2008; Sautter *et al.*, 2005). Studies have shown that this molecule presents anti-inflammatory, chemopreventive and chemotherapeutic activity in the prevention of cardiovascular disease, and in the oxidation of LDL *in vivo*. As a result, interest has grown in accurately calculating the amount of resveratrol found in red wines and therefore it is important that the optimum method employed for its quantification be ascertained and validated in order to produce reliable results. (Fremont, 2000; Sautter, *et al.*, 2005; Souto *et al.*, 2001). The objective of this study was to propose and validate an alternative HPLC chromatographic method for the quantification of *trans*-resveratrol in red wine.

## METHODOLOGY

The equipment and material used were: Agilent© HP liquid chromatograph, reverse phase column C18, manual injection loop of 20 µL, standard *trans*-resveratrol, glacial acetic acid and HPLC grade methanol, purified water, Minisart® (Sartorius) membrane filter of 0.45 µm and Chemstation® data acquisition system. Samples: 3 red wines were obtained from a small-scale producer local to the Taquari valley region, Rio Grande do Sul, Brazil.

The proposed new method for the quantification of *trans*-resveratrol in red wine was made in the mobile phase by replacement of the solvent acetonitrile, frequently used for this analysis, but one that has been missing from the world market for a few months. Methanol was used as the replacement solvent, based on the proximity of their physiochemical properties for HPLC (density, viscosity and solubility). Three locally produced red wines were quantified and the one with the highest *trans*-resveratrol content was selected for validation. A number of parameters were evaluated using a mobile phase containing methanol and a water with pH adjusted with HPLC grade glacial acetic acid 3; varying the flow, proportion and method of gradient and isocratic elution, and column temperature, as shown in Table 1. The chromatographic condition was then selected in which the pressure of the pre-column and column remained low, the peak of *trans*-resveratrol presented a better resolution when compared to the other compounds present in the sample, and with the lower retention time.

**Table 1.** Parameters analysed to determine the best chromatographic condition.

Test	Mobile Phase (metOH:H <sub>2</sub> O)	Mobile Phase Flow	Column Temperature
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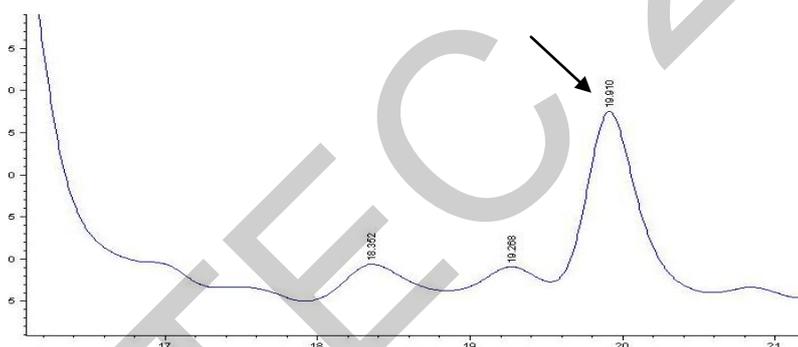
1	Gradient	1.0 mL/min	35 °C
2	17:83	1.0 mL/min	35 °C
3	25:75	1.0 mL/min	35 °C
4	30:70	1.0 mL/min	35 °C
5	30:70	0.5 mL/min	30 °C
6	45:55	0.5 mL/min	30 °C
7	45:55	0.4 mL/min	25 °C

Validation proceeded after establishment of method no. 7. Validation is the process of evaluating the efficiency of an analytical method in the routine of a laboratory, making sure that it meets the necessary requirements of both its analytical application and the experimental study, ensuring the reliability of the obtained results. The validation procedure for this study followed the guidelines set out by the regulatory agencies ANVISA, INMETRO and ICH. (Brasil, 2003.; European Union, *et al.*, 2005; INMETRO, 2007).

The parameters covered were: linearity (linear correlation of 8 points), identification (injections in triplicate with three samples (A, B and C)), precision (repeatability: same operator, same chromatographic conditions and same day), intermediate precision (two analysts in three days of analysis), detection and quantification limits ( $LOD=3.3 \times \sigma / S$ ,  $LOQ=10 \times \sigma / S$ ), robustness (column temperature: 20 °C and 30 °C. pH of mobile phase: 2.8 and 3.2, methanol mobile phase composition: acidic water: 40:60 and 50:50), and mobile phase flow variation (0.3mL/min and 0.5mL/min). The test results underwent statistical analysis by ANOVA and Tukey's test.

## RESULTS

The method chosen was no. 7 (Table 2) as it showed good separation and resolution of the *trans*-resveratrol peak (Figure 1). The defined method was then subjected to validation.



**Figure 1.** Chromatogram of *trans*-resveratrol using the developed method.

The first validation test performed was linearity for which the results showed linearity in the three samples tested (Table 2).

**Table 2.** Linear correlation ( $R^2$ ) and concentration of *trans*-resveratrol for the Wine samples A, B and C.

Sample	Linear Correlation ( $R^2$ )
Wine A	0.9991
Wine B	0.9993
Wine C	0.9992

The identification test showed significant differences in mean levels between samples: A (0.269ppm), B (0.570ppm), C (0.175ppm).

The precision was evaluated by analysis of the repeatability through seven injections of the sample, all made by the same operator, on the same day and under the same chromatographic conditions. A mean sample concentration of 0.560ppm of *trans*-resveratrol was obtained with a standard deviation of 0.01 and variation coefficient (VC) of 2.21%. The results showed compliance of a VC% of up to 5.0%, within the parameters established by ANVISA.

Intermediate precision was determined by two different analysts on three different days, giving satisfactory results when individually analysed and when compared between the two analysts, where the mean concentration was 0.587ppm of *trans*-resveratrol with a standard deviation of 0.027 and variation coefficient (VC%) of 4.53%. These results fall within the requirements set by ANVISA, where the VC% should not exceed 15.0%.

The limits of detection and quantification (LOD & LOQ) determined mathematically through the relationship between the standard deviation of whites and the slope of the calibration curve were 0.088ppm and 0.267ppm, respectively, conforming to those cited by ICH standards.

In relation to the test for robustness, the method presented statistically significant differences, namely, it did not support the variation in the pH of the mobile phase ( $\pm 0.2$  units), column temperature ( $\pm 5$  °C), mobile phase flow ( $\pm 0.1$  mL/min), and proportion of mobile phase ( $\pm 5\%$  methanol). By applying Tukey's test it can be seen that the method was able to withstand an increase of 5 °C in the column temperature in relation to the standard temperature of 25 °C.

## CONCLUSION

The method developed and validated proved to be linear, specific and able to identify differences in levels of *trans*-resveratrol between distinct samples at different concentrations, and was accurate and robust regarding the variation of column temperature of + 5 °C. The method was not seen to support variations in relation to standard chromatographic conditions of: 0.1mL/min in the mobile phase flow, 5% methanol in the mobile phase composition, 0.2 units in the pH of the mobile phase, and 5 °C less in the column temperature. The working chromatographic conditions for the quantification of *trans*-resveratrol in wine can be defined from this data, resulting in reliable and reproducible results.

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## DISCRIMINATING A BOBBIN AND A CONE BY YARN PROPERTIES

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### ABSTRACT

Yarns are wrapped in two different forms, bobbins and cones. This is a visual difference, but we can now discriminate these two by mathematical and statistical methods. The same method in discriminating fabrics of different fibers by using primary hand values is applied to yarn in bobbin and cone form. The advantage of this method is that we can eliminate some measurements and instruments in production and work with more efficiency and less cost and save time. This method can be improved by applying it to other areas of textile productions and even to other production types.

**Keywords :** Discriminant Analysis, Bobbin, Cone, Formulation, Yarn Properties

### Introduction

Textile surfaces are called fabrics which skirts, pants, jackets are made up of. Fabrics are done mainly in three ways, weaving, knitting, and nonwoven. Woven and knit fabrics are made up of yarns, and yarns are made up of fibers, nonwoven fabrics from fibers directly. Fibers which are the main building blocks of yarns are either natural or man-made. Natural fibers are in staple form and man-made fibers are in filament form, then converted to staple form to enable blending with naturals.

Yarns are mostly produced in ring spinning machines and wrapped in bobbins. These bobbins are then wrapped into cones, the main two reasons being cleaning the yarn and putting it into a bigger volume (Fig. 1). A bobbin and a cone are visually two different forms of packaging, but now we can discriminate these two by mathematical and statistical methods according to yarn properties.

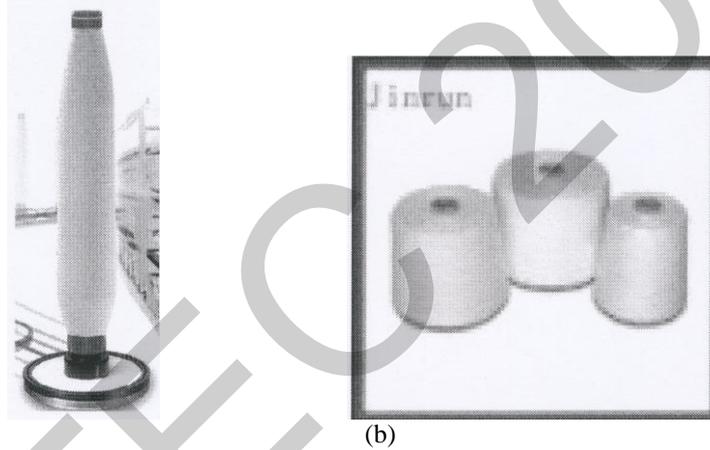


Figure 1 : Yarn in (a) bobbin form and (b) cone form.

Yarn properties is a wide subject. We can define the yarn by its count, the thickness, and its twist, the turns per unit length. But there are many other properties of yarn that are measured such as breaking strength, breaking elongation, work to break, irregularity, imperfections, hairiness, abrasion, moisture, oil content, etc. In our research, we used yarn properties to discriminate between a bobbin and a cone.

### Preliminary Work

Hand evaluation and standardisation of fabrics was first done by Kawabata in 1980 [3]. Besides the mentioned work, there was another interesting work done there. They discriminated the cotton and silk fabrics (Fig. 2), and cotton, silk and polyester fabrics (Fig. 3) by discriminant analysis by using primary hand values of fabrics. Even the fibers which are the main building blocks in those fabrics are visually different, they could determine the difference mathematically and statistically. So the same idea is applied to discriminate a bobbin and a cone by using yarn properties and it worked perfectly well [1].

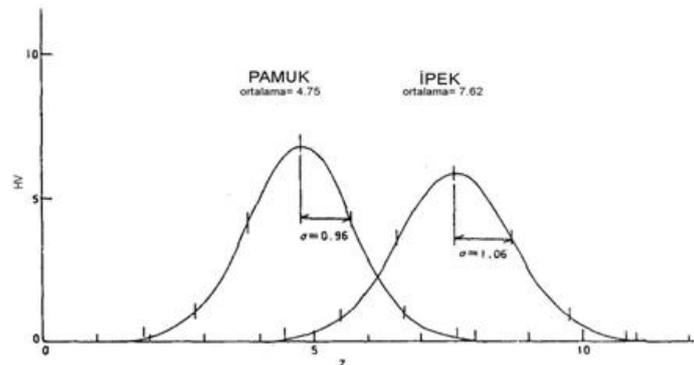


Figure 2 : Z values to discriminate between cotton and silk fabrics [3]

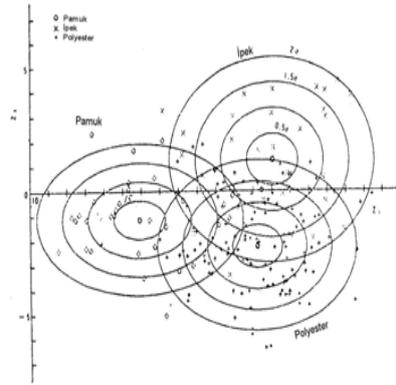


Figure 3 : Z values to discriminate between cotton, silk, and polyester fabrics [3]

**Discriminant Analysis**

The objective of discriminant analysis is to make statistical classification with minimum error with  $p$  number of properties [4]. It is generally assumed that each group have multivariate probability distributions of  $p$  variables and parameters of these distributions are predicted by the selected samples, so we can say that a single data is a random sample which come from these groups [6]. Discriminant analysis is a kind of multivariate analysis which is an extension of single-factor multivariate analysis of variance MANOVA [5]. Discriminant analysis can also be used for finding parameters which have significant properties of its subgroups. In this respect, discriminant analysis have similar properties with ANOVA [2]. As a result of discriminant analysis we want to find a mathematical function that will provide the determination of groups in which the investigated data belong to and with the help of this function to place a new observed data into one of these groups with minimum classification error [8]. Discriminant analysis is a grouping technique used for finding variables that have the most contribution to recognizing differences of groups [7]. Discriminant functions are composed of linear components of predictor variables. Variables that affect the differences between groups are named discriminant (separator) variables [5].

Some assumptions must be valid for applying discriminant analysis. Each group must be taken from a population that has many variables with normal distribution and their covariance matrixes must be equal for each group. On the other hand, there shouldn't be multiple correlation between variables [7].

Discriminant function is obtained so that the discrimination between data is maximum. For this purpose the Eq. 1 is given [6]:

$$(W^{-1}B - \lambda I)V = 0 \tag{1}$$

Discriminant variables can be calculated by using these eigenvectors as in Eq. 2 [6].

$$\begin{aligned} Y_1 &= v_{1,1}X_1 + v_{1,2}X_2 + \dots + v_{1,p}X_p \\ Y_2 &= v_{2,1}X_1 + v_{2,2}X_2 + \dots + v_{2,p}X_p \\ &\vdots \\ Y_s &= v_{s,1}X_1 + v_{s,2}X_2 + \dots + v_{s,p}X_p \end{aligned} \tag{2}$$

Eq. 3 will be found from  $p$  number of variables for discriminant analysis [4]:

$$Y_i = V_1X_{i1} + V_2X_{i2} + \dots + V_pX_{ip} \tag{3}$$

In this equation,  $X_1, X_2, \dots, X_p$  are variables and  $V_1, V_2, \dots, V_p$  are corresponding coefficients. This function is named as discriminating function. While finding such a function, the ratio of change between groups to change within groups must be maximum (Eq. 4) [4].

$$F = \text{Max}(\text{Change between groups} / \text{Change within groups}) \tag{4}$$

Two variance ratio that is identified by Fisher must be as Eq. 5 [4]:

$$L = \frac{v'Av}{v'Wv} \Big|_{\max} \tag{5}$$

If parameters that affect a case with two groups, are identified by a linear equation, Eq. 6 is obtained [2].

$$\text{Group} = a + b_1 \cdot x_1 + b_2 \cdot x_2 + \dots + b_m \cdot x_m \tag{6}$$

In Eq. 6,  $a$  is a constant and  $b_1, b_2, \dots, b_m$  are regression coefficients. Interpretation of such groups, is made in the same way with multiple regression analysis. Variables that have maximum standardized regression coefficients are evaluated as the parameters that make maximum contribution to the group [2].

Coefficients of discriminant function show the partial effect of each variable on discriminant function. Coefficients (weights) of discriminant function are determined to see the contribution of each variable to the function. Canonical analysis is used to determine the most appropriate combination of variables (first function is the most effective and second function's effect is lower etc.). Functions in the analysis must be independent (orthogonal). In other words, contributions of the functions mustn't intersect. In multiple discriminant functions, different functions are tested statistically and important ones are taken into account for further analysis. It is concluded that the parameter that has high coefficient make high contribution [2].

In discriminant analysis, after the discriminant function that determines the difference between groups is calculated, group memberships of the observations are predicted by this function. Classification can be made on the same set of data after the function is determined, but in this case, classification results have the risk of being seen more successful than it is, because the set of data is the same both in determining function and in testing. If the size of sample is enough, it is more reliable to divide the data into two groups as application group and control group. There is not an accurate information about the ratio of application group to control group in literature, but the size of application group must be big enough [7].

**Experimental**

We worked with yarn produced from Adana cotton and the properties measured are from a factory which means directly from production. We have 125 repeats for each property; 30 of them belong to yarn in bobbin form, yarn count Ne20 and twist 19.21 turns/inch, 95 of them belong to yarn in cone form, yarn count and twist the same. So only the form changes, and the yarn properties change. The yarn properties used are maximum breaking force, breaking elongation, work to break, irregularity ( in %U and %CVm units), imperfections (thin places, thick places, neps) and hairiness. PASW statistics program is used and discriminant analysis is applied. The discriminant function obtained has 100% percent of discriminating capability between the form of a bobbin and a cone.

The results of one way ANOVA are given in Table 1 for each property. In Table 2, standardized coefficients are given to compare the properties that are measured with different scales. Structure matrix which shows the correlation of each predictor property of yarn with discriminant function is seen in Table 3 Table 4 gives the within-groups correlation matrix and Table 5 gives the canonical discriminant function coefficients which are the original (unstandardized) coefficients of the discriminant function.

Table 1 : Wilks' Lambda values and the results of ANOVA for each variable [1]

The Tests of Equality of Group Means					
	Wilks' Lambda	F	df1	df2	Sig.
%U	.709	50.603	1	123	.000
%CVm	.731	45.268	1	123	.000
H	.266	338.880	1	123	.000
Thin50	.917	11.197	1	123	.001
Thick50	.973	3.423	1	123	.067
Neps200	.997	.314	1	123	.576
BForce	.988	1.466	1	123	.228
Elongation	.844	22.773	1	123	.000
Rkm	.988	1.478	1	123	.226
BWork	.944	7.290	1	123	.008

Table 2 : Standardized canonical discriminant function coefficients [1]

Standardized Discriminant Coefficients	Canonical Function
	Function
	1
%U	.164
%CVm	.237
H	.884
Thin50	-.159
Thick50	.038
Neps200	-.091
BForce	-1.397
Elongation	-.416
BWork	1.933

Table 3 : Structure matrix [1]

Structure Matrix	
	Function
	1
H	.782
%U	.302
%CVm	.286
Elongation	.203
Thin50	.142
BWork	.115
Thick50	.079
BForce	-.051
Neps200	-.024

Table 4 : Within-groups correlation matrix [1]

Within-groups Correlation Matrix											
		%U	%CVm	H	Thin50	Thick50	Neps200	BForce	Elongation	Rkm	BWork
Correlation	%U	1.000	<b>.993</b>	-.086	.440	.576	.102	.039	.061	.040	.060
	%CVm	.993	1.000	-.123	.443	.639	.176	.050	.084	.051	.084
	H	-.086	-.123	1.000	.042	-.271	-.248	-.185	-.176	-.185	-.205
	Thin50	.440	.443	.042	1.000	.387	-.053	-.106	.085	-.105	-.023
	Thick50	.576	.639	-.271	.387	1.000	.575	.152	.222	.153	.234
	Neps200	.102	.176	-.248	-.053	.575	1.000	.131	.176	.132	.235
	BForce	.039	.050	-.185	-.106	.152	.131	1.000	<b>.704</b>	1.000	<b>.917</b>
	Elongation	.061	.084	-.176	.085	.222	.176	.704	1.000	.704	<b>.905</b>
	Rkm	.040	.051	-.185	-.105	.153	.132	1.000	.704	1.000	.917
	BWork	.060	.084	-.205	-.023	.234	.235	.917	.905	.917	1.000

Table 5 : Canonical discriminant function coefficients [1]

Canonical Discriminant Function Coefficients	
	Function
	1
%U	.330
%CVm	.383
H	2.802
Thin50	-.040
Thick50	.001
Neps200	-.001
BForce	-.058
Elongation	-1.040
BWork	.029
(Constant)	-16.700
Unstandardized coefficients	

By using the original (unstandardized) coefficients of the discriminant function in Table 5, we can write the discriminant function for discriminating the form of a bobbin and the form of a cone as in Eq. 7 :

$$\begin{aligned}
 \text{Equation for Discriminating Packing Type} = & -16.700 + 0.330 U + 0.383 CVm \\
 & + 2.802 H - 0.040 \text{ Thin50} \\
 & + 0.001 \text{ Thick50} - 0.001 \text{ Neps200} \\
 & - 0.058 \text{ BForce} - 1.040 \text{ Elongation} \\
 & + 0.029 \text{ BWork} \tag{7}
 \end{aligned}$$

Calculations according to Eq. 7 are made for yarn properties in both bobbin and cone group. It is found that the threshold value between the two groups is -2. Therefore, if the value from Eq. 7 is lower than -2, that yarn belongs to a bobbin. If the result is higher than -2, that yarn belongs to a cone.

In Table 6, coefficient values of functions that give Z values of two groups are seen.

Table 6 : Classification function coefficients [1]

Classification Function Coefficients		
	Type of Packing	
	Bobbin	Cone
%U	-581.904	-580.277
%CVm	558.113	560.001
H	100.441	114.257
Thin50	-2.134	-2.332
Thick50	-.782	-.778
Neps200	.323	.319
BForce	10.307	10.022
Elongation	518.387	513.261
BWork	-6.102	-5.960
(Constant)	-2746.699	-2822.712
Fisher linear discriminant functions		

Functions for bobbin (Z<sub>1</sub>) and cone (Z<sub>2</sub>) are given as Eq. 8 and 9:

$$\begin{aligned}
 Z_1 = & -2746.699 - 581.904 U + 558.113 CVm + 100.441 H - 2.134 \text{ Thin50} \\
 & - 0.782 \text{ Thick50} + 0.323 \text{ Neps200} + 10.307 \text{ BForce} \\
 & + 518.387 \text{ Elongation} - 6.102 \text{ BWork} \tag{8}
 \end{aligned}$$

$$\begin{aligned}
 Z_2 = & -2822.712 - 580.277 U + 560.001 CVm + 114.257 H - 2.332 \text{ Thin50} \\
 & - 0.778 \text{ Thick50} + 0.319 \text{ Neps200} + 10.022 \text{ BForce} \\
 & + 513.261 \text{ Elongation} - 5.960 \text{ BWork} \tag{9}
 \end{aligned}$$

In the application of discriminant analysis, eigenvalues and Wilks' Lambda tables (Table 7 and Table 8) are obtained to see if the discriminant model is compatible with the set of data as a whole besides measurements that are made for studying the contribution of each variable to the discriminant function. The eigenvalues table gives information about relative efficiency of each discriminant function. If there are two groups, column of canonical correlation is the most helpful measurement. This measurement is equal to Pearson correlation between discriminant scores and groups. Wilks' Lambda is a measurement that shows how well each function places individuals into their own groups. This measurement is the ratio of total variance in unexplained discriminant scores to the variance between groups. If Wilks' Lambda value is low, the capability of the function for classifying individuals is high. In Table 9, classification results are given as both number and percent.

Table 7 : Eigenvalues of the discriminant function [1]

Eigenvalues				
Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	4.506 <sup>a</sup>	100.0	100.0	.905

Table 8 : Wilks' Lambda value of discriminant function and the results of Chi-square test [1]

Wilks' Lambda				
Test of Function(s)	Wilks' Lambda	Chi-square	df	Sig.
1	.182	202.132	9	.000

Table 9 : Classification results [2]

Classification Results				
	Type of Packing	Predicted Group Membership		Total
		Bobbin	Cone	
Count	Bobbin	30	0	30
	Cone	0	95	95
%	Bobbin	100.0	.0	100.0
	Cone	.0	100.0	100.0

**Evaluation of the Results**

According to the values that are given in Table 1, all variables except Thick50, Neps200, BForce and Rkm are statistically significant. It can be understood that averages of two groups are different for %U, %CVm, H, Thin50, Elongation and BWork variables, so these variables contribute to the model. Wilks' Lambda is another measurement of potentials of variables. If Wilks' Lambda value is low for a variable, power of discriminating groups of that variable is high. Therefore, the best variable for discriminating yarns that are in the form of bobbin and cone is H with Wilks' Lambda value of 0.266. %U and %CVm follows H respectively.

The variable that corresponds to the maximum absolute value in Table 2 is the best discriminating variable. In this case, BWork has the best discriminating capability with 1.933. BForce is the second and H is the third variables.

Ordering in Table 3 is the same as that made according to the Wilks' Lamda values in Table 1, but ordering made according to the standardized coefficients in Table 2 is different from them. It means that ordering made according to the standardized coefficients show differences from that made according to the structure matrix (or Wilks' Lamda values) in some aspects. This inconsistency arises from colinearity between some predictor variables shown in bold and red in Table 4. Hence the structure matrix is not affected by colinearity between predictor variables. In Table 4, it can be seen that correlation between BForce-Rkm is 1. For this reason, Rkm value is not included to the analysis. Also there is colinearity between %U-%CVm, BForce-Elongation, BForce-BWork, BWork-Elongation (bold and red values in Table 4).

In accordance with the structure matrix, it is not affected by the colinearity between predictor variables, it can be said that the colinearity between some predictor variables increase the importance of several predictor variables (for example BWork and BForce) in standardized coefficients table. Hence the ordering made according to the structure matrix is more remarkable than others.

The Z values are calculated for both bobbin and cone groups according to Eq. 8 and Eq. 9. When the frequency distribution of calculated Z values is analyzed, it can be possible to see how two groups diverge from each other. In Figure 4, discrimination of yarns, with yarn count Ne20 and twist 19.21 T/inch, that are in the form of bobbin and cone by Z value can be seen.

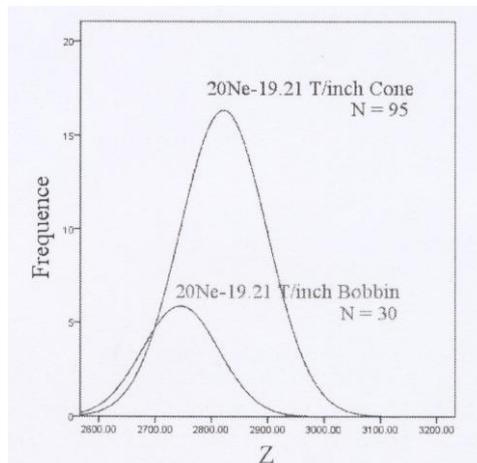


Figure 4 : Discrimination of bobbin and cone, with yarn count Ne20 and twist 19.21 T/inch, by Z values [1]

According to the results in Table 8, classification capability of obtained discriminant function is good. In Table 8, there are also results of Chi-square test and it can be seen that significance value is low. In this case, obtained discriminant function does better than chance at separating the groups.

According to results in Table 9, obtained discriminant model classified total of thirty Ne20 - 19.21 T/inch yarn samples that are in the form of bobbin correctly. Similarly obtained discriminant model classified total of ninety five Ne20 - 19.21 T/inch yarn samples that are in the form of cone correctly. The classification success of the model for both bobbins and cones is 100%.

### Conclusion And Recommendations

The prediction of product properties from raw material properties is very important in textiles and is the primary aspect of research topics. There are many researches needed to be done beside the studied ones. This study is made in the direction of this requirement. In this study, yarn properties are used for prediction by using statistical and mathematical methods and successful results are obtained.

The set of data used in this research is from a factory direct from production. Therefore, it will be easy to adapt the results to the factory. Because the final target is utility in production, the reverse application is successful.

In the light of obtained information, new horizons are broadened for studies that will be done in the future. The same study is suggested to be done with different cotton fibre blends, yarn counts and amounts of twist. For example, cotton fibres that are grown in only Adana are used in this study. Studies that contains cotton fibres grown in different areas must be conducted. Therefore, contents will be expanded for generalization and standardization. On the other hand, a study like this is suggested to be done with different cotton fibre blends, yarn counts and amounts of twist. For example, this study is done with only cotton fibres but it is needed the same study to be done with wool and synthetic fibres and even with mixtures of these. By this way, contents will be expanded and line of vision will deepen. This study is also suggested to be continued and carried to weaving and knitting phases. Hence fabric, which is a different form, will be the research subject. This topic is also suggested to be carried to the garment industry, which means preparing for human use. When all of this process is completed, it will be possible to predict the final product properties, in the phase of human use, from raw material properties.

Elimination of some equipment used before the yarn enters a coner is also possible. This work will also help us to decide if the processes done are achieved according to the purposes ahead. By only taking the regular tests during production we will be able to do process control besides quality control which will save time and costs that are mostly needed in our time. The application of this study in different areas of textile is also an important aspect. It is thought that these studies will be applied successfully in other areas and correct results will be obtained. It is also thought that the application field musn't be only textiles, it should be applied to another branches of science.

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# DIVERSIFIED E-LEARNING SYSTEM A PEDAGOGICAL EXPERIENCE OF STUDENTS AND COURSE CREATORS

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## ABSTRACT

This paper states about a pedagogical experience of the users- the students and the course creators the final year Teacher training students. This e-learning course was prepared for the students of Baniwalid Institute of polytechnic by final year computer science students of College of Education, Baniwalid and Thininai.

Our research experience was an idea of providing e-learning resources by both the learning systems the problem based learning system and knowledge based learning system and thereby giving the option to the students to select their own e-learning method based on their interest and ability and also on the other hand analysis and evaluate the project of the course creator. The goal is to distribute resources for all students taking their interest level under consideration. At the end many innovative ideas in e-learning were invented which will be implemented by our teacher training students in the next generation computer based education system.

**Keywords:** *diversified e-learning system, problem based learning, knowledge based learning.*

## I. INTRODUCTION

"Elearning" is a system that can empower both, students and teachers, for quality education and that too, efficiently. Teachers can clearly communicate more in less time using rich multimedia. It also creates a knowledge resource for the nation. Clearly, this is going to bring the revolution in an education system. Surely, it will bring a clear focus on learners and thus evolve a "Learner-Centric" education system from present "Teacher-Centric" system.

"Elearning" aims to provide excellent learning support to the students, which is as good as face-to-face teaching. These presentations will offer much better learning effectiveness and quality due to clarity of communication and interaction during discussions or tutorials with real teachers and fellow students. Learning will be enjoyable experience due to master trainers and rich multimedia. This also substantially reduces required time for learning. Hence, objectives of Elearning may be summarised as follows:

- Effective Learning
- Improved Quality
- Reduced Duration
- Cost Effectiveness
- Flexibility

The content of this paper refers to the various e-learning courses prepared by the final year computer science students of College of Education. These courses were taught for the students of Baniwalid institute of polytechnic who are in between the age group of 16 to 18. Taking the present education system and the student's role in selection of their own preferred learning system under consideration many e-learning systems was offered to the students. In this diversified e-learning system from the student side since same course which they study in classroom was offered to them in two different learning system they had the choice to select their own interested learning system on the other hand the e-learning projects of the final year computer science students where directly implemented in the school (for whom they developed the project). Their e-learning projects where evaluated by both the professors and the end users i.e. the students.

The main objective of this diversified e-learning education system is to educate the students to explore general, social and practical knowledge subjects through learning systems they are interested, initially without commitment with none of the specific specialties. Thus, students are directed to focus their attention toward the development and application of techniques to solve real problems in problem based learning and increase their knowledge in knowledge based learning system, keeping always in mind their connection to research activities with educational applications.

## II. THE PROPOSAL OF THE DIVERSIFIED E-LEARNING SYSTEM(DELS)

Diversified E-learning system (DELS) was offered for the students of all three years in Baniwalid Institute of polytechnic. The e-learning projects of all the final year Computer science teacher training students were presented before the students of the polytechnic. We ensured that these e-learning projects were also a part of their regular curriculum. All the projects had certain flexibility to expand, to modify or to update this set of options on need the aims of this operation include the study of subjects in a set of areas, through a modern optics, in order to provide a better general formation to the students, with the possibility to handle themes non-usually explored in traditional courses and also to create an exposure to next generation teachers (final year computer science students) to develop and implement this Diversified e-learning system in their future profession, which increases the students involvement and makes the

teacher job much more effective and easier. This has shown to be an efficient way to involve the student and to put option based e-learning system under practice.

The final year Computer science students were given a task of developing projects to bridge the gap between the traditional educational system which is still in use and real time implementation of the acquired knowledge from their four years academic education. The projects developed by our final year students had resources, activities, home works, assignments and feedback.

Intent is to motivate our final year students to explore the computer and its resources for use on day-by-day personal, corporative and social problem solving with respect to their teaching profession. The main characteristics of this method are:

- In-class practical activities
- Development of complete projects during the classes
- Development groups with heterogeneously-skilled members
- Enforcing project specification and use of adequate computational tools to find a good solution for the considered problems
- Enforcing self-learning of concepts needed for using the chosen tools
- Selection of suitable tools to be used in the project
- Enforce learning practical details of the chosen tools

With such a differentiated format for the course, our main intent was to eliminate the usual worry in beginners about direct contact with technology. Additionally, one of the course premises is to stimulate the integration and co-operation with other learning systems, therefore project subjects are encouraged to enclose one or more of the elements below:

- Pedagogical utility
- Social promotion
- Educational contribution

### III. COURSE CREATOR'S PHASE

#### E-LEARNING COURSE - FINAL YEAR PROJECT

In the beginning students were asked to come up with the subjects they would prefer to be implemented as an E-learning course. Among many suggested subjects finally the following subjects were shortlisted

- Computer application using (MS WORD)
- Digital library system
- Computer networks
- Database (MS ACCESS)
- E-Learning Tool (Moodle)
- Computer maintenance

These subjects include the e-learning projects of College of Education, Baniwalid and College of education, Thininai.

Our students highly preferred web programming, multimedia and graphical user interface programming techniques. They were insisted to reach the goal and follow the expectations of the course. The course creators were instructed strictly to follow the specified methodology either (PBL) or (KBL)

Each project consist of 4 to 5 students per team and totally 3 projects where developed by the students of Baniwalid College and 4 projects by students of Thininai College.

The result was analyzed and evaluated based on the following objectives.

This e-learning course content should increase the curiosity learning of the students instead of entertaining.

- Impact of methodology in the course.
- Activities(homework, assignment, discussion, forum)
- Additional resources related to the course.
- Feedback and suggestions.

Among the course creators 30% of the students only come from computer science background from secondary school and the other 70% are new to computer field but as usual only students with mathematics and science background are admitted. What plays the main role in this aspect is that most students came from schools with minimum access to computers and computing resources. There are only 2 private computer centers and since only very few students join the private centers, with this background the result what they produced was remarkable. The resulting projects where analyzed and the following reports where obtained

1. 25.7% projects satisfied the specification up to 70 %
2. 53.9% projects course content was good and the impact of methodology was good
3. 10.5% projects course content was good but methodology of problem or knowledge based was not efficiently implemented 38% the developed projects had fit at least two of the aims delimited in the previous item. Their distribution is illustrated in figure 1

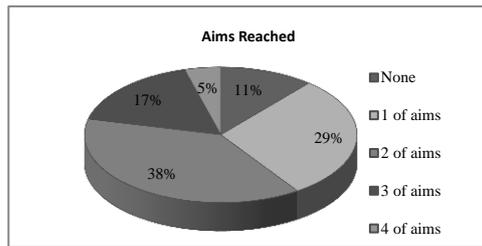


Figure 1: Course aims versus project rates

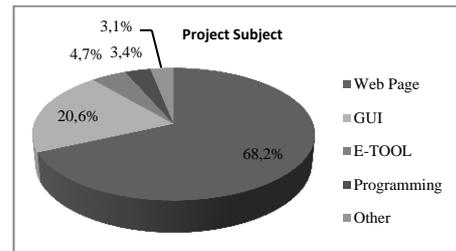


Figure 2: Distribution of projects according to the chosen media

Figure 2 illustrates the choice of distribution for the projects according to the media used in their development. The main choice among the projects has been the design of Web pages 68.2% of the groups.

But since the course creator and the users were totally computer based the transformation of idea into an E-learning course was good. It is evident the projects developed by the groups fit the course aims and expectations. Moreover, developed projects resulted diverse and assorted, despite and high concentration of E-learning based especially due to the freedom of formats.

#### IV. STUDENTS PHASE

Students from Baniwalid institute of polytechnic used the e-learning courses which were developed by our College of Education final year student's projects.

This e-learning course offered by our final year students gave the choice to the polytechnic students to select either problem based e-learning system or knowledge based e-learning system for the same course which they studied in their regular curriculum.

This triangle approach gave the students broad idea to prefer the learning system which they desired and to analysis their works based on usage and feedback.

Naturally students having little previous computer background (first year students) shown slightly greater difficulty to adapt to the method. In contrast, at the end of the course, despite not obtaining the highest grades, they demonstrated an excellent evolution in their accumulated knowledge, showing the best learning performance. Almost all students significantly improved their computer knowledge by employing information technology and communication tools in the development of their projects and or other course activities.

After the course completion all the student were given chance to even view the other learning system so they can acquire more knowledge.

#### V. EVALUATION OF PATICIPANTS IN THIS COURSE

##### A. COURSE CREATOR'S PHASE

Considering e-learning projects, it was observed an expressive number of students with weak problem solving knowledge. What plays the main role in this aspect is that most students came from school with minimum access to computer and computing resources. This was their first course creation attempt. It was observed that at the initial stage course creators just tried to convert to textbook into e-learning course

While the course evolved, students have frequently been, stimulated to use yet unknown computer resources to develop their projects and other course activities. Almost all students significantly improved their computer knowledge by employing information technology and communication tools in the development of their projects and/or other course activities.

By the end of the course, our course creators and many of the polytechnic students had proven their knowledge on how to:

- Access and use the Internet in searching and in research activities
- Locate and use services available in the Internet
- Find, install and use free/open source software
- Adapt available software to fit the needs of specific applications
- Use available software on both standard and nonconventional ways
- Use different and independent software programs in order to perform complex operations that require features not available together in a single program.

**B. STUDENT’S PHASE**

Students with more computer skills had been encouraged to use new computer tools, to explore different technical activities, such as production of video movies, computer language programming, image editing etc. Students had evolved slowly in the first lessons due to the need to learn how to use the basic computer resources. After this stage they had evolved faster until get a consistent domain of basic computer operation and the internet.

When considering the students with more advanced computer skills, it was perceived a continuous and gradual evolution, class by class. For this group of students the evidenced result was the modeling of a personal profile flexible and adaptable on the use of computational resources not previously familiar. By the end of the course the student learned to use the most popular software and their main features. To distinguish between the e-learning system, to use this e-learning system for both theory and practical. Some of the students had problems in starting the projects some required some assistance at the beginning days of e-learning course. Few faced some AV device problem which was rectified immediately.

**VI. DEVELOPMENT OF THE PROJECTS AND LEARNING EVOLUTION OF THE GROUPS**

During the entire course, the students established a gradual and accumulative learning. The projects were developed in groups of up to four people. These projects evolved in five successive phases:

- **Project specification and definition.** The students would have to consider a specific subject. They had to establish goals and the way to reach them
- **Search computational subsidies for the project development,** including new software, new functionalities and the basis for the specification
- **Learning and conducting tests** of the chosen software, and its application to the particular case
- **Project development and implantation**
- **Project documentation and results publication.**

The course was performed following such phases. Students developed their activities in the laboratory with practical lessons, each one in an individual computer. The e-learning projects were designed considering all the project development activities during the classes. At the beginning learning difficulties was higher from the students which course creation skills. This group needed additional time and help, to adapt to the learning method.

**VII. STUDENTS RESULT AND DISCUSSIONS**

It was applied a feedback form for evaluation of the course with the purpose to collect students judgment about the e-learning systems and their perception about the results.

Form was given to the polytechnic students composed of 20 questions about the learning systems, the method, general learning system and student’s behavior and the professor.

After analyzing the results the student opinion with the course creator and the professors perception, both was very close. Considering the method, students were satisfied with the lessons and they had a gradual and consistent learning in both the learning system if compared to the traditional computer class. Students views are represented graphically next.

Figure 3 and 4 illustrates the student’s perception about PBL and fig 5 and 6 about KBL

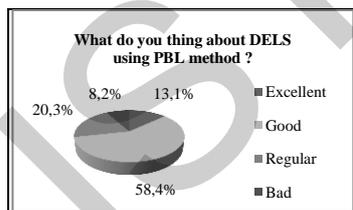


Figure 3 DELS using PBL method evaluation

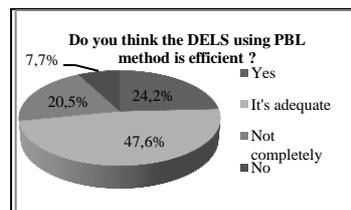


Figure 4: Method efficiency

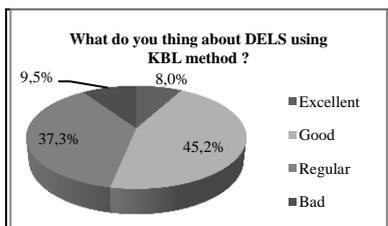


Figure 5 DELS using KBL method evaluation

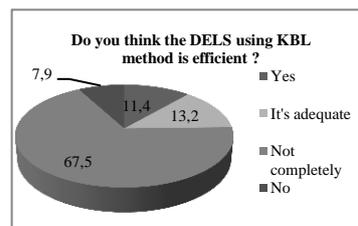


Figure 6: Method efficiency

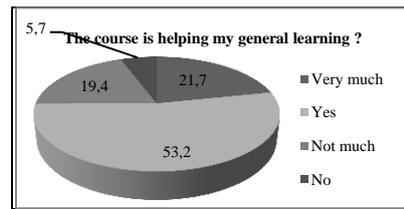


Figure 7: General formation

Students preferred PBL more because they were used to it and they already had the awareness about the learning system.

After the course feedback form was given to the students to evaluate their level of understanding.

When the same project was asked to be viewed by the student will computer background (students who have studied computer in their regular academic we came to a conclusion that they preferred more advanced learning method than others.

### VIII. COURSE CREATIONS RESULTS AND DISCUSSION

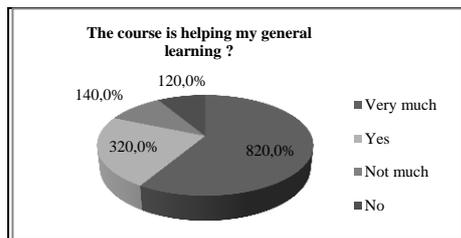


Figure 8: General formation

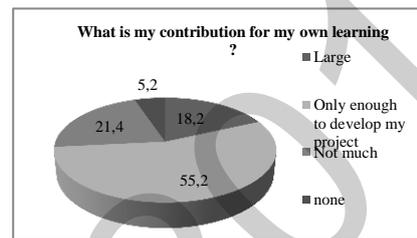


Figure 9: Participation in learning

### IX. A COMPARISON GRAPH OF PBL AND KBL

The problem based e-learning system was approved by 68.5% of the students and knowledge based e-learning system was approved by 31.5% of the students. 65% considered PBL as efficient and 35% KBL as efficient. They are shown in fig 7 and fig 8.

From course creator view 53.2% completely understood the e-learning system through which they are going to implement their selected course, 27.7% had shortage of time and 16.3% stated next time they would do much more better job than this. See fig 9.

### X. DELS RELATION TO PBL

Problem Based Learning (PBL) is a method of learning centered in the student, who becomes the active agent of your own learning. PBL detaches a cyclical context for the learning, it promotes the development of abilities to work in group, and also it stimulates the individual study, according to the student interests and rhythm. The student evolves from passive receiver to the main instrument responsible for your own learning. In PBL, the professor acts as tutor (or facilitator) in the groups and has the chance to know the students difficulties and keep closer of them during the entire course. This method demonstrates very positive results developing new abilities in the students. This method was developed and applied initially in health area, mostly in medicine and nursing, but currently other areas are also adopting the proposal, adjusting to its specific program of study. Also, there are some papers demonstrating applications of this method in other areas, like engineering and computer science undergraduate courses. The education method described in this article, even so inspired in the PBL, is established under a different focus. The similar characteristics to PBL method are summarized below: learning centered in the student, who assumes the main responsibility for your own learning;

- Professors act as facilitators or tutor
- Projects development encourage the students to generate abilities on general problems solving
- New skills are discovered through the auto-learning.[5][4][2]

### XI. THE DELS RELATION TO KBL

Knowledge engineering was carried out in the context of the construction of knowledge systems that were targeted at problem-solving tasks such as diagnosis, assessment and planning. Knowledge engineering was performed in a relatively small, closed area. In the nineties we saw the advent of ontology's as a vehicle for integration of knowledge bases built for different applications. One can view Semantic Web applications as the knowledge systems of this new era, but their knowledge bases have very different properties compared to the closed-world knowledge systems. Knowledge engineers are confronted with a multitude of knowledge sources, multi-lingual, often shallow and heterogeneous.[5][1]

### Principles for knowledge engineering

- Principle 1: Be modest!
- Principle 2: Think large!
- Principle 3: Develop and use patterns!
- Principle 4: Don't recreate but enrich and align!
- Principle 5: Beware of ontological over-commitment!
- Principle 6: The required level of formal semantics depends on the domain!

The most important differences of Diversified e-learning system, PBL and KBL method for both the students and the course creators are summarized below:

- The courses were organized with up to thirty students in each year (or a limit based on the number of computers available in the laboratory);
- All the groups were responsible for: delimiting their problem based on any subject, propose a solution and implement it. Activities during the classes help them to find a solution through the searching subsidies in data communication networks and using computer tools;
- The groups, essentially, were formed by students with different abilities.
- The projects were developed during the classes in four phases: 1) problem definition; 2) search of subsidies for the resolution; 3) development; 4) documentation and publication.[7]

### XII. CONTRIBUTIONS

The presented e-learning system improves the learning process on computer courses, facilitating the access to diversified and updated information. It prepares the student effectively, to handle the most common available software tools, to adapt on using the new technologies, to discover and use free/open source software, it provide them versatility in academic and professional life because of their own preferred learning system. This novel learning system drives the student and the course creators to work not only with the available tools but also to search other subsidies to locate more adequate alternatives to your problem solving and acquiring knowledge. This learning system puts both the students and the course creators involved with new and rich experiences, through a fast learning; the content is easily assimilated and immediately put in practical.

### XIII. CONCLUSION

The DELS method, discussed in this article, revealed to be efficient, and the results had been sufficiently satisfactory. Students as well as the course creators learning were more permanent and solid, after the end of the e-learning course considering the applied concepts and the tools used in the development of the project. An efficient assimilation of practical computer use was also evidenced, as well as the growth of students and course creator's sensitivity on solving new problems and search for the knowledge. This presented e-learning system can be applied to others courses taught on traditional way, especially for basic practical courses or in those the student's computer skills are very heterogeneous. An improvement for the learning system may be proposed: the incorporation of a student and course creator's interaction tool to share difficulties and to stimulate collaboration. It will be put available to the students a resource similar to an on-line daily to accompaniment of projects development process and knowledge development process and also to offer them other way to interchange information and contribution between the groups. Also another improvement may be proposed to evaluate the rarely used learning system versus the ability, attitude towards converting academic curriculum to e-learning education system.

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# DIYARBAKIR İLİ ÇEVRESİNDE MEYDANA GELEN TRAFİK KAZALARININ NEDENLERİ VE RİSK BÖLGELERİNİN BELİRLENMESİ

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## Özet

Türkiye’de yük ve yolcu taşımacılığının büyük kısmı karayolları tarafından karşılanmaktadır. Bu bakımdan karayolları pahalı bir yatırımdır. Şehirlerin büyümesi paralelinde ihtiyaca cevap verebilmesi için yolların artış göstermesi ile birlikte taşıt trafiğini de yoğunlaştırmıştır. Taşıt sayısındaki artış trafik kazalarının da artmasına yol açmıştır. Trafik kazaları beraberinde ekonomik, sosyal ve çevresel etkiler bakımından telafisi çok zor olan sorunlar doğurmaktadır. Bu çalışmada Türkiye’deki kazalar ele alınmış ve Diyarbakır İli’ndeki ve çevresindeki meydana gelen trafik kazaları, nedenleri ve risk bölgeleri belirlenmiştir. Çalışma kapsamında Diyarbakır İli’nde meydana gelen kazalar tespit ve analiz edilerek sırasıyla kazaya sebep olan unsurlar istatistiksel olarak yıllara göre belirlenerek karşılaştırılması yapılmıştır. Sonuç olarak şehiriçi ve şehirler arası yollarda 1997-2010 yılları dönemlerindeki 14 yıllık süre zarfındaki kaza nedenleri ve sonuçları araştırılmış, risk bölgeleri tespit edilerek trafik kazalarının iyileştirilmesine yönelik çeşitli öneri ve yöntemler geliştirilerek sunulmuştur.

**Anahtar kelimeler:** Trafik kazaları, Diyarbakır, Karayolu taşımacılığı

## THE CAUSES OF TRAFFIC ACCIDENTS OCCURRING AROUND THE CITY OF DIYARBAKIR AND DETERMINATION OF THE RISK AREAS

### Abstract

A large portion of freight and passenger transport, are covered by highways in Turkey. This is an expensive investment in highways maintenance. Parallel to the growth of cities to respond to the needs of the road along with the increase in vehicle traffic is concentrated. Traffic accidents with economic, social and environmental impacts raise issues that are very difficult to compensate. This study has been reviewed and Diyarbakır province in Turkey and around the accidents, traffic accidents, the causes and risk regions were determined. The study identified and analyzed accidents in Diyarbakır Province, respectively, based on years of accident-causing factors in determining the statistical comparison is made. As a result, urban and intercity roads meantime, 14-year periods of 1997-2011 the years researched the causes and consequences of accidents, risk areas will be identified and various suggestions for the improvement of road traffic accidents and methods are developed.

**Keywords:** Traffic accidents, Diyarbakır province, Highways transport

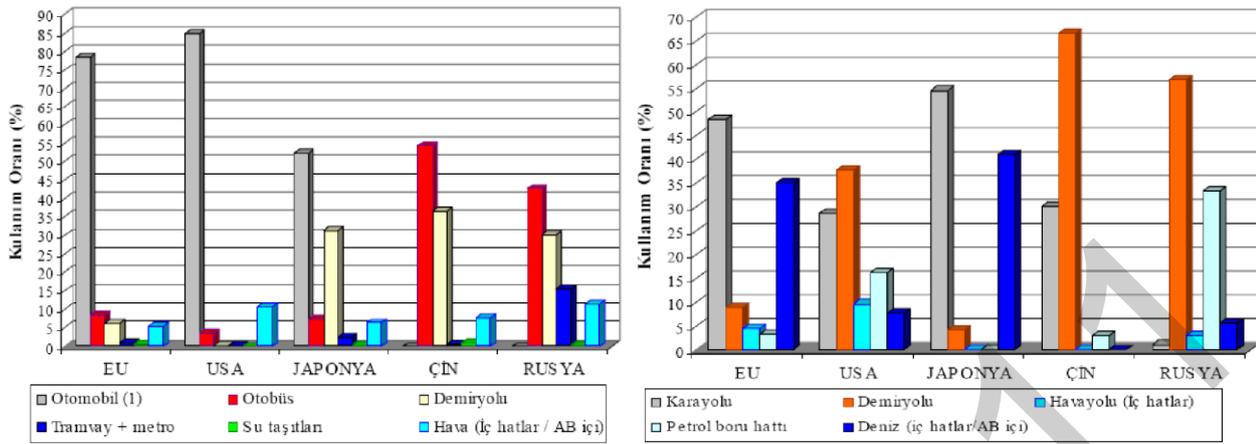
### 1. GİRİŞ

Dünyada olduğu gibi ülkemizde de yolcu ve yük taşımacılığında büyük pay karayolları tarafından karşılanmaktadır. Karayollarında araç cinsi kapasitesi olarak en fazla payı otomobiller kapsamaktadır (Şekil 1). Özellikle kentlerin büyümesi ile yol ihtiyacı artmakta ve taşıt trafiğinde nüfus artışı ve refah düzeyinin artışına bağlı yoğunlaşmalar görülmektedir. Taşıt sayısının çoğalmasıyla birlikte trafik kazalarında da yol, yolcu, araç ve çevreden kaynaklanan sorunlardan dolayı büyük artışlar olmuştur. Kazaların artması, can ve mal kaybı bakımından ülkemizde sıkıntılara yol açmaktadır.

Smeed yaptığı çalışmada değişik ülkelerden elde ettiği trafik verileriyle ölümcül kaza sorunlarını nüfus ve taşıt sayısı oranlarına göre belirlemiş ve kendi modelini geliştirmiştir. Mekky gelişmekte olan ülkelerde taşıtlardaki hızlı artışların ölüm oranlarına etkilerini incelemiştir. Zeeger’e göre şerit genişliği arttıkça yaralı ve hasarlı kaza oranları düşerken ölümcül kaza oranlarında büyük bir değişim olmamaktadır. Bu duruma bakılırsa yollardaki şerit genişlemeleri araçların süratlerinde artışlara yol açarak, taşıt sürücülerinin dikkatlerinin dağılması ve manevra kabiliyetlerinin yavaşlamasıyla kaza riskini çoğaltmaktadır. Partkaya iş ve nüfus ve iş verilerini kullanarak kaza tahmin modeli geliştirmiştir.[1-5].

Ülkemizdeki büyükşehir kapsamında değerlendirilen Diyarbakır İli’de meydana gelen nüfus artışı, köyden kente göçlerin yoğunlaşmasıyla birlikte çarpık kentleşme ile birlikte beraberinde birçok sorunları getirmiştir. Nüfus artışı insanların ulaşım ihtiyacını arttırmış, yeni ve planlı şehirleşmenin olduğu alanlarda bu ihtiyaçlar karşılanmasına rağmen özellikle eski şehirleşmenin olduğu ve çarpık kentleşmenin olduğu alanlarda bu ihtiyaçlar karşılanamamaktadır. Özellikle yapıların yoğun olduğu ve yolların kısıtlı olduğu alanlarda park problemi ve şehir halindeki araç trafiği sıkışıklıkları ve kazaların meydana gelmesi kendini hissettirmektedir.

Çalışmada Türkiye ve Büyükşehir kapsamında yer alan Diyarbakır'daki kazaların tespitine yönelik yıllara göre istatistiksel analizler yapılmıştır. Sırasıyla trafik kazalarına neden olan unsurlar belirlenmiş, trafik kazalarının iyileştirilmesine yönelik çeşitli öneri ve yöntemler geliştirilmiştir. Kapsam olarak 1997-2010 yıllarındaki kazalar baz alınmış nedenleri ve sonuçları araştırılarak kazaya neden olan risk bölgeleri belirlenmiştir.



Şekil 1. Yolcu ve Yük Taşımacılığının Ulaşım Türlerine Göre Dağılımı [6].

## 2. TRAFİK KAZALARININ ÜLKEMİZ SORUNLARI ARASINDAKİ YERİ

Türkiye’de her yıl trafik kazasından yaklaşık binlerce yurttaşımız ölmekte ve yüzünü aşan yurttaşımız yaralanmakta ve sakat kalmaktadır. Bir başka deyişle hergün ortalama 25 yurttaşımız yaşamını yitirmekte 500’ün üstünde insanımız yaralanmaktadır. Trafik kazaları yıllık maliyet bakımından katrilyonları aşmakta ve ülkemize ekonomik anlamda sıkıntılar yaratmaktadır. Son 14 yıl içinde yaklaşık 49.100 yurttaşımız yaşamını yitirmiş ve aynı dönemde 1,8 milyona yakın yurttaşımız yaralanmış ya da sakat kalmıştır. Bu dönemde trafik kazalarından ailesi içinde bir yakınının kaybı ya da sakat kalmasıyla yaklaşık 8,2 milyon kişi etkilenmiştir. Tablo 1’de trafik polisi sorumluluk bölgesinde Türkiye’de meydana gelen kaza verileri görülmektedir.

Tablo 1. Türkiye’de Meydana Gelen Kaza Verileri [7,8]

YIL	KAZA	ÖLÜ	YARALI
	SAYISI	SAYISI	SAYISI
1997	387,533	5,181	106,146
1998	440,149	4,935	114,552
1999	438,338	4,596	109,899
2000	466,385	3,941	115,877
2001	409,407	2,954	94,497
2002	407,103	2,900	94,225
2003	422,272	2,811	95,607
2004	494,819	3,081	109,889
2005	570,025	3,195	123,977
2006	664,539	3,365	135,754
2007	749,434	3,462	149,814
2008	898,451	2,948	145,163
2009	1017,940	2,993	161,719
2010	1073,878	2,738	171,475

Trafik güvenliği bir ülke politikası olarak ele alınıp gerekli önlemler alınmazsa önümüzdeki on yıl içinde de yaklaşık 100.000 insanımız yaşamını yitirecek ve 2011 yılında bir milyonun üzerinde trafik kazası meydana gelecektir. Stratejik bir yaklaşımla sorunun kaynağı olarak trafik kazalarının azaltılması ve yaşanacak travmaların giderilmesi için yalnızca yasal düzenlemeler ve günlük önlemlerle yetinilmemeli sorunların çözümlerinde planlı ve kararlı yaklaşımla sonuca gidilmelidir (Şekil 2).



Şekil 2. Trafik Kazaları ve Yol Açtığı Yaralanma ve Can Kayıpları

### 3. TRAFİK GÜVENLİĞİ YETERSİZLİĞİ NEDENLERİ

Trafik kazalarının azaltılmasıyla ilgili yapılan çalışmalar ülke gündeminin öncelikli konuları arasında yer almamaktadır. Bu alanda ortaya konmuş bir strateji, yakın ve uzun vadeli planlamalar ve hedefler bulunmamaktadır. Böyle bir yaklaşım benimsenmediği için, trafikle ilgili uygulayıcı kuruluşların da plan ve hedefleri bulunmamakta ve günlük rutin çalışmalarla yetinilmektedir. Bu bakımdan sorunların çözümüne yönelik özellikle orta ve uzun vadede alınacak tedbirlere ilişkin kapsamlı Ulusal Trafik Güvenliği Programı ve Projelerinin hazırlanıp belli periyotlarda yenilenmesi, bu konuda çalışma yürüten kuruluşlar arasında gerekli koordinasyonun sağlanarak etkin bir şekilde çalışmaların yürütülmesi gerekmektedir.

Trafik kazalarının yoğun olması, can ve mal kayıplarının artmasına karşın trafik güvenliği gerçek anlamda ülkemizde bir büyük sorun olarak algılanmamaktadır. Ayrıca sorunların ve çözüm önerilerinin tespitinin birden çok bilimsel faaliyet alanının konusu olduğu da bilinmemekte ya da kabul edilmemektedir. Böylelikle, trafikte bulunan ya da görev alan herkes çözüm beyan etmekte ve uygulama kararları hemen çoğu kez, trafikle ilgili bilimsel temellere dayanmamaktadır. Bu durum, uzun vadeli planlamaları hayata geçirmekte zorluklar yaşayan ülkemizde, özellikle kısa dönemli kararlarda ve kaynak tahsislerinde büyük yanlışlıklar yapılması sonucunu doğurmaktadır.

Trafik güvenliği alanın alt disiplinlerinde üniversite ve sonrası eğitim veren kurumlarda araştırma faaliyeti yürütecek bağımsız araştırma birimlerinin bulunmasına yönelik programlar ya yetersiz kalmaktadır.

Ülkemizde ulaştırma sektöründeki dengesizliklerin giderek daha da olumsuz bir durum aldığı görülmektedir. Yolcu taşımacılığında, karayollarının payı %95'e yükselmiştir. Düşük binek aracı sahipliği karşısında bu derece yüksek bir orana sahip olmak, çok büyük bir oranda otobüs taşımacılığı ile açıklanabilir. Yük taşımacılığında, 1980'lerin başında ortaya konan 'Ulaştırma Ana Planı'nda %70'lere çekilmesi hedeflenen karayolları payı tam tersine, %82'lerden %93'lere tırmanmıştır. Bu durum, hiç bir Avrupa ülkesiyle kıyaslanmayacak biçimde kamyon sayısı ve hareketliliğini doğurmaktadır.

Karayollarında otobüs ve kamyon trafiğinin artışı, mevcut yolların kapasitesini ve ömrünü çok olumsuz etkilemektedir. Bu durumda araçların farklı seyir hızları, hatalı sollama nedeni ve bir seferde çok ölümlü sonuçlanan trafik kazalarını ortaya çıkarmaktadır. Bu durum, bazı karayollarında çok şeritli bölünmüş karayolu taleplerini ortaya çıkarmakta ve sınırlı kaynakların diğer ulaştırma türleri ve trafik güvenliğini destekleyecek daha düşük bütçeli yatırımlara yönlenebilmesine neden olmaktadır.

Karayolu projelendirme ve inşaatlarında, özellikle yüksek hızları özendirilen ve erişimi öne çıkaran çözümler yeğlenmekte, trafik güvenliği gerekleri bilgi ve yönlendirme eksikliği nedeniyle yerine getirilememektedir. Bu durum özellikle kent geçişlerinde ve yol kenarı tesis ve diğer yollarla bağlantılarda sorunlar yaratmaktadır.

Yolların işaretlenmesi genelde sorunludur. Araçların periyodik muayeneleri son derece yetersiz ekipmanla yapılmaktadır. Plansız kentleşme, belediyelerdeki ulaşım ve trafik uzmanlarının bulunmaması, kentlerde ulaşım altyapısına ilişkin eksik ve yanlış uygulamalar bulunmaktadır.

Karayollarındaki taşımacılığı disiplin altına alacak, çalışma koşullarını düzenleyerek trafik güvenliğine dolaylı ancak çok önemli ve kalıcı yararlar sağlayacak bir "Taşıma Kanunu" bulunmamaktadır. Trafik güvenliğinin sağlanmasına yönelik mevcut yasa ve yönetmelikler, etkinlikle uygulanamamakta, cezaların yetersizliğinden çok denetimin yaygın yapılamaması ve uygulamadaki sıkıntılar önem taşımaktadır. Şehirleri ve şehirlerarası yolları kapsayan etkin, güvenilir, hızlı işleyen bir trafik veri bankası ve tescil sisteminin bulunmaması, cezaların tahsilinin zamanında yapılamaması ve etkinliğinin azalması sonucunu doğurmaktadır.

Kent içlerinde, özellikle "korunmasız yol kullanıcıları" olarak adlandırılan yayaların güvenlik durumları son derece olumsuzdur. Raylı taşıma olanaklarının uzun süre değerlendirilmemesi ve yetersiz kalması, nüfusları bir milyonu aşmış birçok kentimizde, toplu taşımacılıkta önemli sorunlar yaratmaktadır. Bu durum kent içlerinde özel oto hareketliliğini artırmakta ve tüm mühendislik çözümleri yalnızca bu taşıtların bir yerden diğerine az kesintiyle akıtılmasını öne çıkarmaktadır. Bu durum, artan hızlar ve yetersiz yaya olanaklarıyla birlikte her yıl çocuk, genç ve yaşlı binlerce yayanın ölümüne yol açan ortamı hazırlamaktadır.

Trafik kazalarının nedenleri derinlemesine araştırılmamaktadır. Kaza yerleri ve nedenlerine ilişkin verilerin güvenilir olmaması ve eksik toplanması, bunlara dayanan analizleri sakat ve subjektif yapılması sonucunu doğurmaktadır. Bu durumda, hatalı çözümlerle yüksek maliyetlerle ortaya çıkmaktadır.

Okul öncesinden başlayarak, öğretimin her kademesinde öğrencilere verilen trafik güvenliği dersleri sayıca ve içerik olarak yetersizdir. Özellikle teorik eğitime ağırlık verilmesi, yaş gruplarına uygun, risk bilgisi üzerine yoğunlaşan yaklaşımın mevcut olmaması dikkat çekicidir. Bu eğitimi verecek öğretmenlerin sayısı yetersiz kalmaktadır. Ailelerde trafik güvenliği konusundaki bilinç ve hassasiyet alt düzeydedir ve çocuklarının eğitiminde etkin görev almamaktadırlar. Daha da olumsuz, eksik ve yanlış bilgileri ve çoğu kez kural tanımaz davranışlarıyla yetişkinler ve görevliler, çocuk ve gençlere kötü örnekler teşkil etmektedirler.

Trafik kazalarının oluşmasında en önemli etken insan davranışının geliştirilmesi, rehabilite edilmesine yönelik yasa destekli yaygın programlar bulunmamaktadır. Sürücü adaylarına verilen eğitimin kalitesi, özellikle pratik eksikliği ve bazı durumlarda sınavların güvenilirliği açısından kuşkuyla karşılanmaktadır.

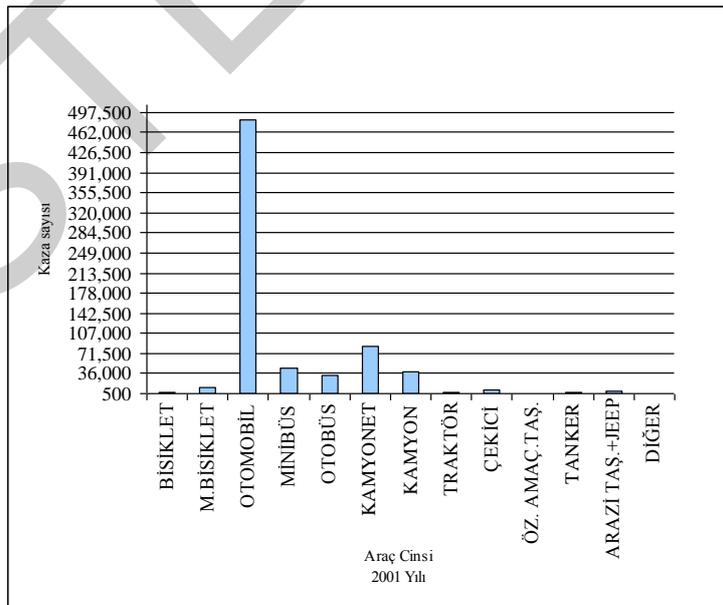
Kamuoyu bilinci ve hassasiyeti yüksek değildir. Medyanın ilgisi son derece azdır. Yazılı medyada, günlük yirmileri aşkın trafik ölümleri bile, eğer kaza bizzat ilgi çekici değilse çok sınırlı yer bulmaktadır.

Trafik güvenliğinin sağlanması yönünde en önemli faktör olan insan davranışının uzun dönemli etkilenmesine yönelik kampanyalar, bilimsel ve koordineli biçimde yapılmamaktadır. Özellikle kaza sonrasında, ölüm ve ağır yaralanmaları azaltacak, güvenlik gereçlerinin araçlarda kullanımı son derece sınırlıdır. Kaza sonrası ölümleri önemli ölçüde aşağıya çekebilecek, kurtarma ve acil yardım hizmetleri yetersizdir. Bundan daha önemlisi, birden fazla kuruluşun işbirliğini gerektiren bu alanda koordinasyon eksikliği yüksek safhadadır [9-11].

#### 4. DİYARBAKIR ÖZELİNDE KAZA TÜRLERİ VE SEBEPLERİ

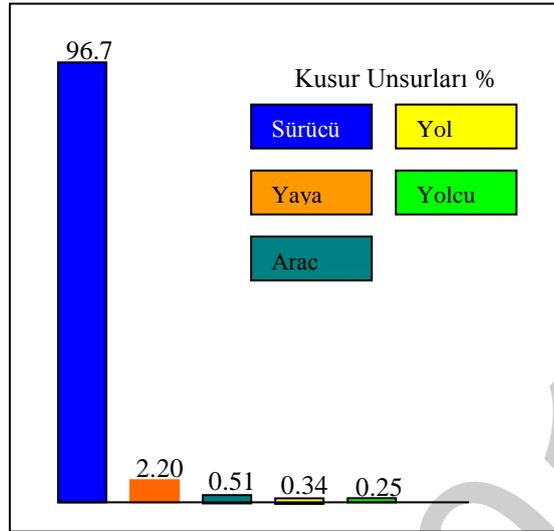
Diyarbakır'da meydana gelen kazaların araç cinsine dağılımı Tablo 2'de verilmiştir. Araçlarda, otomobilin kaza oranı belirgin olarak diğer araç türlerinden yüksektir.

**Tablo 2.** Diyarbakır'da 2001 Yılı İçinde Meydana Gelen Kazaların Araç Cinsine Göre Dağılımı [7,8]



Tablo 3'te 1997-2010 yılları arasında trafik kazalarına sebep olan faktörler görülmektedir. Kusurun büyük oranda sürücü kaynaklı olduğu anlaşılmaktadır. Bu istatistik veri, sürücülerin eğitimi konusunun ivedilikle irdelenmesini gerektiğini göstermektedir.

**Tablo 3.** Trafik kazalarına sebep olan unsurlar [7,8]



Kazaların oluş türleri de bir başka parametre olarak yer almaktadır. Tablo 4'e göre, kazalarda çoğunlukla yandan çarpma, yayaya çarpma, yoldan çıkma ve arkadan çarpma ön plana çıkmaktadır.

**Tablo 4.** Diyarbakır'da Ölümlü-Yaralanmalı Trafik Kazalarının Oluşumlarına Göre Kaza Türleri ve Oranları [7]

KAZALARIN OLUŞUMLARINA GÖRE TÜRLERİ	ORANI(%)
Yandan Çarpma veya Çarpışma	27,0
Yayaya Çarpma	24,0
Yoldan Çıkma	12,73
Arkadan Çarpma	9,79
Devrilme	8,07
Karşılıklı Çarpışma	7,49
Sabit Cisme Çarpma	6,03
Duran Araca Çarpma	3,41
Hayvana Çarpma	0,80
Araçtan Düşen İnsan	0,47
Araçtan Düşen Cisim	0,21
<b>TOPLAM</b>	<b>100,00</b>

## 5. DEĞERLENDİRME

Bu çalışmada 1997-2010 yılları dönemlerine kadar Diyarbakır İli'nde meydana gelen trafik kazalarının nedenleri, sonuçları analiz edilerek risk bölgeleri tespit edilmiştir.

Kazalarda maddi hasar miktarı, yaralı ve ölü sayılarında çarpıcı sonuçlar elde edilmiştir. 2001 yılının trafik güvenliği yılı olması kazalar bakımından bu yılın seçilmesinde önemli etken olmuştur. Kazaların nedenleri olarak teknik nedenler ile sosyal ve toplumsal sebepler birlikte değerlendirilmelidir.

Risk bölgeleri bakımından kazalar;

- 1) Kaza oluş yeri olarak en çok kent içi ve devlet yollarında
- 2) Yolun geometrisi bakımından; geçit olmayan, eğimsiz, düz ve kavşak olmayan yollarda
- 3) Yolların yüzey durumu olarak en çok kaza kuru yüzeylerde olup, ıslak yüzeylerde ise küçümsenmeyecek kadar kaza meydana gelmektedir.
- 4) Yolun kaplama cinsi bakımından en fazla kaza asfalt zeminlerde meydana gelip, en fazla kaza 2005 yılında görülmüştür. En az kaza ise 2002 yılında meydana gelmiş bunda etki olan 2001 yılının trafik güvenliği yılı olmasından ötürüdür.

Kazalarda araçların teknik bakımdan cinsleri, kullanım amaçları ve cinsleride kazaların oluşumunda önemli etkindir. Araç cinsi olarak en fazla kaza taşıt sayısı ve sürat bakımından diğerlerine göre daha üstün olan otomobillerde görülmüş, bunu sırasıyla yük taşımacılığında yaygın kullanılan kamyonetler ve yolcu taşımacılığında kullanılan minibüsler takip etmiştir. Diğer araç cinsleri bunların oransal dağılımından çok daha küçüktür.

Diyarbakır'daki kaza nedenleri teknik nedenler dışında toplum ve sosyal açıdan;

- 1) Toplumsal bilinçsizlik
- 2) Eğitimsizlik
- 3) Denetim yetersizliği
- 4) Sürücü belgesinin herkese verilmesi
- 5) Dikkatsizlik
- 6) Yasalardaki boşluk
- 7) Ahlaki ve kültürel değerlerin yitirilmesi
- 8) Yanlış örnek alma
- 9) Cezaların caydırıcı olmaması
- 10) Karşılıklı saygının olmaması şeklinde sıralanabilir [9-11].

## 6. SONUÇLAR

Diyarbakır'da meydana gelen kazaların teknik sebeplerin yanı sıra sosyal ve toplumsal açıdan kaynaklanan unsurların önemli etkisinin olduğunu kabullenmek gerekir.

Toplum içinde bilinçlenme ve eğitimin artması yaşanabilirliği ve huzuru beraberinde getirecektir. Sürücü belgelerinin verilmesi bakımından önemli olan, belge vermek olmamalı, eğitilmiş ve iyi yetiştirilmiş sürücüler topluma kazandırılmalıdır. Bu bağlamda trafik bakımından denetimler artırılmalı ve verilen cezalar caydırıcı olmalıdır. Aksi takdirde yapılan hatalar tekrarlanabilir. Yapılan hatanın bedelinin ceza makbuzu olacağı sanılır oysaki trafikte yapılan basit bir hata birçok can alabilir. Bu açıdan bilinçli birey olmak son derece önemlidir. Yanlış örnek alma olayı da çok rastlanan bir durumdur. Özellikle gençlerin yanlış örnekleme yaparak yetişmesi, daha sonraki yıllarda trafikte karmaşık ve telafisi mümkün olmayan sorunlar doğuracaktır. Trafikte kusurlu olduğu halde haklı olduğunu savunan insanlar oldukça, bu sorununun çözümü yıllar alacaktır.

Kazaların teknik bakımdan önüne geçilebilmesi için ise de, yollarda trafik uyarı levhalarının ve trafik işaretlerinin kullanılması, taşıt kapasitesinin artışına bağlı olarak bölünmüş yolların ve otoyolların yapılması, yük ve yolcu taşımacılığında karayolu taşımacılığı yükünün azaltılmasına yönelik deniz, tren ve havayolu gibi ulaşım türlerinin de yaygınlaştırılarak teşvik edilmesi gerekmektedir.

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# DYNAMIC ANALYSIS OF A TWO-DIMENSIONAL FRAME WITH ARBITRARILY DISTRIBUTED ELASTIC AND RIGID BEAM SEGMENTS

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## Abstract

The dynamic characteristics of a hybrid beam and a two-dimensional frame composed of any number of *elastic* and *rigid* beam segments are investigated in this paper. To this end, a theory of *elastic-and-rigid-combined beam element* is presented. Firstly, the displacements for the two nodes of a *rigid* beam segment are determined in terms of the displacements of its centre of gravity. Then, based on the above-mentioned nodal displacements of the *rigid* beam segment and those of the two adjacent *elastic* beam elements, the mass and stiffness matrices for the *elastic-and-rigid-combined beam element* are derived. Next, a new transformation matrix is presented in order to transform the state variables of last *elastic-and-rigid-combined beam element* between the local and global coordinate systems. Finally, the overall property matrices of the entire vibrating system are determined with the conventional assembly technique of finite element method (FEM) and its natural frequencies and associated mode shapes are determined with the standard approach. Some important factors, such as length of rigid beam segment, position for the centre of gravity of rigid beam segment, total number of rigid beam segments in the entire vibrating system, etc., are investigated. Numerical results reveal that the above-mentioned parameters have significant influence on the dynamic characteristics of the structure with arbitrarily distributed rigid beam segments.

**Keywords:** elastic beam segment, rigid beam segment, elastic-and-rigid-combined beam element, transformation matrix, finite element method.

## 1. Introduction

Dynamic behaviour of beams carrying multiple masses are important information for structural engineers. Therefore, the literature concerning the last topic is abundant (Low, 2001, etc.). Because the techniques of references (Chan et al., 1998, etc) are developed based on analytical approaches, they are not easy to be extended to the beams or two-dimensional frames composed of arbitrary *elastic* beam segments together with *rigid* beam segments (cf. Figures 10 and 12) with various boundary conditions. To solve this problem, this paper presents an *elastic-and-rigid-combined* beam element such that the natural frequencies and mode shapes of a vibrating system composed of any number of *elastic* beam segments and *rigid* beam segments with various boundary conditions can be easily determined by means of the standard finite element method.

## 2. Property matrices of an *elastic-and-rigid-combined* beam element

If the nodal displacements in the  $x$  and  $y$  directions and the rotational angle about the axis parallel to  $z$ -axis for each node shown in Figure 1 are denoted by  $u_{ix}$ ,  $u_{iy}$  and  $\theta_{iz}$  with  $i = A, B, C$  and  $D$ , then the nodal displacements of the *rigid* beam segment at the left end  $B$ ,  $u_{Bx}$ ,  $u_{By}$  and  $\theta_{Bz}$ , and those at c.g.  $G$ ,  $u_{Gx}$ ,  $u_{Gy}$  and  $\theta_{Gz}$ , have the following relationships:

$$\{\delta_B\} = \begin{Bmatrix} u_{Gx} \\ u_{Gy} - \ell_B \theta_{Gz} \\ \theta_{Gz} \end{Bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -\ell_B \\ 0 & 0 & 1 \end{bmatrix} \begin{Bmatrix} u_{Gx} \\ u_{Gy} \\ \theta_{Gz} \end{Bmatrix} = [R_B] \{\delta_G\} \quad (1)$$

$$\{\delta_B\} = [u_{Bx} \quad u_{By} \quad \theta_{Bz}]^T, \{\delta_G\} = [u_{Gx} \quad u_{Gy} \quad \theta_{Gz}]^T, [R_B] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -\ell_B \\ 0 & 0 & 1 \end{bmatrix} \quad (2)$$

The nodal displacements of the *rigid* beam segment at the right end  $C$  and those at c.g.  $G$  have the following relationships:

$$\{\delta_C\} = \begin{Bmatrix} u_{Gx} \\ u_{Gy} + \ell_C \theta_{Gz} \\ \theta_{Gz} \end{Bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \ell_C \\ 0 & 0 & 1 \end{bmatrix} \begin{Bmatrix} u_{Gx} \\ u_{Gy} \\ \theta_{Gz} \end{Bmatrix} = [R_C] \{\delta_G\}, \{\delta_C\} = [u_{Cx} \quad u_{Cy} \quad \theta_{Cz}]^T, [R_C] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \ell_C \\ 0 & 0 & 1 \end{bmatrix} \quad (3, 4)$$

For conveniences, the stiffness and mass matrices of the *elastic* beam element AB are respectively denoted by

$$[k_e^{AB}] = \begin{bmatrix} [k]_{AA} & [k]_{AB} \\ [k]_{BA} & [k]_{BB} \end{bmatrix}_{6 \times 6}, [m_e^{AB}] = \begin{bmatrix} [m]_{AA} & [m]_{AB} \\ [m]_{BA} & [m]_{BB} \end{bmatrix}_{6 \times 6} \quad (5)$$

where  $[k]_i$  and  $[m]_i$  with  $i = AA, AB, BA$  and  $BB$  are  $3 \times 3$  sub-matrices given by (Przemieniecki, 1985).

Based on Equation (5), the nodal forces for the elastic beam element AB are given by

$$\{F_A\} = [k]_{AA} \{\delta_A\} + [k]_{AB} \{\delta_B\} + [m]_{AA} \{\ddot{\delta}_A\} + [m]_{AB} \{\ddot{\delta}_B\}, \{F_B\} = [k]_{BA} \{\delta_A\} + [k]_{BB} \{\delta_B\} + [m]_{BA} \{\ddot{\delta}_A\} + [m]_{BB} \{\ddot{\delta}_B\} \quad (6a,b)$$

where the overhead dot ( $\cdot$ ) denotes differentiation with respect to time  $t$ ,  $\{\delta_B\}$  is given by Equation (2) and  $\{\delta_A\}$  is given by

$$\{\delta_A\} = [u_{Ax} \quad u_{Ay} \quad \theta_{Az}]^T \quad (7)$$

Substituting Equation (1) into Equations (6a) and (6b) and writing the resulting expressions in matrix form, one has

$$\begin{Bmatrix} F_A \\ F_B \end{Bmatrix} = \begin{bmatrix} [k]_{AA} & [k]_{AB}[R_B] \\ [k]_{BA} & [k]_{BB}[R_B] \end{bmatrix} \begin{Bmatrix} \delta_A \\ \delta_G \end{Bmatrix} + \begin{bmatrix} [m]_{AA} & [m]_{AB}[R_B] \\ [m]_{BA} & [m]_{BB}[R_B] \end{bmatrix} \begin{Bmatrix} \ddot{\delta}_A \\ \ddot{\delta}_G \end{Bmatrix} \quad (8)$$

Similarly, if the stiffness and mass matrices of the elastic beam element CD are respectively given by (Przemieniecki, 1985)

$$[k_e^{CD}] = \begin{bmatrix} [k]_{CC} & [k]_{CD} \\ [k]_{DC} & [k]_{DD} \end{bmatrix}_{6 \times 6}, \quad [m_e^{CD}] = \begin{bmatrix} [m]_{CC} & [m]_{CD} \\ [m]_{DC} & [m]_{DD} \end{bmatrix}_{6 \times 6} \quad (9)$$

then the nodal forces for the elastic beam element CD are given by

$$\begin{Bmatrix} F_C \\ F_D \end{Bmatrix} = \begin{bmatrix} [k]_{CC}[R_C] & [k]_{CD} \\ [k]_{DC}[R_C] & [k]_{DD} \end{bmatrix} \begin{Bmatrix} \delta_G \\ \delta_D \end{Bmatrix} + \begin{bmatrix} [m]_{CC}[R_C] & [m]_{CD} \\ [m]_{DC}[R_C] & [m]_{DD} \end{bmatrix} \begin{Bmatrix} \ddot{\delta}_G \\ \ddot{\delta}_D \end{Bmatrix}, \quad \{\delta_D\} = [u_{Dx} \quad u_{Dy} \quad \theta_{Dz}]^T \quad (10, 11)$$

From Equations (8) and (10), the forces at nodes A, B, C and D can be replaced by those at nodes A, G and D, i.e.,

$$\begin{Bmatrix} F_A \\ F_B \\ F_C \\ F_D \end{Bmatrix} \equiv \begin{Bmatrix} F_A \\ F_G \\ F_D \end{Bmatrix} = [k_{ere}^{AGD}] \begin{Bmatrix} \delta_A \\ \delta_G \\ \delta_D \end{Bmatrix} + [m_{ere}^{AGD}] \begin{Bmatrix} \ddot{\delta}_A \\ \ddot{\delta}_G \\ \ddot{\delta}_D \end{Bmatrix} \quad (12)$$

$$[k_{ere}^{AGD}] = \begin{bmatrix} [k]_{AA} & [k]_{AB}[R_B] & 0 \\ [k]_{BA} & [k]_{BB}[R_B] + [k]_{CC}[R_C] & [k]_{CD} \\ 0 & [k]_{DC}[R_C] & [k]_{DD} \end{bmatrix}_{9 \times 9}, \quad [m_{ere}^{AGD}] = \begin{bmatrix} [m]_{AA} & [m]_{AB}[R_B] & 0 \\ [m]_{BA} & [m]_{BB}[R_B] + [m]_{CC}[R_C] & [m]_{CD} \\ 0 & [m]_{DC}[R_C] & [m]_{DD} \end{bmatrix}_{9 \times 9} \quad (13a,b)$$

The relationships given by Equations (12) and (13) reveal that the *hybrid* beam element shown in Figure 1 can be replaced by a three-node *elastic-and-rigid-combined* (or *elastic-rigid-elastic*) beam element shown in Figure 2 with its stiffness matrix  $[k_{ere}^{AGD}]$  and mass matrix  $[m_{ere}^{AGD}]$  defined by Equations (13a) and (13b), respectively. If inertia effects of the *rigid* beam segments are considered, then Equation (13b) must be replaced by

$$[m_{ere}^{AGD}] = \begin{bmatrix} [m]_{AA} & [m]_{AB}[R_B] & 0 \\ [m]_{BA} & [m]_{BB}[R_B] + [m]_{CC}[R_C] + [m_R] & [m]_{CD} \\ 0 & [m]_{DC}[R_C] & [m]_{DD} \end{bmatrix}_{9 \times 9}, \quad [m_R] = \begin{bmatrix} m_R & 0 & 0 \\ 0 & m_R & 0 \\ 0 & 0 & J_R \end{bmatrix} \quad (13b)', (14)$$

where  $m_R$  and  $J_R$  are respectively the mass and mass moment of inertia of the *rigid* beam segment.

### 3. Transformation matrix of an *elastic-and-rigid-combined* beam element

In Figure 12,  $xy$  represents the local co-ordinate system of an arbitrary *elastic-and-rigid-combined* beam element and  $\bar{x}\bar{y}$  represents the global one of the entire vibrating system. If  $[\delta_A \quad \delta_G \quad \delta_D]^T$  denote the nodal displacements w.r.t. the local  $xy$  coordinate system and  $[\bar{\delta}_A \quad \bar{\delta}_G \quad \bar{\delta}_D]^T$  denote the corresponding ones w.r.t. the global  $\bar{x}\bar{y}$  coordinate system, then according to (Przemieniecki, 1985), one has

$$\begin{Bmatrix} \delta_A \\ \delta_G \\ \delta_D \end{Bmatrix} = [T] \begin{Bmatrix} \bar{\delta}_A \\ \bar{\delta}_G \\ \bar{\delta}_D \end{Bmatrix}, \quad [T] = \begin{bmatrix} \cos \theta & \sin \theta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\sin \theta & \cos \theta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos \theta & \sin \theta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sin \theta & \cos \theta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \cos \theta & \sin \theta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (15, 16)$$

In the last expression,  $[T]$  is the *transformation matrix* between the local  $xy$  co-ordinate system and the global  $\bar{x}\bar{y}$  one, while  $\theta$  is the angle between positive  $x$ -axis and positive  $\bar{x}$ -axis.

## 4. Numerical results and discussions

### 4.1 Validation

In this subsection, a uniform pinned-pinned hybrid beam composed of two *elastic* beam segments and one *rigid* beam segment (cf. Figure 3) is investigated. The *rigid* beam segment is located at the middle of the hybrid beam with length  $\ell_R = 10^{-4} - 10^{-6}$  m,  $\ell_B = \ell_C = \ell_R/2$ , mass  $m_R$  and mass moment of inertia  $J_R$ , while the two *elastic* beam segments are made of steel with length  $\ell_e = (1.0 - \ell_R)/2$ , diameter  $d_e = 0.05$ m, Young's modulus  $E_e = 2.069 \times 10^{11}$  N/m<sup>2</sup> and mass density  $\rho_e = 7.8367 \times 10^3$  kg/m<sup>3</sup>. The total length of the hybrid beam is  $L = 1.0$ m. It is evident that, if the length of the *rigid* beam segment approaches zero, i.e.,  $\ell_R \rightarrow 0$ , then the dynamic effects of the rigid beam segment will approach to those of a lumped mass if the mass and mass moment of inertia of the former and those of the latter are the same and the latter is located at the c.g. of the former. In such a case, the natural frequencies of the hybrid beam composed of 16 *elastic* beam elements and

1 central *elastic-and-rigid-combined* beam element with  $\ell_R \rightarrow 0$  (cf. Figure 3) will be very close to those of the same beam carrying a lumped mass (cf. Figure 4). If the mass and mass moment of inertia of the rigid beam segment are  $m_R = 0.5 \times \rho_e (1.0 - \ell_R) (\pi d_e^2 / 4)$  and  $J_R = 0.0 \text{ kg} \cdot \text{m}^2$ , then the first three dimensionless frequency parameters  $\Omega_j^2 = \omega_j \sqrt{\rho_e A_e L^4 / (E_e I_e)}$  of the above-mentioned two beams are listed in Table 1. In view of the reasonable results, it is believed that the presented *elastic-and-rigid-combined* beam element should be available for the title problem.

#### 4.2 Replacing a rigid beam element by an elastic beam element with infinite elasticity

In this subsection, the standard FEM is used to determine the natural frequencies and mode shapes of the hybrid beam shown in Figure 3. All the physical parameters of the hybrid beam are exactly the same as those of the last subsection except that the total length, mass and mass moment of inertia of the rigid beam segment  $\ell_R = 0.1 \text{ m}$ ,  $m_R = 1.5387 \text{ kg}$  and  $J_R = 0.0 \text{ kg} \cdot \text{m}^2$ , respectively. Because, in the standard FEM, all beam elements are *elastic*, one must let the Young's modulus to approach infinity (i.e.,  $E \approx \infty$ ) for modelling a *rigid* beam element. From the numerical results shown in Table 2, it is seen that the standard FEM is not suitable for the beams composed of the conventional *elastic* beam elements together with the *elastic-and-rigid-combined* beam elements studied in this paper.

#### 4.3 Influence of length of the rigid beam segment

All parameters for the beam carrying a central *rigid* beam segment (cf. Figure 3) studied in this subsection are the same as those studied in the last subsection except that the physical properties of the rigid beam segment are: mass  $m_R = 10.0 \text{ kg}$ , mass moment of inertia  $J_R = 10.0 \text{ kg} \cdot \text{m}^2$ , length  $\ell_R = 0.1, 0.3$  or  $0.5 \text{ m}$  and  $\ell_B = \ell_C = \ell_R / 2 = 0.05, 0.15$  and  $0.25 \text{ m}$ . Besides, the boundary conditions of the hybrid beam are replaced by "clamped-clamped". The first three natural frequencies of the above-mentioned hybrid beam are listed in Table 3. Figures 6-8 respectively show the 1<sup>st</sup>–3<sup>rd</sup> mode shapes of hybrid beam with length of the rigid beam segment  $\ell_R = 0.1, 0.3$  or  $0.5 \text{ m}$ .

#### 4.4 Influence of position for centre of gravity (c.g.) of rigid beam segment

All parameters for the current example are the same as those of the last example except that the length of the central rigid beam segment is  $\ell_R = 0.5 \text{ m}$  and several sets of  $\ell_B$  and  $\ell_C$ , with  $\ell_B + \ell_C = \ell_R = 0.5 \text{ m}$ , are used. The first three natural frequencies of the hybrid beam are listed in Table 4. The 3<sup>rd</sup> mode shapes of the hybrid beam, for the cases of  $\ell_B = 0.05 \text{ m}$  and  $\ell_C = 0.45 \text{ m}$ ,  $\ell_B = 0.15 \text{ m}$  and  $\ell_C = 0.35 \text{ m}$ , and  $\ell_B = 0.25 \text{ m}$  and  $\ell_C = 0.25 \text{ m}$ , are shown in Figures 9(a), 9(b) and 9(c), respectively.

#### 4.5 Influence of mass and mass moment of inertia of the rigid beam segment

For the case studied here, all parameters of the hybrid beam are the same as those of the last example except that  $\ell_B = \ell_C = \ell_R / 2 = 0.25 \text{ m}$  and three sets of mass and mass moment of inertia are studied:  $m_R = 1.0 \text{ kg}$  and  $J_R = 1.0 \text{ kg} \cdot \text{m}^2$ ;  $m_R = 5.0 \text{ kg}$  and  $J_R = 5.0 \text{ kg} \cdot \text{m}^2$ ;  $m_R = 10.0 \text{ kg}$  and  $J_R = 10.0 \text{ kg} \cdot \text{m}^2$ . Table 5 shows the influence of mass  $m_R$  and mass moment of inertia  $J_R$  of the rigid beam segment on the first three natural frequencies,  $\omega_j$  ( $j = 1$  to  $3$ ), of the hybrid beam.

#### 4.6 A hybrid beam composed of multiple elastic and rigid beam segments

The multi-span hybrid beams, with clamped-clamped (C-C), pinned-pinned (P-P), clamped-pinned (C-P) and clamped-free (C-F) boundary conditions, composed of four identical *elastic* beam segments and three identical *rigid* beam segments (cf. Figure 10), are investigated in this subsection. The diameter, Young's modulus and mass density of the elastic beam segments are the same as those of the last examples, while the physical parameters for the three identical rigid beam segments are: mass  $m_R^{(1)} = m_R^{(2)} = m_R^{(3)} = 5.0 \text{ kg}$ , mass moment of inertia  $J_R^{(1)} = J_R^{(2)} = J_R^{(3)} = 5.0 \text{ kg} \cdot \text{m}^2$ , length  $\ell_R^{(1)} = \ell_R^{(2)} = \ell_R^{(3)} = 0.1 \text{ m}$  and  $\ell_B^{(j)} = \ell_C^{(j)} = \ell_R^{(j)} / 2 = 0.05 \text{ m}$ , where the superscripts  $j$  ( $=1$  to  $3$ ) represent the numberings of the rigid beam segments. Note that the  $\bar{x}$  positions for the c.g. of the three identical *rigid* beam segments are:  $\bar{x}_1 = 0.225 \text{ m}$ ,  $\bar{x}_2 = 0.5 \text{ m}$  and  $\bar{x}_3 = 0.775 \text{ m}$ . The first three natural frequencies of the multi-span hybrid beams, with various boundary conditions, are presented in Table 6. To save space, only the first three mode shapes of the multi-span hybrid beam with clamped-pinned (C-P) boundary conditions are shown in Figure 11.

#### 4.7 A two-dimensional frame composed of multiple elastic and rigid beam segments

A two-dimensional frame, with clamped-clamped boundary conditions, composed of multiple elastic and rigid beam segments (cf. Figure 12), is investigated herein. In Figure 12, the solid rectangles represent the rigid beam segments, while the solid thick lines represent the elastic beam segments. The diameter, Young's modulus and mass density of the elastic beam segments are the same as those of the last examples, while the physical parameters for the rigid beam segments are: mass  $m_R^{(j)} = 5.0 \text{ kg}$ , mass moment of inertia  $J_R^{(j)} = 5.0 \text{ kg} \cdot \text{m}^2$ , length  $\ell_R^{(j)} = 0.1 \text{ m}$  (or  $0.1414 \text{ m}$ ) and  $\ell_B^{(j)} = \ell_C^{(j)} = \ell_R^{(j)} / 2 = 0.05 \text{ m}$  (or  $0.0707 \text{ m}$ ), where the superscripts  $j$  ( $=1$  to  $12$ ) represent the numberings of the rigid beam segments. The first five natural frequencies of the two-dimensional frame are presented in Table 7. To save space, only the first two mode shapes of the two-dimensional frame are shown in Figure 13.

5. Conclusions

By means of the *elastic-and-rigid-combined beam element* presented in this paper, the free vibration characteristics of a hybrid beam and a two-dimensional frame composed of arbitrary *elastic* and *rigid* beam segments have been studied. From the numerical results, one finds that some important factors, such as length of *rigid* beam segment, position for the centre of gravity (c.g.) of *rigid* beam segment, total number of *rigid* beam segments in the entire vibrating system, etc., have significant influence on the dynamic characteristics of the vibrating system with arbitrarily distributed *rigid* beam segments.

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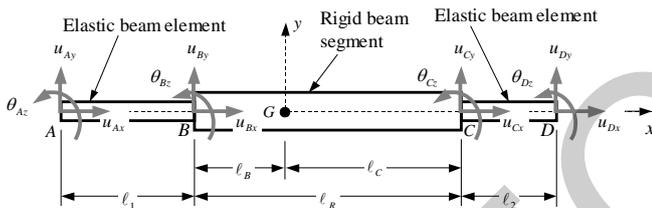


Figure 1 A two-node *rigid* beam segment BC connected with two *elastic* beam elements, AB and CD.

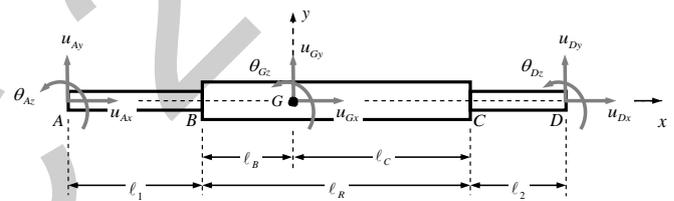


Figure 2 Figure 1 can be replaced by a three-node elastic-and-rigid-combined beam element.

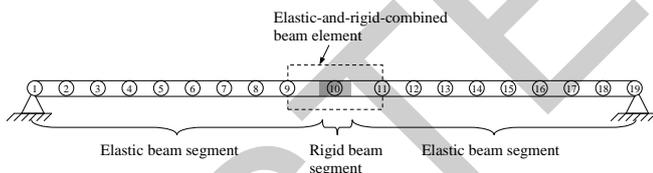


Figure 3 Mathematical model for a hybrid beam composed of 16 *elastic* beam elements and 1 central *elastic-and-rigid-combined* beam element.

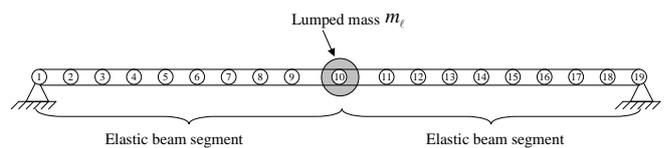


Figure 4 Mathematical model for an elastic beam carrying a lumped mass at its mid-length.

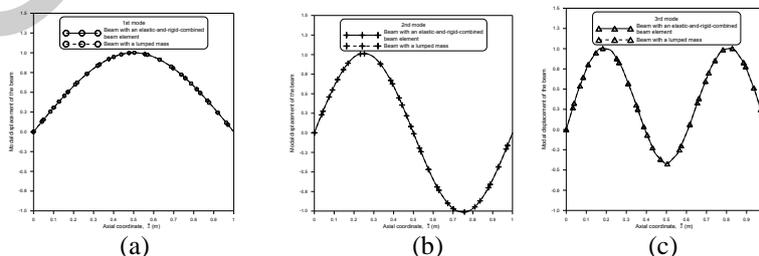


Figure 5 (first) three mode shapes for the beams shown in Figures 3 and 4.

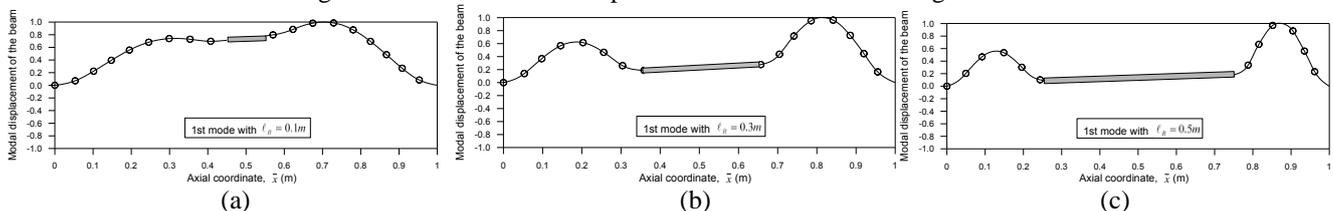


Figure 6 Influence of length of the rigid beam segment on the 1<sup>st</sup> mode shape of the beam.

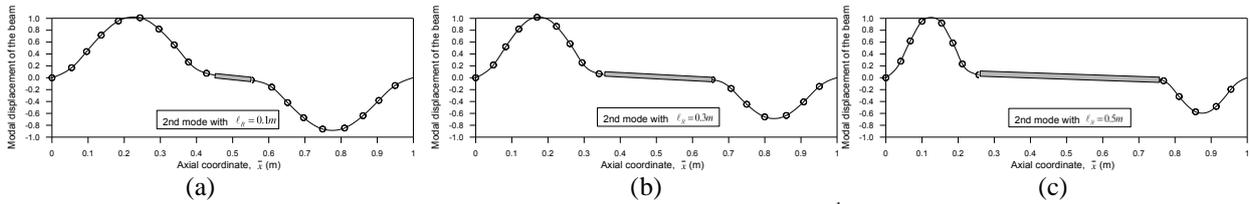


Figure 7 Influence of length of the rigid beam segment on the 2<sup>nd</sup> mode shape of the beam.

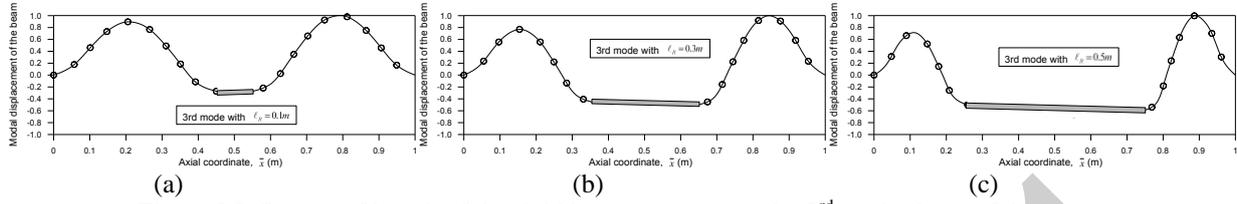


Figure 8 Influence of length of the rigid beam segment on the 3<sup>rd</sup> mode shape of the beam.

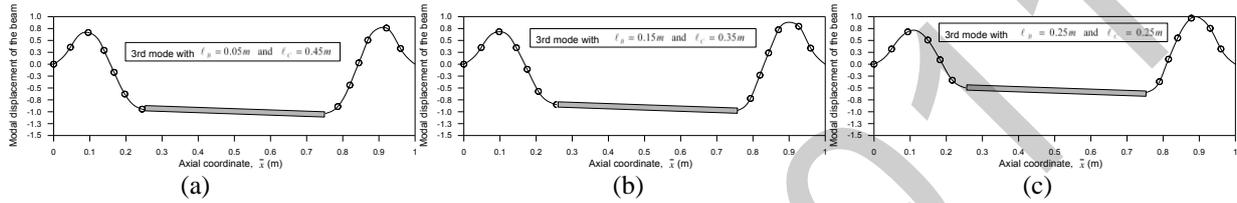


Figure 9 Influence of distances  $l_B$  and  $l_C$  for c.g. of the rigid beam segment on 3<sup>rd</sup> mode shape of the hybrid beam.

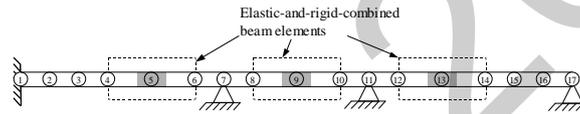


Figure 10 A multi-span clamped-pinned hybrid beam composed of four elastic beam segments and three rigid beam segments.

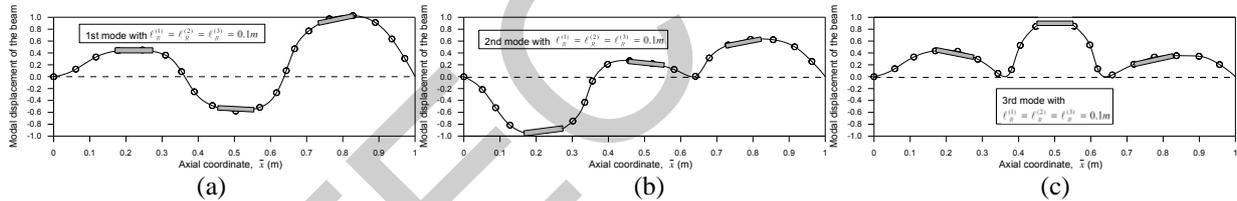


Figure 11 First three mode shapes of a multi-span clamped-pinned hybrid beam (see Figure 10).

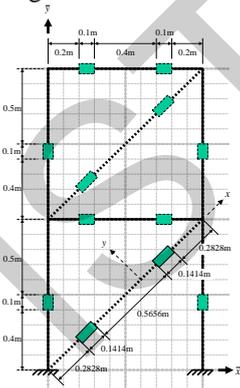


Figure 12 Mathematical model for a two-dimensional frame composed of multiple elastic and rigid beam segments.

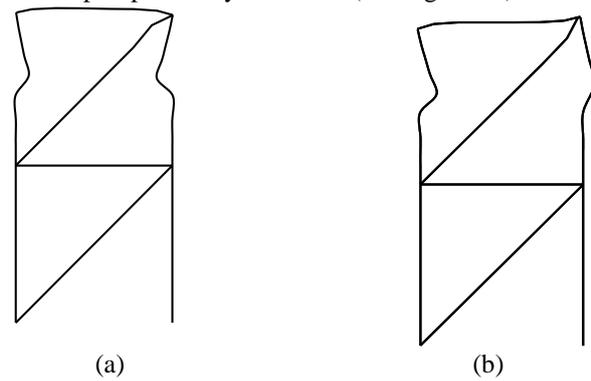


Figure 13 The first two mode shapes of the two-dimensional frame shown in Figure 12: (a) 1<sup>st</sup> mode, (b) 2<sup>nd</sup> mode.

Table 1 The first three dimensionless frequency parameters,  $\Omega_j^2 = \omega_j \sqrt{\rho_e A_e L^4 / (E_e I_e)}$  ( $j = 1$  to 3), for the *hybrid* beams shown in Figures 3 and 4.

Models	Length $\ell_R$ (m)	Dimensionless frequency parameters, $\Omega_j^2$		
		$\Omega_1^2$	$\Omega_2^2$	$\Omega_3^2$
Beam with an elastic-and-rigid-combined beam element	$10^{-4}$	6.892	39.490	71.831
	$10^{-5}$	6.965	39.479	71.819
	$10^{-6}$	6.966	39.478	71.817
Beam with a lumped mass (i.e., $\ell_R = 0$ (Banerjee and Sobey, 2003))		6.966	39.478	71.816

Table 2 Influence of Young's modulus on the first five natural frequencies,  $\omega_j$  ( $j = 1$  to 5), of the elastic beam.

Methods		Natural frequencies, $\omega_j$ (rad/s)				
		$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$
Standard FEM	$E = 10^{15}$ N/m <sup>2</sup>	707.69	2543.82	6464.22	10267.05	16168.71
	$E = 10^{25}$ N/m <sup>2</sup>	1988.46	3449.81	7118.62	10574.71	15672.71
	$E = 10^{35}$ N/m <sup>2</sup>	4890.38	4890.38	15851.69	15851.69	33101.49
Presented approach (a beam with an elastic-and-rigid-combined beam element and $\ell_R = 0.1$ m)		4794.82	4988.03	15168.13	16168.75	16478.96

Table 3 Influence of length of the rigid beam segment,  $\ell_R$ , on the first three natural frequencies,  $\omega_j$  ( $j = 1$  to 3), of the hybrid beam.

Length $\ell_R$ (m)	Natural frequencies, $\omega_j$ (rad/s)		
	$\omega_1$	$\omega_2$	$\omega_3$
0.1	4815.70	7109.13	7864.65
0.3	10810.74	11754.67	14128.83
0.5	22007.08	23037.72	28567.48

Table 4 Influence of distances  $\ell_B$  and  $\ell_C$  for c.g. of the rigid beam segment on the first three natural frequencies,  $\omega_j$  ( $j = 1$  to 3), of the hybrid beam.

Distances (m)		Natural frequencies, $\omega_j$ (rad/s)		
* $\ell_B$	* $\ell_C$	$\omega_1$	$\omega_2$	$\omega_3$
0.05	0.45	22828.04	23003.63	38954.88
0.15	0.35	22694.68	23021.59	34251.38
0.25	0.25	22007.08	23037.72	28567.48

\*  $\ell_B$  and  $\ell_C$  are the distances between c.g. of the rigid beam segment and its two ends B and C (cf. Figure 1), respectively.

Table 5 Influence of mass  $m_R$  and mass moment of inertia  $J_R$  for the rigid beam segment on the first three natural frequencies,  $\omega_j$  ( $j = 1$  to 3), of the hybrid beam.

Mass (kg)	Mass moment of inertia (kg · m <sup>2</sup> )	Natural frequencies, $\omega_j$ (rad/s)		
$m_R$	$J_R$	$\omega_1$	$\omega_2$	$\omega_3$
1.0	1.0	22797.56	23130.59	58597.69
5.0	5.0	22587.78	23068.87	37886.55

Table 6 The first three natural frequencies,  $\omega_j$  ( $j = 1$  to 3), of the multi-span hybrid beams, with clamped-clamped (C-C), pinned-pinned (P-P), clamped-pinned (C-P) and clamped-free (C-F) boundary conditions, composed of four identical *elastic* beam segments and three identical *rigid* beam segments (cf. Figure 10).

Boundary conditions	Natural frequencies, $\omega_j$ (rad/s)		
	$\omega_1$	$\omega_2$	$\omega_3$
Clamped-Clamped	10948.93	12825.85	17583.33
Pinned-Pinned	10392.50	12080.80	17334.03
Clamped-Pinned	10493.28	12533.83	17464.59
Clamped-Free	6905.64	11011.64	12803.57

Table 7 The first five natural frequencies,  $\omega_j$  ( $j = 1$  to 5), for the two-dimensional frame shown in Figure 12.

Natural frequencies, $\omega_j$ (rad/s)				
$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$	$\omega_5$
763.08	868.02	1124.28	1229.66	1322.95

# DYNAMIC ANALYSIS ON CUTTING TORSOR DURING THE MILLING PROCESS

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## Abstract:

In the manufacturing process the interaction tool/chip/machine-tool generates the cutting forces and also the moments (a complete torsor) on the tool in three directions. These moments represent a significant proportion of energy consumed in cutting process. This paper proposes a method of dynamic analysis in order to carry out the monitoring and diagnostics of the milling process quality based on torsor measurement. The method used in our research refers to an advanced analysis of mechanical actions to obtain the answer of the milling tool during the cutting process and also to identify various defects. An experimental device was designed and developed for the acquisition, processing and analyzing three-dimensional signal. The envelope analysis of mechanical actions and vibration is proposed to detect the cutting capacity of the tool with the optimization application of cutting parameters. The research is focused on Hilbert transform optimization to evaluate the dynamic behavior of the machine/tool/workpiece contact.

**Keywords:** torsor, milling, vibration, envelope

## 1. Introduction

The cutting process represents the widely used method to manufacture the mechanical parts. The new machine tool offer higher possibilities in high speed rotation, high feed velocity, and more and more flexibility. Optimization of cutting parameters in these conditions for the conventional materials and especially to the composite materials is a very important objective to achieve the quality conditions, productivity and costs (Teti, et al., 2010), (Altintas & Budak, 1995), (Quintana & Ciurana, 2011). A series of cutting models for determining power consumption are made in two-dimensional even tri-dimensional configuration, but cannot be used in global form and only local and is often far from reality (Cahuc , Darnis & Laheurte, 2007). The aim of this paper is a dynamic analysis applies to the mechanical actions (the complete torsor) and the mechanical vibrations to develop a 3D dynamic milling model. That model concerning the moments generated during the milling process and takes in account your contribution. Previous studies have shown the presence of moments at the tooth of the cutter mill (Laheurte, 2004). The mechanical power consumed during the cutting process depends on every one of the six components of the mechanical actions, and the part consumed by the moments cannot be neglected. This term can represent up to 50% of the total consumed power (Cahuc , Darnis & Laheurte, 2007), (Laheurte, 2004). This study present two analysis methods (direct and indirect) of the moments evolution, according to the torsor kinematics measured during the milling process. By the complete torsor determination the dynamic analysis is focused on the tool quality evolution during the cutting process. Dynamic analysis is performed using the method Synchronous Envelope Analysis (SEA), (Bisu, et al., 2011), (Zapciu, et al., 2009).

## 2. Objective of research

This paper aims at determining a dynamic three-dimensional model applicable to milling by moments integration generated by the cutting process. To understand the dynamic phenomena due to the milling process a complex experimental protocol is designed and realized. Research takes place in two aspects: the first one represent the qualitative dynamic analysis process of the moments generated by the process, but measured in the center of the dynamometer and second aspects is the moments analysis on the tooth of the mill cutter by determining the position of the tool during processing.

### 3. Experimental procedure

Tests were carried out on a 3 axis CNC milling machine FIRST MCV300 which can supply a maximum power of 11 kW and 8000 rpm rotational speed. A special device has been installed on the milling CNC machine in order to recover the 3 linear axes positions. Thus, the position of the cutting edge is continuously known allowing to determine the torsor parameters.

The workpiece material is 42CrMo4 (close to AISI 4142 steel) with 260 HV Hardness, 900MPa limit stress and 210 GPa Young modulus. Wait for our goal the recording data of vibrations and cutting forces signals in the same time with rotational speed is absolutely necessary, (Bisu, et al., 2011). A Kistler 9257B stationary dynamometer Quartz 3 - Component, a National Instruments NI USB-6216 analogical/digital data acquisition board and Fastview software were used for three axis cutting force measurements, figure 2. The dynamic answer of the machine/tool/chip/workpiece contact is achieved by a three-dimensional PCB piezoelectric accelerometer fixed on the workpiece. The milling tool were used here is 490-025C5-08M a Capto C5 system for a BT40 tool holder, with 25 mm diameter and 3 teeth. The cutting parameters is 1 mm depth of cut, with 157 m/min the cutting speed and 0.1mm/tooth feed rate.

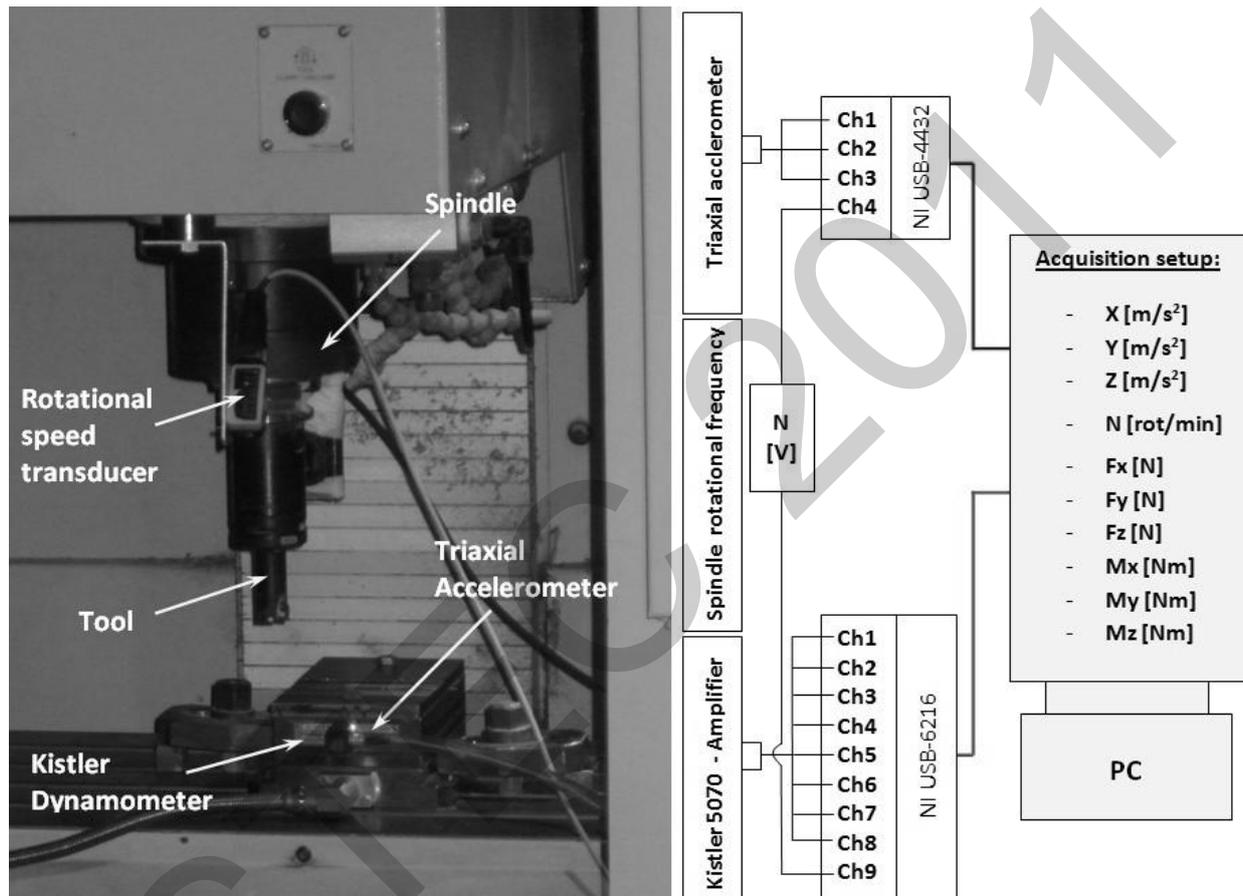


Fig.1. Experimental setup

### 4. Torsor Analysis

The main aim of the reported research is to investigate the possibility to assess the workpiece surface quality in milling by use of process monitoring. Correlation between the output signals (cutting forces, vibration) and the type of features which appeared on the workpiece surface were investigated by use of time and frequency analysis of the output signals (Bisu, et al., 2011). In order to analyze the quality monitoring tool during the cutting process is carried out an analysis of the mechanical action of the forces and moments generated by the torque tool/ chip/workpiece. Thus for the above cutting conditions is obtained the evolution of forces ( $F_x$ ,  $F_y$ ,  $F_z$ ) and moments ( $M_x$ ,  $M_y$ ,  $M_z$ ) in amplitude type pick to pick, fig.2. In this paper we analyze the dynamic behavior of the milling process applying the envelope method in the case of the forces and the moments. It can be observed the amplitude variations of the forces and the moments generated by the vibratory system machine/tool/workpiece and allow a good correlation with accelerations. In these conditions we will study the effects of dynamic data on the cutting tool through the measured parameters. The forces analysis method was developed in the another paper (Bisu, et al., 2011) obtaining significant results by correlating the vibration signals of forces. Further research continues by addressing the dynamics of the moments generated by the milling process.

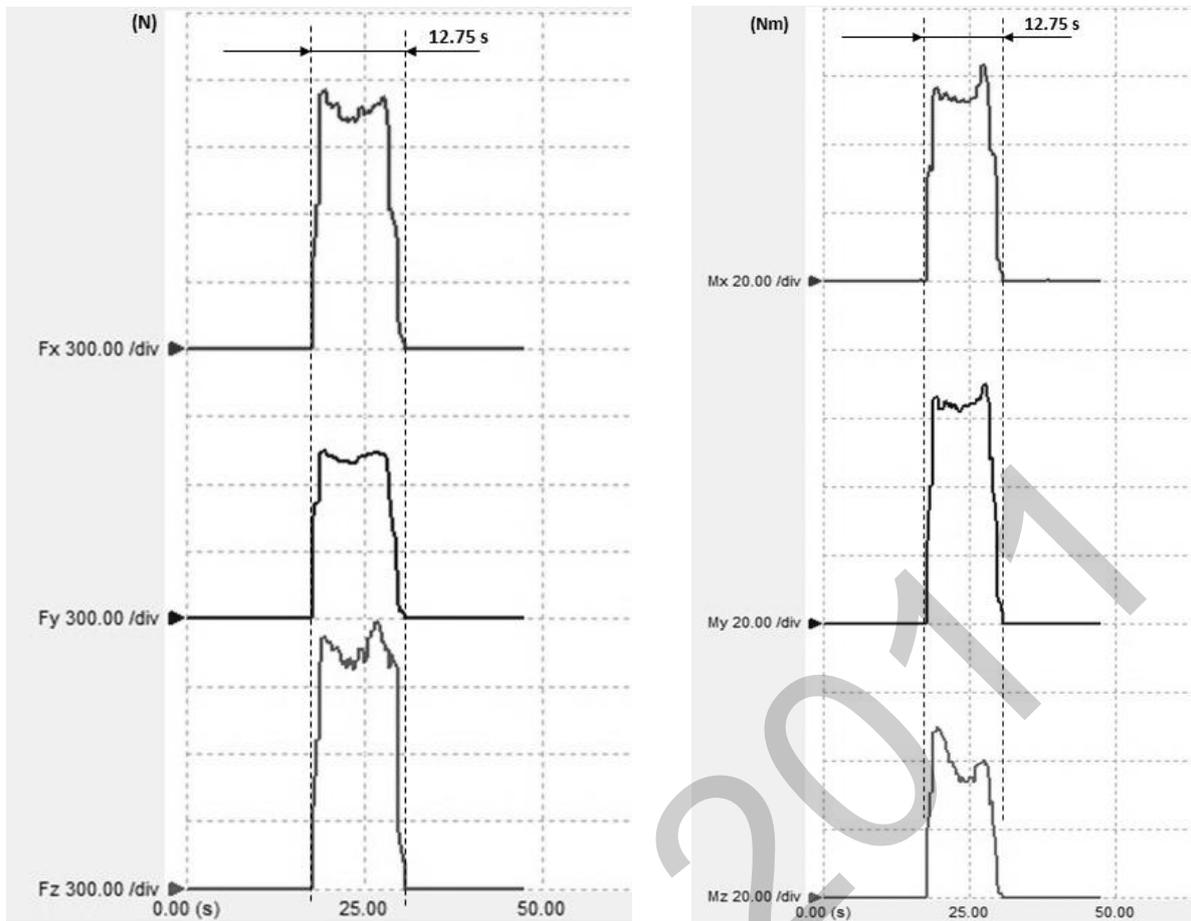


Fig.2. The forces evolution on x, y and z direction.

Dynamic behavior of the tool is highlight by the waveform signal (Mx, My and Mz) measured in center of the dynamometer, fig.3, through supply chain shown in Figure 1.

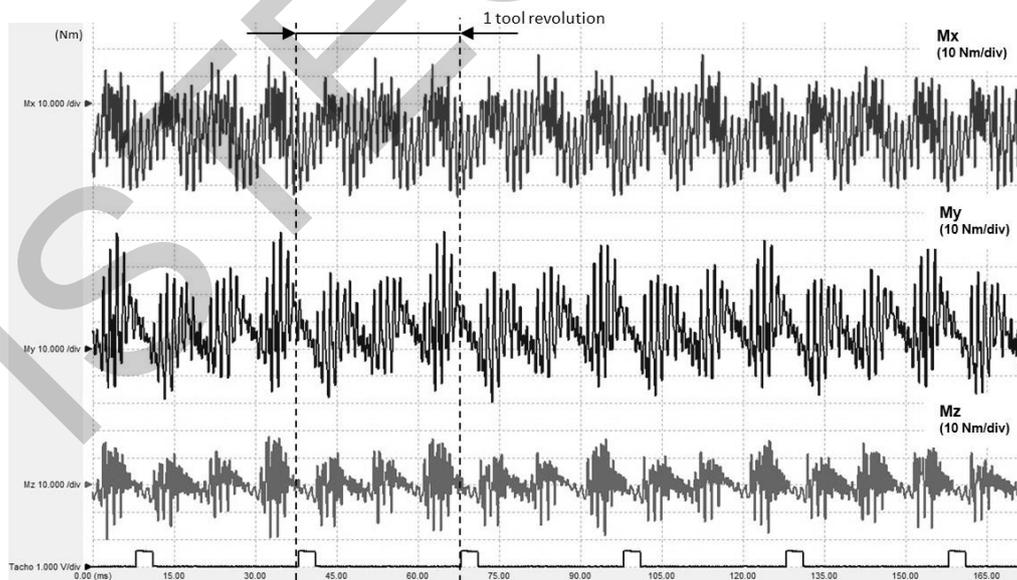


Fig.3. The waveform signal for the moments in x, y and z direction.

It can be seen in Figure 3 the evolution of cutter teeth during a complete rotation of the cutting tool. The moments analysis continues to apply FFT on the signal measured in time and obtain frequency spectrum due to the milling process, shows in figure 4 for 1mm depth of cut. Considering that in this first part of the work the moments are determined in center of dynamometer the spectral moments analysis is important to identify the resonance filters bands, necessary to perform the method of applying Synchronous Envelope Analysis (SEA), (Bisu, et al., 2011).

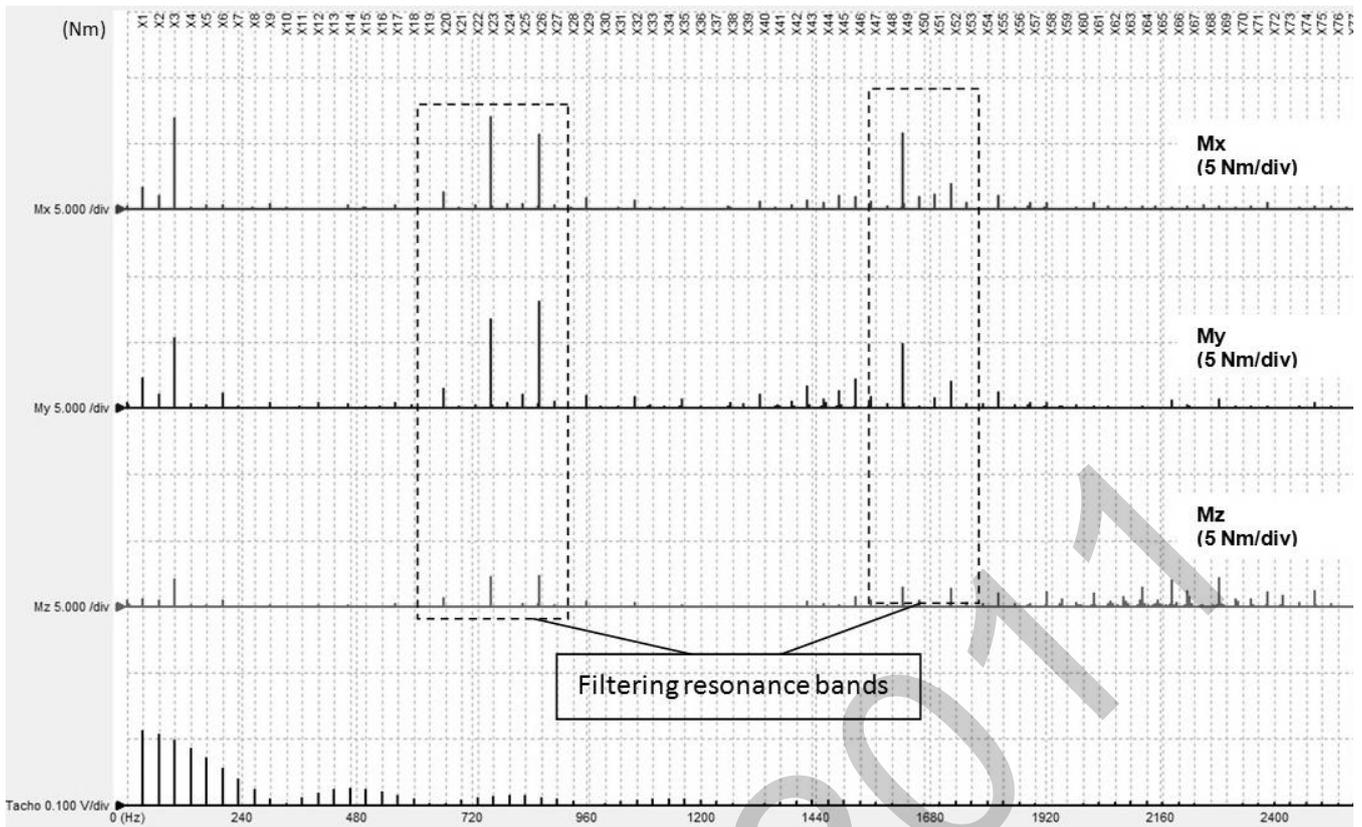


Fig.4. The FFT spectrum for the moments in x, y and z direction.

After identification of the filter ranges equivalent with the frequency impact of the cutter teeth for a qualitative and quantitative analysis a SEA method is applying for Mz moments. This method is based on the analysis of input signals, respectively when measured Mz, followed by application of Synchronous FFT transform which to identify and locate the filtering resonance bands (Fig. 4). Next we apply the Hilbert transform followed by IFFT transformed (fig. 5). To find the impact frequency of the milling tool we apply again the Synchronous FFT transform and by harmonic and interharmonics analysis we are able to evaluate the tool work quality during the cutting process (Bisu, et al., 2011). The figure 5 presented the moments Mz envelope, following their evolution during the cut. It can be seen that the frequency of tooth impacts in material influences both vibrations, forces (Bisu, et al., 2010), (Bisu, et al., 2011) and moments. By the time the signal enveloping for the Mz moments as one of the cutter teeth is more loaded than the other two given that all teeth are new, without wear. We can quantify this difference, obtaining a value for enveloping were the tooth  $z_1$  is two times higher than the other two teeth,  $z_2$  and  $z_3$ . A first conclusion of this is related to the inadequate quality of the reference position of the teeth on the tool diameter, and more an misalignment of these teeth in the plan can be made in discussion.

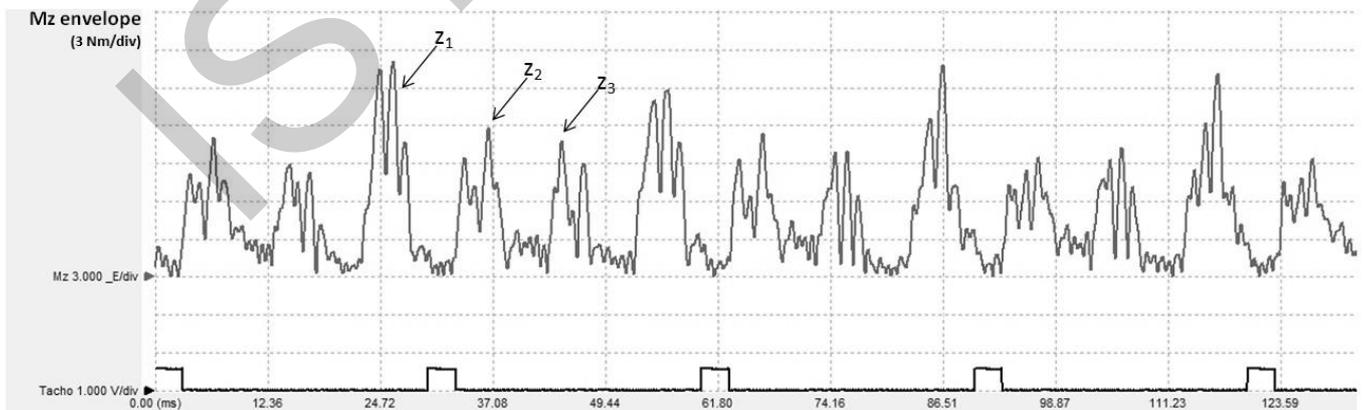


Fig.5. The envelop of the Mz moment.

Hilbert transform allows the integration of resonance phenomena and fault analysis tool by identifying frequencies teeth impacts in material and quality of their evolution.

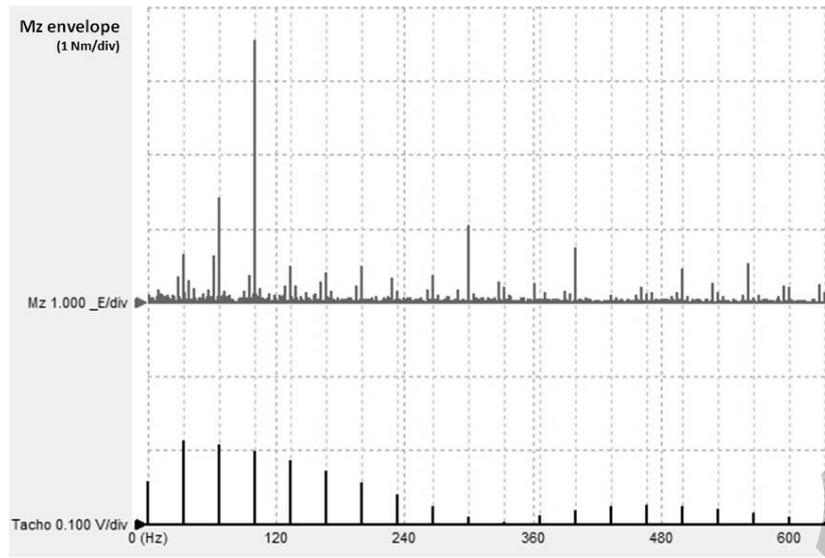


Fig.6. The envelop of the Mz moment.

Analysis of envelope frequency synchronized with the speed provide qualitative and quantitative information about cutter teeth during the milling. Moreover, the Mz moments has a special importance in energy consumption during milling process (Cahuc, Darnis & Laheurte, 2007), (Laheurte, 2004).

**5. The moments Mz determination**

To accomplish the objectives a QZZ2 dynamometer (Couetard, 1993) is used to measure simultaneously 6 components (forces and moments according to each direction) in the same time with the tool position. This procedure is designed to obtain the second aspect, the moments determination at the milling tooth by the position identification during the cutting process. The tool used is a cutter mill with 63 mm diameter with positive cut geometry. The cutting parameters used here is: 120 m/min the cutting speed, 0,1 mm/tooth the feed rate, and 2 mm the cutting depth.

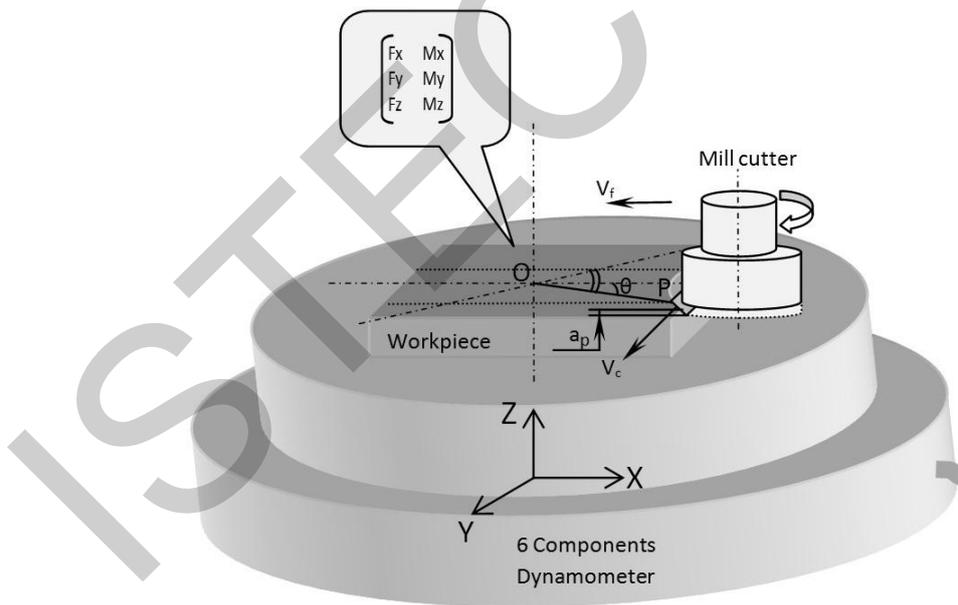


Fig.7. Experimental setup for torsor determination.

The cutting moments determination is done by the transfer moment method, equation no.1

$$\vec{M}_P = \vec{M}_O + \vec{P}_O \otimes \vec{R} \quad (1)$$

The moments at the cutting teeth is induced by two methods: the first one is directly by measuring the positions starting from the CNC feed chain and the second one the indirectly method by identifying the first point of entry into cutting tool and the calculation based on a mathematical algorithm based on time advance and the angular position of the tool (eq.2).

$$P = f(t, f, V_f, \theta) \quad (2)$$

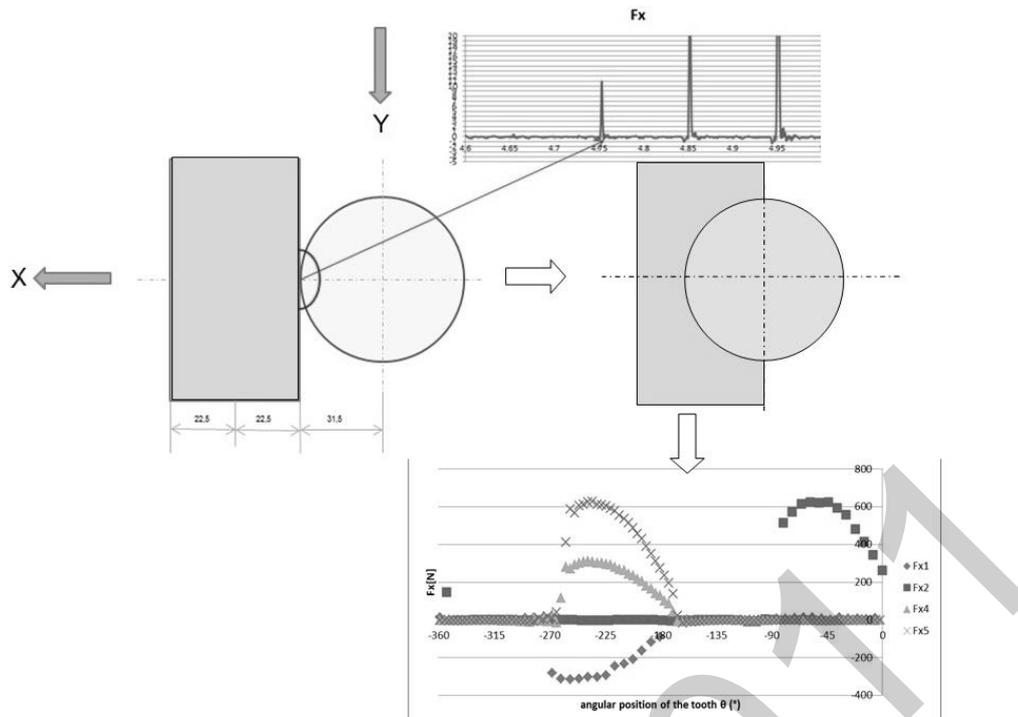


Fig.7.Tool position determination.

Knowledge of the cutting moments is an important achievement in metal cutting field, offering an important information on the process quality, optimizing cutting parameters but also monitoring and machine/ tool /work piece system maintenance.

## 6. Conclusion

In the context of economical current where costs, productivity and quality are indispensable conditions for competitiveness in industrial, developing methods and tools to help meet these conditions is essential. This paper aims at developing a method for analyzing complex dynamic parameters based on a series of purchase through a series of equipment and tools to obtain the requirements of quality and quantity. This analysis is based on Hilbert transform method using enveloping method and is applied to milling in order to identify the dynamic behaviour of the milling tool during the cutting process. The purpose of this method of analysis is to obtain qualitative and quantitative results of the torsor provided by the interaction of machine/tool/workpiece to develop a dynamic 3D model optimization and maintenance process. The moments determination of the x and y directions is the important future of the dynamic analysis validation based on the SEA method (Bisu, et al., 2011). In the future research is focused on creating a dynamic three-dimensional model useful in optimizing the milling process which takes into account these results.

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# DYNAMIC SOLUTION FOR LEADER FAILURE IN HYPERCUBE NETWORK

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## ABSTRACT

Most of the previous solutions for leader failure in hypercube are static algorithms, that didn't consider any changes in processes and links states during algorithm execution. This research propose dynamic algorithm to solve this problem despite these changes. The new algorithm solves leader failure problem when the ID number is not distinguished and with the probability of presence of Intermittent or complete link failure. Algorithm is analyzed and its Performance is evaluated. In a network of  $N$  nodes connected by a Hypercube network the proposed algorithm uses  $O(N)$  messages to elect a new leader in  $O(\log N)$  time steps with the presence of link failure and process Identification Number (ID) is not distinguished.

**KEYWORDS:** Dynamic Algorithm, Leader Failure, Link failure, Hypercube Network, Time Complexity, Identification Number.

## INTRODUCTION

Leader election Algorithm (LEA) is a program distributed over all processes, it starts when one or more process detect that leader has failed, it terminates when the remaining processes know who the new leader is. In other words it moves the system from an initial state, where all the processes are in the same computation state without leader in the network, to a new state in which one of these processes is a leader or coordinator, and the rest aware of this leader [29].

Distributed systems are widely used to increase the speed of solving computing problems. These systems use many computers cooperate with each other to execute the program. The control of these systems may be centralize made by one process called leader or distributed among the processes. In centralized control, Fault tolerant from coordinator or leader crash is a very important issue in these systems. LEAs used to solve this problem by substitute failed process by deserved new leader [6], [17], [26],.

LEAs are widely used in centralized distributed. For example, in client-server, LEAs are used when the server fails and the system needs to transfer the leadership to another station. It is also used in token ring. When the process that has the token fails, the system should select a new node to take over the token [16].

In distributed systems, there are many network topologies like hypercube, meshes, ring, bus,...etc[12] [19] . These topologies may be either the hardware processors, or the software processes embeded over the other hardware topology [15]. This research focuses on the hypercube network where one process works as a leader. It proposed a dynamic solution to solve leader failure problem in spite of the presence of link failure and it considered the state when process ID is not distinguished.

This paper is organized as following. Section 2 presents related work. Section 3 describes the hypercube structure and its desirable properties. Section 4 describe proposed algorithm. Section 5 gives a mathematical proof for time steps and message complexity. Section 6 concludes the results and suggests future work.

## RELATED WORK

Leader election algorithms have been studied in different perspectives as follows: The nature of the algorithms (Dynamic vs. Static) [8] , Node Identity (ID) (unique identity vs. anonymous ID) (Distinguished vs not distinguished) [21],[28] , Topology Type (ring, tree, complete graph, meshes, torus, hypercube ...etc) [1], [5], [7],[20],[22],[27], Communication mechanism used (synchronous vs. asynchronous) [3] , transmission media (wired vs. wireless or radio) [2],[14],[18],[25]. Some of the previous work dealt with the link failure [22], [23]. The leader election solution was first thought of at the end of the seventies, it was started by the ring and complete networks ([24], [21], [30]) . In the nineties meshes, hypercube and tree were studied. To date, these topologies and wireless networks are still being studied ([14], [20]).This section will look over some previous work in election algorithms and focus on the most relevant researches.

In [3] leader election was studded by using a hybrid protocol that Combined Time-Free and Timer-Based Assumptions to Obtain Eventual Leadership. In [9] researchers propose a formal definition for the timed asynchronous distributed system model. They present extensive measurements of actual message and process scheduling delays and hardware clock drifts. These measurements confirm that this model adequately describes current distributed systems such as a network of workstations. They also give an explanation of why practically needed services, such as consensus or leader election, which are not implemental in the time-free model, and implemental in the timed asynchronous system model.

In [2], a self-stabilizing leader election algorithm that can tolerate multiple concurrent topological changes is proposed.

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In [23] he proposed a protocol for leader election tolerant to intermittent link failure in the complete graph network. In [18] they present two new leader election algorithms for mobile ad-hoc networks. In [25] they proposed two asynchronous distributed systems in which the various rounds of election proceed in a lock-step fashion.

In [4] researchers presented an algorithm to solve the link failure for complete network, and in [11] the study assumes the processes are physically or logically ordered, so that each process knows who its successor is.

In [12] he proposed an election algorithm for oriented hypercube, where each edge is assumed to be labeled with its dimension in the hypercube. The algorithm exchanges  $O(N)$  messages and uses  $O(\log 2N)$  time steps to solve the problem and In [11] The problem in hypercube networks was studied, by using two models with sense of direction, the dimensional and the distance models. The proposed algorithm needs  $\theta(\log 3N)$  time steps using  $\Omega(N)$  messages and in [20, 21] different perspectives for the algorithm was considered. In [1] Intermittent Link Failures was studied.

## MODEL DESCRIPTIONS

A hypercube  $H_n$ , of order  $n$ , is defined to be regular symmetric graph  $G = (V, E)$  Where  $V$  is the set of  $2^n$  vertices =  $N$ , each representing a distinct  $n$ -bit binary number and  $E$  is the set of symmetric edges such that two nodes are connected by an edge if the Hamming distance between the two nodes is 1 i.e., the number of positions where the bits differ in the binary labels of the two nodes is 1. For example, in  $H_3$ , the node 010 is connected to three nodes 110, 000 and 011. It is known that the number of edges in  $H_n$  is  $n \times 2^{n-1}$  and the diameter of  $H_n$  is given by  $D(H_n) = n$ . [27]

The diameter and radius of the hypercube equal  $(\log N)$ . The shortest path between any two nodes is less than or equal  $(\log N)$ . This path can be founded using Exclusive Or (EXOR) operation between the source label and destination label. The Hypercube graphs have an elegant recursive structure. To construct a labeled  $(d+1)$  dimensional hypercube, take two  $d$ -dimensional hypercube and extend all labels in the first one with a 0 and all labels in the second a 1. For each process in the first one adds an edge (of direction  $d$ ) to connect it with the associated node in the second hypercube.

This study assumed the following Assumptions:

- ⇒ One intermittent link failure is recoverable.
- ⇒ Routers working all the time even at the fault process.
- ⇒ All communication links are bidirectional.
- ⇒ Leader process could fail due to different reasons which lead to lose of the leadership property. Other processes can detect this failure, when the time out exceed without acknowledgement. Nodes detect this failure start the election algorithm.
- ⇒ Each node calculates a weight that defines its relative importance to be the new leader. This weight is represented by identification Number (ID) for each node. This algorithm considers the state when the IDs for two or more processes are same.
- ⇒ Each process is in one of the following States: leader or normal or candidate.

## PROPOSED ALGORITHM

Proposed algorithm consists of three phases. Phase one is started, when one or more nodes detect leader failure. After  $\log N$  time steps, phase one reduces the count of participated nodes in the election algorithm to  $N/2$  nodes aware of the election process. In second phase our algorithm uses the reduction all-to-one communication operation to have the result in one node with address  $(X10203...0d)$  ( $X$  means 1 or 0). Finally, in the third phase node  $(X10203...0d)$  broadcasts the leader message to all nodes in the network. During each step in phases one and two, received ID is compared with the local ID and Greater ID is passed to the next step. When the two IDs are equal the summation of ones in processes label is compared and select the greater to complete with. Detail description for all phases is as follow:

**Phase One:** This phase starts when one or more nodes detect the leader failure. Each node detect the failure change its state to candidate and initiate the election:

- Step1:** Send an election message to the node differs in the right most bit through link 1. Election message composed of (phase, step, winner ID, and winner position). The election message changes the state of receiving node from normal state to candidate state.
- Step2:** The sender and receiver in the previous step (nodes in the candidate state) send an election messages to the two associated nodes differ in the second right most bit through link 2.
- Step r (r > 2):** The senders from the previous step send an election messages to the nodes differ in the  $r-1$  left bit through the link  $r-1$ . The receiver nodes send an authentication message (election message) through link  $r-2$  to insure that the election message reached the node or not due to the link failure. After the send of the authentication message the node wait for acknowledgement or time out to send election in step  $r$ .

Nodes that receive the authentication message may be received the election message in advance, so the authentication message is ignored after get the greater ID. In the second case when the authentication message is

received by a node in normal state. To tolerate the probability of link failure the node sends the election message through link (r-1). In both cases the nodes that receive the authentication message send an acknowledgement to the sender.

Nodes that received the authentication message send the election messages through link r + 1 to continue the algorithm. Surely any node send any election or authentication message must use the greater ID it knows.

**Step Log N :** N/2 processes (the senders and receivers from the Log N –1 step) send an election messages to the nodes differ in the Log N left bit through log N link. End the phase 1.

During the execution of phase one, if the receiver is aware of the failure and is in progress with its own initiated election step, it will complete the greater step and terminate the smaller one. Each node receives the election message, it compare its own ID with received ID then complete the next step with the greater ID. **If the received ID equal the local ID, algorithm select the ID with greater in process label bits to complete with.**

After this phase leader ID is included in N/2 nodes one half of the hypercube. These nodes will continue to phase 2.

**Phase Two:** second phase uses the reduction all-to-one operation. We add some alterations to tolerate the link failure. Reduction operation applied to N/2 nodes hypercube that was resulted from phase 1, to have the result in one process that have the address  $X_10_2...0_d$ , "X means 0 or 1 depends on which half to complete" As follows:  
**Step1 To Step Log N –3 :** nodes that reach phase 2 and with the (step + 1) and (step + 2) left most bit =1 ( $X_111X_4...X_d$ ) exchange the greater id with the nodes with the same properties except the (step + 2) left most bit = 0 through the link (log N – step –1). The participants in the exchange needs acknowledgement or wait until time out to progress. After the exchange these nodes send election message to nodes with the second left bit = 0 ( $X_10X_3...X_d$ ) through link Log N – step. These steps conclude the result inside a two dimensional hypercube in spite of the probability of the link failure.

**Step Log N -2:** the receivers in the previous step and with the two right bits (10, 01) send election to node with the two right bits(11).

**Step Log N-1:** After comparison and get the greater ID node (11) send the winner to nodes(10,01).

**Step Log N:** In last step nodes(10,01) send election message to the node ( $X_10_20_3...0_d$ ).

After the end of phase 2 the last node ( $X_10_20_3...0_d$ ) is the only node knows about the leader ID.

**Phase3:** In this phase the node ( $X_10_20_3...0_d$ ) broadcasts the result to all nodes considering the link failure. Leader message contains new leader ID and position. The broadcast will be as follows:

**Step 1 :** node ( $X_10_20_3...0_d$ ) send leader message through link (step) to node ( $X_10_20_3...1_d$ ).

**Step 2 :** the two nodes in phase 1 send the message through link (step).

**Step 3 to Log N:** Each node receive the leader message send it through the link step. To consider the link failure for this phase each node receives the leader message send another message through link step – 2 to check if the message reach the other side. Node that receive the extra message may knows about the broadcast so it ignore the extra message. If the node doesn't know about the message it send the extra message through link step -1. The last step isn't needed after the step Log N.

## PERFORMANCE EVALUATIONS

Proposed algorithm is analyzed by computing number of messages and time steps overall execution of the algorithm. Analyses process is carried out for two cases, Simple case and the worst case.

**Theorem 1:** Assume that we have N number of nodes in hypercube network. Then, leader election algorithm needs  $O(N)$  messages to complete.

### Proof.

To find the number of messages, we compute it for each phase, and then calculate the total for the entire algorithm.

**In Phase One** the algorithm use three types of messages: election messages where each node receives one message except the first node. The number of election messages is equal (N-1) .

$$1 + 2 + 4 + \dots + N/2 = \sum_{i=0}^{\text{Log}N-1} 2^i = N - 1 \quad (1)$$

The second type is the authentication message which start from step 2, where each process send one authentication message until the end of this phase. The total number of this type is N-2 messages.

$$2 + 4 + \dots + N/2 = \sum_{i=1}^{\text{Log}N-1} 2^i = N - 2 \quad (2)$$

The third type is the acknowledgement message. Each node receive the authentication message send an acknowledge message except in the last step. The number of the acknowledgement messages is N/2 –2.

$$2 + 4 + \dots + N/4 = \sum_{i=0}^{\text{Log}N-2} 2^i = N/2 - 2 \quad (3)$$

If there is a link failure we need one message to inform the previous node about the election. So the total messages for phase 1 is equal:

$$(N-1) + (N-2) + (N/2 - 2) + 1 = 5N/2 - 4 \quad (4)$$

**Phase Two:** Half of the participants' nodes in phase 2 send two messages for each. One message to avoid the probability of link failure and the second to go on the reduction process. This process valid until the result becomes inside 4 nodes. Then the algorithm needs 6 messages to obtain the leader ID in one node.

$$N/4 + N/4 + N/8 + N/8 + \dots + 4 + 4 + 6 = 2 \sum_{i=2}^{\log N - 2} 2^i + 6 = 2(N/2 - 5) + 6 = N - 4 \text{ messages} \quad (5)$$

**Phase Three:** Broadcast needs N-1 messages, since each node receives one leader message except the initiator.  $1 + 2 + 4 + 8 + \dots +$

$$N/2 = \sum_{i=0}^{\log N - 1} 2^i = N - 1 \quad (6)$$

to cover the probability of link failure we need

$$2 + 4 + 8 + \dots + N/2 = \sum_{i=1}^{\log N - 1} 2^i = N - 2 \quad (7)$$

if there is a link failure we need another message so the number of messages for phase 3 is equal to:

$$(N-1) + (N-2) + 1 = 2N - 1 \text{ messages} \quad (8)$$

**Total : From equations 5,6,7 the total number of messages over all the algorithm is :**

$$(5N/2 - 4) + (N - 4) + 2(N - 1) = (11N/2) - 10 = O(N) \text{ messages} \quad (9)$$

**Theorem 2** Assume that we have N number of nodes in hypercube network. Then, leader election algorithm needs at most  $O(N \log N)$  messages to complete.

**Proof.**

To find the number of messages, we compute it for each phase, and then calculate the total for the entire algorithm.

**In Phase One:** When the failure is detected by all nodes, Each node sends one message during each election step in the first phase. The algorithm needs Log N election step so the number of messages during the election steps is N Log N messages. The number of authentication and acknowledgement messages adaptive depends on the number of nodes that detect the error and the time of detection. But in any case it doesn't increase N messages for each step. The total isn't increase 3N Log N messages.

**Phase Two and Phase Three** are the same as in the simple case.

$$\text{Total : } 3N(\log N) + (N - 4) + (2N - 1) = O(N \log N) \text{ Messages} \quad (10)$$

**Theorem 3** Assume that we have N number of nodes in hypercube network. Then, election algorithm return stable with a new leader by  $O(\log N)$  steps .

**Proof.**

To find the total time steps we compute the time steps for each phase and then add the results to find it for the entire algorithm.

**In Phase One:** Reducing the processes containing the leader ID to the half nodes of the model needs Log N time steps as follow:

Step 1: node detect the failure sends the election message to node differ in the first right bit needs one time step, no need for the authentication and the acknowledgement.

Step 2 to log N : each step needs 3 time steps, one for election message, one for the authentication message and one for the acknowledgement. The last step doesn't need the acknowledgment. The total for phase one is equal:

$$1 + 3(\log N - 1) - 1 = 3 \log N - 3 \text{ Steps} \quad (11)$$

**Phase Two:** this phase continuo the election process with d-1 dimensional hypercube with all its nodes are knowing about the election and have the result from the first phase. The first stage of this phase needs 3 time steps: two steps for the exchange and one for reduction step. phase 2 needs  $3(\log N - 3)$  steps , and 3 steps for the two dimensional hypercube

$$3(\log N - 3) + 3 = 3 \log N - 6 \text{ Steps} \quad (12)$$

**In Phase Three:** Broadcasting (One-To-All), the leader message in hypercube needs Log N time steps. In the case of link failure the algorithm needs another two time steps to inform the unreachable node as described above. Phase three needs :  $\log N + 2$

The total steps over all the algorithm from 11,12,13

$$3 \log N - 3 + 3 \log N - 6 + \log N + 2 = 7 \log N - 7 \text{ Steps} = O(\log N) \text{ Steps} \quad (14)$$

**CONCLUSIONS AND FUTURE WORK**

In this research dynamic solution for leader failure problem in hypercube network is presented. Link failure besides leader failure is solved. Proposed algorithm considered the state when Identification number is not distinguished. Link congestion consideration and precedence synchronization are used in the algorithm. Proposed algorithm performance is evaluated. The algorithm uses  $O(N)$

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messages to elect a new leader in  $O(\log N)$  time steps. For **Future Work**, the work presented can be improved by carrying out the following: I plan to design effective algorithm to solve the leader failure in meshes with the presence of links failure.

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# **EDUCATIONAL LEADERSHIP SKILLS IMPLEMENTATION AND DEVELOPMENT: PROJECT BASED DATA MODELING GE COURSE AT ZAYED UNIVERSITY**

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## **ABSTRACT**

This work aims to explore the importance of educational leadership skills in the domain of higher education, and to investigate how may leadership skills be implemented for university students and how may this implementation affect their academic performance as well as the quality of students' future.

The concept of leadership and educational leadership had emerged in recent years. More and more business oriented concepts had found their ways to the field of education. Few of these concepts are: mission-stating, goal-setting, monitoring and evaluating and those have been heavily implemented in the educational domain years ago in many of western and eastern countries and very good results have been obtained.

This study seeks to implement and/or develop educational leadership skills within Zayed University students' community throughout a partially project based General Education course as well as educational leadership awareness. The effect of such efforts on students' performance was investigated and very promising indications were detected.

## **INTRODUCTION**

Education is an international/global scale enterprise, in every country in the world, school based education is a firmly established component no matter what the social, economical and political directions are. On the other hand, in comparing education within many countries and societies, it can be observed that the educational provision is characterized by many contrasts that can be summarized into social, economic, ethnic, religious factors. All these factors and others shape the patterns that are observed in the organization and management of the educational system. (Nick. F) Much work and effort have been given to the analysis of the reasons behind discrepancies between the developed countries' educational system and the Arab educational system, especially at the university level. Many would argue that human resources, financial issues, curriculum development problems are behind these great differences in the two systems. (Akkabar. A) Yet, there is a great belief that the real component is the lack or non efficiency of a proper educational leadership skills list within this system.

This work investigates educational leadership skills as being educational components that have to be presents not only in managers and conventional leaders but rather in all contributors to educational system in higher education especially within students' communities. A comparative study shows that the concept of leadership skills is very relative as it changes from west to East. Nevertheless, all agrees that acquiring knowledge and leadership skills is what helps countries and societies to develop. For this purpose, a descriptive study has taken place in Zayed university in the UAE to analyze the output of developing curriculum using project based learning (PBL) concepts. In parallel, another field study has also taken place in order to increase awareness of the importance of such skills. Results were hoped to be positives and promising, and to prove once more that in order for students to succeed they should acquire few of the leadership skills besides knowledge. The work concludes by providing studies' summaries and recommendation that were presented to work further in this field of higher education in order to prepare capable and competent graduates who would help in developing their societies, their country and the region.

## **EDUCATION LEADERSHIP SKILLS**

A growing recognition that leadership development involves more than just developing individual leaders has now led to a greater focus on the context in which leadership is developed. In fact, thoughtful and careful consideration about how to best use leadership competencies in various domains have been carried out and programs and

curriculum have been developed all over the world. Furthermore new ways of thinking about the nature of leadership and leadership application have been explored by inspiring its ideas and concepts from business like fields and domains. Recently, effective leadership has been commonly viewed as central to organizational and institutional success, and more and more importance is placed on leadership implementation and development than ever before.(Alldredge. M)

**Leadership Concept Interactions:** In the education field and approaching leadership concepts and educational leadership skills, it has well been acknowledged that of all the work that occurs at every level of the education system in general and of the university level in specific, there are many types of interactions that are taking place within the educational institution. Examples of these interactions are: the interaction between professors and students, administration and professors, administration and students, students and curriculum, professors and curriculum,...In this work, the focus will be given to curriculum and students, and how can they be affected by leadership concepts and leadership skill implementation and/or development.

*Curriculum:* In addition to administration and professors, university curriculum has been recognized to have a great input and role on the academic environment in the educational institutions. Good and well developed curriculum helps university professors and students to achieve their academic goals. In addition, curriculum has been considered to be the real heart of education improvement. It is not only a list of topics to be taught to students in educational institutions, it can serve several purposes simultaneously, indeed, curriculum may be viewed as a powerful tool for the administration, professors in their attempts to develop their own educational institutions, to increase equal access for all students and to raise the quality of teaching and learning.

Also, it is worth stating that curriculum development is an ongoing process and it is not a product, thus to proceed to a curriculum development in a leadership environment is to change it from project thinking to a process thinking. This curriculum development is in general a process that requires expertise and continuous production of new knowledge and skills. Thus, there is a need to stronger research and potential directions and curriculum models as well as to a systematic assessment and analysis on the implementation of the new curriculum in the educational institutions.(Joyce. B) For a curriculum that is meant to be adopted in a academic leadership environment, direct copying and transfer of any of curriculum types, of any one of the academic systems in any of the developed countries, has to fail due to cultural, social, economical and political differences. A real challenging and relevant academic curriculum could move from one type to another or can take part of one type and parts of other types. Courses' outlines and courses' outcomes should be carefully planned and designed accordingly, and tested afterward. In addition, when working a curriculum that will help implementing and developing educational leadership skills, it is always needed to search for interesting experiences, problems and their solutions that may be useful as resources in the ongoing curriculum design and assessment. For instance, in Zayed University, this specific approach was carefully taken into account in the development of general education courses. For example in the introduction to environmental course that deals with environmental problems and solutions, issues related to the UAE environment were heavily discussed and UAE statistics were presented and studied. Students' enthusiasm and involvement during all those discussion were very noticeable. UAE as being a young country(40 years), its education and higher education in specific a being even younger, there is a great chance that needs to be embraced by educators, administrators and researchers to introduce new educational concepts and procedures in order to help graduating students with competence, knowledge and skills.

*Students:* At the college and university level, it is worth mentioning that these relations and interactions between all educational components are even stronger and critic as the students have only few years a head to embrace the job's world. Now a days, most leadership trainings and programs specially those conducted and established in the western world are based on the traditional concept of leadership. For university students and in college classes today, few students learn the leadership skills they need for their future jobs or to serve their communities. In most universities, the development of student leadership skills is not part of the academic curriculum but attributed to "extra-curricular" activities, thus, it is mostly regarded as part of students' non academic activities in clubs and organizations rather than being part of the students' every day life. Yet, it has been found that the most effective leadership trainings and programs occur in everyday settings that includes the course of learning, the course of a community group planning an event and ...(Renate. N) These everyday venues can potentially serve as opportunities for leadership development for all university students. In this regard, students' courses, student organizations (students' council and students' clubs) contain many good opportunities for leadership skills implementation and development. In fact, if a professor/student group consciously conducted leadership development for members as part of the ongoing work of the group, if each semester members of the group did a leadership development exercise and each member identified one skill to develop in the course of that semester, if

that same exercise were conducted each succeeding semester and became part of that organization's ongoing activities, and there fore many new leadership skills would be implemented and developed for each member by the time he or she graduated from college. The success would be tremendous if the similar strategies are adopted in every class of the university, in all other universities and institutions and that will with no doubt have a great impact on communities and societies development.(Wheatley. M)

As a summary, leadership concepts in the educational field at universities and colleges is a complicated matter and process. Many components are overlapped and should be taken into consideration. The focus in this study has been directed to curriculum and students and it has been proven that these two components need to have access to the preparation, trainings, on-going support, recognition, and collaboration opportunities.

#### **FIELD STUDY AT ZAYED UNIVERSITY**

**Curriculum: Project Based Learning in a GE course:** It has been demonstrated that PBL (Problem based learning) may be the most effective approach to lifelong learning and assessment. This academic approach can train students, and learners in general, in such characteristics as: teamwork, enthusiasm, motivation, leadership skills, interpersonal skills, organizational skills. All these skills are very desirable talents in the 21<sup>st</sup> century both in career axis, jobs axis and people lives in general. For instance, PBL is a curriculum design and a teaching/learning strategy which simultaneously develops higher thinking order, disciplinary knowledge bases and practical skills by placing students in the active role of practitioners (or problem solvers) confronted with a situation or a structured problem which reflects the real world.(Boud. D) The basic characteristics of PBL are that it is context based using real life cases and problems. It focuses on thinking skills, it requires integration of interdisciplinary knowledge and can be applied in small groups. Students are driven by a posed real life problem and become interested in its solution. As for the university professor's role, it is considered as one of support, rather than direction, and facilitating rather than instructing. It is obvious therefore, that PBL is a student centered teaching and instructing approach rather than professor centered teaching.

Although, the PBL approach has been extensively used in academia all over the world, this method interestingly has recently emerged as a tool for the development of leadership skills given the new challenging roles of leaders to act in the fast changing global societies.(Yeo.R) For this reason, a careful study has been carried out using courses offered in Zayed University. The discussed course here is a partially PBL course(GE) and the main objective behind using such approach is to develop and improve leadership skills for undergraduate students. The following is an example of a partially PBL course taught at Zayed University at the General Education level. This course (Data Modeling) is designed to provide Zayed University students with a broad general education in quantitative reasoning and critical thinking. It also provides a foundation for the development of their ability to function competently and confidently in majors' programs. The course is focused on analytical reasoning and thinking to solve real world problems in business, finance, economics, computer science, education and the natural sciences. The content of the course is delivered through classroom activities and project to introduce the students to the various topics. For some topics or case studies, data can be from primary sources connected with other courses, such as Environmental Science, Health Science and other general education courses. In each area, knowledge, analytical skills, critical thinking and understanding are developed using relevant examples for discussion, analysis and interpretation in class with follow up exercises or assignments of a similar nature to be done individually or in groups outside the classroom. To be able to take this course, students should have suitable mathematics placement test results. The course emphasis is on applications of quantitative reasoning in the context of real world problem that are mostly related to the United Arab Emarites. Using the knowledge and skills learned and discussed in classroom, students were provided with a course project. The project has three different sets of data and students should first complete these sets by gathering primary data using either data collection or surveys. Afterwards, students needed to model all the data and make sense out of it by using some or all knowledge and skills learned in classroom activities. Students needed to work in groups, and therefore get involved in project group planning, results discussions and projects challenges were looked at inside the classroom. Toward the end of the semester, a survey was administered for the "Data modeling" course students. The following charts present students perception and attitude toward the Data Modeling GE course project:

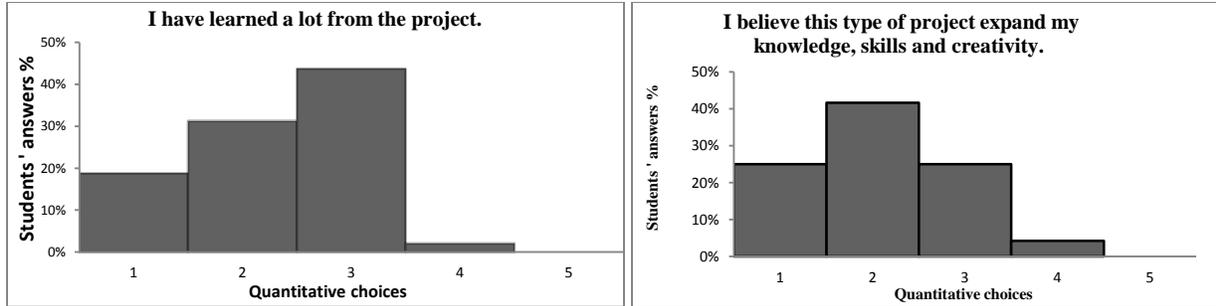


Chart 1 and Chart2: Statistics of educational leadership skills perceived by 2011 ZU undergraduate students. (1,2,3,4,5) were converted respectively from (Strongly agree, Agree, Neutral, Disagree, Strongly disagree).

Students perception toward this style of learning was mostly positive. Good percents of students have liked the project and believe to have learned a lot from it. Other portion of interviewed students were either neutral or they disagreed about the project concept. This shows that more effort is needed to be directed on curriculum development, and that most if not all general education courses should be developed toward PBL concepts. As a summary, this type of courses that are offered at Zayed University are real good cases where students can develop leadership skills. These courses were discussing issues that are related to the students' lives and that will help them better understand and work efficiently later on for their societies and countries.

**Students: Educational leadership awareness:** It has been proven in the previous study and other studies as well that students' attitudes and approaches to educational leadership skills in courses in general and quantitative courses in specific can profoundly influence their motivation to learn and develop their expertise.(Lahkim. M) And as discussed previously in the introduction, there is a list of leadership skills in general and educational leadership skills in specific that should be acquired by students in order for them to get skills as well as knowledge. This list includes skills such as objective (goal), communication, working with others... The previous courses' description as per new teaching and learning concepts and approaches (PBL) had proven to successfully help students learning as well as earning educational leadership skills both from a personal and interpersonal point of view. These leadership skills have been known to hold a great importance in determining the success of students. Nevertheless, resistance to the new approach from both professors' sides and students' side and lack of awareness of the importance of these educational skills could be a challenge in the trial of implementing these leadership skills within the educational institutions. An other major challenge to applying PBL concepts in general educations courses is that there are many sections (around 50) and an average of 25-28 students(For the Data modeling course taken in the study). The language skills, varied backgrounds, and attitudes toward teaching vary from one professor to another. In an effort to maintain quality teaching in all sections, general course outcomes were specified and general assessments were applied, yet all of that limit the flexibility and openness of the PBL nature. In a trial to reinforce the acquisition of educational leadership skills within Zayed University students population from another axis, a parallel effort was lunched in few of the Zayed University general education courses (Data modeling course was one of them). The aim behind conducting the following field study (academic experiment) is basically to help Zayed University undergraduate students focus on one or two items of the above educational leadership skills` list, be aware of it, then study its effect on the student's academic performance at a further phase. That leadership attitudes and approaches have been developed and validated in a daily basis, and the procedure was carried out by implementing in a day to day base few educational leadership skills then by detecting its impact on students toward the end of the semester via survey2a. An example of how the course objective and units' specific objective were discussed is illustrated in the flow chart below:(as per the data modeling GE course)

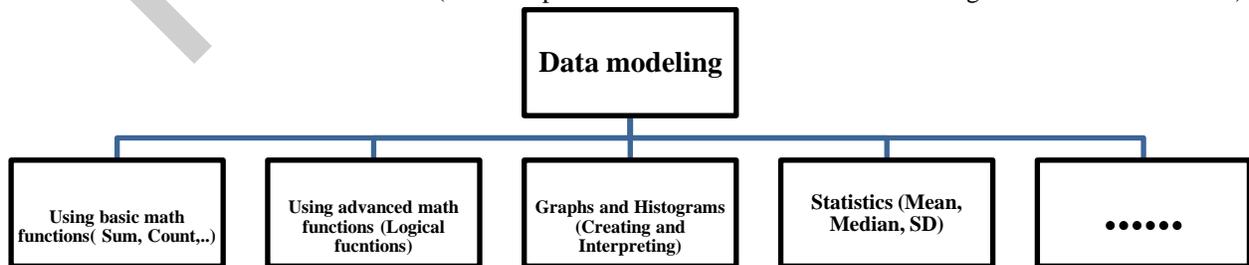
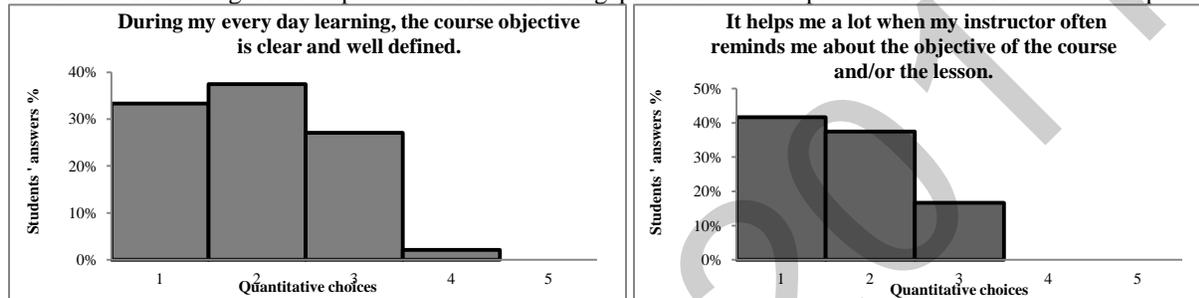


Figure 1: Example of flow chart used to illustrate course and unit objectives in a daily basis.

The results of this educational leadership skills awareness study and the comparison of students' responses to the survey questions provides good insight into their expertise and their academic performance. The other aim of the field study reported in this section is to examine Emirati students' educational performance in Zayed University as related to the impact of educational leadership skills awareness and PBL (Partially applied in the data modeling course) on students' performance. The purpose of this part of the study is to evaluate qualitatively and quantitatively the relationship between leadership skills and student's performance. For this reason, an online survey was administered to ZU female students toward the end of 2011 spring semester in Dubai campus. Students are in their third and fourth semester of study. From a general point of view, the survey focused on two main targets that are the education leadership skills acquisition, and the influence of the implementation of few educational leadership skills and the partially applied PBL model on the performance of students. The influence has been studied and analyzed qualitatively and quantitatively. Surveys2a' questions were meant to investigate students' implementation of few discussed educational leadership skills in the course work. The answers has shown an interesting trend, A good percentage of the students' population has shown great appreciation of identifying course objective and the continuous reminding of it importance. The following plots show data presentation for few selected questions.



Charts 3 and Chart4: Statistics of educational leadership skills awareness perception. (1,2,3,4,5) were converted respectively from (Strongly agree, Agree, Neutral, Disagree, Strongly disagree).

The above plots show that in general there is a students' positive attitude toward educational leadership skills awareness. The results are very encouraging and there are showing very good students' perception and understanding of educational leadership skills and their importance for students.

In addition to conducting survey2a that helps us to study quantitatively students' perception of educational leadership skills awareness, a comparative study has been performed for students' grades in the beginning of the semester and those at the end of the same semester. The purpose of this comparison study was to determine if spreading the awareness concepts and implementing few of the educational leadership skills within the course work has built leadership skills beyond classroom learning. For this reason, two sections of the same general education course GE were investigated and student's test grades were compared. The following chart was obtained:

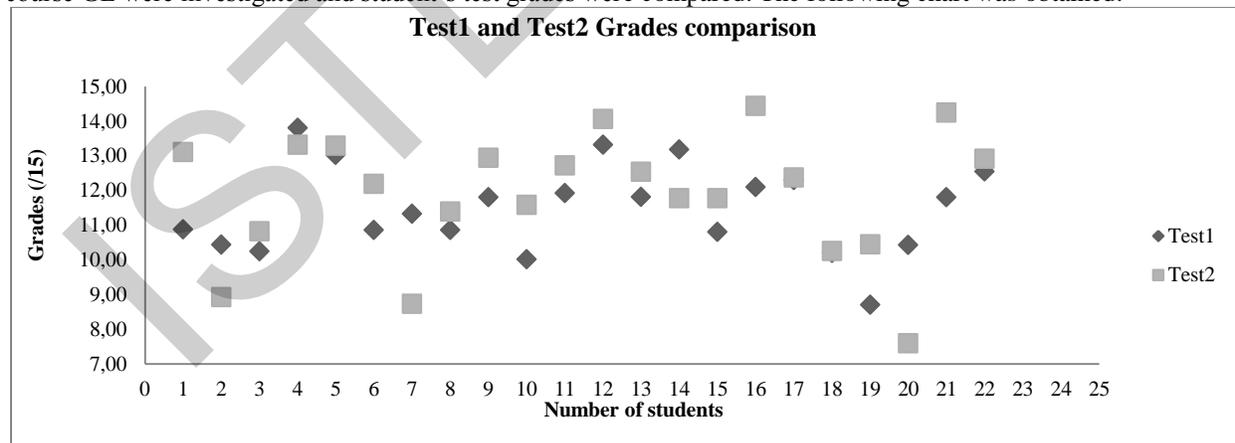


Chart 5: Example of a GE course COL110 grades comparison.

The study comparison lunched for the Data modeling GE course during the same semester has shown that the majority of students have got better grades as the semester goes on. Many factors can be behind this positive grades' change and there is a good chance that the educational leadership skills awareness and implementation has a greater role in this change. In order to confirm this result further studies need to be undertaken and more quantitative data comparison is needed.

## CONCLUSION

Concluding the whole research conducted in Zayed University within General Education students population, it has been found that leadership development skills are highly effective. Therefore, these skills should be developed and implemented by educational institutions to improve performance at various level. Various challenges such as the nature of GE courses (high number of sections and students, assessment, professors...), students resistance and ignorance of the learning concept could all be overcome. At Zayed University and other universities in the Arab world, more work and effort should still be directed to curriculum development and students leadership skills awareness.

In addition to applying non classical pedagogical ways of instructing such as problem solving (PBL) and case studies, and direct incorporation of few of the educational leadership skills within the university courses. Special courses could be designed to help implementing these skills within the students populations at the university level. One leadership course could be incorporated each semester for students during their General education period or prior to entering the GE level. These courses could discuss educational leadership skills, their importance in the education field and job market, Various themes related to students' culture, background and environment could be suggested for each course and within the university course outlines. On the other hand, professors and administrators should also be part of the educational leadership implementation experiment. Thus, creating a leadership environment within the educational institution would affect with no doubt the performance of students, professors and administrators. Therefore, ongoing leadership workshops, ongoing curriculum development and ongoing educational leadership research should be part of Zayed University priorities in order to raise the level of education.

Also, educational leadership skills should also be perceived from many other sources, not just from inside classrooms courses and activities, even though the usual sources are likely to be still the most influential. Efforts to improve students' recruitment, training, evaluation and ongoing development via university clubs, extra curriculum activities, independent studies and ...should be considered highly cost effective approaches to successful students' improvement. These efforts will be increasingly important for university students as those practices converge into establishing a new education system, improving its overall quality and substantially adding value to students' learning.

In Zayed University and other universities in the Arab world, much work is still needed at the level of curriculum development, students readiness (leadership skills), professor competence and administrator cooperation. Further research is planned to increase the educational leadership awareness within Zayed University students' population as well as conducting research on curriculum development, professor and administrators' involvement in the domain of educational leadership.

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# EFFECT OF H<sub>2</sub> REDUCTION ON CARBON NANOTUBE SYNTHESIS

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## ABSTRACT

Carbon nanotubes (CNTs) with their high mechanical, electrical, thermal and chemical properties are regarded as promising materials for many different potential applications. Chemical vapor deposition (CVD) is a common method for CNT synthesis especially for mass production. There are important parameters (synthesis temperature, catalyst and calcination conditions, substrate, carbon source, synthesis time, H<sub>2</sub> reduction, etc.) affecting the structure, morphology and the amount of the CNT synthesis. In this study, CNTs were synthesized by CVD of acetylene (C<sub>2</sub>H<sub>2</sub>) on magnesium oxide (MgO) powder substrate impregnated by iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O) solution. The synthesis conditions were as follows: at catalyst calcination temperatures of 400 and 550°C, calcination time of 0, 15 and 30 min, hydrogen concentrations of 0, 5, 10, 20, 50 and 100 % vol, synthesis temperature of 550°C and synthesis time of 30 minutes. The synthesized materials were characterized by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), and Raman spectroscopy. Effect of H<sub>2</sub> reduction on catalyst calcination and CNT synthesis were investigated.

**Key words:** H<sub>2</sub>, reduction, carbon nanotubes, CVD, synthesis, fluidized bed

## INTRODUCTION

Since the carbon nanotubes discovery of by Iijima in 1991 (Iijima,1991), Carbon nanotubes (CNTs) have attracted much attention due to their exceptional electrical, optical and mechanical properties. Therefore, they can be implicated to many fields such as electronics, chemicals, sensors, energy storage, and biotechnology. However, currently major obstacles are present in the application of carbon nanotubes. Specifically, the exact growth mechanism of CNTs and their resulting properties are not yet well understood. Hence, there has been an ungoing effort to understand the growth of CNTs. Various methods were used for carbon nanotubes growth, both single-walled and multi-walled nanotubes (SWNTs and MWNTs), including arc-discharge (ADE) (Maiti et al., 1994), laser beam evaporation (LBE) of graphite (Guo et al., 1996) and chemical vapor deposition (CVD) of carbon through catalytic decomposition of hydrocarbons (Hernadi et al.2000; Trimm,1977) . The catalytic chemical vapor deposition method is a very efficient technique for the large-scale and low-cost synthesis of carbon nanotubes. Recently, several groups have started academic and engineering researches on the CVD in the fluidized bed reactor process (Pérez-Cabero et al., 2003; Corrias et al., 2003; Qian et al., 2004) based on the catalytic decomposition of carbonaceous gases on a catalytic material that contains transition-metal nanoparticles. For large-scale production, the use of a fluidized bed reactor has been proposed as an alternative to avoid obstruction of the carbon deposited and damage to fixed bed reactor walls (Pérez-Cabero et al., 2003). There are different parameters (synthesis temperature, catalyst and calcination conditions, substrate, carbon source, synthesis time, H<sub>2</sub> reduction, etc.) affecting the structure, morphology and the amount of the CNT synthesised. In the growth of CNTs, it is clear that hydrogen is an essential element having been implicated in a number of surface morphology change of the catalyst. The activity of hydrogen with the hydrocarbon gas is also important. During recent decades, many studies have been reported in this subject (Chang Chung et al., 2004; Kim et al., 2006). In a study conducted with the effect of H<sub>2</sub> addition on synthesis yield of CNT was investigated and the relation between the reduction degree and reaction temperature, the ratio of H<sub>2</sub>/CO concentration in the synthesis was observed. It was reported that the high reduction degree of catalyst before synthesis is an essential condition for high yield of CNTs because low reduction degree means the insufficiency of an active catalyst required to make CNTs. Optimum gas flow rate of H<sub>2</sub> on CNT synthesis was determined. Also it was found that when content of H<sub>2</sub> was higher this critical value, the shapes of CNTs became worse due to transition into inactive surface of catalyst (Chang Chung et al., 2004). In another study, the effect of growth temperature on the CNT synthesis was examined with H<sub>2</sub> reduction. It was found that the H<sub>2</sub> reduced the iron oxide to different oxidation states, depending on the time of H<sub>2</sub> introduction. When H<sub>2</sub> was introduced at 200°C, very little growth was achieved. As the H<sub>2</sub> was introduced at 400°C and 600°C, the growth was curbed with very little CNTs resulting on the samples. When H<sub>2</sub> was introduced at 600°C, CNTs were seen only on the edges of the substrate (Kim et al., 2006).

In this study, the effects of H<sub>2</sub> reduction on catalyst calcination and multi-walled carbon nanotubes (MWCNTs) synthesis were investigated. MWCNTs were produced by CVD of (C<sub>2</sub>H<sub>2</sub>) on magnesium oxide (MgO) powder substrate impregnated by iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O) solution. While catalyst calcination and CNTs synthesis, parameters such as calcination temperature and time, H<sub>2</sub>% concentration in catalyst calcination and CNT synthesis were optimized to investigate the effects on the carbon efficiency and quality of CNTs. The synthesized materials were characterized by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM), Raman spectroscopy.

## EXPERIMENTAL STUDY

### Synthesis of Carbon Nanotubes

Multi-wall carbon nanotubes were synthesized by the fluidized-bed CVD synthesis of acetylene ( $C_2H_2$ ) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) solution which has MgO to Fe weight ratio of 5%. The system was composed of a "Protherm" furnace that can operate up to 1100°C and a quartz reactor with a diameter of 2.5 cm and length of 94.5 cm. In the middle of the reactor is a nano porous silica disc allowing gas flow. The furnace is placed vertically and the quartz reactor is placed in it with the nano porous silica disc placed in the middle of hot region of the furnace. MWCNT synthesis was held on the 5 to 10 cm length region around the quartz disc of the reactor. To fluidize the bed a certain flow rate of gas was necessary for a given substrate catalyst mixture. For this purpose argon was used as carrier and inert gas and acetylene was used as carbon source. The gas was fed to the system through the bottom of the reactor and it left the system from the top. A magnesium oxide ( $100 \text{ m}^2 \text{ g}^{-1}$ ) supported iron oxide powder produced by impregnation in an iron nitrate ethanol solution is used as precursor powder. To get a precursor with a MgO to Fe weight ratio of 5%, MgO were suspended in ethanol and iron nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) previously dissolved in 100 ml ethanol was stirred together and sonicated for 20 min in order to homogenize the mixture. Afterwards the precursor was dried and grinded into a fine powder. The catalyst and substrate mixture was placed homogeneously on the disc. For MWCNT synthesis while heating the system to calcination temperatures of 400°C and 550°C by an increase of 10°C/min, 100 ml/min argon was fed to the system to maintain inert atmosphere and to make flow of other gases existing in the system. As the temperature reached calcination temperature,  $H_2$  flow started with argon to form reduction on iron oxide catalyst. To investigate the effect of  $H_2$  reduction in calcination, hydrogen concentrations in gas mixture were varied as 0, 5, 10, 20, 50 and 100 % vol. Calcination times were selected as 0, 15 and 30 min. After calcination, the furnace was heated to the synthesis temperature (550 °C). The synthesis was started with the introduction acetylene mixed with argon and different  $H_2$  concentrations (0,5, 20 and 50 % vol) for 30 min. After synthesis, the MWCNTs were cooled in inert gas (argon). The total experimental time varied from 2 to 3 h with duration of actual growth stage 45 min. All experimental conditions were given in Table 1.

Table 1. Calcination and synthesis experimental conditions

Exp. No	Calcination Experiments					Synthesis Experiments			
	Ar flow rate (ml/min)	$H_2$ flow rate (ml/min)	Calcination temp. (°C)	Calcination time (min)	$C_2H_2$ flow rate (ml/min)	Ar flow rate (ml/min)	$H_2$ flow rate (ml/min)	Synthesis time (min)	Synthesis temp. (°C)
1	410	0	400	30	41	369	0	30	550
2	410	0	550	30	41	369	0	30	550
3	0	0	550	0	41	369	0	30	550
4	410	0	550	15	41	369	0	30	550
5	369	41	550	15	41	369	0	30	550
6	328	82	550	15	41	369	0	30	550
7	205	205	550	15	41	369	0	30	550
8	0	410	550	15	41	369	0	30	550
9	369	41	550	30	41	369	0	30	550
10	328	82	550	30	41	369	0	30	550
11	205	205	550	30	41	369	0	30	550
12	0	410	550	30	41	369	0	30	550
13	369	41	400	15	41	369	0	30	550
14	328	82	400	15	41	369	0	30	550
15	205	205	400	15	41	369	0	30	550
16	0	410	400	15	41	369	0	30	550
17	369	41	400	15	41	369	0	30	550
18	328	82	400	15	41	369	0	30	550
19	205	205	400	15	41	369	0	30	550
20	0	410	400	15	41	369	0	30	550
21	0	410	550	30	41	348,5	20,5	30	550
22	0	410	550	30	41	287	82	30	550
23	0	410	550	30	41	164	205	30	550
24	0	0	550	30	41	348,5	20,5	30	550
25	0	0	550	30	41	287	82	30	550
26	0	0	550	30	41	164	205	30	550

### Characterization of Materials

The synthesized MWCNTs were characterized by transmission electron microscopy (TEM) -FEI-Tecnai-G2 F-20 instrument, raman spectroscopy-Horiba Jobin-YVON HR 800UV instrument and thermogravimetric analyzer (TGA)-TA-Q600 SDT instrument.

## RESULTS AND DISCUSSIONS

### Structure Characterization of Multi Wall Carbon Nanotube

By the synthesis temperature of 550°C at a fixed iron content of 5%, a synthesis time of 30 min. and acetylene as carbon source the yield was obtained in multi-wall nanotube type. TEM image of this yield was given in Fig. 1. It has obviously been seen from Fig. 1 that the diameter of the CNTs is 10 nm and their appearance is darker in the picture. One possible explanation for the dark parts is a result of the impurities within the structure. This observation lead to a conclusion: in the temperature of 550°C MWNTs were grown.

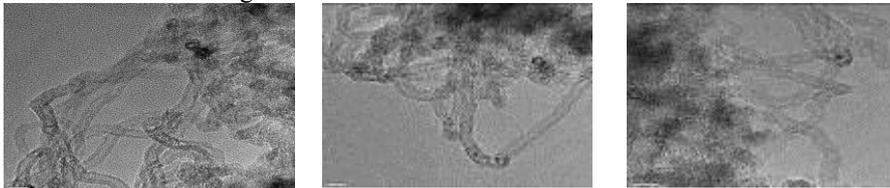


Fig.1. TEM images of MWNTs

Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. Fig. 2 shows Raman spectrum for carbon deposits excited by 633 nm laser. As seen from Fig. 2, the spectrum in RBM band which is a characteristic of SWNT was also observed in the sample. The reason of this spectrum which was observed at MWCNT is that the innermost tube diameter was below 2 nm.

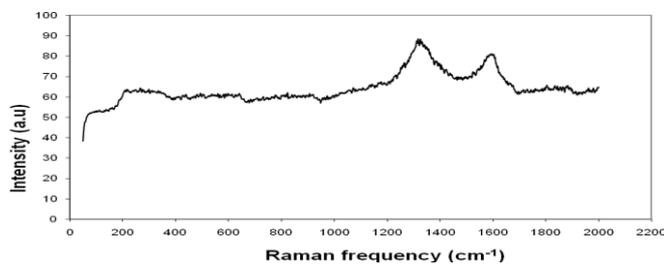


Fig. 2. Raman spectra of MWNT

### Effect of Hydrogen Reduction

The effects of H<sub>2</sub> reduction were investigated into two parts: catalyst calcination and MWCNT synthesis. The carbon efficiency of the synthesized MWCNTs was calculated according to TGA measurement. In order to eliminate any differences which may be caused due to moisture content of synthesized samples, in the calculations the initial temperature was selected as 200°C to have the dry weight percent and the final temperature was taken as 800°C to have the same temperature value for all samples. The formula of carbon efficiency is:

$$\text{Carbon efficiency (\%)} = \frac{\text{Weight\%}(200^\circ\text{C}) - \text{Weight\%}(800^\circ\text{C})}{\text{Weight\%}(200^\circ\text{C})} \times 100 \quad (1)$$

Thermogravimetric (TG) analysis is used to characterize the total carbon loading and determine the residual metallic catalyst. The amorphous carbon is completely oxidized at temperatures below 350 °C and graphite burns above 750 °C. The oxidation temperatures of the CNTs depend on the nanotube type and MWCNTs is generally oxidized at the temperatures above 400 °C. In this study, the TG analysis of MWNTs was conducted in air atmosphere with a ramp of 10 °C/min between 200 and 800°C. Carbon efficiency (%) of the MWCNTs were obtained from TG analysis. TGA results were given in the Table 2.

Table 2. TGA results of MWCNTs

Exper. No	Calcination Temp. (°C)	Calcination Time (min)	H <sub>2</sub> % in calcination	H <sub>2</sub> % in synthesis	Carbon Efficiency %
1	400	30	0	0	42
2	550	30	0	0	45
3	550	0	0	0	49
4	550	15	0	0	44
5	550	15	10	0	23
6	550	15	20	0	35
7	550	15	50	0	41
8	550	15	100	0	39
9	550	30	10	0	32
10	550	30	20	0	37
11	550	30	50	0	38
12	550	30	100	0	53
13	400	15	10	0	40
14	400	15	20	0	44
15	400	15	50	0	41
16	400	15	100	0	43
17	400	30	10	0	40
18	400	30	20	0	46

19	400	30	50	0	49
20	400	30	100	0	42
21	550	30	100	5	58
22	550	30	100	20	59
23	550	30	100	50	55
24	550	0	0	5	54
25	550	0	0	20	57
26	550	0	0	50	64

### Effect of H<sub>2</sub> Reduction on Catalyst Calcination

#### Calcination Temperature

The effect of calcination temperature on carbon efficiency was examined for 100 % H<sub>2</sub> and two calcination times (15, 30 min). The selected calcination temperatures were 400 and 550°C. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig. 3. It is seen that there is a tremendous increase in carbon efficiency (from 42% to 53%) of 30 min calcination time whereas there exists a slightly decrease in carbon efficiency of 15 min calcination time (from 43% to 39%). With this result it can be said that with the increase in calcination time there becomes an increase in the carbon efficiency. In summary the order of the carbon efficiency of given temperature of 400°C for 100% H<sub>2</sub> concentration is 30 min > 15 min, whereas for 550°C it is 30 min > 15 min.

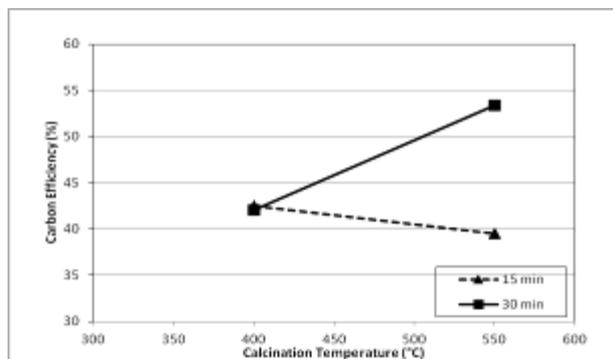


Fig. 3. Calcination temperature vs. carbon efficiency for 100 % H<sub>2</sub>

#### Calcination Time

The effect of calcination time on carbon efficiency was examined for 100 % H<sub>2</sub> and two calcination temperatures (400°C, 550°C). The calcination times were selected 15 and 30 min. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig. 4. It is seen that there is a tremendous increase in carbon efficiency (from 39% to 53%) of 550°C calcination temperature whereas there exists a decrease in carbon efficiency of 400°C calcination temperature (from 43% to 42%). With this result it can be said that with the increase in calcination temperature there becomes an increase in the carbon efficiency. In summary the order of the carbon efficiency of given time of 30 min for 100% H<sub>2</sub> is 550°C > 400°C, whereas for 15 min it is 400°C > 550°C.

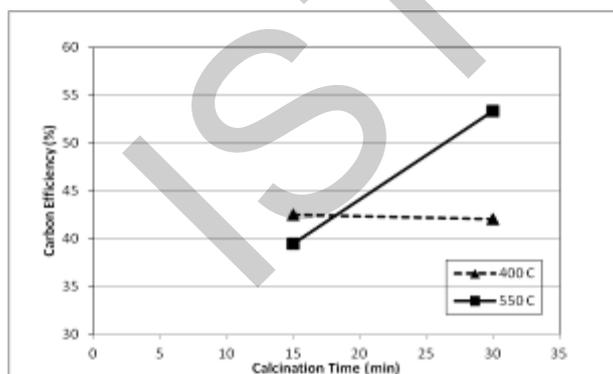


Fig. 4. Calcination time vs. carbon efficiency for 100 % H<sub>2</sub>

#### H<sub>2</sub> Concentration (%) in Calcination

The effect of H<sub>2</sub> concentration on carbon efficiency was examined for calcination time of 30 min and calcination temperatures of 400 and 550°C. The H<sub>2</sub> concentrations were selected as 10, 20, 50 and 100 % vol. Carbon efficiency of these synthesized materials from TG analysis are shown in Fig. 5. It is seen that there is a tremendous increase in carbon efficiency (from 32% to 53%) at 550°C whereas there exists an increase in carbon efficiency at 400°C (from 40% to 42%). With this result it can be said that with the increase in H<sub>2</sub> concentration % there becomes a regular increase in the carbon efficiency for 550°C of calcination temperature. Besides this for 400°C calcinations temperature, carbon efficiency increased between 10% and 50% H<sub>2</sub> concentration, then a decrease was found between 50% and 100% H<sub>2</sub> concentration. Depending on these results, it was examined that the highest carbon efficiency % was obtained with 100% H<sub>2</sub> concentration, 30 min calcination time at 550°C

calcination temperature.

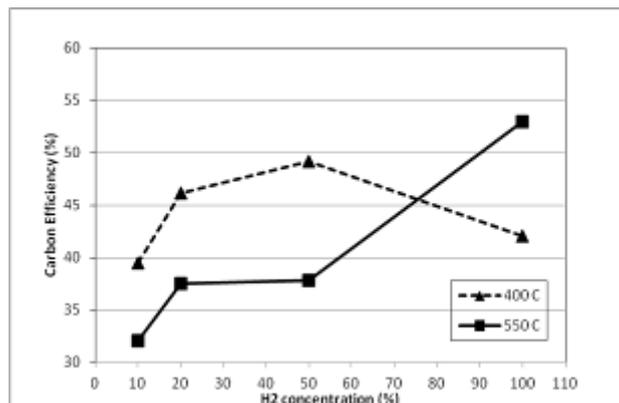


Fig. 5. H<sub>2</sub> concentration vs. carbon efficiency

### Effect of H<sub>2</sub> Reduction on CNT Synthesis

According to the TGA results of experiments which were carried out without H<sub>2</sub> reduction (0%) in CNT synthesis, the highest carbon efficiency values were obtained as 49% and 53% at 550°C calcination temperature for 0% and 100% H<sub>2</sub> calcination, respectively (Table 2). To examine the effect of H<sub>2</sub> reduction in CNT synthesis, H<sub>2</sub> was added into synthesis gas with three different concentrations of 5, 20 and 50% vol for 0 and 100% H<sub>2</sub> calcination. Carbon efficiency (%) of these synthesized materials from TG analysis are shown in Fig.6. According to the H<sub>2</sub> concentrations of 5, 20 and 50% vol in the CNT synthesis for 0% H<sub>2</sub> calcination there is a regular increase (from 49 % to 64 %) in carbon efficiency. Also TG analysis showed that for 100% H<sub>2</sub> calcination, there is an increase (from 58% to 59%), then a decrease (from 59% to 55%) in carbon efficiency. As a result of these values, it was found that H<sub>2</sub> concentration (%) in the CNT synthesis is important for increasing of carbon efficiency and this results are consistent with other studies found in literature (Uoo-Chang Chung et al., 2004). In the study of Uoo-Chang Chung et al., they investigated the shapes and structures of CNTs with H<sub>2</sub> addition in CO using a cheap iron oxide catalyst for CNTs synthesis. They found that the synthesized carbon weight increased with H<sub>2</sub> addition, and the value showed maximum in the H<sub>2</sub> gas with a flow rate of 0.7 L/min at 680°C with CO gas of 0,3 L/min. When H<sub>2</sub> value was higher than 0.7 L/min, carbon weight decreased as H<sub>2</sub> contents increase. Also it was found that when content of H<sub>2</sub> was higher than this critical value (0.7 L/min), the shapes of CNTs became worse due to transition into inactive surface of catalyst. It was also found that H<sub>2</sub> addition had an influence considerably on the shape and structure of CNTs.

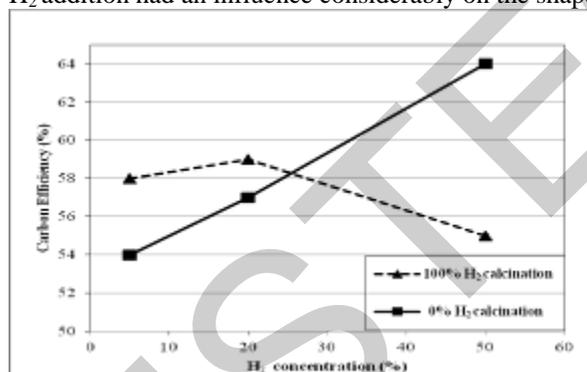


Fig. 6. H<sub>2</sub> concentration vs. carbon efficiency

## CONCLUSIONS

The present study has shown that calcination temperature, calcination time and H<sub>2</sub> concentration (%) are important parameters in catalyst calcination and MWCNT synthesis. As a result of TGA measurements, at highest calcination temperature (550°C), carbon efficiency (%) was increased with calcination time (15, 30 min) and H<sub>2</sub> concentrations (10, 20, 50, 100%). In addition to these results, with increase in H<sub>2</sub> concentration (5, 20, 50%) in synthesis gas, higher carbon efficiencies were obtained. Experimental evidences and measurements showed that the carbon efficiencies of synthesized MWCNTs are positively affected with increase the calcination temperature, calcination time and H<sub>2</sub> concentration (%) in CNT synthesis.

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# EFFECT OF ILLUMINATING ANGLE AND ROUGHNESS ON THE ANGULAR SCATTERING LIGHT

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## ABSTRACT

The vision of vehicles drivers is influenced by the scattered light which depends on various factors such as the inclination angle, the intensity of the light source and the surface state of the windshields. In this context, we studied the effect of illuminating angle and projected sand masses on scattered light. For the incidence  $\alpha = 30^\circ$ , the results show that the number of created defects increases with the projected sand mass until reaching a saturation state at 50g ( $Ra \geq 2.50 \mu\text{m}$ ) in the chosen test conditions. The specular transmission and reflexion decreases regularly and reaches a constant value of 15% and 0.5% respectively. At the same time, the illuminating angle affects the transmission and the reflection and therefore the light scattering. We can notice that for  $\alpha = 60^\circ$ , the specular transmission and reflection drop of 46% and 36% respectively. The variation of the transmission and the reflection according to projected mass shows an inflection point at ( $T = 70\%$ ,  $Mp=18\text{g}$ ) and ( $R = 4\%$ ,  $Mp = 18\text{g}$ ). This points seems to separate two domains: a transparent field ( $Ra < 0.4 \mu\text{m}$ ) and a blur field ( $Ra > 0.4\mu\text{m}$ ).

Keywords : Glass, Sandblasting, Scattering, Transmission, Roughness.

## 1 INTRODUCTION

The visibility of objects through a car glass windshield can be affected by its surface state. The exterior windshield surface is differently exposed to damaging effect caused by dust, hail or sand according to the geographical region where the car is [1-2]. Their surface damage can induce different effects on the diffused light [3].

In Saharan regions for instance, sandblasting during sandstorms can affect tremendously the vehicles windshields surfaces. This inevitable and undesirable glass erosion phenomenon induces stray light that is harmful to drivers' vision particularly at night and during sunset or dawn.

The visibility loss is caused by light diffusion that occurs when structural heterogeneities appear either in the propagation medium volume or at the interface between two materials of different optical characteristics [4].

In this work, we studied the diffusion induced by surface heterogeneities caused by sandblasting on glass samples. We're concerned with elastic diffusion (without wavelength changes) that is related to the samples geometric characteristics.

## 2 MATERIALS AND TEST CONDITIONS

The samples were prepared from a soda-lime glass manufactured by AFRICAVER (an Algerian company located at Jijel region). The dimensions used were  $50 \times 50 \times 3 \text{ mm}^3$ . In order to simulate the effects of the sandstorm on the surface state of a glass, a sand blower apparatus was used (Figure.1). The erosion tests were realized in the following conditions:

Fixed parameters:

- Size range of the sand grains :  $\approx (200 \div 250) \mu\text{m}$
- Speed of the air flow :  $16 \text{ ms}^{-1}$
- Impact angle :  $90^\circ$
- Distance between the nozzle and the target : 50mm

Variable parameters:

- Mass projected :  $Mp = (10, 20, 50, 100) \text{ g}$

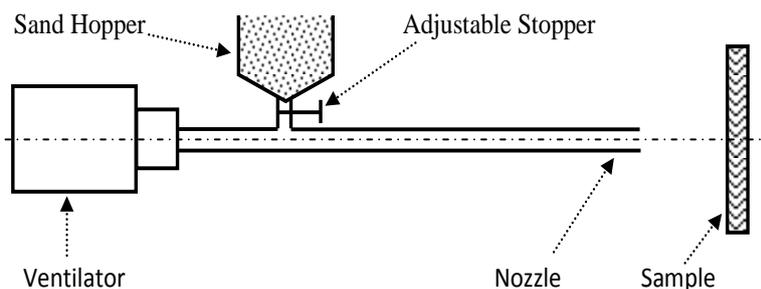


Fig.1 Schematic illustration of the used sand blower

Figure 2 shows typical photos of the glass samples damaged by different sand masses. For low masses, there are individual impacts, but for higher projected sand masses, the damages extend and cover the entire exposed surface which reaches a saturated state.

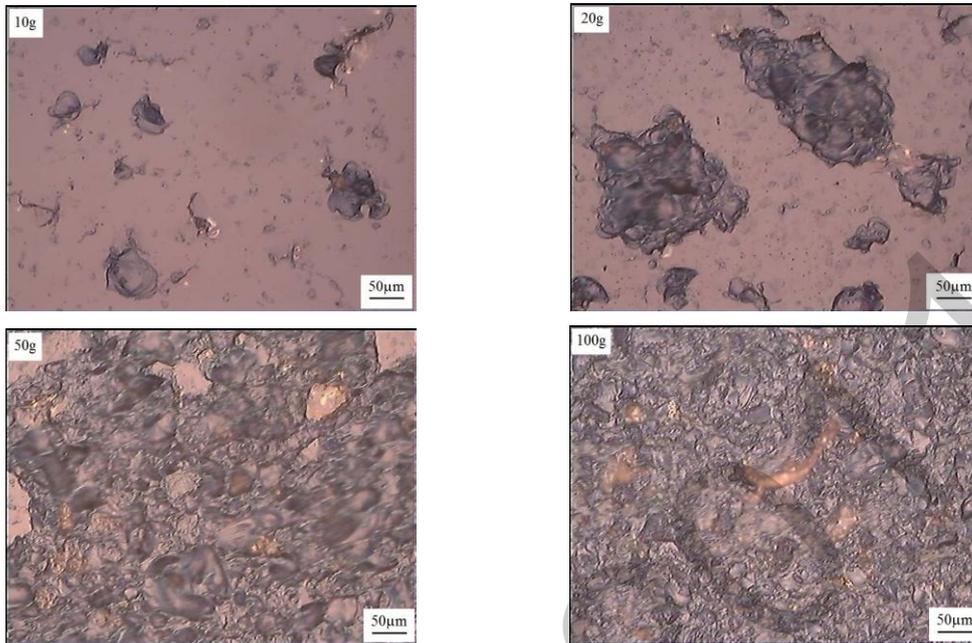


Fig.2 Optical micrographs of the eroded surfaces for different low masses.

## 2 OPTICAL EXPERIMENTAL APPARATUS

Figure 3 shows the schematic principle of the optical apparatus prepared for the purpose of this study. It consists in illuminating a sample fixed on the vertical goniometric plane at variable incidence ( $\alpha = 30^\circ$  and  $60^\circ$ ) from a 300W white light xenon source. The emitted light beam is collimated by a Koehler system composed of two lens ( $L_1$  and  $L_2$ ) and two diaphragms (DO and DC) before being diffused by the eroded analyzed surface area whose diameter is 3mm.

The transmitted and reflected beams are captured by a phototransistor (T) which is mounted on a mobile arm which is solidly attached to goniometric rotating table. The phototransistor (T) is placed at a distance of 50 mm from the analyzed surface where the measuring elementary solid angle corresponds to  $d\Omega = 4.10^{-4}$ sr. It allows converting the luminous energy into electrical energy expressed in EVA type nano amperes (10 nA-1 mA). The position of the phototransistor (T) in relation to the normal direction at the surface determines the diffusion angle  $\theta$ . The goniometer is composed of a fixed table graded from  $0^\circ$  to  $360^\circ$  and a moving table equipped with a graded jack between  $0^\circ$  à  $30^\circ$ . The optical system resolution is of  $1'$  ( $1/60^\circ$ ). In this

study, we determined the variations of the diffused light normalized intensity using the solid angle unit  $\frac{d\phi_{diff}}{\phi_0 d\Omega} = f(\theta)$  with variations of angle  $\theta$  at a pace of  $10'$ .

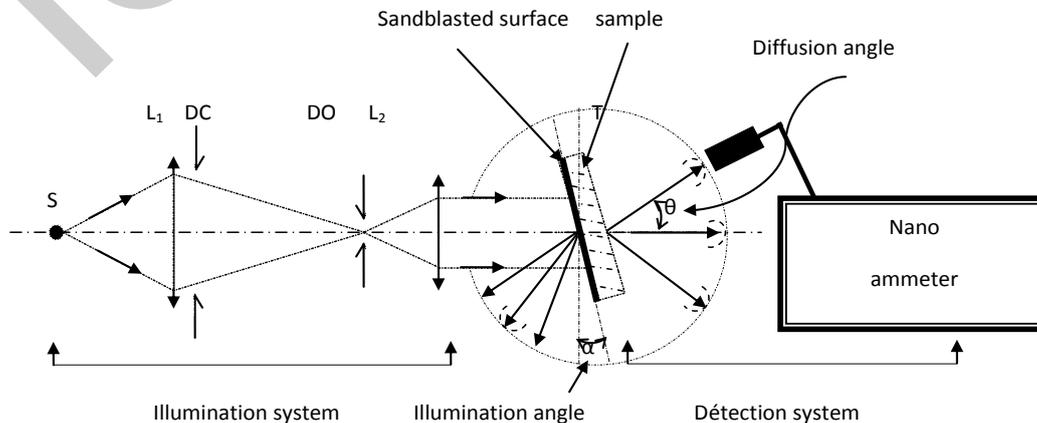
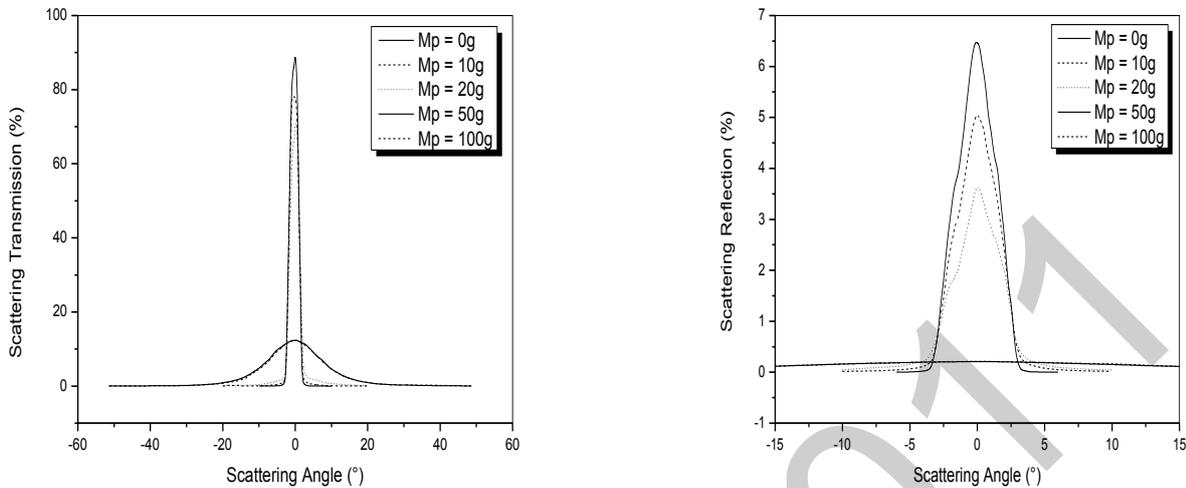


Fig.3 Schematic principle of the experimental apparatus

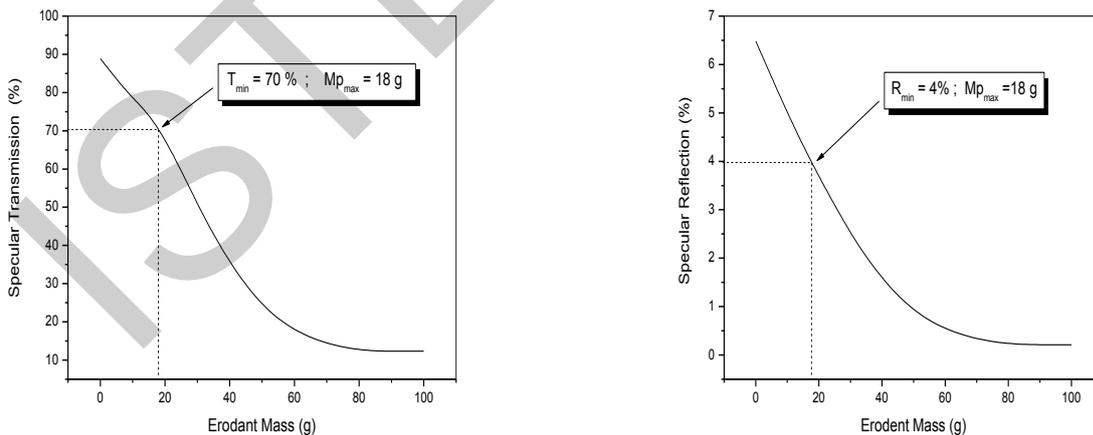
### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of the projected mass on the angular scattering transmission and reflection at $\alpha=30^\circ$ .



**Fig.4** Angular scattering transmission and reflection in relation to the projected mass at  $\alpha = 30^\circ$  for :  $M_p = (0, 10, 20, 50$  and  $100)g$

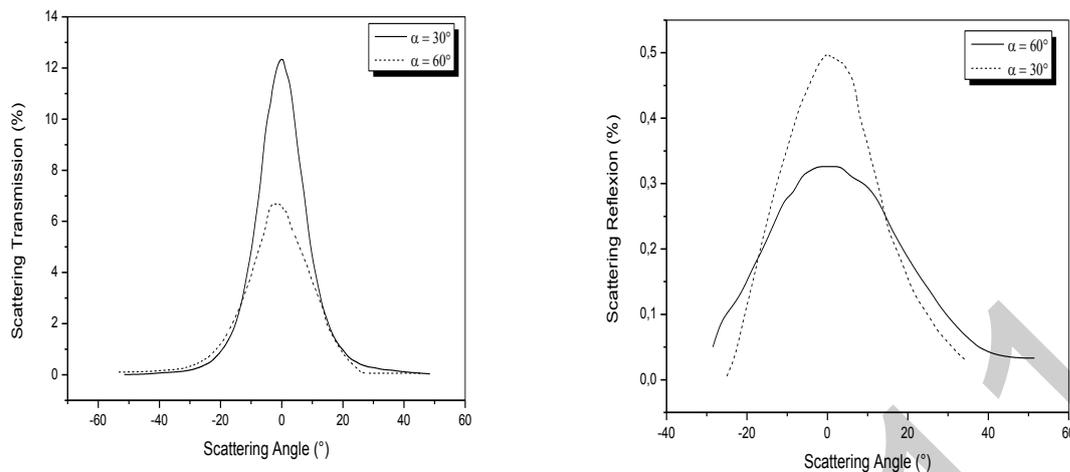
It appears of the figure.4, that as the projected sand mass increases, the angular scattered transmission and reflection increases. We can see that the diffused light is very important as the projected mass is high ( $M_p \geq 50g$ ). In this case, the surface state is more damaged. In the case of low mass we see that most of the incident light energy is concentrated in the specular direction. As the projected mass increases, the intensity of the specular beam decreases and the transmitted and reflected radiation becomes more diffuse. Furthermore, a very important widening effect was showed on the curves which correspond to the high projected mass. The increase of the widening effect was the result of the increase of the degradation of glass surface. At the same time, the degradation of surface state induces a loss of specular transmission and reflection. Figure. 5 show the variation of the specular transmission and reflection versus the sand mass projected. For both the transmission and the reflection cases, the energy loss in the specular direction decreases regularly before reaching saturation at 15 % and 0.5 % respectively



**Fig.5** Specular transmission and reflection in relation to the projected mass for  $\theta_i = 30^\circ$  : 0g, 10g, 20g, 50g et 100g

#### 3.2 Effect of the incidence angle on the angular scattering transmission and reflection for $m_p = 50g$

Parallely to the influence of the projected mass on the light scattered, the illuminating angle alleviates the optical transmission and favors the light scattered. Figure 6 represents the illuminating angle effect on the scattered transmission and reflection for sand mass project equal 50g. It clear, that the illumination conditions have an important influence on diffusion. We can notice that the specular transmission and reflection drop of 46% and 36% respectively. The diffusion that reduces the specular light transmission and reflection induces angular opening of the beams that are revealed by the curves spreading.



**Fig.6** Scattered light angular distribution for sandblasted samples  $M_p = 50g$  in relation to the incidence angle  $\alpha = 30^\circ$  and  $\alpha = 60^\circ$

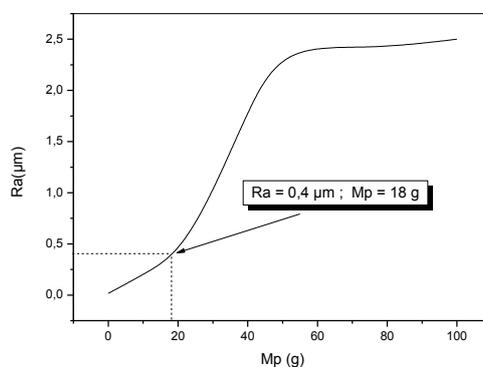
#### 4 DETERMINATION OF THE TRANSPARENT AND THE FUZZY DOMAINS

According to the figure 5, we can define two optical domains.

- A first transparency field where the optical transmission is rather high and the roughness is rather low.
- A second blurry field where the optical transmission is weak enough and the roughness is high

The determination of the limit between the two domains is based on the intersection between the line of the transmission value limit  $T_{min}$  and the curve of the variation of the transmission on function of the projected mass. According to B. Savaète[5], the tolerated visibility limit which corresponds to a minimal value of the valid transmission in Europe is 75% while it is 70% in Japan and in the United States of America. In this work, we opted to  $T_{min} = 70\%$ . In this case, the limit of the two domains is  $M_p = 18g$  which corresponds to  $Ra^{max} = 0.4 \mu m$  (show figure. 7). Since the transparent field which corresponds to a slow decrease of  $T$  and for roughness values lower than  $0.38 \mu m$ , and a fuzzy field corresponding to a sharp decrease of  $T$  and for roughness values greater than  $0.4 \mu m$ .

We based on the limit determined from the transmission curve, since we can be proposed a limit of reflection as a “limit value”. In our test conditions, this value corresponds to an optical reflection limit of about 4%.



**Fig.7** Variation of the arithmetic roughness  $Ra$  versus the projected sand masses  $M_p$ .

#### 5 CONCLUSION

In this work, we simulated the effect of sand blasting on the surface of a soda-lime glass. We have studied the effect of illuminating angle and the projected mass on the angular scattering light. The results show that the roughness increases with

the increase in the projected mass whereas for both the transmission and the reflection cases, the energy loss in the specular direction decreases regularly before reaching saturation at 15 % and 0.5 % respectively. For the low projected masses, the optical transmission and reflection is maximal in the specular direction. As the projected mass increases, a spreading out of the curves is observed. By varying the illuminating angle, we noticed a decrease of the specular transmission and a progressive spreading of the scattering curves.

The aim of this study is to define a roughness and an optical reflection limit that separates the acceptable transparency domain from the harmful fuzziness. The variation of the optical transmission and reflection according to the arithmetic roughness allows to define a visibility limit which is localized at about ( $T=70\%$  and  $Ra = 0.4\mu\text{m}$ ) and ( $R=4\%$  and  $Ra = 0.4\mu\text{m}$ ).

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## EFFECT OF PLANTING ENVIRONMENT AND INPUT APPLICATION ON NATURAL DISTRIBUTION PATTERN OF ENTOMOPATHOGENS

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### Abstract:

The effect of environmental factors was determined on the occurrence and diversity of entomopathogens in soils of southern and central Punjab, Pakistan. Effect of Soil types, tillage practices and pesticide applications on test population was investigated through Gallaria bait method. All three categories (minimum, moderate and maximum cultural practices) differ in soil types, cultural practices and pesticide applications. Four species of entomopathogenic fungi found were *Beauveria bassiana*, *Conidiobous globosum*, *Metarhizium anisopliae* and an unknown species with various frequencies in different categories. Total frequency of occurrence of these fungi was the highest in category 01 (minimum cultural practices) that was found to be 16.66 % among all types of observed fungal species in comparison with that of 12.5% in category 02 (moderate cultural practices) and 15.38 % in category 03 (maximum cultural practices). As concerned the variation in frequency of occurrence of individual entomopathogenic fungi species in all the categories; *Beauveria bassiana* and an unknown species was observed in category 01 with the same frequency of 8.33%. While *M. anisopliae* and *C. coronatus* was totally absent. *M. anisopliae* was the only species present in category 02 with frequency of 12.5% and in category 03, *M. anisopliae* and *C. coronatus* was only present with same frequency of 7.69%. While both *Beauveria bassiana* and unknown species were absent in this category. The absolute value of Beta Diversity ( $\beta$ ) of entomopathogenic fungi was 05 in different categories.

Key words: Entomopathogenic fungi, Gallaria bait method, *Beauveria bassiana*, Distribution frequency, Beta Diversity ( $\beta$ )

### INTRODUCTION

Fungi that infect insects have received considerable attention by scientists due to their potential for biological control of pests. Many research works have focussed the selection of virulent strains for target pests and their development as biological control agents. In contrast, it is surprising that very little is known about the fundamental ecology of most of these fungi in nature. This knowledge is essential in order to receive the most ecosystem services provided by entomopathogenic fungi in agricultural production. Knowledge of the basic ecology of the fungi is also necessary to include them in conservation biological control. In this biological control strategy, agricultural practices and/or habitat manipulations are applied to the farming system to favour living conditions for specific natural enemies of pests (Eilenberg *et al.*, 2001).

Studies of biodiversity in agroecosystems and the delivery of ecosystem services to agricultural production have usually ignored the contribution of entomopathogens in the regulation of pest populations (Altieri, 1999; Gurr *et al.*, 2003; Tschardtke *et al.*, 2005). However, entomopathogens are among the natural enemies of arthropod pests in agroecosystems. An authentic understanding of the ecology of indigenous populations of these beneficial organisms is a prerequisite for the evaluation of their contributions to pest control and for predicting the impact of agricultural practices on their populations.

Annually cropped agroecosystems are highly disturbed mostly due to tillage regimes and this affects the populations of natural enemies of crop pests. The communities of entomopathogenic fungi in the arable soil environments are different from communities of less disturbed habitats (Steenberg, 1995; Bidochka *et al.*, 1998; Meyling and Eilenberg, 2006) and fewer disturbances in the cropping system also affect the populations of the fungi. Likewise, conservation tillage regimes, using strip-till and no-till was more favorable to *B. bassiana* and *M. anisopliae* populations in the soil than conventional tillage regimes employing ploughing and disking (Hummel *et al.*, 2002a). These findings of higher fungal densities in reduced tillage and no-till systems could be observations of indirect effects caused by increased levels of host populations of non-pest insects. High population levels of non-pest insects have been observed in reduced tillage systems (Hummel *et al.*, 2002b). The observations cited above may therefore not necessarily be a direct result of mechanical disturbance on fungal population levels.

Chemical insecticides, herbicides and fungicides are usually applied in conventional farming practices. These compounds, especially fungicides applied against plant pathogens, might also negatively affect the populations of entomopathogenic fungi with reduced pest regulation potential as a consequence. However, most of the studies were performed in vitro with fungal cultures and extrapolation from studies in laboratory experiments to field conditions may not be straightforward. In vitro experiments further showed that the fungicide triadimefon inhibited the growth of *B. bassiana*, but fields previously treated with this product showed a higher frequency of occurrence of the fungus in soil samples than in samples from untreated control soils (Mietkiewski *et al.*, 1997; Chandler *et al.*, 1998). The fungicidal product albicarb even increased activity of in vitro cultures of *B. bassiana* (Mietkiewski *et al.*, 1997). This emphasizes that due to the complex interactions and composition of agroecosystems, applications of specific

fungicides are not necessarily detrimental to the occurrence of entomopathogenic fungi in the soil. Selected compounds could thus possibly be used in integrated pest management (Mietkiewski *et al.*, 1997).

Here, we present the effect of different cultural practices and input applications aspects of different agroecosystems in Punjab, Pakistan. Recent research work aims at the foundations to be laid for future focus on the indigenous populations of insect associated fungi as biological control agent in different cultural practices and input fertilizers and pesticides using CBC strategy.

## MATERIALS AND METHODS

### Site Description and Soil Collection:

In “Nawan Kot” Layyah, nine different chickpea fields with same climatic conditions, soil type (sandy) and altitude (145 m) were selected to check the occurrence and diversity of insect associated fungi. Five year history of all selected fields was acquired by means of collaboration with local farmers as well as Directorate of Agriculture Extension, Government of the Punjab and Directorate of Pest Warning and Quality Control of Pesticides, Government of the Punjab. The selected fields were divided into three categories and three fields from each category were selected for further research work.

**Table 1: Division of selected fields on the basis of cultural Practices**

Sr. no	Categories	Tillage/ annum	Irrigation/ annum	Sprays/ annum	Cultivated Crops
1	Minimum Cultural Practices	0-2	0-2	0-4	Chickpea, Barley
2	Moderate Cultural Practices	3-4	3-6	4-7	Chickpea, Wheat, Fodder, Millet,
3	Maximum Cultural Practices	5-10	7-12	7-12	Cotton, wheat, Barley, fodder

Soil samples were collected by digging out soil in agro-ecological system at different spots around plant rhizosphere covering an area of 5 meter square at the depth of 12 cm

with the help of either soil core sampler ( $\phi= 20\text{mm}$ ) or through auger. Five soil samples from each field were collected, pooled and mixed together into a single upto 01 kilogram. The altitude and geographical location of each site was measured by Global Positioning System. The soil from different categories sites were collected in dry conditions and packed in 15-20-cm polyethylene bags. Plastic bags were labelled with date, place, and source of collection.

### **Insect Bait Bioassay**

Rearing was performed in plastic boxes incubated in the dark in a climate controlled room at temperature  $20^{\circ}\text{C}$ . Adult moths were provided with a solution of water and honey. Under the lid of the box containing adults, strips of folded paper were provided for oviposition. The females were attempted to place their eggs in crevices as the folded paper represents. The paper was then easily removed with the eggs attached.

Paper strips containing eggs were placed in a new box with a ball of food for early instars. When the eggs hatch, the neonate larvae moved toward food themselves and started feeding. When the larvae grew approximately 1 cm in length they were provided with food for late instars. Larvae of approximately 2.5-3 cm length (4 weeks after hatching) were suitable for baiting soil samples.

When *G. mellonella* were reared at  $20^{\circ}\text{C}$ , four weeks old larvae were most suited for baiting to avoid that they pupate in the soil. To prepare the heat treatment:

1. Beaker was placed with 500 ml of water in a water bath at  $56^{\circ}\text{C}$ .
2. Larvae (+10%) were taken out of the rearing containers and placed in a box. Placed a sheet of paper in the box and the larvae crawled under this for hiding.

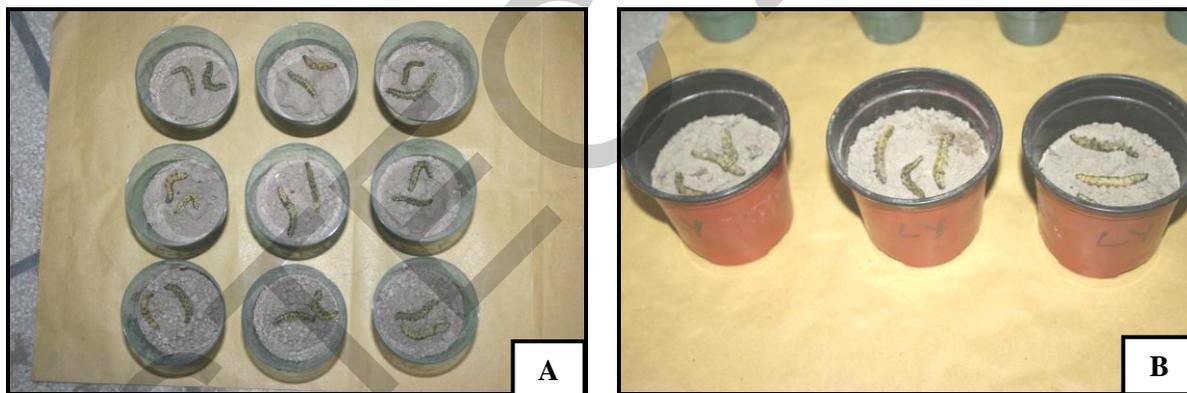
Thus they didn't crawl out.

3. The paper was removed and the box was trembled so that the larvae could not cling to webbing in the box. All the larvae were poured the larvae into the beaker with hot water for 10-15 seconds. The water was poured through a sieve and cooled the larvae in cold running water for 30 seconds. The larvae were placed on dry tissue paper and then placed in the dark for 3-5 hours.

4. When the larvae had recovered from the treatment (they appeared dead at first) placed them in the soil containers. Samples were not inverted because the larvae could squash and die.

Zimmermann (1986) recommended the insect bait method for the selective isolation of entomopathogenic fungi. Numerous studies have been carried out using insect baits, especially *G. mellonella*.

- Each soil sample was passed through 2-mm pore sieve to remove plant tissues and molding gravels or blocks, and then mixed thoroughly and placed in a plastic bag. Soil samples were sufficiently moistened with sterile distilled water.
- Soil samples were air dried and re-moisturized afterwards to appropriate levels to avoid infections by entomopathogenic nematodes.
- Three to five larvae were used for each sample.
- Baiting of each sample was replicated 5 times.
- The samples were incubated at  $21\pm 1^{\circ}\text{C}$  in the dark and individual containers were inverted daily in the first week.
- The samples were inspected for the first time after 5 days. After initial baiting, this inspection was repeated regularly after every 3-4 days for a period of 3 weeks.



**Figure 1:** Treatment of *Galleria mellonella* larvae with soil (A) Soil of Different Zones treated with *Galleria mellonella* larvae (B) Soil of different cultural categories treated with *Galleria mellonella* larvae.

### Isolation and identification of fungi

The dead bait larvae were surface sterilized with 1% Na-Hypochlorite for few seconds and inoculated to PDA petriplates at  $25^{\circ}\text{C}$  in incubator for 7 days. Insect-associated fungi were isolated from *Galleria* larvae and identified by their morphological

characteristics like colony color and shape of culture on PDA, conidiophore shape, and conidia shape and color with the help of several taxonomic keys (Domsch *et al.*, 1980; Nelson *et al.*, 1983; Samson *et al.*, 1988).

### **Preliminary Pathogenicity Test (Koch's postulates)**

Infections of isolates with unknown pathogenicity to the *G. mellonella* larvae were bioassayed. The tested fungus was grown on PDA plate for 10–12 days and its spores were washed with 1 ml sterile water into 1.5 ml tubes. The final instar larvae of *G. mellonella* were immersed into the spore suspension with forceps for about 3–5 s, and then transferred into 9 cm diameter Petri dishes with moistened filter paper. Petri dishes were sealed with parafilm to maintain the humidity, and were incubated at the temperature of 20–25°C in darkness. Infected larvae were inspected daily till death or pupation. Fungal structures growing out of the dead larvae were identified to evaluate whether the fungus was the same as inoculated. Five larvae were treated for a fungus and the experiment was carried out three times to evaluate the pathogenicity of the fungus. On the basis of pathogenicity, the isolated fungi were divided into following three categories as described by Sun and Liu, 2008:

- Entomopathogenic Fungi or Entomopathogens
- Opportunistic Fungi
- Secondary Colonizer

#### **Entomopathogens**

The isolated fungi that showed 100% mortality rate on larvae of *Galleria* were categorized as Entomopathogenic Fungi or Entomopathogens.

#### **Opportunistic Fungi**

The isolated fungi showing mortality rate from 1-90 % on the larvae of *Galleria* were categorized as Opportunistic Fungi.

#### **Secondary Colonizers**

The fungi isolated during *Galleria* baiting method that did not show any mortality on the larvae of *Galleria* were categorized as Secondary Colonizers.

## Data analysis

The frequency of occurrence of insect associated fungi was measured by following simple formula:

$$\text{Frequency of Occurrence (\%)} = \frac{\text{No. of Individual Specie}}{\text{No. of total Species}} \times 100$$

The species diversity was measured using beta diversity ( $\beta$ ) which is the total number of species that are unique between communities (Meffe *et al.*, 2002). Beta diversity was determined by the following equation:

$$\beta = (S_1 - C) + (S_2 - C)$$

Where, “ $S_1$ ” represents the total number of species recorded in the first community, “ $S_2$ ” represents the total number of species recorded in the second community, while “ $C$ ” represents the number of species common to both communities. All the data were analyzed by analysis of variance followed by Duncan’s Multiple Range Test (Steel and Torrie, 1980) using computer software COSTAT.

## RESULTS AND DISCUSSION

Nine soil samples from selected fields with different cultural practices (Minimum, Moderate and Maximum Cultural Practices with respect to general recommendations of Agriculture Extension department) were analyzed for distribution and frequency of occurrence of insect associated fungi.

Four species of Entomopathogenic fungi found were *Beauveria bassiana*, *Conidiobous globosum*, *Metarhizium anisopliae* and an unknown species with various frequencies in different categories. Total frequency of occurrence of these fungi was the highest in category 01 (Minimum Cultural Practices) that was found to be 16.66 % among all types of observed fungal species in comparison with that of 12.5% in category 02 (Moderate Cultural Practices) and 15.38 % in category 03 (Maximum Cultural

Practices). As concerned the variation in frequency of occurrence of individual Entomopathogenic fungi species in all the categories; *Beauveria bassiana* and an unknown species was observed in category 01 with the same frequency of 8.33%. While *M. anisopliae* and *C. coronatus* was totally absent. *M. anisopliae* was the only species present in category 02 with frequency of 12.5% and in category 03, *M. anisopliae* and *C. coronatus* was only present with same frequency of 7.69%. While both *Beauveria bassiana* and unknown species were absent in this category.

The phenomenon that *B. bassiana* preferred natural habitat and *M. anisopliae* preferred cultivated habitats were observed by several authors (Mietkiewski *et al.*, 1991; Vanninen, 1995; Bidochka *et al.*, 1998). Quesada Moranga *et al.* (2007) reported no significant effect of habitat on the occurrence of *B. bassiana*, but strong association between *M. anisopliae* and soil from cultivated habitats. More studies on the effect of habitat type on occurrence of insect associated fungi are needed.

A significant difference in occurrence of *M. anisopliae* among minimum, moderate and maximum cultural practices was observed. In case of *B. bassiana* and unknown species, such difference was observed only in minimum cultural practices as compared to moderate and maximum cultural practices. While there was no significant difference observed in its occurrence between moderate and maximum cultural practices. Significant difference of *C. coronatus* was observed only in maximum cultural practices as compared to minimum and moderate cultural practices (Figure 2).

Likewise, conservation tillage regimes, using strip-till and no-till was more favorable to *B. bassiana* and *M. anisopliae* populations in the soil than conventional tillage regimes employing ploughing and disking (Hummel *et al.*, 2002a). These findings of higher fungal densities in reduced tillage and no-till systems could be observations of indirect effects caused by increased levels of host populations of non-pest insects. High population levels of non-pest insects have been observed in reduced tillage systems (Hummel *et al.*, 2002b). The observations cited above may therefore not necessarily be a direct result of mechanical disturbance on fungal population levels.

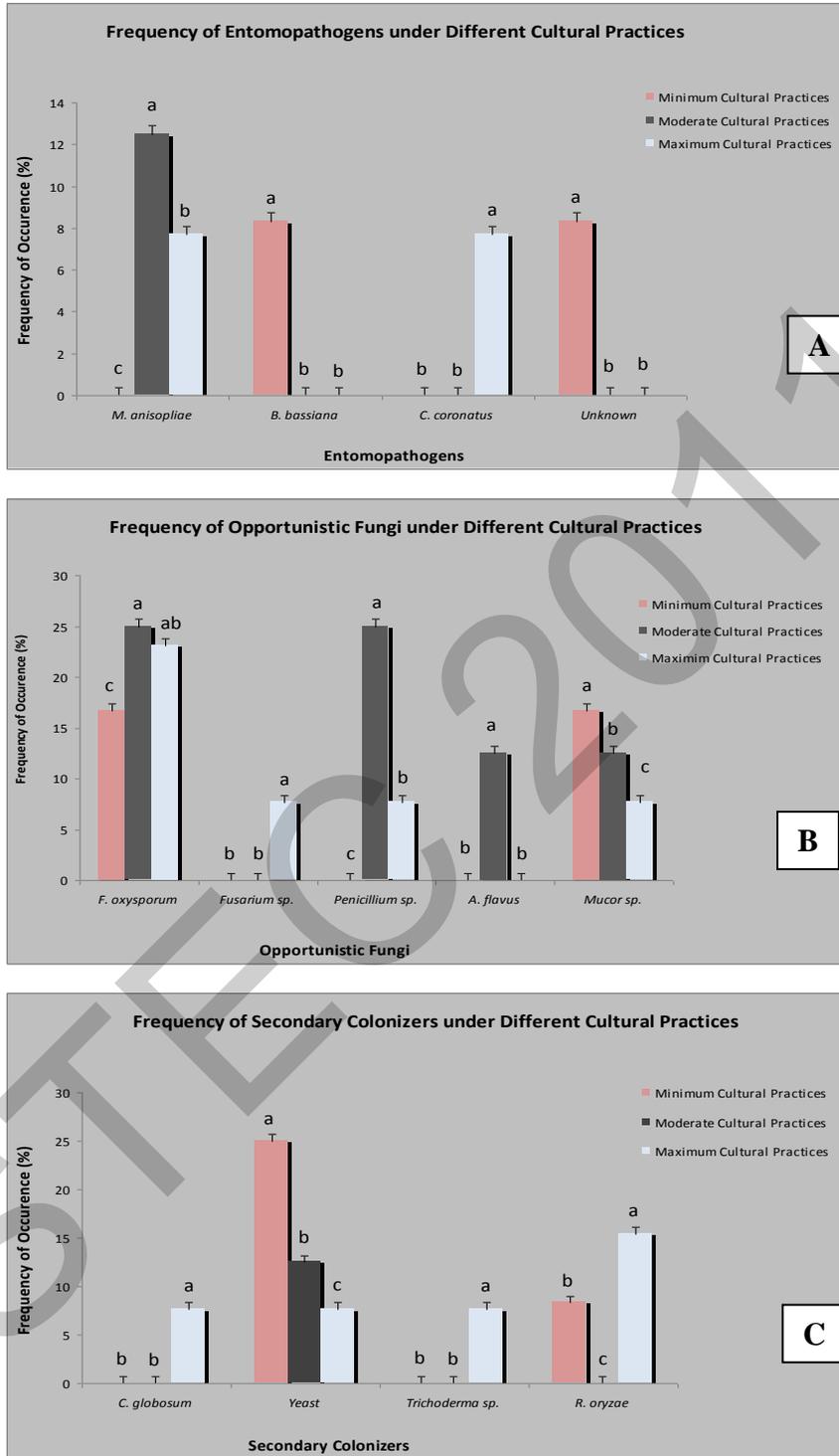
Total five species of Opportunistic fungi *Fusarium oxysporum*, *Fusarium sp.*, *Penicillium sp.*, *Aspergillus flavus*, and *Mucor sp* were found in all categories among various frequencies of occurrence. Total frequency of occurrence of these fungi was the highest in category 02 that was found to be 75.00% among all types of observed fungal

species in comparison with that of 50.01 % in category 01 and 46.15 % in category 03. The frequency of occurrence of individual Opportunistic fungi species was variable among categories; *Fusarium oxysporum*, *Penicillium sp.* and *Mucor sp.* were found in category 01 with same frequencies of occurrence of 16.67%. *Aspergillus flavus* and *Fusarium sp.* was absent in this category. While in category 02, *Penicillium sp.*, and *Fusarium oxysporum* were found with highest frequencies of occurrence that was 25.0% for each. In category 03, *Fusarium oxysporum* was found with the highest frequency of 23.08% and *Fusarium sp.*, *Penicillium sp.* and *Mucor sp.* was found with frequency of 7.69% for each.

A significant difference in occurrence of *Penicillium sp.* and *Mucor sp.* was observed among minimum, moderate and maximum cultural practices. In case of *F. oxysporum*, significant difference was found only in minimum cultural practices. While in case of *Fusarium sp.* and *A. flavus*, significant difference was observed in maximum and moderate cultural practices respectively (Figure 2).

Four species of Secondary colonizers found in all categories were *Chaetomium globosum*, yeast, *Trichoderma sp.* and *Rhizopus oryzae*, with various frequencies among different categories. Collective frequency of occurrence of these fungi was the highest in category 03 that was found to be 38.45 % among all types of observed fungal species in comparison with that of 33.33 % in category 01 and 12.5 % in category 02. The frequency of occurrence of individual Secondary colonizer species was variable among different categories. The frequency of yeast was the highest in category 01 and 02 with the rate of 25.0 % and 12.5% respectively. *Rhizopus oryzae* was found 11.46 % in category 03 while *Chaetomium globosum*, *Trichoderma sp.* and *Rhizopus oryzae* were lacking in category 02.

A significant difference in occurrence of yeast and *R. oryzae* among minimum, moderate and maximum cultural practices of hot arid zone was observed. While in case of *C. globosum* and *Trichoderma sp.*, the significant difference was only found in maximum cultural practices (Figure 2).



**Figure 2:** Occurrence Frequency of Insect associated Fungi under different cultural Practices. (A) Frequency of Entomopathogens. (B) Frequency of Opportunistic Fungi. (C) Frequency of Secondary Colonizers

The absolute value of Beta Diversity ( $\beta$ ) of entomopathogenic fungi was 05 in different categories. In case of opportunistic fungi its value was 02 while in secondary colonizers, its value was 04 (Table 2).

Table 2. Diversity of insect-associated fungi in soils in soils under different Cultural Practices					
Fungal Community		Category 01	Category 02	Category 03	Absolute value of Beta Diversity ( $\beta$ )
		Present/ Absent	Present/ Absent	Present/ Absent	
Entomopathogens	<i>M. anisopliae</i>	--	+	+	05
	<i>B. bassiana</i>	+	--	--	
	<i>C. coronatus</i>	--	--	+	
	Unknown	+	--	--	
Opportunistic Pathogen	<i>F. oxysporum</i>	+	+	+	02
	<i>Fusarium sp.</i>	--	--	+	
	<i>Penicillium sp.</i>	+	+	+	
	<i>A. flavus</i>	--	+	--	
	<i>Mucor sp.</i>	+	+	+	
Secondary Colonizer	<i>C. globosum</i>	--	--	+	04
	yeast	+	+	+	
	<i>Trichoderma sp.</i>	--	--	+	
	<i>R. oryzae</i>	+	--	+	

**CONCLUSION:**

Consequently, to understand more about the insect pathogen dynamics in different cultural practices and input applications, studies on the natural occurrence and distribution of insect pathogenic fungi in various soil types and cultural practices are necessary. Ecological studies on the occurrence of all insect associated fungi in the soil are needed too.

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# EFFECT OF RF POWER ON PROPERTIES OF ZnO:Al THIN FILMS PREPARED BY RF-MAGNETRON SPUTTERING FOR SOLAR CELLS APPLICATIONS

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## Abstract

ZnO:Al thin films were deposited onto glass substrates by RF-magnetron sputtering system. 13.56 MHz RF power was supplied by an RF generator matched to the target. The crystallographic orientation of the films was determined by an X-ray diffractometer (XRD). Single-phase ZnO:Al is formed and the intensity of the peak (002) increase with increasing RF power from 25 to 50 W. The grains are densely packed as shown in the surface micrograph. The resistivity of the films depends on the working pressure. Carrier concentration and Hall mobility of the films also varies with the working pressure. The optical transmittance of the films was measured with an UV-VIS scanning spectrophotometer. The values of band-gap energy,  $E_g$  of doped ZnO thin films for different working pressure were found that increase by increasing working pressure and the values obtained are 3.18 eV and 3.44 eV for 25 and 50 W respectively.

**Keywords:** Transparent conductive oxide, solar cell, RF-magnetron sputtering

## 1. INTRODUCTION

Zinc oxide has attracted a significant amount of attention in the past several years since this wide band gap semiconductor finds a number of applications in catalysis, gas sensing, and the fabrication of varistors and other microelectronic devices. ZnO has a hexagonal wurtzite crystal structure ( $a = 3.25 \text{ \AA}$  and  $c = 5.206 \text{ \AA}$ ). This structure can be described schematically as a number of alternating planes of O and Zn ions stacked along the c-axis.

Undoped and impurity-doped ZnO thin films have been widely used in thin film solar cells, because of their higher thermal stability in hydrogen plasma atmosphere, non-toxic nature, low price, easy fabrication and good electrical and optical properties, compared with other possible materials such as ITO, or SnO<sub>2</sub> [1-3]. Additionally, ZnO is the material that possesses a direct band-gap (3.3 eV at room temperature). These advantages prove that, it is one of the promising candidate in the number of optoelectronic applications like a transparent conductive contact [4,5], an n-type conducting window in thin film solar cells based on CdTe [6,7], CuGa<sub>x</sub>In<sub>1-x</sub>Se<sub>2</sub> [8-12] and others [13].

## 2. EXPERIMENTAL

ZnO:Al films with a thickness of about 50 nm are deposited by rf- magnetron sputtering (Fig. 1) from a ZnO/Al<sub>2</sub>O<sub>3</sub> (97/3 wt.%) target on soda lime glass as substrate. The glass substrates were ultrasonically cleaned in acetone bath before loading into the sputtering system. The sputtering chamber was evacuated with rotary pump and turbo-molecular pump. In this work, the room temperature is used and a thickness of films is controlled by microbalance quartz placed near the substrate. The working pressure was  $9 \times 10^{-5}$  Pa.

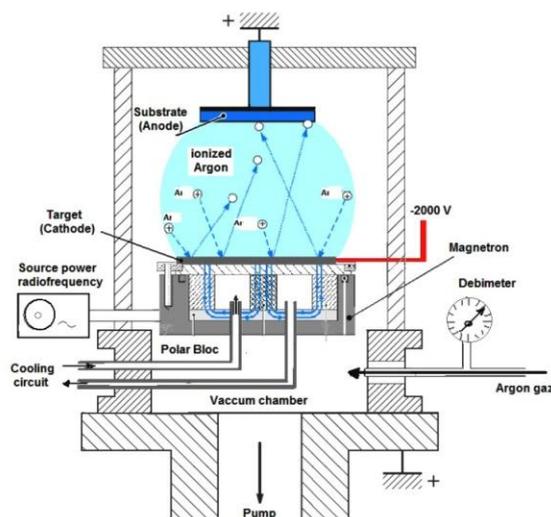


Fig. 1. Rf-magnetron sputtering system.

High purity (99.99% pure) Argon, and Oxygen were introduced into the chamber and controlled by two digital mass flow controllers. During sputtering, the total gas flow and the argon gas flow ratio was fixed at 2. The Ar/O<sub>2</sub> ratio was varied from 0:20 to 20:0. The sputtering target was pre-sputtered for few minutes before the deposition. Films were deposited at 25 and 50 W for 15 min. We successfully prepared n-type ZnO:Al thin films using reactive rf-magnetron sputtering in Ar-O<sub>2</sub> mixture atmosphere in this work. By controlling the Ar to O<sub>2</sub> ratio in ambient treatment, n-type ZnO films with low resistivity were obtained.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Structural properties

Fig. 2 (a and b) shows typical XRD patterns of the ZnO:Al films deposited at RF powers of 25 and 50 W, using a working gas pressure of 1.0 Pa and a room temperature substrate. The measurements were taken on the central region of the samples. The (002) peak is observed at a  $2\theta$  value of  $35^\circ$  for all samples, which agrees well with the value reported in the literature for single-crystal films grown on other substrates [14,15]. This indicates an oriented film growth, with the crystallographic c-axes perpendicular to the substrate surface. The observed increase in the XRD intensity with increasing RF power reveals that increasing the sputtering power improves the crystallinity of the film. The weak diffraction intensity (less than 50%) and the appearance of the (102) peak both indicate that a higher RF power cause a degradation of the preferred orientation of crystallinity.

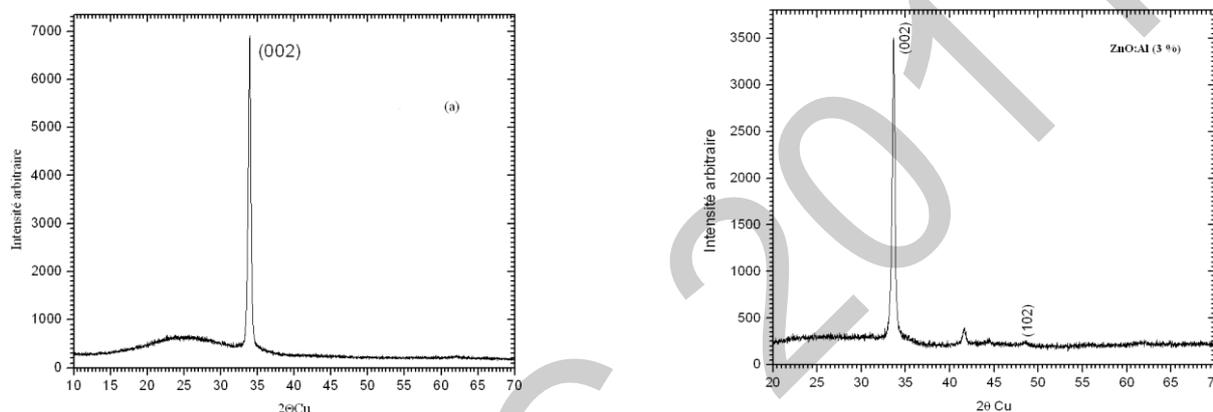


Fig. 2. The XRD pattern of the ZnO:Al films deposited at various rf powers  $P_{RF}$ : (a) 25 W and (d) 50 W.

Fig. 3 consists of SEM micrograph show the effect of RF power on surface morphology. We can see that the morphology evolves considerably for lower RF power. The size of grains is approximately 100 nm, the substrate surface being entirely covered for the film thickness retained. The SEM indicate that a higher power cause a degradation of the preferred orientation of crystallinity witch agree with X-ray results.

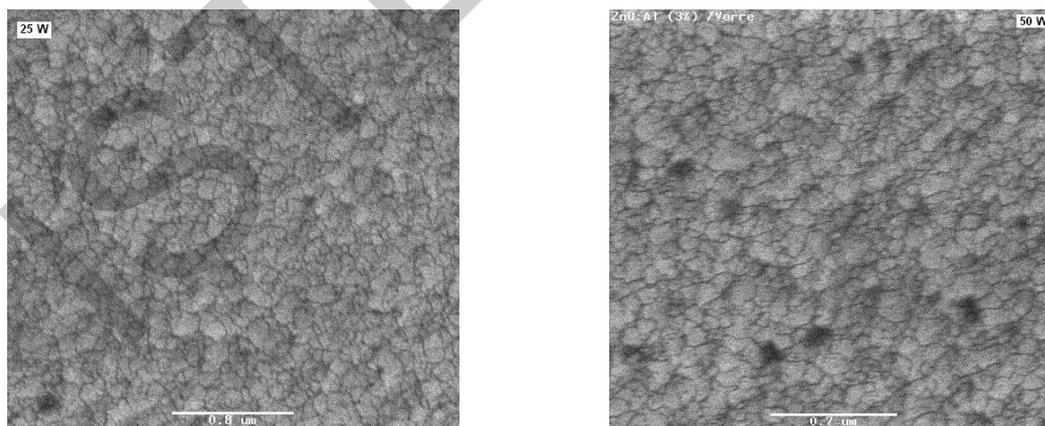


Fig. 3. SEM micrograph of ZnO:Al films at various RF power.

#### 3.2. Electrical properties

The results of the Hall Effect measurements are listed in Table 1. The resistivity of ZnO:Al films was very low, typical value was about  $0.018 \Omega \cdot \text{cm}$  and  $0.076 \Omega \cdot \text{cm}$ , which are in good agreement of the values reported in [16].

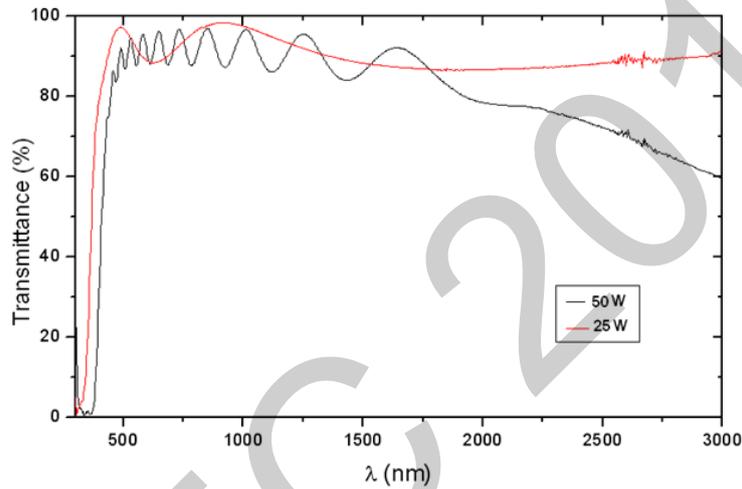
From Table 1, we find that the mobility of the films is not affected by RF power and the highest hole concentration have been obtained. The change of the carrier concentration is attributed to the oxygen vacancies which serve as acceptor should be considered. When the N<sub>2</sub>/O<sub>2</sub> ratio is high as 25:5, the amount of the oxygen vacancies exceeds that of the activated nitrogen atoms. Then, when the N<sub>2</sub>/O<sub>2</sub> ratio is lower than 30:10, nitrogen atoms in the films are more than the oxygen vacancies. As decreasing the N<sub>2</sub>/O<sub>2</sub> ratio, the acceptor decrease, which leads to the decrease of hole concentration.

**Table 1.** Electrical measurements

Power source (W)	Temperature substrate (°C)	Type	Resistivity (Ω.cm)	Mobility (cm <sup>2</sup> /Vs)	Concentration (cm <sup>-3</sup> )
25	Ambiant	n	7,64.10 <sup>-2</sup>	0,249	3,48.10 <sup>21</sup>
50	//	n	1,81.10 <sup>-2</sup>	0,311	1,11.10 <sup>21</sup>

**3.3. Optical properties**

In Fig. 4, we see that bellow 1500 nm, the impact of RF power on transmission is very small. The best average transmission (~90%) is obtained for both RF power, whereas the average transmission drops slightly to ~80% for P<sub>RF</sub> = 25 W. Considering the change of resistivity with RF power, this slight decrease in transmission may be attributed to an increase in the free-carrier concentration. Therefore, lower resistivity of films and higher transmission in the visible range are not entirely compatible. Above 1500 nm, the RF power has a very strong impact on transmission. While a low power (50 W) maintains a high optical transmission (and a low reflectance up to wavelengths of ~1800 nm), a power of 25 W reduces the transmission to 60% at 1800 nm. This reducing transmission with increasing power corresponds well with the decreasing film resistivity and is explained by free-carrier absorption. The cut-off behaviour at the blue end of the spectrum is determined by direct electronic transitions from the valence band to the conduction band.

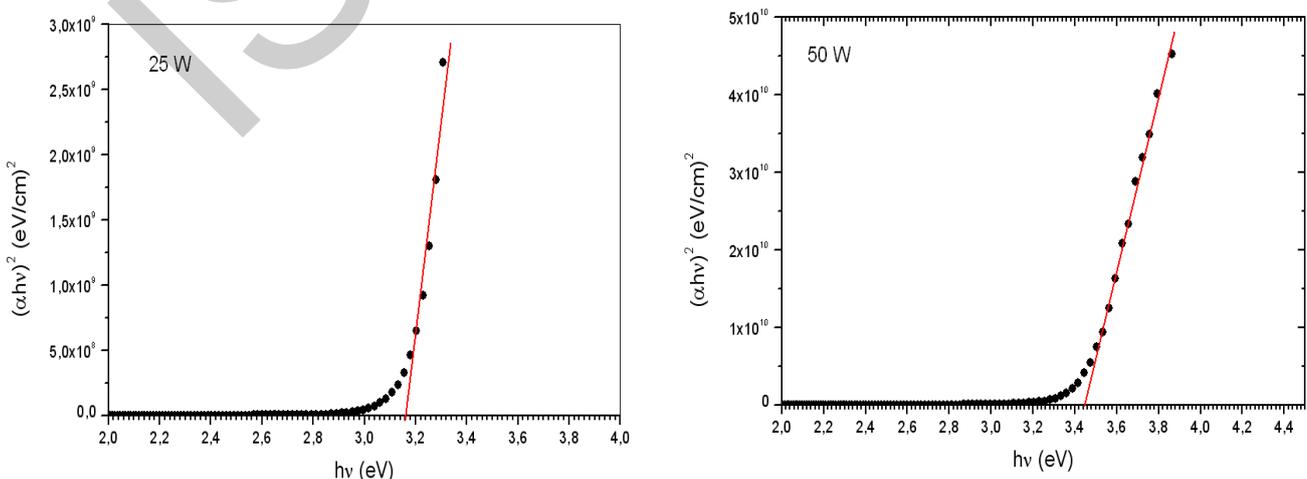


**Fig. 4.** Transmission of the ZnO:Al films deposited at different rf powers of 25 and 50W.

Therefore, the direct optical bandgap  $E_g$  of the ZnO:Al can be determined from the transmission and reflection data measured at short wavelengths. The theoretical relation between the  $E_g$  and the absorption coefficient is given by :

$$\alpha = A(h\nu - E_g)^{1/2}$$

where  $A$  is a constant,  $h$  is Planck's constant, and  $\nu$  is the frequency of the radiation. By determining  $\alpha$  from the measured transmission curve and by plotting  $(\alpha h\nu)^2 = f(h\nu)$ , a straight-line behaviour is expected from which the  $E_g$  can be determined :  $E_g = 3.18$  eV and  $3.44$  eV for 25 and 50 W respectively (Fig. 5).



**Fig. 5.**  $(\alpha h\nu)^2$  versus  $h\nu$  of the ZnO:Al films grown at various P<sub>RF</sub> of 25 and 50W.

#### 4. CONCLUSION

In this paper, the preparation of low-resistive p-type ZnO:Al films by rf- magnetron sputtering has been investigated. The weak diffraction intensity and the appearance of the (102) peak both indicate that a higher power cause a degradation of the preferred orientation of crystallinity. The results of the Hall effect measurements show that the resistivity of AZO film was very low, typical values was about 0.02 and 0.08  $\Omega\cdot\text{cm}$  but the resistivity of samples not affected by power source and carries concentration about  $10^{21}\text{ cm}^{-3}$ , then Zn:OAl is a good optical window for thin film heterojunction solar cells with bandgap of 3.18 eV and 3.44 eV for 25 and 50 W respectively.

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# EFFECTS IN VITRO ON BIOEROSION OF PLA, PGA BIOMATERIALS

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## ABSTRACT :

Functionalized monomers such as cyclohexanone, lactic acid, glycolic acid and other glycolic compounds give by copolymerization some biomaterial composites with changing bioresorption as a duality function between mechanical properties versus porosity (a). In the other side, some functionalized monomers show after polymerization process properties which reinforce mechanical parameters versus porosity parameters. This phenomenon decreases the bioresorption mechanism and push it at lower limits. Consequently, these biomaterials composite will show zero bioresorption. This is the case of polyamides (Nylon and Perlon), polycondensation products of hexamethylene diamine and adipic acid, terephthalic polyesters which are paraxylene (issued of fuel) and ethylene glycol products, polyolefines, polytetrafluoroethylene expanded PTFE. The bioresorbable polymers are mainly aliphatic polymers issued from lactic acid (PLA) or glycolic acid (PGA). This last polymer is well known on fiber surgery activity since twenty years ago. Most used polymers are polylactide PLA (as PDLA or PdLA), or polyglycolide PGA, then their copolymers also. Polyglactins 910 and 370 are frequently used in order to prepare bioresorbable biomaterials. Polyglactins are mixtures of PLA and PGA. Normal Vicryl and Rapid Vicryl have been the subject of our investigation on bioerosion of biocomposite materials from polyglactins. It was shown that bioresorption of Rapid Vicryl is most easy and follows a kinetic way different from this followed by Normal Vicryl, as shown by microphotographies from polarizing microscope Zeiss with integrated camera. Zwick machine using Test Expert logiciel provided measures on mechanical parameters of Normal Vicryl and Rapid Vicryl (b,c).

**Key words:** PLA, PGA, PLGA, polyglactin, bioerosion, cracks, scission, Normal and Rapid Vicryl.

## 1. INTRODUCTION:

Biodegradable polymers are two main types: natural and synthetic. Natural biopolymers include cellulose, starch, chitin, while the more common synthetic polymers consist of poly(lactic acid) (PLA), poly( $\epsilon$ -caprolactone) (PCL), and poly(glycolic acid) (PGA). Poly(lactic-co-glycolic acid) (PLGA) is known as a copolymer of PLA and PGA. This paper seeks to examine the effects of biodegradation in vitro on samples of Normal Vicryl and Rapid Vicryl.

## 2. PLA, PGA, PCL, AND COPOLYMERS (POLYGLACTIN):

PLA: PolyLactic Acid  
PGA: PolyGlycolic Acid  
PCL: PolyCaproLactone

Three polymers PGA, PLA and PCL play a vital role in key aspects of properties of Normal Vicryl and Rapid Vicryl which are made up of Polyglactin 910. Spectroscopical studies have proved the same qualitative chemical identity of Normal and Rapid Vicryl. Normal Vicryl is a catgut, while Rapid Vicryl is a synthetic biomaterial. Both of them reply to the molecular formula:  $(C_2H_2O_2)_m (C_3H_4O_2)_n$ . (d,e).

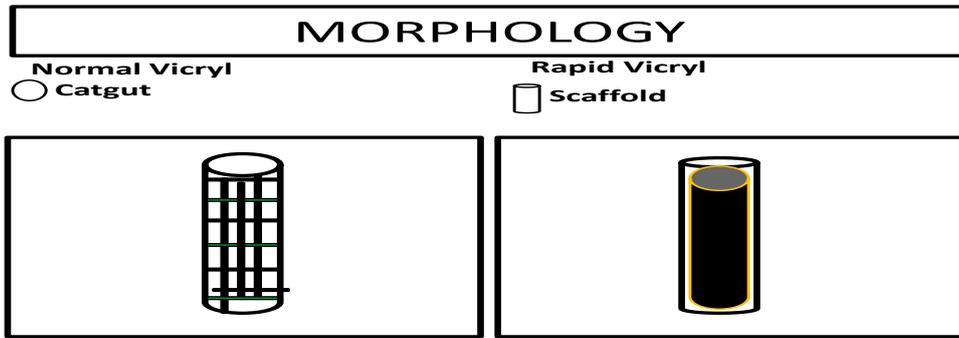


Fig.n°1

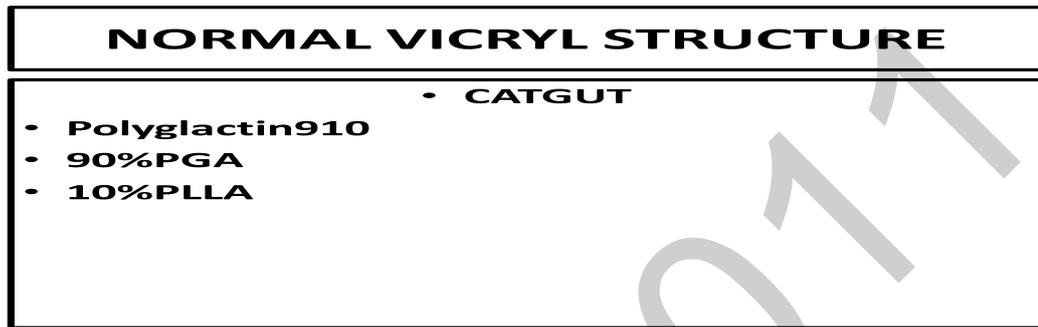


Fig.n° 2

<b>Normal Vicryl</b>	<b>Rapid Vicryl</b>
<b>Catgut</b>	<b>Scaffold</b>
<ul style="list-style-type: none"> <li>• <b>collagen derived from submucosa of bovine or bovine intestine.</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>SR (self - reinforced), die- drawing ,in hot conditions , by extrusion.</b></li> </ul>

Fig.n°3

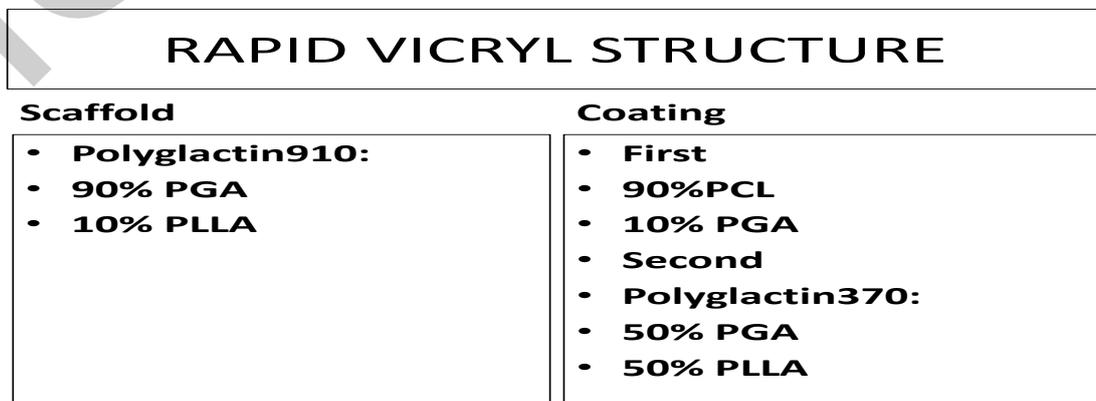


Fig.n°4

Poly(lactide) PLA is chiral in nature. This chirality is seen in the carbon with four different substituents (hydrogen, oxygen, carbonyl, and methyl), the reason which causes two different PLA polymers : PDLA and PLLA ( D , L conventional stereochemistry notation for sugars). PLLA has a crystallinity of 37%, a glass transition temperature between 50 and 80°C, and a melting temperature of 173-178° C. A polymerization of the racemic mixture produces amorphous PDLA, which due to the interference stereochemistry in the chain alignment. Polyglycolide shows more performant properties than poly(lactide), partly due to its greater stereoregularity: a crystallinity between 45 and 55%, a glass transition temperature between 35 and 40°C, a melting temperature between 225 and 230° C and a higher strength and modulus of 7 GPa(f). While all PLGA copolymers show a glass transition temperature between 40 and 60 °C, their melting point, percent crystallinity, porosity, mechanical properties, and bioresorbability, depend on the percent composition of PLA and PGA. Incorporate of P(D-LA) or P(L-LA) decrease tensile strength but incorporate P(L-GA) or P(D-GA) is more efficient in order to decrease tensile strength ,enhancing bioresorption (f,g).

PCL( poly ε-caprolactone) : Literature reported that PCL is a biocompatible, semi-crystalline polymer particularly known in scaffold engineering for its strongest hydrophobic properties which enhance its mechanical properties random polymerization or copolymerization processes. PCL has a slower degradation rate than most biopolymers, a glass transition temperature of -60°C, a melting temperature of 58-60°C, and a decomposition temperature of 350°C. Its mechanical properties include a tensile strength of 16 MPa, tensile modulus of 400 MPa, flexural modulus of 500 MPa, elongation at yield of 7%, and elongation at failure of 80% .PCL is also an important member of the aliphatic polyester family. It has been used to effectively entrap antibiotic drugs and thus a construct made with PCL can be considered as a drug-delivery system, being used to enhance bone ingrowth and regeneration in the treatment of bone defects . The degradation of PCL and its copolymers involves similar mechanisms to that of PLA, proceeding in two stages: random hydrolytic ester cleavage and weight loss through the diffusion of oligometric species from the bulk. It has been found that the degradation of PCL system with a high molecular weight (Mn of 50,000) is remarkably slow, requiring 3 years for complete removal from the host body(h) .

According to the Consensus conference of the European Society for Biomaterials:

- Biodegradation: A biological agent (an enzyme, or cell) is responsible for degradation.
- Bioerosion: contains both physical (such as dissolution) and chemical processes (such as backbone cleavage). E.g. a water-insoluble polymer that turns water-soluble under physiological conditions.
- Bioresorption, Bioabsorption: polymer or its degradation products removed by cellular activity(e.g. phagocytosis).

3..SYNTHESIS:

3.1. Lactic acid is obtained from corn starch or cane sugar or potatoes by fermentation. Oligomerized, it is then catalytically dimerized into lactide monomer, which is a di-ester ring. Glycolic acid can be similarly reacted into a glycolide, which can then be polymerized using a ring-opening polymerization. The ring opening polymerization is a multistep process that begins with the low molecular weight lactic or glycolic acid polymer. After the low molecular weight polymer is obtained, the glycolide is distilled by heating at low pressure. Although there are a variety of catalysts available such as antimony compounds, zinc compounds, and alkoxides, stannous octoate is preferred because it is approved by the FDA as a food stabilizer. Second process is polymerization across opening cycles of lactide and glycolide. Lactic acid undergoes preferentially a bulk polymerization at higher temperature, 140-180°C, low pressure, in presence of catalyst. This reaction occurs also in solution. Several mechanisms have been studied: cationic, anionic and coordination-insertion. . The ring-polymerization is started with the initiator and glycolide or lactide at a temperature of 195°C. After two hours at this temperature, the temperature is increased to 230°C. After the polymer solidifies, the high molecular weight polymer is obtained. The side-product salts can be easily removed by washing the polymer with water. Another simple process is to use a condensation reaction to polymerize glycolic acid. However, this process yields a lower molecular weight polymer than the ring-opening polymerization due to the side products of the condensation reaction(M<5000 g/mol). PLAGA statistical copolymers follow the same way on synthesis as PGA or PLA, but this occurs in a slightly lower range of temperature (i,j,k),(figures n°5,6,7,8) .

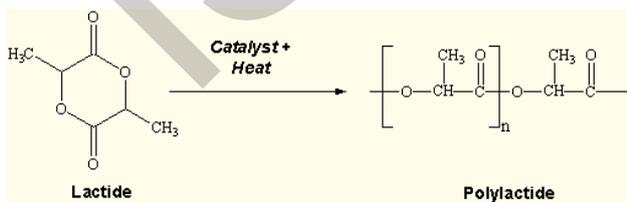


Fig.n°: 5

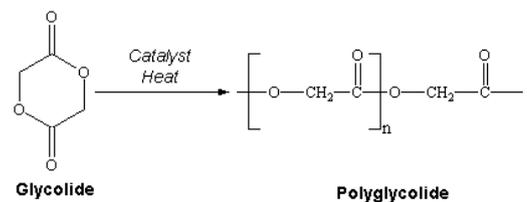


Fig.n°:6

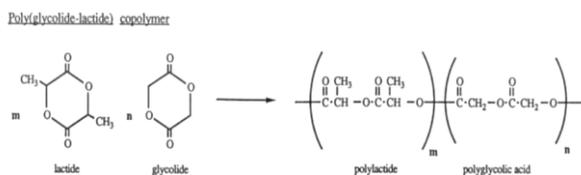
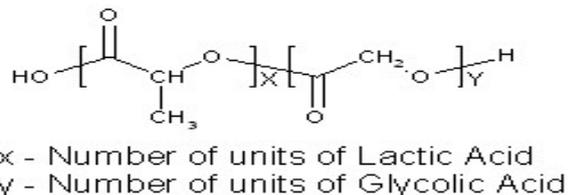


Fig.n°:7



x - Number of units of Lactic Acid  
y - Number of units of Glycolic Acid

Fig.n°:8

3.2. PCL is obtained by homopolymerization of  $\epsilon$ -caprolactone in glass reactor, in presence of stannous octoate as catalyst, under nitrogen atmosphere for 24 h at 120°C. The monomer/catalyst ratio is 1700 : 1 (mol/mol). Low-molecular-weight residuals are removed by a dissolution-precipitation method in which chloroform and methanol are used as solvent and precipitant, respectively (1).



Fig.n°:9

#### 4. EXPERIMENTAL

##### 4.1 MICROSCOPIC STUDY:

The type of material selected for this in-vitro study is a commercial form of polyglactin (910 and 370) sold under the tradename Normal Vicryl, Rapid Vicryl, obtained from Ethicon (Johnson-Johnson company) in sterile packages. The samples are 0.4 mm thick, 75 cm long. Samples of Normal Vicryl 3 (subject to degradation by erosion during nine months) and Vicryl Rapid (subject to degradation by erosion for three months) were analyzed by the Zeiss microscope (Germany), using rectangular glass slides (ref.803495, Polylabo, France). The samples are observed in natural light microscopy and fluorescence microscopy. Fluorescence microscopy exploits the potential of certain molecules which emit light when they are illuminated with light of higher wavelength. The light emitted by a white light source is filtered to isolate the wavelength that will excite the sample and is focused on the observation area by the lens. The resulting image is the reverse of that obtained in direct light, the observed objects stand out bright against a dark environment, the final contrast is then higher (m).

##### 4.2. MECHANICAL STUDY:

Mechanical experiments were carried out by using Zwick machine, driven by Test Expert logiciel.

The samples subject to mechanical study are: undegraded Normal Vicryl, Normal Vicryl 1, Normal Vicryl 2, Normal Vicryl 3, and undegraded Rapid Vicryl. The terms of degradation to which were submitted Normal Vicryl, 1, 2, 3 are respectively 3, 6 and 9 months.

Symbols:

Rm: tensile stress ( $N/mm^2$ ), Module: Young module ( $N/mm^2$ ), FR: breaking strength ( $N/mm^2$ )  
 $\epsilon$ -Rm: essay elongation (percent)  $\epsilon$ -Rupture: rupture elongation (mm or percent)

The tests were performed according to ISO, or ASTM at a speed traction 250 mm/mn or 500 mm/mn. Zwick machine is equipped with jaws Zwick and Zwick load cell for low tractions (up to 2000N ( $N/mm^2$ )) (n).

#### 5. RESULTS :

##### 5.1. MICROSCOPIC OBSERVATION OF NORMAL VICRYL :

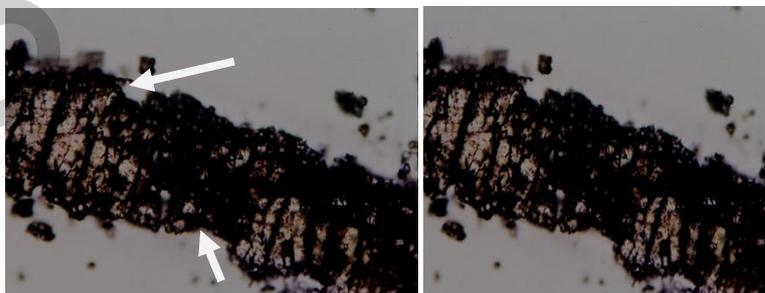


Fig.n°10

Fig. n°11

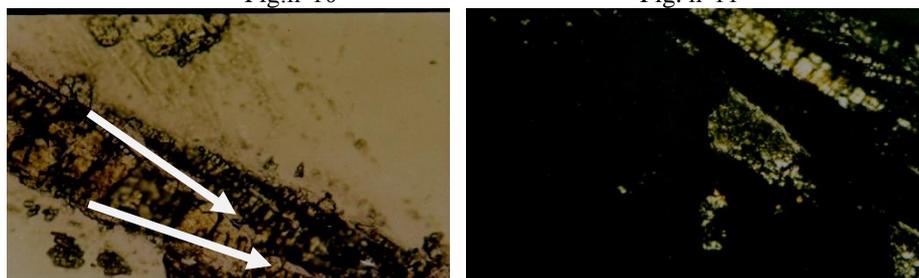


Fig.n°12

Fig.n°13

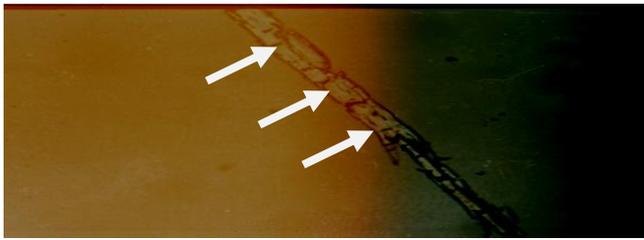


Figure 14



Figure15

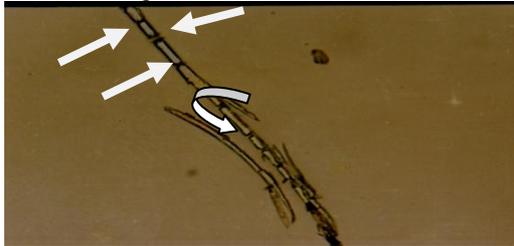


Figure 16



Figure17

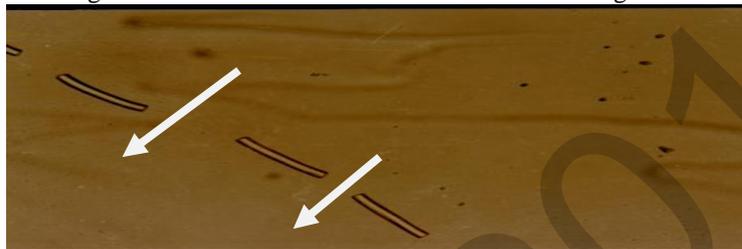


Figure18

**5.2 MECHANICAL STUDY:**

	Rm(N/m <sup>2</sup> )	Young module(N/mm <sup>2</sup> )	ε-Rm(%)	Fr N/mm <sup>2</sup>	ε-Rupture(%)
Undegraded Rapid Vicryl	696.80	9919.78	15.41	696.80	15.54
	689.94	7957.02	16.95	689.94	16.95
Undegraded Normal Vicryl	827.08	5015.31	30.50	827.08	30.50
	772.70	6185.11	27.04	772.70	27.17
Normal Vicryl 1	409.04	461.37	43.04	404.56	26.71
Normal Vicryl 2	349.59	1645.03	21.97	349.59	21.97
	380.72	1054.51	11.52	376.50	11.55
Normal Vicryl 3	291.13	3452.02	10.52	278.05	10.55

Table n°1: main mechanical features of Normal Vicryl and Rapid Vicryl,

**6. DISCUSSION:**

**6.1 NORMAL VICRYL BIOEROSION:**

Bioerosion operates the molecular chain irregularities of the PLGA co-polymers by random attacks to their crystallinity. It creates the first cracks in the structure of the biomaterial. Bioerosion appears as a regioselective phenomenon (in regard to figures 10,11) which occurs according to topologic considerations. Bioerosion hollows out catgut by the sides (fig.10,11,19). Ester bonds gather inside of the biomaterial. Molecules water start on penetration, via the cracks, inside the molecular chains of Polyglactin, in direction of ester bonds. It's the starting point of trans-esterification of catgut, beginning on PGA ester bonds (Fig.20). The catgut undergoes by sides penetration of molecules water. Process of de-esterification will continue, enhanced by the increase of products acidity and by uptake of water, followed by the irreversible process of breaking down ester bonds and backbone PGA units. Eviction of PGA units will continue in axial direction. The biodegradation products: oligomers, monomers, carboxylic acid end-groups, are responsible for the autocatalytic bulk biodegradation which is able to break down ester bonds of the hydrophobic units of PLLA. This process leads at the end to the complete bioresorption of Normal Vicryl by metabolism process. The mechanism of (bioresorption) of Normal Vicryl differs from the one followed by Rapid Vicryl essentially on:

morphologic evolution of bioerosion and biodegradation phenomenons (o, p).

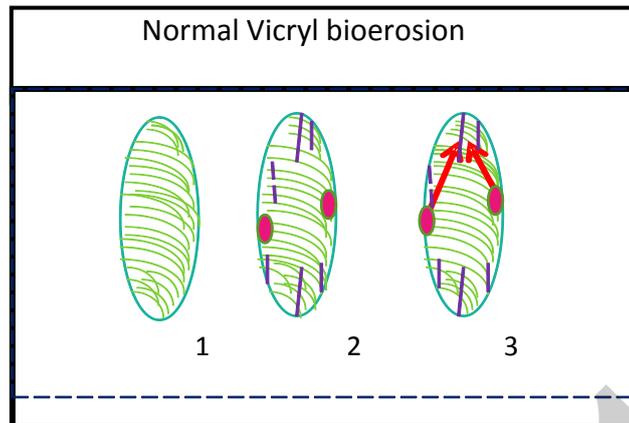


Fig.n°19

1:undegraded , 2:cracks and side holes, 3:side breakthrough erosion

Esterbonds COO will break down , by hydrolysis of PGA, in first ,as shown in the equation below:

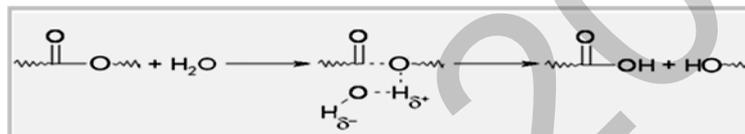


Fig.n°20 : Hydrolysis of ester bonds

Surface bioerosion	Bulk bioerosion	Biodegradation
<p>Surface erosion:                      water penetration limited,                      degradation occurs on the surface.                      thinning of the component over time.                      integrity is maintained over longer time when compared to bulk erosion.                      hydrophobic polymers experience surface erosion since water intake limited.                      acidic byproducts are released gradually                      acid burstless likely, lower chance of inflammation.                      surface erosion can also occur via enzymatic                      Bioerosion causes:                      changes in the appearance of the biomaterial                      changes in the physicommechanical properties:                      swelling                      deformation                      structural disintegration                      weight loss of function</p>	<p>Bulk erosion:                      water enters polymer                      causes hydrolytic degradation                      component hollowed out,                      finally crumbles (like sugar cube in water)                      releases acid groups : possible inflammation</p>	<p>PGA and PLA                      Most widely used biodegradable polymers.                      PGA is the simplest aliphatic polyester:                      highly crystalline, high melting point                      chemical degradation mediated by water,                      enzymes, microorganisms.                      Mechanisms of chemical degradation:                      cleavage of cross-links between chains                      – cleavage of side chains                      – cleavage of polymer backbone                      – combination of above                      Hydrolysis of biodegradable polymers                      breakdown of a molecule in the presence of water.                      Hydrolysis of the ester bond results in formation of an acid and an alcohol.                      Hydrolysis of the anhydride bond results in formation of two acids.                      Copolymers of PGA and PLA used to adapt material properties suitable for wider range of applications.                      PLA is more hydrophobic than PGA.                      Hydrophobicity uptake of thin films to about 2% and reduces the rate of hydrolysis compared with PGA                      geometry of the implanted device (surface/volume ratio)                      Polymer less permeable to water in glassy state:                      Tg of the polymer should be greater than 37 °C to maintain resistance to hydrolysis under physiological conditions</p>

Table n°2: mechanism of bioerosion

This study proves that Zeiss microscopy images can be used to follow the bioerosion process of PLA , PGA , and copolymers (Normal Vicryl and Rapid Vicryl).

Images captured in natural light, figures:10,11,12,14,16,18.

Images captured in fluorescence light, figures :13,15,17.

Figure 10 shows the digging of lateral cavities by surface erosion. This is the first step of bioerosion process: surface bioerosion. It shows a swelling of the sample (swelling, then elasticity, can reduce the risk of trauma to surrounding tissues by irritation). Figure 13 shows changes in the appearance (black areas) which is due to loss of functions. The orange light is returned from areas that have not been modified by surface erosion and retain their functional groups. Figure 13 shows the bioerosion in bulk that continues to draw a V channel. This is the second step. And that's the appropriate step to the intervention of bacteria, enzymes, and macrophages to digest the products of erosion. Finally, and it's the third step: all debris will convert via Krebs cycle in ATP, CO<sub>2</sub>, and H<sub>2</sub>O(q,r).

### 6.2 RAPID VICRYL BIOEROSION:

In the case of Rapid Vicryl, bioerosion process follows an entirely different mechanism from that of normal Vicryl as reveal the figures 14 until 18. Overall, the samples retain their luster and shine by fluorescence, this shows that there is no important loss of functional groups ester. Figures 14 and 15 show a swelling of the sample (Hydrolysis of ester functions thus occurs transversely as indicated by the straight arrows in figures 14 and 16). The arrows are also pointing to areas of transverse fission. The dark circular areas do not return light by fluorescence microscopy. Figures 16 and 17 show the phenomenon of bursting of first coating and second coating. Final step is the ejection of the scaffold out of first and second coatings (fig. 18). This phenomenon of Rapid Vicryl bioerosion is certainly conditioned by the extrusion process and the factors of sterilization (gamma irradiation and ethylene oxide). It's known that gamma irradiation causes backbone linkages and this is the case in regard to figure 18 where backbone scaffold appears sectioned without damage of bioerosion, after three months exposition (a,b,c), (table n°2).

### 6.3. ZWICK MACHINE DATA:

Theoretically, the traction experienced by a material is reflected in the curve (stress-elongation) by the appearance of three distinct deformation zones: an elastic deformation zone, a plastic deformation zone and a third zone, called breaking zone. If the sample breaks in its elastic range, without any plastic deformation before breaking, it is considered a brittle material. According to data of table n° Normal is more elastic than Rapid Vicryl. Young's modulus is related to the length of the macromolecular chains. If the extent of degradation is high, Test expert gives statistically contradictory measures of Young module. Data show an increase in rigidity of Normal Vicryl versus the extent of degradation, accompanied by a decline in the elongation at breaking (table n°1).

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# EFFECTS OF BIOBASED PLASTICIZER ON THE MECHANICAL AND DYNAMICAL PROPERTIES OF POLY(VINYL CHLORIDE)

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## ABSTRACT

Epoxidized soybean oil (ESBO), is one of the most commonly used epoxides because of its typical combined roles as a plasticizer and heat stabilizer. In this study, a novel plasticizer of poly(vinyl chloride) (PVC) resins, epoxidized sunflower oil (ESO), was synthesized, and its performance was evaluated. ESO was designed to act as a coplasticizer and a heat stabilizer like ESBO. ESO is used as organic coplasticizer for plasticized PVC containing Ca and Zn stearates as primary stabilizers and stearic acid as lubricant. Di-(2-ethylhexyl) phthalate (DEHP), a conventional plasticizer for PVC, was partially replaced by ESO. Mechanical properties (tensile and shore D hardness) were investigated. The performance of ESO to ESBO (20 g) for comparison, indicated that ESO could be used as secondary plasticizer for PVC in combination with DEHP. All mechanical and dynamical properties of plasticized PVC sheets varied with the oxirane oxygen of the ESO.

**Keywords:** PVC, epoxidized sunflower oil, mechanical properties, glass transition temperature, DMA.

## INTRODUCTION

The use of plasticizers is one of the most efficient ways to modify the thermal and mechanical properties of polymers [1-8]. Plasticizers are often low molecular weight compounds that lower the glass transition temperature ( $T_g$ ) and convert rigid polymers into flexible ones. To be effective, a plasticizer must distribute itself between the polymer chains and interact with functional groups, thereby reducing the interactions between the polymer chains and softening the matrix. Plasticizers are required for nearly all polymers used in film coating to reduce the polymers brittleness, improve flow, import flexibility and increase toughness, strength, as well as shear resistance [7-10]. They are classified into primary, secondary, and extenders, esters, phosphates, and epoxides are the most suitable plasticizers for poly(vinyl chloride) (PVC). Since PVC is polar in nature, mostly ester type plasticizers such as dioctyl phthalate (DOP) and dibutyl phthalate are used for its compounds.

Today, one of the most important epoxidized vegetable oil is epoxidized soybean oil (ESBO) [10-12] its worldwide production is about 200,000 t/year.<sup>13</sup> Fats and oils are renewable resources that can be chemically or enzymatically treated to produce materials that can often act as a replacement for materials derived from petroleum. Fatty epoxides are used directly as plasticizers that are compatible PVC and as stabilizers for PVC resins to improve thermal stability. Because of high reactivity of the oxirane ring, epoxides act as raw materials for a variety of chemicals compounds. Epoxidation is defined as the addition of an oxygen atom across a carbon-carbon double bond to create epoxide (or oxirane) functionality. Epoxidation reactions are typically performed with percarboxylic acids or other peroxy compounds. Epoxidized oil with higher oxirane oxygen value and lower iodine value is considered to be of better quality.<sup>14</sup> This work is part of a program concerned with the effects of epoxidized sunflower oil (ESO). Sunflower oil is a renewable resource that can be readily epoxidized as described previously [15,16]. ESO has the potential for use as an environmentally friendly reactive material. In this study, mechanical and dynamical properties of PVC/ESO in presence of DEHP are evaluated and compared with the traditional coplasticizer ESBO.

## EXPERIMENTAL

### Materials

Algerian PVC from ENIP-SKIKDA with K value 65-67 which is a measure of the relative viscosity according to the standard DIN 53-726, Zn stearates from Aldrich (Germany), Ca stearate from Prolabo (France), di-(2-ethylhexyl) phthalate (DEHP) (BASF, Germany) and stearic acid from SOGIS (Italy) were used as received.

### Epoxidation process

Sunflower oil with iodine value  $I(\text{iod})$  of 130 [g  $I_2$ /100 g], from Cevital-Bejaia, Algeria, was used as received. The saponification value, the acid number, and the viscosity were: 193.5 [mg KOH/g], 0.2, and 1476.3 [MPa S] respectively. The epoxidation was carried out according to C=C double bond/acetic acid/hydrogen peroxide molar ration of 1/0.5/1.5, as the acetic acid, which is converted to peracid, is regenerated. The 50% relative excess of hydrogen peroxide versus double bonds was considered as reasonable. Toluene was used as solvent at 50 wt % to sunflower oil. Dried resin and glacial acetic acid were introduced in a 250-mL three-necked flask fitted with a mechanical stirrer, sunflower oil and toluene were then added and the flask was immersed in a thermostated oil-bath. Stirring was started at moderate rate and the temperature was raised up to 55-60°C. Hydrogen peroxide (30%) was added dropwise over a period of 15 min to avoid overheating. After the required reaction time, the oil and aqueous phases were decanted; the organic phase was washed successively with water and 0.1N  $\text{Na}_2\text{CO}_3$  solution, and rinsed with water. The toluene phase was dried over sodium sulphate and the solvent removed with a rotary evaporator to give the epoxidized oil.

### Characterization methods

$^1\text{H}$  NMR of SO and ESO,  $^1\text{H}$  NMR data of ESO were recorded using a Bruker AM 300 spectrometer, operating at 500 MHz using a 5-mm broadband inverse Z-gradient probe in  $\text{CDCl}_3$ .

**Table 1.** Formulations realized with ESO or ESBO

Formulations	1	2	3	4	5	6	7
Poly(vinyl chloride)	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1
Ca/Zn stearates 1/1	1	1	1	1	1	1	1
Di-(2-ethylhexyl) phthalate	30	-	-	30	30	30	30
Epoxidized sunflower oil	-	10	-	10	20	30	-
Epoxidized soybean oil	-	-	10	-	-	-	20

**Table 2.** Formulations realized with ESO containing various oxirane oxygen levels

Formulations	8	9	10	11	11	12	13
Poly(vinyl chloride)	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1
Ca/Zn stearates 1/1	1	1	1	1	1	1	1
Di-(2-ethylhexyl) phthalate	30	30	30	30	30	30	30
Epoxidized sunflower oil	20	20	20	20	20	20	20
Oxirane Oxygen (O.O%)	(0)	(1)	(2)	(3)	(4)	(5)	(6)

### Preparation of PVC sheets

Samples were prepared using the recipes given in Table 1 and 2. PVC and additives were mixed in a roll mill at  $160^\circ\text{C}$ . The sheets were compression molded to make plaques, which were required for some of the tests. The operating temperature was  $160^\circ\text{C}$  for 12 min with hydraulic pressure of 20 tons.

### Measurements

#### Discoloration

The evolution of discoloration was measured using ten degrees color scale (Synmero).

#### UV-visible analysis

The PVC materials with different components were pressed into films with the thickness about  $100\ \mu\text{m}$ . UV-visible spectra of films PVC were obtained by using a Shimadzu 120-02 UV-visible spectrophotometer.

#### Dynamical mechanical analysis

All experimental data were collected on a TA instruments DMA 2980 machine, using the tension film clamping arrangement. Specimens were excited using a  $20\text{-}\mu\text{m}$  dynamic displacement, and a small preload (0.2 N) to insure that the specimens were always in tension. The measurements of the complex Young's modulus were made over a temperature range from  $-50$  to  $130^\circ\text{C}$ , in  $2^\circ\text{C}$  intervals, at the following frequencies: 1, 3, 5, 10, 15, 20, 35, and 50 Hz. The temperature was allowed to come to equilibrium and held constant while measurements were made at each frequency.

## RESULTS AND DISCUSSION

### $^1\text{H}$ NMR of SO and ESO analysis

From the spectra  $^1\text{H}$  NMR measurement on ESO (6.4% oxirane oxygen) shows the disappearance of the signals of vinylic protons at 5.3–5.5 ppm and indicates that the epoxy group is present in the  $\delta$  3.0–3.2 ppm region. The methane proton of  $-\text{CH}_2-\text{CH}-\text{CH}_2$  backbone at  $\delta$  5.1–5.3 ppm, methylene proton of  $-\text{CH}_2-\text{CH}-\text{CH}_2$ - glycerol's backbone at  $\delta$  4.0–4.4 ppm,  $\text{CH}_2$  proton adjacent to two epoxy group at  $\delta$  2.8–3.0 ppm,  $-\text{CH}-$  proton of the epoxy ring at  $\delta$  3.0–3.2 ppm,  $\alpha\text{-CH}_2$  to  $\text{C}=\text{O}$  at  $\delta$  2.2–2.4 ppm,  $\alpha\text{-CH}_2$  to epoxy group at 1.7–1.9 ppm,  $\beta\text{-CH}_2$  to  $\text{C}=\text{O}$  at  $\delta$  1.55–1.7 ppm,  $\beta\text{-CH}_2$  to epoxy group at  $\delta$  1.4–1.55 ppm, saturated methylene group at  $\delta$  1.1–1.4 ppm and terminal  $-\text{CH}_3$  groups at  $\delta$  0.8–1.0 ppm region.

#### Discoloration measure

Plasticizer performance data were obtained on milled sheets prepared on a laboratory roll mill. For our preliminary study the Synmero scale has been used. Figure 1 shows the discoloration curves of PVC sheets containing various plasticizers systems. In the absence of DEHP, ESO has no effect on the retardation of the development of discoloration. The ESO in presence of DEHP uniformly showed excellent effect on the initial coloration. This efficiency generally was equal to or better than ESBO alone or combined with DEHP. The coloration decreases with increasing the weight of ESO in presence of DEHP. ESO exhibits a relatively better effect than ESBO on the development of discoloration.

Figure 2 presents the influence of the levels of the oxirane oxygen in the ESO in presence of DEHP. The increase of oxirane oxygen of ESO decreases the discoloration degree of PVC sheets. The epoxy group of the plasticizer is excellent hydrochloric acid scavenger; hydrochloric acid absorption occurs readily [18-20]. The formation of polyene sequences was investigated by UV-visible spectroscopy. The influence of the weight of the epoxidized oil and the amount of oxirane oxygen in the ESO were considered. The inherent stabilizing action is indicated in the accompanying. Figures 3 and 4 illustrating the performances of the epoxidized oil at different weights in purified milled sheet formulations.

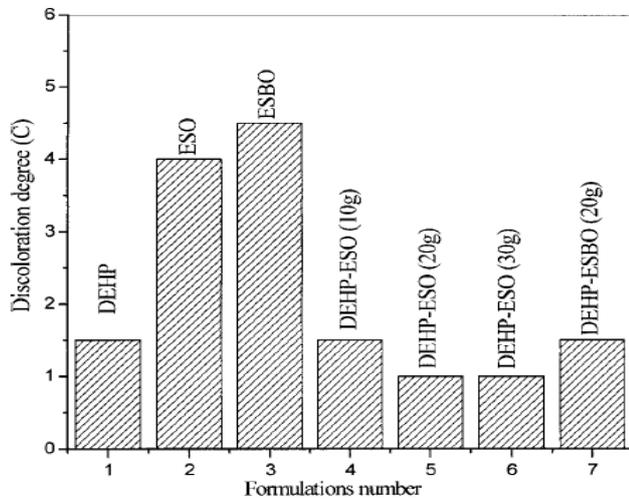


Figure 1. Discoloration of PVC sheets with various weight plasticizers system.

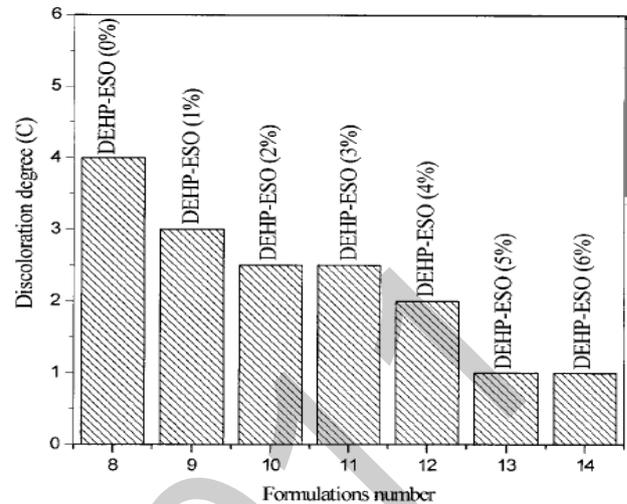


Figure 2. Discoloration of PVC sheets plasticized with ESO containing various levels of epoxidation.

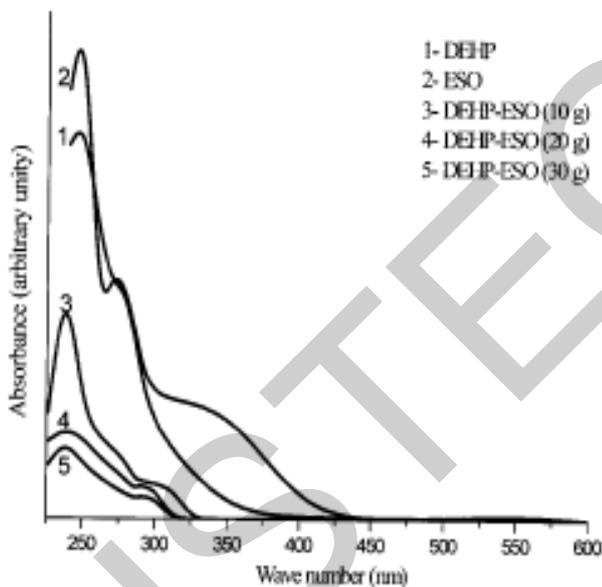


Figure 3. UV-visible spectra of purified PVC sheets with various weights of epoxidized sunflower oil.

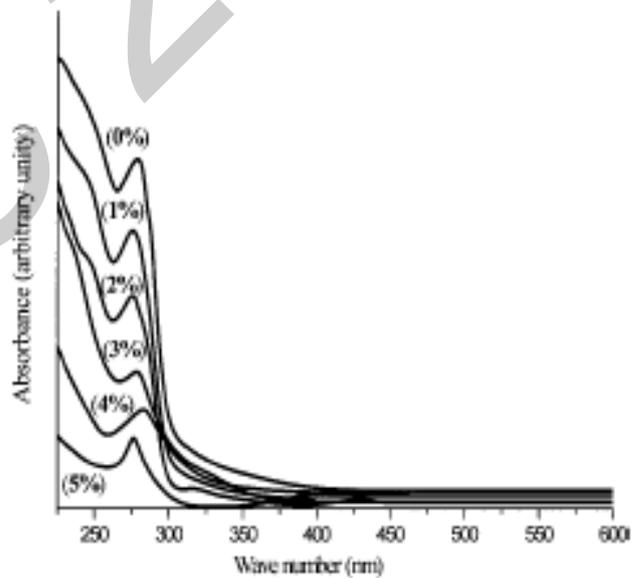


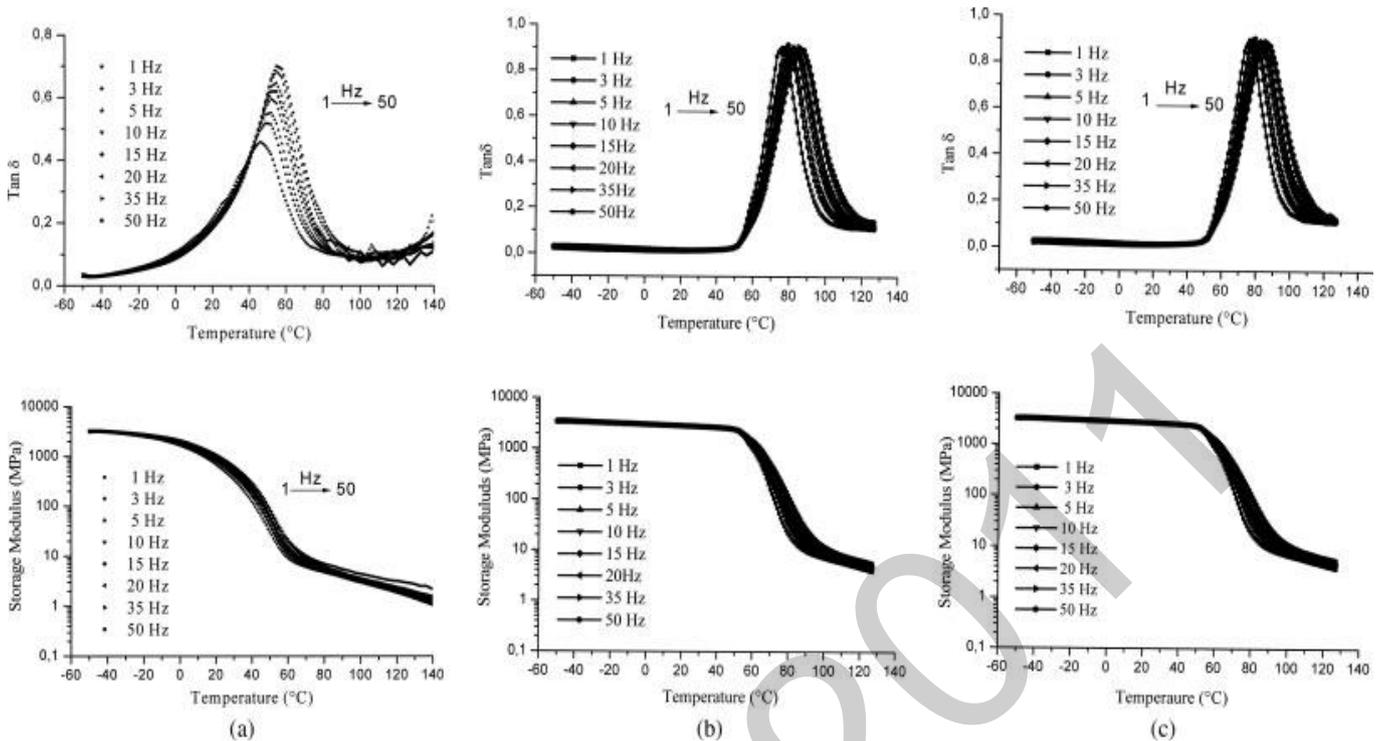
Figure 4. UV-visible spectra of purified PVC sheets plasticized with epoxidized sunflower oil containing various levels of epoxidation (0-5% O.O).

### Dynamical mechanical analysis

The loss tangent spectra are typical of a miscible system by showing one Tg and there is only a moderate broadening of the main Tg relaxation. This suggests that the blends PVC-DEHP-ESO are homogeneous. The DMA of PVC-DOP shows a lower tan  $\delta$ ; and a broad peak; or a lower homogeneity. The incorporation of oxirane in sunflower oil reduces the degradation of PVC and reduces it progressively with the increase of oxygen oxirane. It is accepted that the higher the tan  $\delta_{max}$  the greater the mechanical loss; these losses are related to high energy input required for the motion of the molecular chains of the polymer as the transition is being approached. The results also suggested that increasing the weight of ESO content caused an increase of elastic behavior (reduced tan  $\delta_{max}$ ).

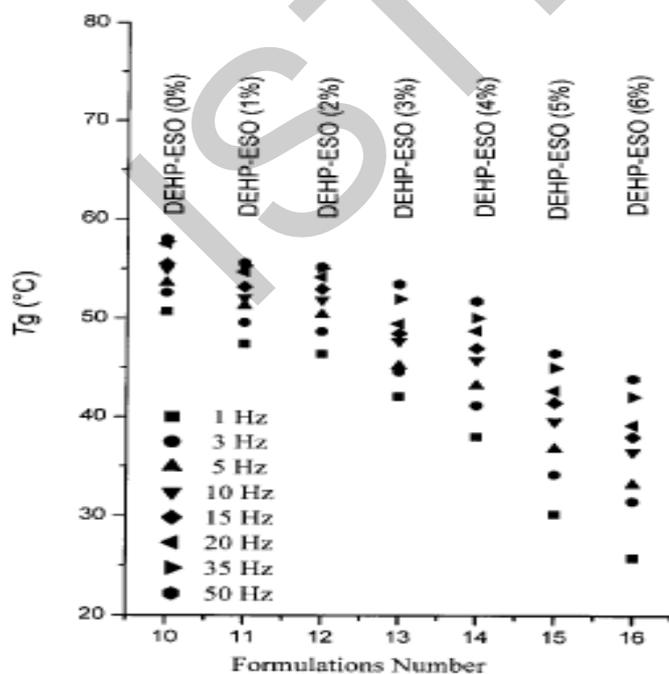
In the tan  $\delta$  presentation, a narrow relaxation peak dominated over the entire temperature of measurement from 250°C to about 130°C. Peak temperatures measured tan  $\delta$  at various frequencies is tabulated. As expected, the higher content plasticizer samples had lower glass transition temperatures. In other words, the plasticization effect of ESO on the PVC increases with increasing ESO content. Finally, another interesting observation relating to the Tg behavior of ESO is that the increase of

oxirane oxygen decreases the Tg of PVC sheets. Substantial physical property changes occur with increasing level of epoxidation; thus as the level of epoxidation goes up the glass transition temperature (Tg) decreases.

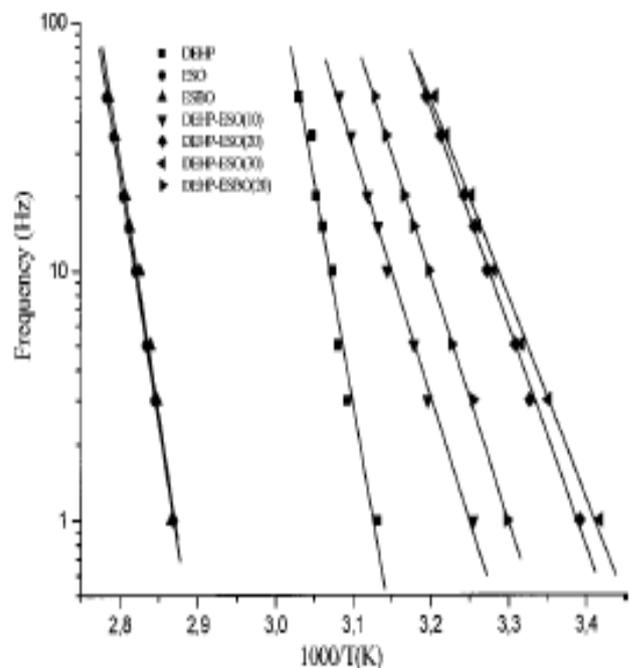


**Figure 5.** Loss tangent curves and storage modulus as function of temperature for plasticized PVC with: (a) DEHP, (b) ESO, and (c) ESBO.

Figure 7 also shows that the epoxidation levels of ESO in combination of DEHP are divided into two groups: with less (sample 8, 9, and 10) and those with more than 3% O.O (sample 11, 12, 13, and 14); this also reflected on tan  $\delta$  max versus their optimum composition behavior and its affinities. In the first group from 0 to 2% O.O Tg decreases slowly, but in the second group from 3 to 6% O.O Tg decreased rapidly. Increase in frequency of the testing displaced the Tg value to higher temperatures. It was interesting to plot the value of tan  $\delta$ max to verify the effect of frequency on the change in activation enthalpy by using Arrhenius law. From the frequency dependence of the Tg peak, the values of activation enthalpy for the plasticized samples are calculated, showing the thermally activated character of this process (Fig. 8) and given in Table 3, where  $\Delta H$  is the activation enthalpy for the relaxation process.



**Figure 7** Glass transition temperatures for plasticized PVC sheets with various oxirane oxygen of ESO.



**Figure 8** Activation enthalpy for different system lasticizers of PVC sheets.

It appears that there is a monotonic dependence of the activation enthalpy on the measured T<sub>g</sub>. This dependence could have arisen from the complete miscibility between the dominant amorphous phase of PVC and the DEHP-ESO. The points corresponding to the plasticized PVC samples are shifted toward lower value of activation enthalpy. Epoxidation of sunflower oil is essential, as it improved compatibility as well as thermal stability. This study demonstrates some of potential industrial applications of sunflower oil, many of which have yet to be fully exploited.

**Table 3.** Activation Enthalpies Values

Notation (Formulation)	Activation enthalpy ( $\Delta H/\text{kcal mol}^{-1}$ )
F1 (DEHP 30g)	18.1
F2 (ESO 10g)	20.2
F3 (ESBO 10g)	21.2
F4 (DEHP 30-ESO10g)	10.1
F5 (DEHP 30-ESO20g)	8.9
F6 (DEHP 30-ESO30g)	8.1
F7 (DEHP30-ESBO20g)	9.9

### CONCLUSIONS

Existing results give evidence that the presence of ESO in PVC mixtures brings about an appreciable decrease in degradation of PVC and contributes to preservation of the color of the mixture. The study shows that ESO could be used as a secondary plasticizer for PVC. ESO is suitable above all for its cooperative effects. It can be regarded as stabilizer as well as good plasticizer. The physical interaction or solubility of ESO seemed to be more likely reason for such changes in the properties of flexible PVC. When the plasticizer content was increased, there was a decrease in tensile strength and shore D hardness.

The presence of ESO in formulation with DEHP greatly enhances the thermal and mechanical characteristics. Dynamical mechanical analysis reveals that ESO can function as coplasticizer for PVC-DEHP systems by the lower T<sub>g</sub> values obtained for various oxirane oxygen. The plasticizing effect of ESO was higher than that of ESBO because of the lower molecular weight of ESO and its higher compatibility with PVC.

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# EFFECTS OF TWO LOBE WAVE SQUEEZE FILM DAMPER IN THE SUPPORT OF AN UNBALANCED RIGID ROTOR

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## ABSTRACT

A possible improvement of the performances of squeeze film damper (SFD) for supporting the rotors of high-speed turbomachinery has been sought adopting a two lobe, wave (2LW) geometry of the bearing bore. A statically unbalanced, symmetrical, rigid rotor supported with 2LW-SFD has been theoretically examined through numerical continuation, assuming laminar, isoviscous oil flow within the damping film and incomplete centering action of the retainer springs mounted parallel to the film. Despite nonlinearity which still affects the system, the obtained results highlight the potential of the unconventional geometry as a mean for a possible reduction of the typical drawbacks in the response with conventional SFD, mainly consisting in undesired whirling motions with too large journal orbits and/or nonsynchronous character, so as to assure more safe conditions for the rotor operation. Yet, further theoretical and experimental investigation is desirable in order to confirm such an outcome.

Keywords: lubrication, squeeze film damper, rotordynamics, bifurcation.

## NOMENCLATURE

$C, L, D, R$	= reference radial clearance, axial length, reference diameter and radius of the bearing
$F_{SFx}, F_{SFy}$	= fluid force component, in function of dimensional coordinates and velocities
$m$	= half rotor mass
$\varphi$	= angular orientation of the 2-lobe bearing (2LB)
$U$	= $(\rho/C)$ dimensionless static unbalance
$\omega$	= angular speed of rotor
$k$	= stiffness of the SFD restraining springs
$\mu$	= lubricant viscosity

## INTRODUCTION

The poor quality and drawbacks which affect the dynamic behaviour of turbomachinery on rigid supports equipped with simple rolling bearings, in terms of forces transmitted to the frame and vibrations, fostered the concept of combining the bearing to an oil film since from the Thirties of the past century (Birmann, 1933). As a device capable to work in this way, in order to assure enough damping to the rotor-system, the squeeze film damper (SFD) has received substantial and systematic scientific attention in the last five decades (Della Pietra & Adiletta, 2002). This huge research work has been mainly addressed to fluid dynamic and structural aspects of the damping device, like oil cavitation and inertia or oil feeding and seals effects, which highly influence the pressure distribution in the film and hence the film forces. The said factors, together with the basic nonlinear character of the film forces, represent a crucial issue as regards the dynamic response of the supported rotor. Here the nonlinearity, possibly exalted under some circumstances, can give rise to undesirable or unexpected whirling motions of the rotor with very large orbits described by the journals within the relative bearings and/or characterized by nonsynchronous nature. General consequences of these effects are high levels of vibrations and force transmissibility, shortening in the life of the bearings, damage of the damper bearing, possible failure of the rotor due to the fatigue mechanism connected to the nonsynchronous whirl. Therefore, a consistent part of the research from literature has been just focused onto the dynamic behaviour of the rotor-support system with SFD, represented by practical or experimental real rotors, often theoretically characterized by very simple flexible or rigid models, provided with supports of the uncentralized or centralized type (Adiletta & Della Pietra, 2002). Regarding to this last option, it is worth mentioning that the rotor journal is let free to whirl within the damping film, i.e. subjected to the only hydrodynamic forces of the squeeze film, or it is further supported by springs which work in parallel to the film and allow a preliminary centering of the journal within the bearing clearance when the rotor is at rest. Nevertheless, the registration of the static position can be carried out in practice with higher or lesser accuracy and the complete, full centering turns out to be only theoretical. Bistable conditions with jump in rigid rotors were investigated, among others, by White (1970) and Hahn (1979). Mohan & Hahn (1974) analyzed the horizontal centralized rotor, where the flexibility of supports is due the spring elements mounted in parallel to the damping film, and pointed out the importance of a critical value of the unbalance beyond which the squeeze film bearing with flexible mount behaved worse than a rigid support. The influence of the initial conditions, when numerical integration is carried out for solving the nonlinear equations of the rotor-support system, was investigated by Taylor & Kumar (1980). They

observed on this basis the dominant character of one of the two solutions present in intervals of speed with bistable behaviour. Li & Taylor (1987) showed the coexistence of nonperiodic and synchronous solutions after numerical study of the unbalanced rigid rotor on SFD with centralizing springs. Also, they investigated into the effects of incomplete centering and pointed out the importance of the complex characteristic roots about the degree of attraction of the different coexistent motions. Similar analyses were carried out by Zhao & Hahn (1993) and Zhao et al. (1994) who analyzed the bifurcating behaviour of the rotor system. In the latter paper, successive bifurcations along rotor run up, respectively representing changes from synchronous to quasi-periodic, sub-harmonic and again to synchronous whirl, were reported and explained with the study of Floquet multipliers. More recent examples of research works about nonlinear behaviour of rigid rotors on SFD are represented by Bonello, Brennan, & Holmes (2002), focused onto receptance harmonic balance method that was adopted to determine periodic solutions, and Inayat-Hussain, Kanki, & Mureithi (2003), where the bifurcating dynamics of the nonlinear systems was dealt with by means of a numerical case study and recourse to continuation technique. Besides the rigid rotor case, flexible rotor systems have been extensively studied too, especially in the simple symmetrical model with rigid disk, flexible shaft and SFD end supports (Inayat-Hussain, 2009). Furthermore, particular research efforts have been addressed to innovative design of the squeeze damper, in order to improve the dynamic performances of the supported rotor (de Santiago et al. 1999, El-Shafey & El-Hakim, 2000). In this regard, the present work is aimed to test the adoption of a two lobe, wave (2LW) geometry of the bearing bore, in place of the common circular profile. Such a concept, with adoption of different shapes, is well known in journal bearing design (Pinkus, 1956). The three lobe wave profile, in particular, has been thoroughly investigated for gas bearings application (Dimofte, 1995) putting in evidence its advantages and the present authors have recently focused their attention onto the 2LW geometry for oil lubricated journal bearings (Adiletta, Mancusi, & Strano, 2011). In this case, wave amplitude and angular phase of the profile represent, in respect of the conventional circular geometry, two further parameters that influence the behaviour of the rotor-support system and are possibly at hand to optimize the dynamic response. On this basis, a statically unbalanced, symmetrical, rigid rotor supported with 2LW-SFD has been theoretically examined under the hypotheses of laminar, isoviscous oil flow within the damping film and incomplete centering action of the retainer springs mounted parallel to the film. The analysis has been carried out with use of numerical integration of system equations and continuation algorithm.

**THE EQUATIONS OF MOTION AND THE FLUID FILM FORCES IN THE SFD**

A statically unbalanced, rigid rotor is in horizontal disposition and supported at each end by roller bearing plus squeeze film damper (SFD) with retaining springs. The whole system is assumed to be symmetrical, so that cylindrical whirl can be assumed for the rotor motion and the following equations are written for a single half of the rotor-support system:

$$\begin{cases} m\ddot{\bar{x}} + \sigma\dot{\bar{x}} + k\bar{x} = m\rho\omega^2 \cos \omega t + F_{SFx} \\ m\ddot{\bar{y}} + \sigma\dot{\bar{y}} + k(\bar{y} - \bar{y}_S) = m\rho\omega^2 \sin \omega t + F_{SFy} \end{cases} \quad (1)$$

Equations (1) are written assuming a reference fixed frame placed in the bearing center, with the  $\bar{y}$  axis parallel to the gravity force, upward directed, and  $\bar{z}$  direction parallel to the rotor axis. A gravity residual  $\bar{y}_S$ , due to hypothesized incomplete centering of the springs, is defined as:

$$\bar{y}_S = \bar{y}_0 + f_S,$$

where  $f_S$  represents the static deflection of the spring system, i.e.  $f_S = -mg/k$ , and  $\bar{y}_0$  is the coordinate of journal center of the rotor in the absence of weight. Substitutions:

$$\begin{aligned} x = \frac{\bar{x}}{C}, \quad y = \frac{\bar{y}}{C}, \quad y_S = \frac{\bar{y}_S}{C}, \quad \omega t = \tau, \quad \dot{x} = \frac{dx}{d\tau} \frac{d\tau}{dt} = x'\omega, \quad \dot{y} = \frac{dy}{d\tau} \frac{d\tau}{dt} = y'\omega, \quad \zeta = \frac{\bar{z}}{L}, \\ \omega_R = \sqrt{\frac{k}{m}}, \quad \Omega = \frac{\omega}{\omega_R}, \quad \omega_B = \frac{\mu RL^3}{mC^3}, \quad f = \frac{\omega_B}{\omega_R}, \quad U = \frac{\rho}{C}, \quad q = \frac{\sigma}{2\sqrt{mk}}, \\ \lambda = \frac{L}{D}, \quad F_{SFx} = \frac{\mu\omega_R LR^3}{C^2} f_{SFx}, \quad F_{SFy} = \frac{\mu\omega_R LR^3}{C^2} f_{SFy}, \quad (2) \\ f_{SFx} = - \int_{-1/2}^{1/2} \int_{\delta 1}^{\delta 2} \gamma \cos \delta d\delta d\zeta, \quad f_{SFy} = - \int_{-1/2}^{1/2} \int_{\delta 1}^{\delta 2} \gamma \sin \delta d\delta d\zeta, \quad \gamma = p / \left( \mu\omega_R \frac{R^2}{C^2} \right), \end{aligned}$$

$$w_1 = x, \quad w_2 = y, \quad w_3 = x', \quad w_4 = y', \quad w_{2,S} = y_S,$$

yield the following system of first order ODEs equivalent to (1):

$$\begin{cases} w_1' = w_3 \\ w_2' = w_4 \\ w_3' = -\frac{2q}{\Omega} w_3 - \frac{1}{\Omega^2} w_1 + \frac{f}{4\Omega\lambda^2} f_{SFx} + U \cos \tau \\ w_4' = -\frac{2q}{\Omega} w_4 - \frac{1}{\Omega^2} (w_2 - w_{2,s}) + \frac{f}{4\Omega\lambda^2} f_{SFy} + U \sin \tau \end{cases} \quad (3)$$

Components  $F_{SFx}$  and  $F_{SFy}$  of the fluid film force were obtained from the pressure distribution determined solving the Reynolds equation written for finite SFD, in the presence of non circular bearing profile and incompressible, isothermal, isoviscous, laminar flow:

$$\frac{1}{R^2} \frac{\partial}{\partial \vartheta} \left( \frac{\bar{h}^3}{\mu} \frac{\partial p}{\partial \vartheta} \right) + \frac{\partial}{\partial \bar{z}} \left( \frac{\bar{h}^3}{\mu} \frac{\partial p}{\partial \bar{z}} \right) = -12 \left( \dot{\bar{x}} \cos \delta + \dot{\bar{y}} \sin \delta \right) \quad (4)$$

The fluid film region with  $\delta \in [0, 2\pi]$ ,  $\zeta \in [-1/2, 1/2]$  was discretized by means of a two-dimensional mesh of  $N+1$  columns by  $M$  rows, with cell dimension  $\Delta\delta \times \Delta\zeta$  and  $\Delta\delta=2\pi/N$ ,  $\Delta\zeta=1/(M-1)$ . Finite differences solution of the Reynolds equation was carried out by means of a forward-time, centered-space FD scheme, with  $M=5$ ,  $N=81$ , and a subsequent SOR algorithm for solving the algebraic system. Ambient pressure was adopted at film borders and to replace sub-ambient values obtained from the FD routine. Equations (3) were numerically integrated with a Runge-Kutta routine. The determination of trajectories and Poincaré sections was carried out together with numerical continuation of periodic solutions after suitable choice about the set of the system parameters.

According to (2), Fig. 1 and Adiletta, Mancusi, & Strano, (2011) the bearing of the damper presented a two-lobe, wave profile characterized by dimensionless amplitude  $B$  and angular orientation  $\varphi$ . In the present investigation,  $B$  was given values 0, 0.05, 0.1, 0.15 and 0.2 (the null value was included in the set in order to represent the circular bearing case) while  $\varphi$  was assigned in the set  $\pi, -3\pi/2, -\pi/2, -\pi/4, 0, \pi/4, \pi/2, 3\pi/2$ . Figure 1a illustrates the modification of the original circular bearing clearance as an effect of  $B$  and  $\varphi$ . Fig. 1b shows three examples with  $B = 0.2$  and  $\varphi = \pi, 0$  and  $\pi/4$ . The geometry of the bearing was further specified by means of a length to diameter ratio  $\lambda$  that was assumed equal to 0.125, as typical of short-bearing aspect.

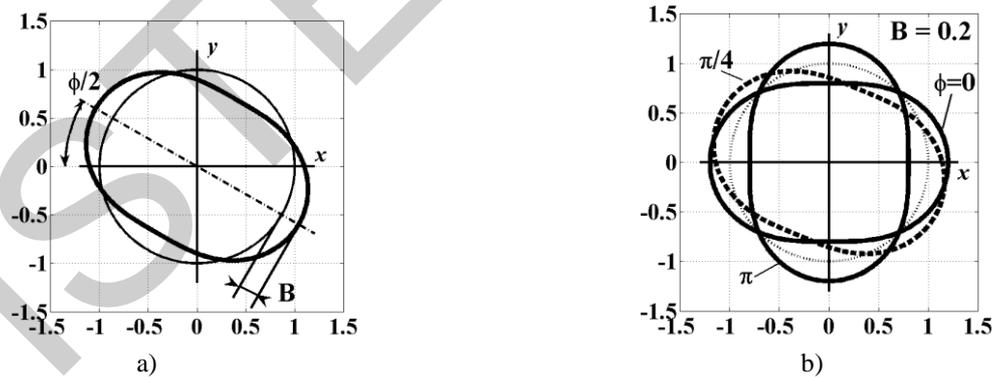


Fig. 1

The effects of damper geometry and orientation onto the dynamic behaviour of the rotor were tested once suitable set-up conditions of the system had been fixed. In this regard, the results from Zhao and Hahn (1995), relative to a common circular bearing case in the presence of severe unbalance, suggested to assign:  $f = 0.072$ ,  $U = 0.3$ ,  $w_{2,s} = -0.7$ , given the remarkable nonlinearity which affected the rotor response under these conditions. A specific, dimensional case study was conceived in congruence with the above parameters, fixing  $k = 929752$  N/m,  $m = 50$  kg,  $R = 0.04$  m,  $C = 0.00015$  m and  $q = 0.005$ . The angular speed was given in the interval  $I\omega = [100, 1200]$  rad/s. Then the remaining quantities  $\omega_R$ ,  $L$ ,  $\mu$  and  $\Omega$  could be inferred:

$$\omega_R = \sqrt{\frac{k}{m}} = 136.36 \text{ rad/s}, \quad L = 2R\lambda = 0.01 \text{ m}, \quad \mu = f \frac{m\omega_R C^3}{RL^3} = 0.0414 \text{ Pa s}, \quad \Omega = [0.733, 8.80] .$$

**RESULTS OF NUMERICAL ANALYSIS**

Bifurcation analysis of periodic and *k*-periodic solutions was carried out by means of a continuation algorithm, based onto AUTO 97 (Doedel *et al.*, 1997), which traced the fixed point locus of the discrete-time “equivalent” system constructed via the Poincaré sections. The branches of the fixed points were computed together with Floquet multipliers. These quantities made it possible to check the stability of the branches. On the other hand, numerical integration of Eq. (3) based on Runge-Kutta method made it possible to check some of the results from continuation through direct observation of the journal orbits. Only two significant examples of the obtained numerical results have been reported here below:

a) The resonance curves of the synchronous response (1*T*), respectively obtained for different  $\phi$  values, when the bifurcation parameter  $\omega$  varies in the interval  $I_\omega$ . The angular positioning of the damper bearing not only modifies the resulting orbit magnitude, here expressed by means of the maximum orbit radius, but determines too the presence or absence of the saddle-node bifurcation connected to the well known jump effect. In Fig. 2a, the curves obtained with  $\phi = \pi$  and  $-3\pi/4$  are deprived of the “nose” followed by instable branch (not reported) that characterized the curves with  $\phi = -\pi/2$  and  $-\pi/4$ . In Fig. 3a waterfall picture of the resonance curves has been plot in the whole interval  $I_\omega$ . Fig. 3b shows a from-the-top view of the same plot, evidencing the sub-intervals of  $I_\omega$  where the synchronous motion turns out to be stable (absence of line represents instability). Three examples of the journal orbits about resonance are put in comparison in Fig. 4a-c.

b) Two continuation diagrams of the 1*T*, obtained at given values of *B* and  $\omega$ , assuming  $\phi$  as the bifurcation parameter which varies in the interval  $[0, 2\pi]$ . In Fig. 5a, b the angular speed has been assumed equal to 600 and 500 rad/s, respectively, i.e within a zone of  $I_\omega$  that is generally characterized by instability of the synchronous solution (compare Fig. 3b). Fig. 6 illustrates a particular from Fig. 5b. The plots point out that the existence of the stable motion, at given speed, is conditional on the choice of suitable values for *B* and  $\phi$ . In the diagrams the response of the circular bearing case has been further reported to allow comparison.

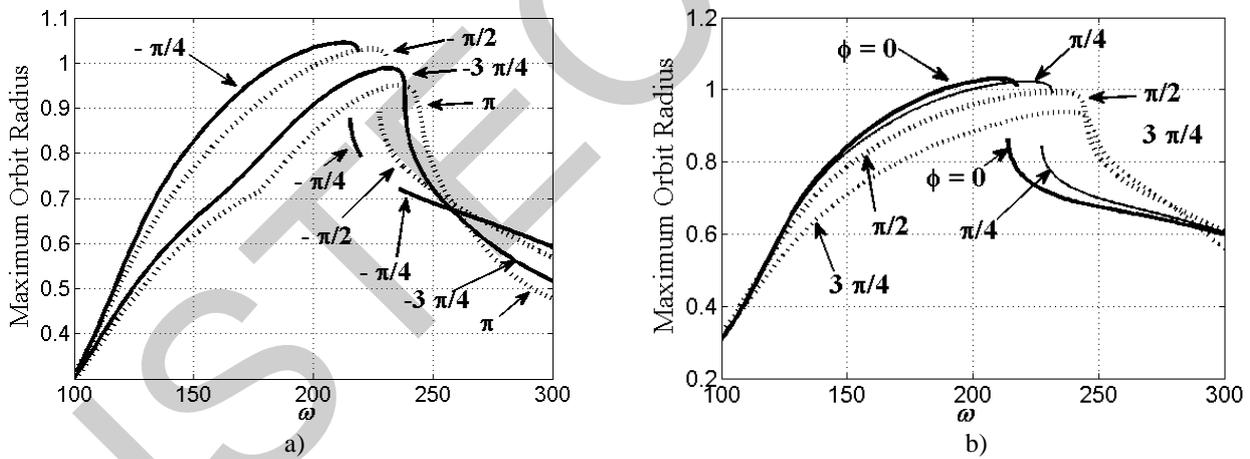
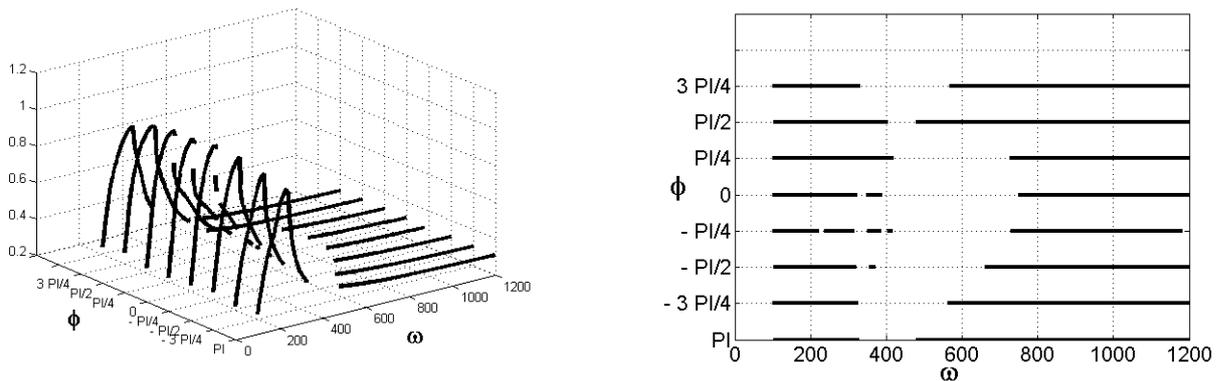


Fig. 2



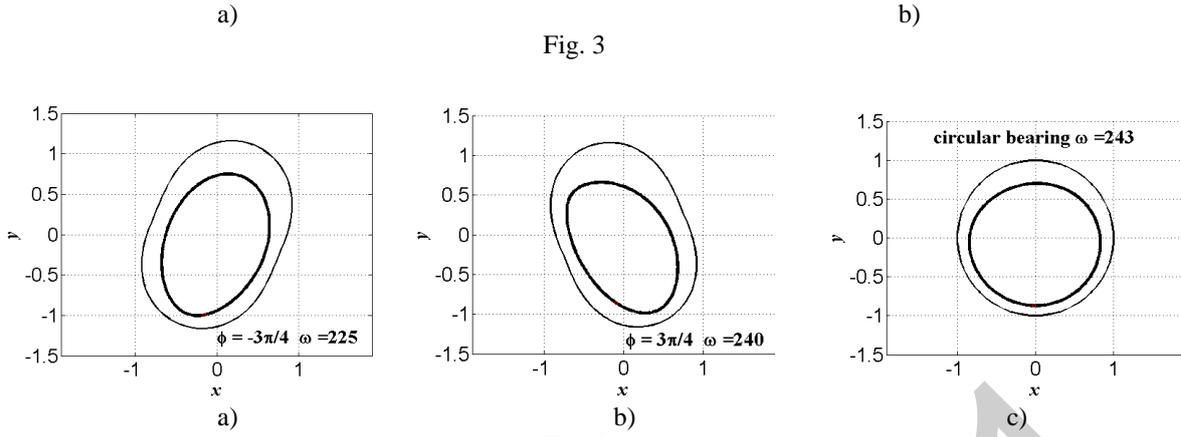


Fig. 3

Fig. 4

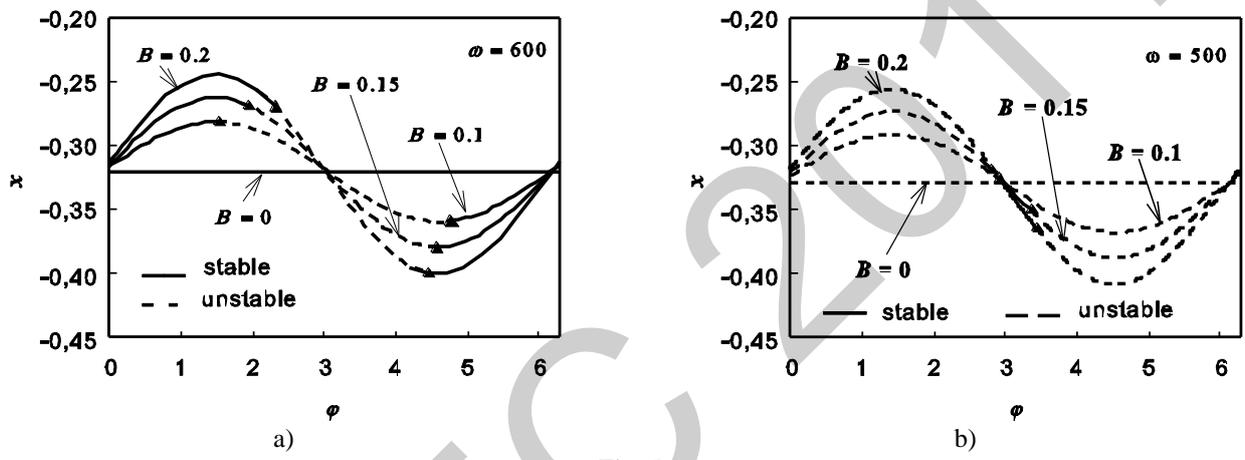


Fig. 5

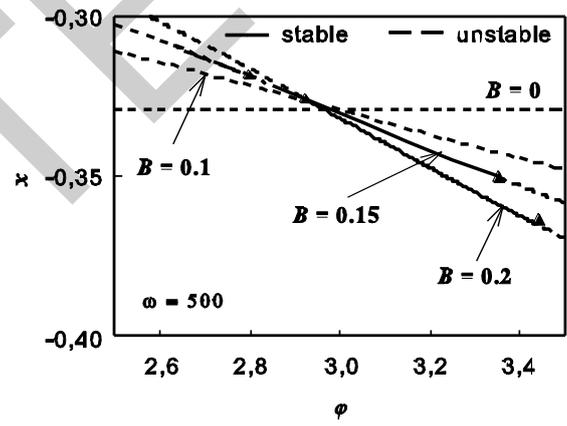


Fig. 6

**CONCLUSIONS**

The use of 2LW-SFD for supporting a rigid unbalanced rotor has been investigated through numerical continuation method, with particular attention to the effects of the bearing geometry onto the synchronous response. A case study with given unbalance, gravity residual, lubricant viscosity, wave amplitude of the bearing profile, and different values for the angular position of the 2LW bearing has been selected for the analysis. The obtained results, despite the restriction of the investigation to the synchronous response, put in evidence the substantial effect of the choice of such a bearing geometry, with particular regard to the jump phenomenon and the recover of stable solutions. Further investigation, both theoretical and experimental, is desirable in order to assess possible practical benefits of the device.

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# EFFECTS ON THE STUDENTS' PERSONAL COMPETENCES OF THE USAGE OF PBL METHODOLOGIES IN PROFESSIONAL REALITY SIMULATION ENVIRONMENTS: STUDENTS, TEACHERS, GRADUATES AND EMPLOYERS' PERCEPTIONS

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**ABSTRACT:** Trying to ensure that every student who enters the work market bears a set of personal attributions acknowledged as essential, higher education institutions (HEIs) have been being confronted with the need to activate new ways to produce and disclosure knowledge, compatible with the transition from an educational to a work environment. This research analyses the effects on the development of the students' personal competences of the PBL methodologies in a simulation environment for the business reality. Setting off from a case study of a vocational HEI, we resorted to the interview technique with teachers and employers and the questionnaire technique with the students and graduates. Students, graduates and teachers support that the PBL methodologies contribute for the further development of personal competences, mainly at the level of resource use (management, planning and work methodology) and at the level of knowledge construction (critical analysis, grounds for decisions and initiative). By the employers, one can easily detect a persistent trend not to acknowledge the PBL methodologies as directly responsible for an improvement of the graduates' personal competences, with the exception of the valorisation of more consistent grounds and more confident attitudes.

## 1. INTRODUCTION

The society's current conditions require an extraordinary educational commitment in favour of the training for the new generations. The higher education system itself does not go unharmed by the social, political and economical transformations we experience. Bearing this context in mind as a reference, it is possible to realize a society which generates challenges over a set of professional, but also personal and social competences. The expectation that the graduates will be able to evidence a vast set of much needed attributes for a lifelong learning process is shared not only by the employers and graduates, but also, with grand centrality, by higher education institutions (HEIs). As cited in Radloff, de la Harpe, Dalton, Thomas & Lawson (2008), the graduates who prove to have relevant attributes are taken into great consideration by the employers and regarded as citizens who generate social rise in value. In this sense, it is quite important to tend to the mutual influence dynamics among the varied agents involved and the structures which they consist of (students, teachers, graduates and employers). Trying to ensure that every student who enters the work market bears a set of personal attributions acknowledged as essential, confronts HEIs with the need to activate new ways to produce and disclosure knowledge. Some authors insist in the idea that it is central to change learning and teaching strategies, in order to develop students' horizontal competences (e.g. Silén & Juhlin, 2008). The arguments involved in such methodologies are multidimensional and diversified.

In the present study we highlight PBL methodologies (either in a perspective of project-based learning or a problem-based learning), based upon the principle of using contextualized problems of a professional nature as a starting point for the acquisition and integration of knowledge (Kolmos, 1996). Throughout this work we reflect upon the need for the HEIs to answer to new ways of knowledge production and dissemination, which value not only the *know-how* and the *do*, but also the *know how to be with others* and the *know how to be*. Against the background of this problematic, the general goal of this project is to try to contribute for the theoretical discussion on the way change movements associated to the PBL methodology produce implications at the level of the higher education students. We did, however, limit our field of study to the context of personal competences, trying to render more viable the control of the existing complexity and diversity in the PBL methodology paradigm. Specifically, we will centre our analysis on the set of perceptions and positions assumed by the main groups involved and with particular interests in the learning processes: students, teachers, graduates and employers. Based on the pointed outlines, and more specifically, we intend to: (1) inquire about the role which the PBL methodology plays in the development of the students' personal competences; (2) find out if the methodology improves the personal competences of the PBL graduates when compared to others; and (3) perspective the role of the PBL methodology at the level of personal competences, in the construction of a graduate profile for the third millennium.

This article is organized into five key points. After the introduction we try to contextualize PBL methodologies within the changing learning and teaching paradigm in vocational higher education. The next section focuses on the methodological aspects of the study, including the context of the case study used in the research and techniques for collecting and processing data. The fourth section is devoted to presenting and discussing the results obtained from students, graduates, academics and employers. The paper ends with the main conclusions of the study.

## 2. PBL METHODOLOGIES AND THE CHANGING PARADIGM IN VOCATIONAL EDUCATION

In the Report made for UNESCO by the International Commission on Education for the Twenty-first Century (International Commission on Education for the Twenty-first Century, 1996) a complementary mission for education is immediately referred:

that of fructifying the creative talents and potentialities of all individuals. In that very same report, the need for a lifelong learning process is strengthened, as one of the keys to access education. The idea conveyed by the group of rapporteurs sustains that, in order to be able to answer its set of assignments, education must be built upon the symbiosis of four basilar learning processes: learning to know (acquiring not only a set of codified knowledge, but also, and most importantly, the domain of those instruments), learning to do (adjusting training to the future professional activity, in such a way as to apply the knowledge obtained), learning to live together (cooperating with others in the resolution of common projects) and learning to be (allowing for the full development of the person, rendering him/her apt to create autonomous and critical thoughts, capable to judge different circumstances in life). However, if traditional teaching (which is understood as a model of transmission of both knowledge and values, in the unequivocal direction teacher to student) is primarily oriented by the learning of how to know and, especially in the field of higher vocational training, by the learning of how to do, according to the authors of the above mentioned report, it will be necessary to provide education with structured methodological ways, capable to involve both the learning of how to live together and the learning to be. In such a perspective, it is possible to sustain the idea of focusing on learning, thus realizing that the latter can not occur without people or a reference to its subjectivities and personal and social contexts (Fyrenius *et al*, 2007).

All together, the adequacy of the higher education system to the teaching-learning model sustained by the Bologna Process, did also jeopardize a profound change of paradigm: in order to confront the European student profile, the HEIs should emphasize horizontal competences which render students responsible for their learning processes, thus leaving the teachers with the task to facilitate and orient those processes. The implementation of these guidelines does inevitably create the need to re-evaluate the pedagogical activities at the level of goal definition and assessment, as well as, particularly, at the level of execution and follow-up of the methodological processes. In the Portuguese case, the higher education network is developed upon a binary system, accentuating the distinctly professional prominence of the polytechnic higher education, as opposed to more conceptual and theoretical features of the university education. Hence we find two distinctive logics: in the university education and in sequential periods of time, we may distinguish *knowledge* and *know-how*, whereas in the polytechnic education, at the same time, *knowledge*, *know-how* and *do* coincide. So, and particularly in polytechnic education it is possible to understand the importance to rethink the training of its students adjusting it, as far as possible, to the professional needs demanded by employers. In order to strengthen such a position, new pedagogies centred in the relation between pedagogical practices and professional practices have been revealing themselves as an important methodological paradigm (e.g. Musal, Taskiran & Kelson, 2003).

A possibility to establish the transition between educational practice and professional practice is that of fostering the change of a traditional teaching system to a PBL model. Developed by Howard Barrows and Robyn Tamblyn as of the late sixties and initially associated to medical schools, the PBL methodology has been used in various professional areas and programs, already gathering 40 years of experience (Nel, *at al.*, 2008). The PBL methodology is based upon the principle of using contextualized problems of a professional nature as a starting point for the acquisition and integration of knowledge (Barrows & Tamblyn, 1980). So being, and ontologically speaking, the use of professional problems works, simultaneously, as a learning incentive and a focus. In PBL methodology, students work in small groups, analysing the problem they are presented with, identifying the necessary information for its solution, directing their learning activities according to the knowledge needed to process the problem presented and, finally, formulating possible solutions. Throughout this process and by means of self-learning mechanisms, one may assume students develop competences which allow them not only to achieve the desired professional results, but also to work different personal and social features (Papinczack, 2009). In this way, it is supposed for the profile of a graduate who recurred to a PBL methodology to include not only basic knowledge, which will allow him to research, understand and critically explain the existing literature on a certain matter, but also the aptitude to communicate with others or the ability to solve problems which his professional experience enables him with, both as a person and a technician. On the other hand, and accepting the perspective of several authors (e.g. Tate & Grein, 2009) that learning has its place when there is an active and committed participation of the learner, it becomes fundamental for him to reconstruct knowledge, adjusting it to his needs and image. PBL methodology conceptually predicates an active construction of meanings for those who learn it, promoting, as a result, a more lasting internalization of the learning experiences. In such a perspective, this custom made concept stimulates, on the one hand, personal and social competences of intellectual growth and, on the other, it makes those competences more effective ones. Following the PBL methodology, the students who are looking for the answers to the questions they asked themselves, will select which may in fact answer their doubts and justify the solutions «found». As a result, it is possible to refer the acquisition of competences at three different levels: technical (referring to the quality of the service rendered), social (associated to the nature of interpersonal relations) and self-developing (regarding questions of organization, argumentation and communication) (e.g. Albanese & Mitchell, 1993; Musal, Taskiran & Kelson, 2003). In particular, some studies of PBL in the accounting area can be consulted. According to the analysis of the state of the art about accounting and education, Rebele *et al.* (1998), Apostolou *et al.* (2001) and Watson *et al.* (2003, 2007), reveal that that between 1991 and 2005 only three articles refer to PBL. Nevertheless, some other studies may be point out. More recently, Tate and Grein (2009) or Xu and Yang (2010) have done some work on it. So, it is precisely the condition of the existence of few readings about PBL methodologies in accounting that instigates us to consider the paradigm of the effects on the students' personal competences of the usage of PBL methodologies in professional reality simulation environments.

### 3. METHOD

Within the problematic discussed, the main objective of our work is to contribute to the theoretical discussion of how changes related with PBL methodologies produce implications on personal competences in vocational higher education. Supported on the several authors that frame the conceptualizing of our study, it is possible to sustain the thesis that PBL methodologies develop and reinforce students' personal competences (e.g. Tate & Grein, 2009). In more specific terms, we intend to inquire about the role which the PBL methodology plays in the development of the students' personal competences. Simultaneously,

we want to find out if the methodology improves the personal competences of the PBL graduates when compared to others. Finally, we want to perspective the role of the PBL methodology at the level of personal competences, in the construction of a graduate profile for the third millennium.

### 3.1 The Case Study: Business Simulation

As previously referred, the case study which shapes this work is based upon the curricular unit of Business Simulation (running since 1997), included in the last semester of the last year of the study plan of the first cycle of studies of the accounting course available at the ISCA-UA. The origin of the idea to create a subject which aims to present a new teaching solution which brings the later closer to the business reality derived, mainly, from the conjugation of two primordial factors: a first factor which results from the difficulty to introduce a curricular training period in the course (which meant professionally placing about 160 students per year) and a second factor which resulted from the need to place upon the market accountants who were potentially more apt and advantageously competitive for the exercise of their profession, facing the growing offer of graduates qualified to exercise it.

Methodologically, the need to build bridges between the theoretical knowledge and its practical applications, among the conceptions teachers had on the professional needs and the competencies required by employers, motivated the use of a contextual learning process, integrated in a reality which mirrored the professional environment of the future graduates, following an ideological line of learning by doing. Parallel to this, there is the idea to simulate, within the school, the business reality which tried to offer a greater follow-up to the passage from a purely academic life to an active professional one and, at the same time, complement the initial training of the future graduates, by means of a holistic integration of the knowledge achieved during previous academic years. Such a context revealed itself a window of opportunity for the structuring of a systemic model inspired in PBL methodologies. The structure of the model chosen for the subject of Business Simulation completely unfolds around projects which imply themes from different subject areas, thus fostering learning by the resolution of problems that emerge during the formulation or implementation of those very projects. Based on teamwork, the model privileges self-learning and comprises, in its logical structure, the figure of the group's tutor who has a role of guidance.

The Business Simulation method consists of a simulated market of virtual companies, which small groups of students must manage and administer. The number of groups created annually is, roughly, 75, comprising the most varied fields of activity, with special attention to the fact that the interconnection among them demands for the existence of supplier and consumer companies, as well as competitive companies, just like it occurs in the real market. The subject takes place in 15 real weeks, which correspond to a virtual year, thus allowing students to perform the accounting simulation of the beginning and the end of the exercise. In order to maximize the real character which the Business Simulation is intended to have, the subject has similar goals to those established for analogous situations in the real world, with the delivery being the only true fictional aspect. The approximation to the professional activity is also ensured by the collaboration of three centrals which simulate the products and services necessary for the full operation of the business network: public, financial and commercial. While the public central emulates the role of different public entities, the financial central focus on assuring a set of diversified financial products and services. Finally, the commercial central has the role to promote the necessary dynamic to the functioning of the various sectors of business activity represented in the simulated market.

The importance granted to the subject is acknowledged by the Chartered Accountants Association Council (OTOC), which means that ISCA-UA is one of the schools which is exempt of the training period requested by the OTOC in order to have access to the enrolment as a chartered accountant. As that training period has the triple goal supplying professional experience, complementing social and professional competences and enabling a stronger articulation between the school and the world of work, the Business Simulation fulfils, according to the OTOC's perspective, the goals established for a training period. So being, it brings an added value to the profession of the future graduates.

### 3.2 The research design

After the definition of the main objective and the investigation questions that circumscribe this investigation, we elected a case study methodology. As a means of research, the methodology of case study enables, as far as Bell (1998) is concerned, to broaden the limitations of the existing knowledge and enable future researchers to confront their decisions with those referred to on the study. Yin (1994) also refers the fact that the most important aspect of a case study is not the statistical generalization of the phenomenon, but rather the analytical generalization in itself. So, our option derives from the belief that it can confirm and complete conceptual knowledge and from the opportunity of interest it represents, namely at a vocational level in accounting courses. More, we add the fact that a single case study can be a pilot case in future studies of multiple cases. On the other hand, we considerer important to elect the main groups involved and with particular interests in the learning processes: students, teachers, graduates and employers. In the empirical study we developed, we used the technique of interviews with the teachers and employing entities and that of questionnaire with the remaining participants. When observing the data collected we also resorted to varied strategies: the qualitative approach elects content analysis techniques to deal with the information gathered, whereas the quantitative approach chooses a statistical treatment of the inquiries performed.

The scripts for the semi-structured interviews made to teachers and employers were basically outlined according to the literature review and to the specific object and goals defined for the research. It must be properly highlighted that during the qualitative collection of information, all the interviews transferred a role of informer, rather than that of respondent, on to the interviewees, as they were free to express facts and convictions in their own language (Lessard-Hébert, Goyette & Boutin, 1997). All interviews were recorded with the proper consent of the authors and their answers were studied with the QSR NUD\*IST software (*Non-numerical Unstructured Data Index Searching and Theorizing*). The questionnaires proposed to the students and graduates were conceived similarly to the interviews, as of the revised theoretical setting and the specific object and goals established. In each question, it was explored whether the PBL methodology of Business Simulation did or did not originate the changes in the students' personal competences. The answers were pre-oriented on a Likert scale with 5 points,

with a neutral possibility, and the respondent had to mark that which was closer to the way he/she perceives things. All questionnaires were prepared for an optical reading and the answers were examined following descriptive statistics. The software used was the SPSS (*Statistical Package for Social Sciences*).

While selecting the teachers, we choose to include all those who had at least four years of experience in the subject, admitting that punctual collaborations dispersed throughout several years would result in less limited perspectives on the methodological functioning of the curricular unit. 14 interviews were made. In order to confirm the diversification principles and in such a way as to ensure the most broad overview possible of the problems and situations which take place within the group of the employing entities, we choose to only retain entities with graduates from ISCA-UA who were carrying out duties related to the accounting area, but spread out in several departments. Such a choice returned five entities, which corresponded to thirty-two graduates (twenty-three of which had attended Business Simulation as opposed to nine who hadn't). In this study we also involved all the students enrolled in the subject when the empirical part of the project was developed, which meant a total of 138 students. The return rate achieved was of 96%. Given that it was quite relevant to streamline the questionnaires to all the graduates from ISCA-UA who had attended Business Simulation, the 881 graduates present in the process since its beginning were taken into account. In this group, the return rate was of 84%.

Finally, it is also very important to mention that the adoption of a PBL methodology within Business Simulation presented itself as a challenge accrued both for students and for teachers. In fact, with the total development of the curricular units of the accounting degree running according to traditional teaching methodologies (identified, as previously mentioned, as a uniform model for the transmission of knowledge in the univocal direction teacher to student), the methodological organization of the Business Simulation suddenly supervenes as a model which opposes to the traditional one. This factual situation rises, namely by students and teachers, an inevitable comparison between the methodological philosophies inherent to the two models. In terms of this study, the fact that students, graduates and teachers tend to compare their traditional methodological experiences with the PBL experience of the Business Simulation, presents itself as a unique opportunity which adds up to the research the possibility to understand every opinion reported on the empirical part, as considered under the light of the PBL methodology *versus* the traditional teaching methodologies.

#### 4. RESULTS AND DISCUSSION

As formerly referred, the sudden introduction of a PBL methodology in a course formatted according traditional teaching moulds, constitutes, *per se*, a fundamental element for the comparison of the learning experiences reported by students and by teachers of the institution. Methodologically and within the scope of this work, we resorted to the possibility to confront the two teaching methods (traditional and PBL) by the intervening elements (students, teachers and graduates) was a way to conceptualize the same study group and control group. So being, we argued that, although it is possible to introduce external variables in the analysis, such a fact allows for the reduction of the latter, as each analysis unit is built in a paired manner: before and after the use of a PBL model. Ergo, and as an aspect prior to the whole discussion, we assumed that each element (student, teacher and graduate) is his/her own control, with each group simultaneously becoming a test and a control group, where the samples gathered concern the records of the same element exposed to different aspects of the situation under study: traditional and PBL methodologies.

In this stage of our analysis, we tried to account for a set of perceptions expressed by the varied elements from the samples under study, who conceptualized the positions of students, teachers, graduates and employing entities regarding the features of the students and graduates' competences at a personal level. We included items relating to written and oral communication, critical analysis, time management, task planning, synthesis capability, creativity, setting of goals, decision reasoning, initiative capability, personal organization, dynamism and work methodology. With the dimension regarding the self-development abilities, we were able to circumscribe a set of assertions in on how the surveyed intervenients interpret the ways how the teaching-learning processes which use the PBL methodologies may eventually interfere in the structuring of the students and graduates' personal competences.

##### 4.1 The Students' Perspective

The information presented in Table 1 characterizes the set of answers collected by the inquiry presented to the students, thus allowing us to establish an approximate picture regarding the reflection they make on possible alterations of their personal competences due to the PBL methodology implemented in the Business Simulation.

Table 1. Characterization of the percentage results of the group of students

Degree of alteration or non-alteration of the personal competences at the level of	Tendency to decrease	Unaltered	Tendency to increase
written communication	5.3	31.1	63.6
oral communication	3.8	35.6	60.6
critical analysis	6.8	15.9	77.3
time management	12.1	7.6	80.3
task planning	7.6	12.1	80.3
synthesis capability	3.1	26.5	70.4
creativity	4.6	25.8	69.6
setting of goals	6.1	26.7	67.2
decision reasoning	4.6	20.6	74.8
initiative capability	4.5	21.4	74.1
personal organization	9.1	31.1	59.8
dynamism	2.3	23.1	74.6
work methodology	3.0	22.0	75.0

Focusing on the students' answers in positive positions regarding the question of the influence of learning in the development of their personal competences, some items seem to reveal a stronger convergence of positions. Therefore, at a first level of analysis, it is possible to find an accentuated positive influence of the methodologies implemented in two terms: that of the planning and organization (time management and task planning); and that of knowledge construction (critical analysis, synthesis capability, creativity, decision reasoning, initiative capability, dynamism and work methodology). At a second level of analysis, the empirical study points to the development, although slightly less accentuated, of competences referring to communication (oral and written), personal organization and setting of goals. Although the results need to be carefully processed, an hypothetical interpretation of the values gathered (especially for the first three items) may refer to the fact that the competences regarding communication and personal organization transit, in a more direct manner than the others, from the traditional learning methodologies previously used by students. In fact, the whole traditional path run by the student during his/her schooling process, had always, generally speaking, relied on written and (probably less, but also) oral communication. On the other hand, the personal organization, in turn, had always been a present element in the student's traditional schooling.

#### 4.2 The Teachers' Perspective

It was also of great interest for us to study, from the teachers' point of view, if the PBL methodology in Business Simulation did have any impact in the personal competences of the students. In this category, we included the following items: oral and written communication, critical analysis, synthesis capability, creativity, initiative capability, personal organization, dynamism, work methodology, reflection and self-esteem and self-confidence. By means of the detailed exhibition of the results gathered, we tried to understand how teachers perceive the effective possibility of changes at the level of the student's personal competences.

As far as the critical analysis is concerned, almost all the interviewees state that the methodology applied allows students to develop their critical reasoning in a constructive perspective. Another perspective referred by two teachers, presents us with the idea that the varied opinion presented by them is not a weak point, but rather an asset which is capable of adding analytical capability to the students' activity. Regarding the decision reasoning there are unanimous positions by the teachers: the PBL methodology enables them to develop, within the student, the ability to consolidate the resolutions he/she chooses to take. Also regarding personal organization aspects, the interviewees state that the methodology followed in the subject provides for mechanisms which go beyond life at school. Prolonging the aspect of personal organization, teachers refer to the urgency of a work methodology motivated by the PBL process, that forces students to have a constant and permanent flow of work. Based upon the answers intentions which were presented, it seemed to us beyond the shadow of a doubt, that there are, throughout the course of the subject, several moments which promote oral and written communication. Exactly as described in literature (e.g. Kirschner, Vilsteren, Hummel & Wigman, 1997) the interviewed teachers state that the methodology crates, in fact, synthesis mechanisms upon students, in such a way as to enable them to manipulate much information with which it is daily confronted. Within the self-development area, the interviewed teachers refer it is possible for students to collect, form the methodology, competences referring to creativity, initiative capability and dynamism. Such an active participation of the students in the construction of their learning processes is, equally, accompanied by a reflexive potential. In fact, teachers are unanimous when underlying the fact that the methodology is an important instrument for the process. In the perspective of one of the teachers, there is also an extra fact, which is the fact that Business Simulation provides the student with self-esteem and self-confidence competencies, capable of rendering him/her more apt to take on a Professional career. Particularly interesting to us seems to be the suggestion by the same teacher in the sense of assessing the number of graduates who choose to start off their career on their own. This choice referred by the teachers seems to understand the methodology as a dynamic process capable of encouraging business opportunities among associates.

#### 4.3 The Graduates' Perspective

The statistical analysis performed on the matter of the data collected by this group, aim at analysing the perspective of those as far as the alteration degree of their personal competences is concerned, my means of the methodology followed in the subject. The data presented on table 2, characterizes the set of answers collected.

Table 2. Characterization of the percentage results of the group of graduates

Degree of alteration or non-alteration of the personal competences at the level of	Tendency to decrease	Unaltered	Tendency to increase
written communication	2.4	46.0	51.6
oral communication	1.2	36.7	62.1
critical analysis	1.4	18.8	79.8
time management	3.1	14.7	82.2
task planning	2.6	14.0	83.4
synthesis capability	2.4	32.5	65.1
creativity	2.1	34.5	63.4
setting of goals	1.7	22.4	75.9
decision reasoning	1.9	19.1	79.0
initiative capability	2.1	25.4	72.5
personal organization	1.4	33.4	65.2
dynamism	1.7	30.6	67.7
work methodology	1.6	20.6	77.8

The analysis of the set of items which comprise the personal competences block allows us to, broadly, underline the positive tendency evidenced by the graduates on the possibility to register alterations, caused by the PBL methodology followed in the Business Simulation. The statistical treatment described, besides allowing the identification of some more relevant themes in terms of the results gathered, does also induce hypothetical interpretations in terms of the configuration of the subjects'

answers. Despite certain optimism, it soon becomes quite obvious that there are different valorisations of the items under study, somehow allowing the creation of a hierarchy of two distinctive answer profiles. The analysis of the table allows the verification of a markedly positive profile, which comprises critical analysis, time management, task planning, setting of goals, decision reasoning, initiative capability and work methodology. However, there is also another shade in the opinions of the graduates. According to this second profile, it is possible to detect more moderate positions which, surely, continue to express the perception that there is a positive trend which promotes oral and written communication, synthesis capability, creativity, personal organization and dynamism. One must particularly highlight the graduates' judgement, as far as the written communication item is concerned, where opinions are divided between a neutral assessment and weak positive evaluation.

#### 4.4 The Employers' Perspective

With the interviews made to the employers we intend to perspective a set of questions referring to the personal competences of the graduates. In order to better circumscribe changes at this level, we now describe the results extracted from the meaning units associated to the items approached by entities, being that they only referred the items decision reasoning, personal organization, self-esteem and self-confidence.

According to all the employers interviewed, the Business Simulation enables graduates to develop their ability to reason decisions, limited not only by theoretical concepts, but also by practical aspects which have already been experienced. Upon such a basis, the graduates who attended the curricular unit of Business Simulation present themselves, this way, more valued and professionally acknowledged, while achieving certain levels of the profession, when compared to other colleagues who choose not to attend the subject. When observing the sense of the answers, generally speaking, employers do not acknowledge personal organization as a competence which benefits from the attendance of the Business Simulation subject. As far as self-esteem and self-confidence are concerned, only one of the employers approached the subject, assuring that the experience acquired during the Business Simulation subject, while granting them with more preparation, renders graduates more confident and secure of their actions. The very same employing entity meets the opinions presented by some teachers, referring that attending the subject is an asset in terms of ability to assume a positive attitude. An element worthy of mentioning has to do with the fact that all employers who were interviewed were aware of the existence of the subject of Business Simulation at ISCA-UA, a fact which seems to reveal the attentions schools who train graduates within the scope of companies' needs deserve.

### 5. CONCLUSIONS

This work investigates the expression modes of the use of PBL methodologies at the level of personal competences by students and graduates at a higher education level. It is not our intention to generalize results. In fact, the data we processed does not allow for it. Nevertheless, based upon the indicators we examined it is, already, possible to conclude that the teaching-learning methodologies grounded on PBL models, validate some conceptual propositions of the already existing theoretical production on this theme. Still, there are others which do not seem to be corroborated by the practical results collected. Based upon some reflections we have been establishing, it is possible to ponder new perspectives, capable of contributing for the activation of a debate around the dynamics of self-development competences, associated to the use of PBL methodologies. Hence, despite the fact that, theoretically, the research reveals methodologies under study tend to affect the students' personal profile, it is not clearly evident how such alterations are perceived by the various agents involved in the educational process (students, teachers, graduates and employers). Such as it was observed, we identified two trends in the perceptions evidenced by the interviewees and the respondents.

On the one hand, the results collected with the group which comprised students, graduates and teachers leads us to sustain that the methodologies under study contribute to the development of personal competences, mainly at the level of resources' usage (management, planning and work methodology) and knowledge construction (critical analysis, decision reasoning and initiative capability). Such specificities are eventually identified with the characteristics of the profile of the graduate who used a PBL methodology on his training process, as Albanese (1993) and Kolmos (1996) refer. Another conclusion of the study is the fact that the communication skills (oral and written) appear far less valued, when compared to the remaining items for self-development. One may perhaps find a justification in the fact that traditional methodologies already explore these aspects. Another possible perspective refers to the circumstance that teachers may not present uniform solutions, which, likewise, encourages debate among the students. In this sense, it seems that the discussion of ideas which often occurs bears an underlying methodology which significantly increases the argumentative power of students, though they appear to develop more comfortable attitudes in more traditional environments. One must also underline that teachers have been questioning the choice on the possibility to establish a professional career on their own (entrepreneurship). To some extent, this aspect acknowledges that methodologies have the ability to foster self-esteem, and self-confidence in students, also being able to, together with several other factors, contribute for the assumption of the idea to create companies in the field. As literature does not approach this matter, it seems possible to us to sustain the possibility of inserting the entrepreneurship logic, motivated by the new methodologies under study in this work, in the existing theories.

On the other hand, the perception manifested by the group of employing entities seems, however, not to acknowledge, at least not so noticeably, the impact of those methodologies at the level of the trainees' personal development. Following a certain path, we find a tone of speech which values methodology as a potentiating force for more consistent groundings, enhanced by the practical experiences the students have already gathered. The same positive tone is evidenced in the items referring to attitudes of a more confident posture and greater security. It is, however, possible to find a persistent tendency for employers not to acknowledge PBL methodology as responsible, at least not directly, for the improvement of the graduates' personal competences. These facts lead us to conclude that the methodological models which sustain alterations in the students at a personal level are rather simplistic rendering it, in our opinion, unreasonable to generalize this problem, at least as far as employers are concerned.

The results achieved with the analysis of the data collected also require some lateral reflections. A possible consideration has to do with the understanding of a strategy which potentially favours the development of personal competences, but which does not have the same effect on every student or context. Another pertinent reflection: if, as the European Centre for the Development of Vocational Training refers, the forecasts for employability for Europe in 2020 point at eighty million jobs, the bottom question which arises is the need to understand what kind of competences will be necessary to fulfil these vacant jobs, according to the employers' needs. On this page, a potential uneasiness refers to the need to know how we may be able to assure the early identification of competences which will secure the needs of a multifaceted market.

Simultaneously, we reflected on the need to open the worlds of education and training, namely at a higher level, making them more reactive to the needs of learners and employers, by means of the development of relevant competences, centred on tangible studies and results. Nonetheless, and according to the HEIs role while cultural diffuser, it is important to carefully analyse the equilibrium aspect between theoretical conceptualization and its practical applicability. We are, therefore, before the pressure of a flexibility exercise at the level of competence management, not only professionally, but, more intensely, at a non-cognitive level and, particularly, at a personal one. This because modernizing in order to meet new challenges places a considerable pressure on the current education and training systems, especially in developing countries.

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# ELECTRIC-ARC FURNACE SLAG UTILIZATION in HOT MIX ASPHALT

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## ABSTRACT

In the meantime, as natural supplies of high quality granular materials used in highways have become less abundant, the highway engineer is faced with the challenge of finding alternative materials to meet the requirements for these materials. Both environmental and economic factors also contribute to the growing need for the use of reclaimed materials in asphalt pavements. One of these reclaimed materials, electric-arc furnace slag (ferrochromium slag), has not been used extensively in pavements even though it has got promising features. In this study, ferrochromium slag has been obtained from an electrometallurgy establishment in Turkey. Various percentages of binder, limestone filler and slag filler were used to prepare specimens; then stability and flow tests and creep test were carried out on the specimens. In addition, particle size analysis, specific gravity, SEM observation, chemical analysis was performed on the materials prior to performance tests. Consequently, laboratory test results showed that asphalt mixtures containing ferrochromium slag are as good as or better than those of limestone aggregate.

**Keywords:** Electric-Arc Furnace Slag, Mixture Design, Permanent Deformation, Mineral Filler.

## 1. INTRODUCTION

The main flexible pavement material is use in today is asphalt concrete. This is a high-quality pavement surface composed of asphalt cement and aggregates, hot-mixed in an asphalt plant and then hot-lid. Asphalt concrete must provide a stable, safe and durable road surface. The properties of asphalt concrete depend on the quality of its components, binder, aggregates and filler, and the mix design proportions. Relative amounts of aggregate, binder and air void are very important [1].

In the meantime, as natural supplies of high quality granular materials used in highways have become less abundant, the highway engineer is faced with the challenge of finding alternative materials to meet the requirements for these materials. Some of these alternative materials are hydrated lime, Portland cement, marble dust [3], fly ash [4], coal dust [5], pumice dust [6], sewage sludge ash [7], steel slag [8] etc. Both environmental and economic factors also contribute to the growing need for the use of reclaimed materials in asphalt pavements. One of these reclaimed materials, ferrochromium slag, has not been used extensively in pavements even though it has got promising features.

A certain amount of filler is necessary in bituminous mixtures to obtain the required density and strength. The filler particles fill a portion of the space between sand and gravel particles, and thus contribute to increase density. The filler also influence the optimum binder content in bituminous mixtures by increasing the surface area of mineral particles. Several studies; Puzinauskas [2], Anderson et al. [9], Kandhal et al. [10], Shahrour and Saloukeh [11], Ishai et al. [12], Ishai and Craus [13], Tayebali et al. [14], Hussain Bahia [15] conclude that fillers largely influence the asphalt mixture performance. Different filler materials may have different mechanical properties in the asphalt mixture. Dukatz and Anderson [16] have investigated eight different filler materials to investigate the mechanical properties of asphalt and they found that different filler materials have different effects on stiffness and had almost no effect Marshall stability and void ratio.

In this study, various percentages of asphalt cement, limestone filler and FeCr slag filler were used to prepare the Marshall specimens and then stability and flow tests and creep test were carried out on the specimens. After getting design parameters, utilization of slag filler in asphalt mixtures was investigated in comparison with limestone filler.

## 2. MATERIALS

### 2.1. Properties of Mineral Filler

Mineral filler is usually defined as a material which passes No.30 (0,600 mm) standard sieve. Moreover; at least 70 percent of this material passes No.200 (0,075 mm) standard sieve [18]. Mineral filler plays an important role in arranging the properties of the mixture; however, it covers a very little part of all aggregate. Filler is generally used at low rates such as 3% – 9%. This component change the aggregate gradation by filling air voids until a certain amount and this provides more touch points between aggregate particles and this contributing to obtain denser mixtures [19]. This situation is particularly important for surface layers, because increased composite and increased density gets good impermeability.

The function of mineral filler is more than filling voids. In addition, filler shows binder and slippery effects in the bituminous mixtures and helps to get mortar, this dual role differs mineral filler from other aggregates.

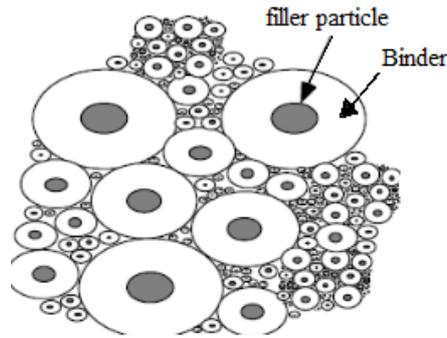


Figure 1 : Fillers’ interaction with bitumen

2.2. Properties of Slag Filler (FeCr slag)

Ferrochromium slag dust is used as artificial filler in this study. Slag was obtained from ETİ Electrometallurgy Establishment (ETİ E.E.) which is founded in Antalya-Turkey. Every day, approximately 70-80 tons of Ferrochromium slag (FeCr slag) are produced in ETİ E.E. and disposal of the waste slag constitutes a problem. Chemical analysis of FeCr Slag is shown in Table 1.

Table 1 : Chemical Properties of Electric-arc Furnace Slag (Ferrochromium slag)

Element	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	S	C
Percentage	0.52	31.18	1.02	8.66	45.58	12.78	0.08	0.11

During the Ferrochromium and Silico-ferrochromium production process in the electric-arc furnaces, unreduced oxides and some SiO<sub>2</sub> form a liquid slag layer on the pots. Slag is poured into the slag molds and let to cool in open air. Air cooled FeCr slag is gradually transformed into powder form and it gains a crystal structure because of slow cooling process.

Only the minus No.200 sieve (0,075 mm) fraction of FeCr slag was evaluated in this study. Scanning electron microscopy (SEM) was used to observe the microstructure of slag filler particles (Figure 2). The SEM micrographs were obtained from Akdeniz University, Antalya/Turkey. The micrograph shows that the slag filler particles have rough and sharp surface with crystal structure. This phenomenon may cause the higher friction inside the samples.

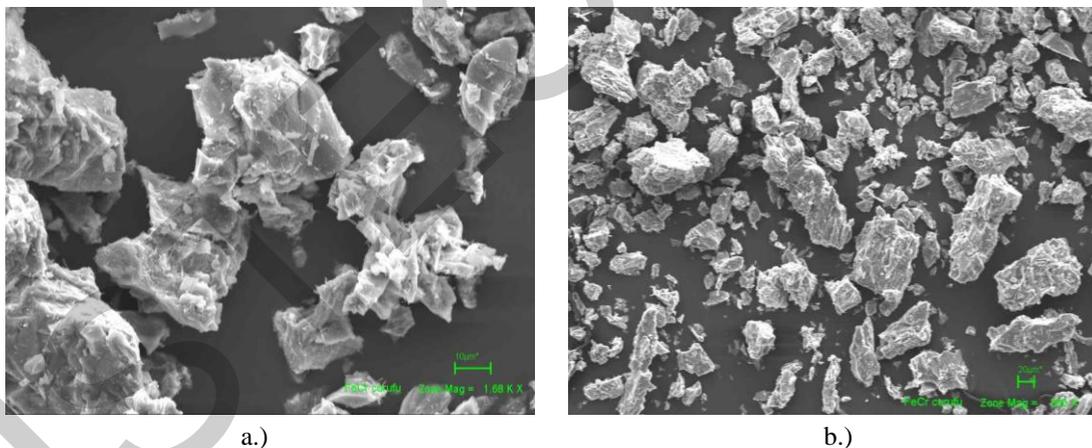


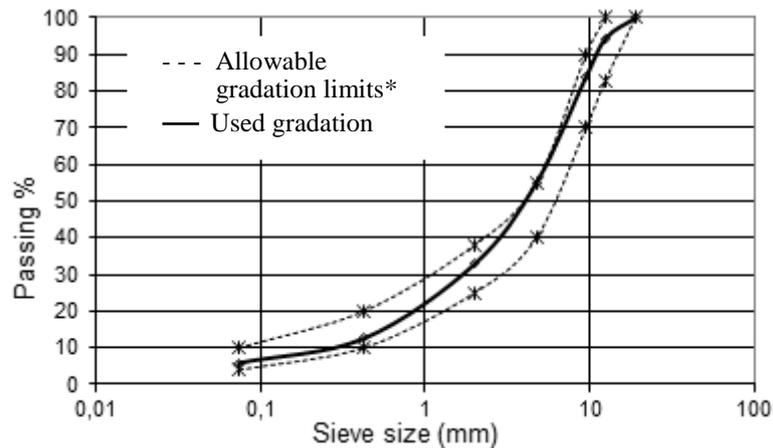
Figure 2 : SEM images of FeCr slag (a- 1680x , b- 365x magnified)

2.3. Mineral Aggregate

Crushed aggregate of Antalya region was used in this study, aggregate gradation shown in Figure 3. Physical properties of aggregate and filler are shown in Table 2.

2.4. Asphalt Cement

50-70 penetration grade asphalt cement is selected. Determined properties of asphalt cement are shown in Table.3.



**Figure 3 : Aggregate gradations** (\* Turkish Highway Administration’s suggested gradation limits for hot climate regions)

**Table 2 : Physical Properties of Aggregate and Filler**

Properties	Value	Limits	Standard
Specific gravity of course aggregate	2,70 gr/cm <sup>3</sup>	-	TS-EN 1097-6
Course aggregate, water absorption	0,37 %	Max 2,0	TS-EN 1097-6
Specific gravity of fine aggregate	2,65 gr/cm <sup>3</sup>	-	TS-EN 1097-6
Los Angeles abrasion loss of aggregate	20,2 %	Max 30%	TS EN 1097-2
Freeze thaw test with Na <sub>2</sub> SO <sub>4</sub>	4,3 %	Max 12%	TS-EN 1367-2
Aggregate stripping resistance	72 %	Min 50%	ASTM D 1664
Limestone filler bulk specific gravity	2,69 gr/cm <sup>3</sup>	-	ASTM D 854
FeCr slag filler bulk specific gravity	3,16 gr/cm <sup>3</sup>	-	ASTM D 854

**Table 3 : Properties of Asphalt Cement [21]**

Properties	Unit	Value	Related Standard
Penetration, 25°C, 100 g, 5 sec	1/10 mm	62	TS EN 1426
Ductility, 25 °C, 5 cm/min.	cm	100+	TS EN 13398
Softening point (ring and ball method)	°C	50,1	TS EN 1427
Flash point (Cleveland open pot)	°C	339	TS EN ISO 2592
Specific gravity	gr/cm <sup>3</sup>	1,023	TS 1087

\*TS: Turkish Standards

### 3. PERFORMANCE OF ASPHALT MIXTURE

Diameter of 101.7 mm and a height of 63.5 mm Marshall specimens were prepared with various asphalt contents to determine the optimum bitumen content for each filler type. 7 different asphalt content at 0,5% increments (3,5% - 4,0% - 4,5% - 5% - 5,5% - 6% - 6,5%) and two filler materials (slag filler and limestone filler) were used for specimens.

The initial filler content was 7%. Marshall mixture design method, described in ASTM D.1559 was applied in the study. Stability and flow test were carried out on these specimens. The specimens were also tested for density and voids analysis. According to Marshall design method optimum bitumen contents were determined for each filler type. Average of the two optimum bitumen contents determined as optimum bitumen content (5,1%).

Marshall specimens were prepared with 75 standard compaction blow for each side, considering heavy traffic level. This is better simulates the required density for pavement construction. Mixing and compaction temperatures were controlled to produce viscosities of 170±20 cst and 280±30 cst, respectively [22]. Three specimens were manufactured for each combination.

In further tests, defined optimum bitumen content (5,1%) and various filler contents (2,5% - 5% - 7% - 10%) were used to prepare specimens. Aggregate gradations used for new specimens are shown in Table 5. When the filler content was increased from 0 to 10 percent, in order to accommodate the increased quantity of filler, an equal volume of fine aggregate (minus No.10) was removed and replaced by an equal volume of filler. Specimens were than tested for stability and flow,

permanent deformation, air void content, density, voids filled with bitumen, voids in mineral aggregate. Test results are shown in Figures 4 to 9.

**Table 4 : Hot Mix Asphalt Design Specifications (KGM\* 2006)**

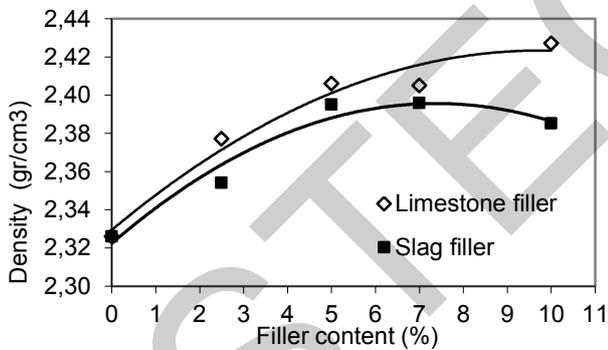
Specification	Binder Course		Friction Course	
	Min	Max	Min	Max
Std. Impact Number	75		75	
Stability, KN	7.5	-	9.0	-
Air voids in mixture, VTM %	4	6	3	5
Voids in Aggregate, VMA %	13	-	14	-
Flow, 1/100 in (mm)	8 (2)	16 (4)	8 (2)	16 (4)
Bitumen %	3.5	6.5	4	7
HMA Density*	2.30 – 2.50			

\*Turkish Highway Administration Office

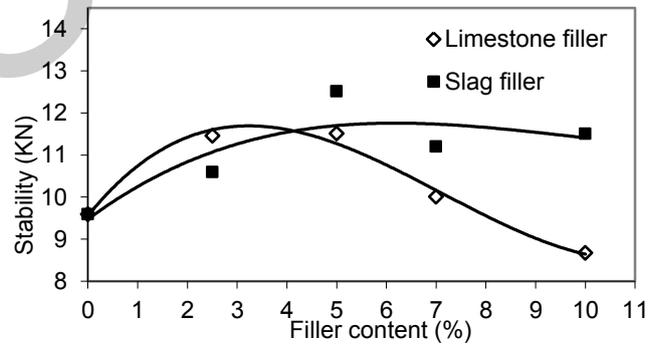
Minimum stability criteria suggested by Asphalt Institute for heavy traffic condition is 8006 N [23].

**Table 5 : Gradations for Mixtures Containing Various Filler Percentages**

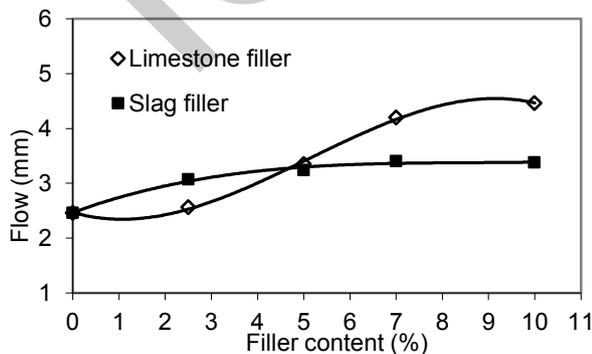
Filler content (%)	0	2,5	5.0	7.0	10
Sieve Grade	Total Percentage Passing				
¾"	100	100	100	100	100
½"	91,5	91,5	91,5	91,5	91,5
3/8"	80	80	80	80	80
No.4	47,5	47,5	47,5	47,5	47,5
No.10	30	30,5	31	31,5	32
No.40	12	13	14	15	16
No.200	0	2,5	5	7	10



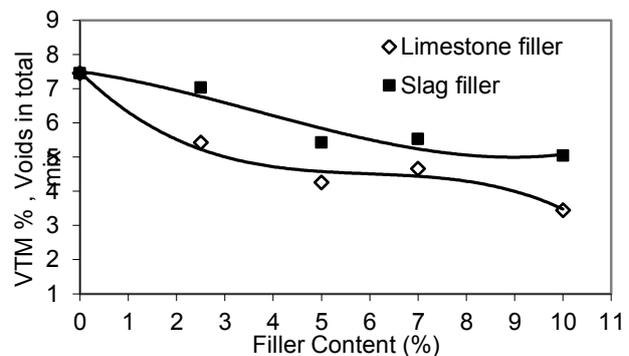
**Figure 4 : Filler content versus specimen density**



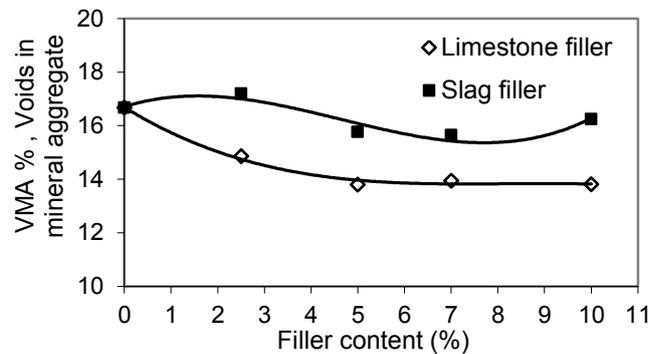
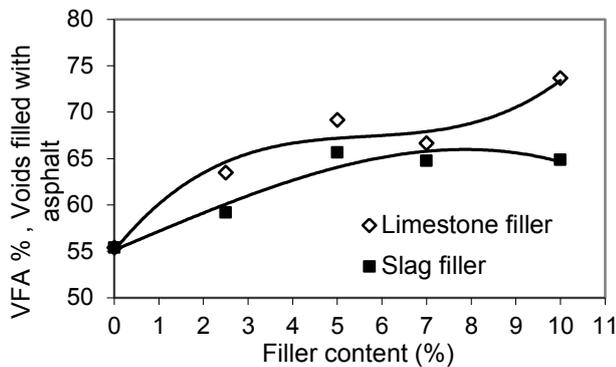
**Figure 5 : Filler content versus Stability**



**Figure 6 : Filler content versus Marshall flow**



**Figure 7 : Filler content versus Voids in total mixture**



**Figure 8 : Filler content versus Voids filled with asphalt** (Suggested VFA criteria by KGM, min: %65 – max: %75) **Figure 9 : Filler content versus Voids in mineral aggregate**

Test results analyzed according to design parameters of hot mix asphalt and filler materials evaluated comparatively for use in asphalt pavements. With increasing of filler percentages, the densities of specimens were increased as expected (Figure.4). Densities of samples made with FeCr slag showed similarity to limestone filler.

Stability and flow results of the specimens produced with FeCr slag filler showed better performance than limestone filler. Especially at the higher filler percentages (7%, 10%), the significant improvement was observed with FeCr slag filler. Specimens made with slag filler showed 15% improved stability in comparison with control specimens.

According to flow results, specimens with FeCr slag showed quite satisfactory values which doesn't go over criteria limits of 4 mm, also at 10% filler (the highest flow result was only 2,4 mm). On the other hand, flow result of the limestone filler were went up to max limit of flow at 7% and 10%percent. This situation can be explained by microstructure and surface properties of filler materials. The filler particles were observed by SEM as shown in Figure.2. The micrograph shows that the slag filler particles have rough and sharp surface with crystal structure. This phenomenon can be the possible reason of FeCr slag's lower flow and higher stability results. Mainly flow value of specimens could be assessing as a major indicator of inner friction. Hence, the increment of inner friction due to crystal structure and sharp surfaces of specimens are expected.

Specimens with slag filler showed higher VTM (voids in total mix) values compared to limestone filler (see Figure.7). However this is cannot asses as a preferred situation, until a certain amount of air void increment, it plays a preventive role to bleeding of asphalt pavements, particularly in hot climate regions bleeding is a key factor of proper pavement design.

McLeod [24] developed the volumetric criteria for the specimens compacted with a Marshall hammer with 75 blows on each side of the specimen. Since, McLeod recommended that the VMA, which is the volume of voids between the aggregate particles, should be restricted to a minimum value of 15%; also KGM recommends the minimum VMA value of 14%. Mainly, VMA value varies with air voids and aggregate size. Specimens with slag filler show higher VMA values than limestone filler specimens (see Fig.9). Test results range between 15.6 – 17.2 for slag filler and 13.8 – 16.6 for limestone filler.

### 3.1. Dynamic Creep Test

The Dynamic creep test is a test that applies a repeated pulsed uniaxial stress on an asphalt specimen and measures the deformations in the same direction using Linear Variable Differential Transducers (LVDT's) [25]. The samples were prepared for dynamic creep test with different FeCr filler ratios and optimum bitumen content (5.1%). Three samples (101 mm diameter and 63.5 mm height) from each mix were tested and the average values of the accumulated (permanent) deformations were recorded [26].

After sample preparation, the samples have been kept overnight in room conditions then those have been put into the cabinet in which temperature is controlled and conditioned to the test temperature. The permanent deformation tests have been carried out at 40 °C. The samples are preconditioned to the testing temperature overnight. The samples were mounted into the testing frame for dynamic creep test. 5000 cycles of 100 kPa axial stresses was applied on each sample. At the beginning, 100 cycles of 100 kPa axial stress was applied on each sample for conditioning. Five different types of samples which contain FeCr slag filler were prepared. Figure.10 shows the relationship between the number of cycles and the axial accumulated permanent deformation for the tested groups.

Control mixture (0% FeCr filler) has maximum permanent deformation about 240 microns at the end of test. For the mixes containing FeCr slag at different filler ratio, the plastic deformations decrease until 7% FeCr content, after that plastic deformation increase (Fig.10). Therefore it can be concluded that up to a certain value of the FeCr filler content in the sample plastic deformations decrease, after that it is increases. The reason behind is that certain amount of filler, fills the void inside the samples and increases the stability, but after a certain value, the filler material avoids the bounding between the grains and the asphalt.

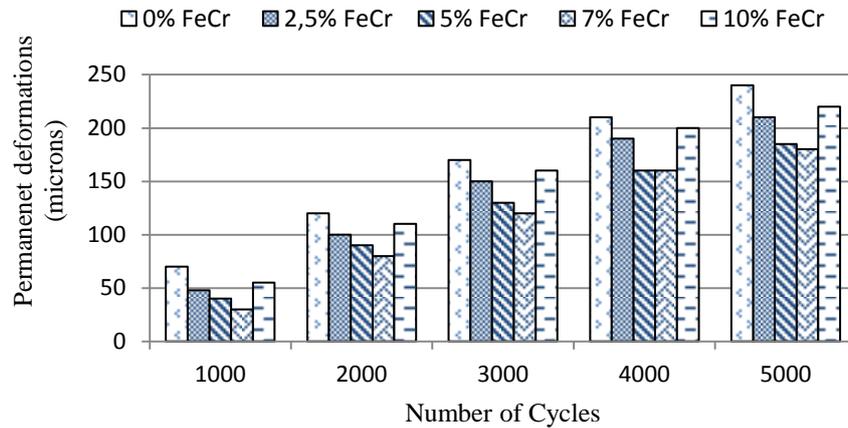


Figure 10 : Relationship between axial accumulated permanent deformation and loading cycles

#### 4. CONCLUSIONS

This investigation was mainly undertaken to evaluate the FeCr slag performance of asphalt concrete mixes having different percentages of slag filler and find the optimum replacement percentage of the limestone filler by the slag. To fulfill this objective, laboratory evaluation of asphalt concrete mixes with different combinations of FeCr slag filler and limestone filler were conducted. Stability and flow properties, density and voids analysis of Marshall specimens were studied, including different types and various percentages of fillers. Marshall mix design procedures and suggested criterions of Asphalt Institute and KGM were taken into account.

The test results showed that the use of FeCr slag as filler material in asphalt mixtures instead of limestone filler may be promising to obtain a material suitable for engineering purposes. It's recommended to use slag filler in current hot mix asphalt up to 7% where they are abundant. After 7% slag content, HMA density slightly decrease and plastic deformation of samples increases. Therefore it can be concluded that up to a certain value of the FeCr filler in the sample, fills the voids inside the sample and increases the stability, but after a certain value, the filler material avoids the bounding between the grains and the asphalt.

Consequently, electrometallurgy establishments generally don't expect an income from slag waste. They are looking for the utilization of slags which occupy large areas in factories. In fact, with the assistance of elements mentioned above, using FeCr slag as filler material in road pavements would provide economic and environmental benefits compared to conventional filler materials.

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# ELECTRODEPOSITION OF COPPER (Cu) ON INDIUM AND TITANIUM OXYDE (ITO)

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## ABSTRACT

The deposition of metal films on foreign substrates (metal or semiconductor) plays an important role in many modern technologies, and is used widely in various applications such as microelectronics, high density magnetic recording, MEMS sensors and energy conversion devices [1]. The development of thin films having a precise and controlled microstructure, a crystal orientation, and properties at low scale are required. The aim of this work is to analyze the mechanisms of electrodeposition of metals on a semiconductor surface such as ITO. Indeed, the study of nucleation and the properties of nanostructures of copper electrodeposited on an ITO surface by the electrochemical method contribute to the understanding of the mechanisms of electrodeposition of magnetic nanostructures on such surfaces. In this work several characterization techniques have been used: cyclic voltammetry (CV), coulometry, chronoamperometry (CA), and atomic force microscopy (AFM).

**Key words :** Electrodeposition, Copper, Indium titanium oxide (ITO), Voltammetry, AFM

## INTRODUCTION

The deposition of metal films on foreign substrates (metal or semiconductor) [2] plays an important role in many modern technologies, and is used widely in various applications such as microelectronics, and conversion devices energy [3]. Also the development of thin films with controlled microstructure and precise crystal orientation, and scales very small properties are required.

The interest of this work was focused on studying mechanisms of electrodeposition of metals on a semiconductor surface such as ITO. The study of nucleation and properties of electrodeposited copper nanostructures on a surface of ITO by electrochemical methods gives the contribution to the understanding of the mechanisms of electro-magnetic nanostructures on the surface.

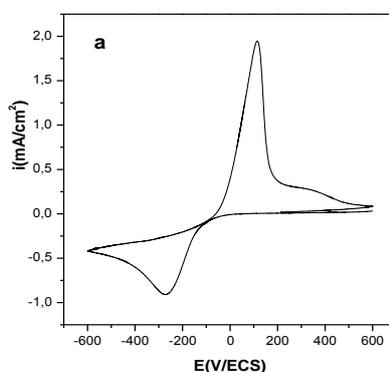
## 2.EXPERIMENTAL

The substrates used as working electrode is an ITO (indium tin oxide), an area well determine  $0.32\text{cm}^2$ , this electrode is cleaned with acetone and ethanol, respectively, for 10 minutes and then wash thoroughly with water distilled. Finally, the activation in a solution of hydrochloric acid (1M) for one minute. The electrodeposition was carried out in a Pyrex glass cell and a double wall with a capacity of 75 ml with three electrodes. The counter electrode was a platinum wire and the reference electrode is a saturated calomel electrode (SCE) potassium chloride (KCl). The standard potential of the reference electrode relative to the standard hydrogen electrode temperature  $25^{\circ}\text{C}$  is equal to  $+0.24\text{V}$ . The copper layers are obtained in a solution containing  $0.008\text{M CuSO}_4 + 0.5\text{M Na}_2\text{SO}_4 / \text{H}_2\text{O}$  at pH 5.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical study of copper on ITO by cyclic voltammetry

Figure (1 a) shows a cyclic voltammogram corresponding to the electrodeposition of a copper layer obtained on an ITO plate.



**Figure 1:** Electrodeposition of Cu / ITO ( $S = 0.32\text{cm}^2$ ) between  $-0.6$  to  $0.6\text{V/ECS}$  with  $v: 0.05\text{V/s}$

The curve obtained is characterized by the presence of a cathodic peak around  $-0.27\text{ V / SCE}$ , attributed to the reduction of copper cations in copper metal.

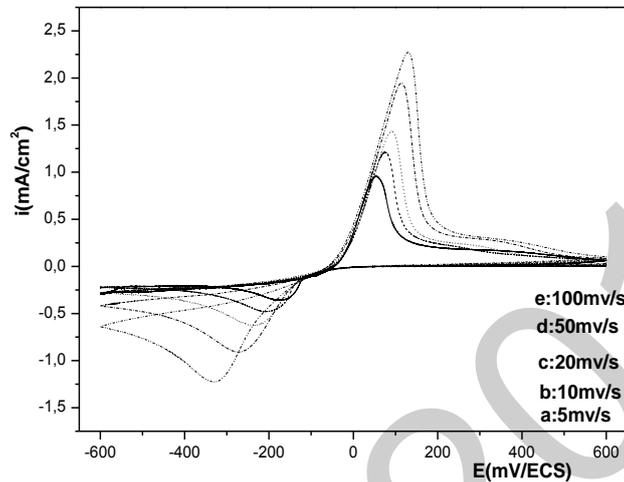


Back to scan an oxidation peak is observed at  $0.1\text{V/ECS}$ , corresponding to the redissolution of the deposited copper.

### 3.2. Kinetic study of copper deposits on ITO

#### \* Influence of scan rate

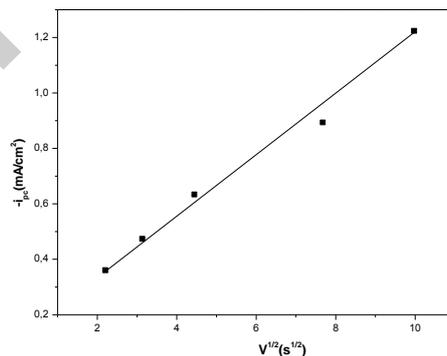
To see the influence of scan rate on the electrochemical behavior of copper, we carried out a study on several voltammetric scan rates: 5, 10, 20, 50 and 100  $\text{mV / s}$ , Fig. (2) [4].



**Figure 2:** Electrodeposition of Cu / ITO at different scan rates a) 5; b) 10; c) 20; d) 50; e) 100  $\text{mV / s}$ .

All the curves shown in this figure are characterized by peaks of copper reduction. These peaks appear at a potential of about  $-0.32\text{ V / SCE}$  for high speed scanning. A shift in the peak potential is observed when the change in scanning speeds. This behavior makes us believe that at low sweep speeds can be achieved with a stable course voltammograms copper deposit uniform and almost uniform over the entire surface of ITO electrode studied.

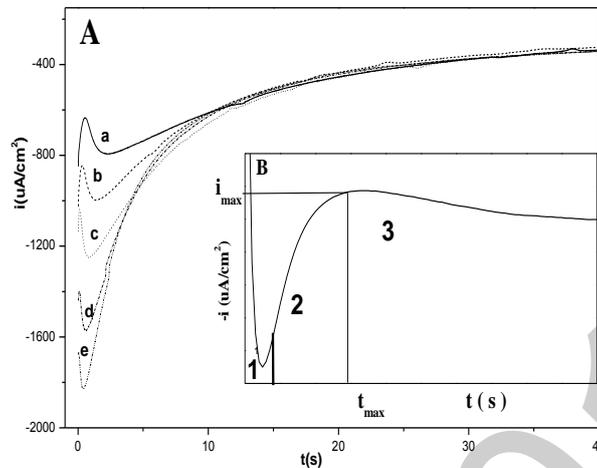
Analysis of the cathodic peak currents as a function of the square root of the scan speed figure (3), gives a straight curve implying that the process of dissolution of copper is controlled by diffusion.



**Figure 3:** Variation of peak currents as a function the square root of scan rate

### 3.3. Electrochemical study of Cooper on ITO by chronoamperometry

The previous study conducted cyclic voltammetry allowed us to choose the applicable differential to the electrode potential for the development of ITO copper layers desired. The terms of deposits are set at 60s and the current response time is recorded in Fig 4.



**Figure (4):** transition current after the application of several potential A: a) -225 b) -250 c) -275 d) -300, e) -325 mV / SCE on an ITO electrode with a theoretical model B

We note that the plots obtained with the same shape can be divided into three time intervals: In the first interval (1, B), the current increases sharply before falling. This current corresponds to the load of the double layer. In the second interval (2, B), an increase in current is observed. This increase is due to the growth of independent nuclei which is added the development of new nuclei.

The third interval (3, B) results in a decrease in current are observed which explains the growth of the film formed is governed by a diffusional regime. This behavior is described by Cottrell's law. The decrease in current is probably due to a decrease in the concentration of electroactive species on the surface of the electrode.. The decrease in current is probably due to a decrease in the concentration of electroactive species on the surface of the electrode.

#### \* Study of nucleation and growth through the use of current transients

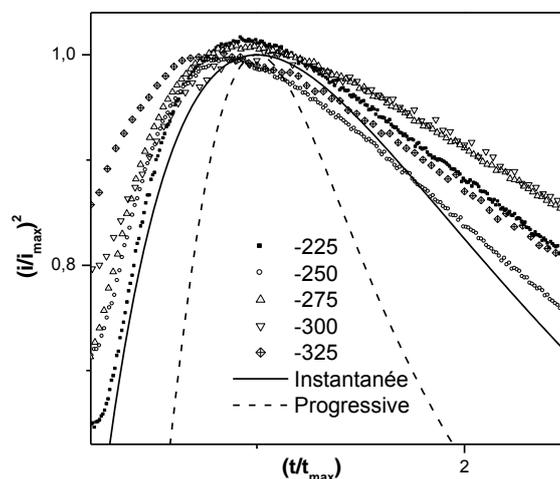
The study of the evolution of the current function of time after application of different potentials provides access to information of nucleation and growth of a film in a liquid underworld. This part is devoted to the processes of nucleation during electrodeposition of copper on a semi-conductive substrate by the use of theoretical models of Scharifker Hills [5, 6]. These authors have shown that it is possible to determine the type of nucleation involved in an electrodeposition of metals deferens through chronoamperometric curves, in the case of a three-dimensional nucleation model. The theoretical relationship between the current and the time for 3D nucleation is given by the following equations: In the case of an instantaneous nucleation (I):

$$\text{I: } (i/i_{\max})^2 = (1.9542) (1/x) [1 - \exp(-1.2564x)]^2$$

And progressive nucleation (II):

$$\text{so : } x = t/t_{\max} \quad \text{II: } (i/i_{\max})^2 = (1.2254) (1/x) [1 - \exp(-2.3367x^2)]^2$$

According to the equations I and II, the experimental points, normalized to  $I_{\max}$  and  $t_{\max}$  are shown in Figures 5, and compared to standard models of a three-dimensional nucleation.



**Figure 5:** 3D nucleation curves  $(i / i_{\max})^2 = f(t / t_{\max})$  obtained from the chronoamperometric curves performed on ITO substrate at different potentials.

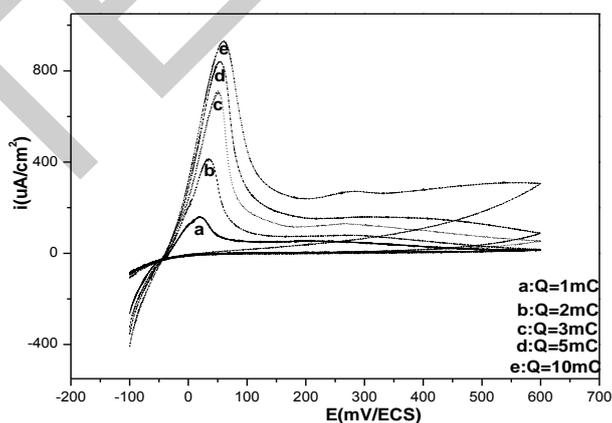
These curves are obtained from Figure 4 by previous normalization of two variables  $t$  and  $i$  to the maximum current  $i_{\max}$  and the time  $t_{\max}$ . By comparing the experimental curves with theoretical curves, a single nucleation mechanism of copper electrodeposition on ITO surfaces was observed, it corresponds to the instantaneous nucleation process.

This is in perfect agreement with the work of the literature [7]. It is important to note that the atoms are incorporated at the nucleation sites previously without creating new nucleation centers and germination occurs regardless of the time.

### 3.4. Electrochemical study of Cu / ITO by coulometry

#### \* Effect of the amount of electricity consumed on the behavior electrochemical Cu

Figure 6 shows the cyclic voltammograms for the deposition of copper, after the passage of the following charges: 1 mC (a), 2 mC (b), 3 mC (c) 5 mC (d) and 10 mC (e). The analysis of the deposited layer is formed in a solution containing no copper.

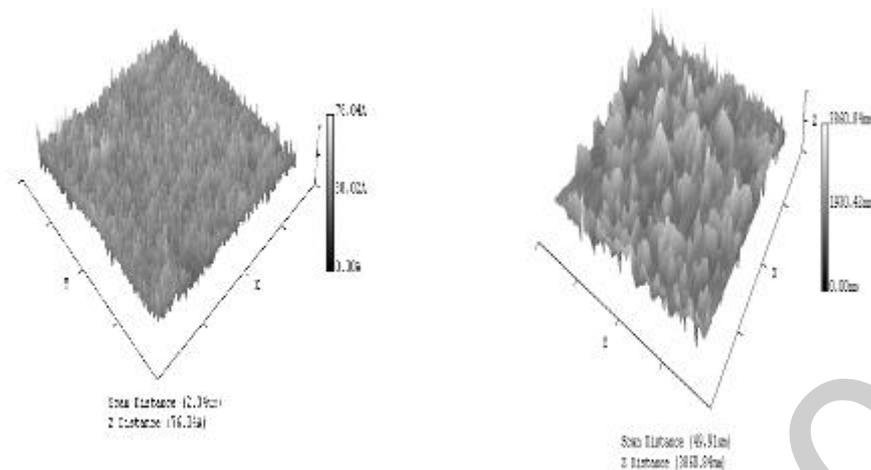


**Figure 6:** Curves of anodic dissolution of copper deposited at  $-250\text{mV}$  on ITO in  $0.008\text{M CuSO}_4$ , at  $v = 20\text{mV s}^{-1}$  after passage of the charge  $Q$ : (a) 1 mc, (b) 2mc, (c) 3mc, (d) 5mc, (e) 10 mc

To determine the amount of copper deposited on the electrode used, we performed the direct reduction of metal several potential imposed followed by a forced dissolution by cyclic voltammetry. It is found that the peak intensity of oxidation of copper increases with increasing charge ( $Q$ ) passed.

### 3.5 Morphological characterization by AFM

Figure (7,A) shows a topographic AFM 3D image of bare ITO and figure (7,B) shows an image of electrodeposited copper in 3D on the same substrate. The analysis of this image gives an RMS value of 279 nm for the copper layer deposited. The deposition of copper is with germs three-dimensional (3D), because of the weak interaction energy between the surface and the semi-conductive metal deposited.



**Figure 7:** Images obtained by AFM of electrodeposited copper by cyclic voltammétry  $v = 10\text{v/s}$  on ITO

It seems that the ITO surface is completely covered by copper and distribution of grains is homogeneous. This is in agreement with the instantaneous nucleation mechanism observed previously. The seeds of nucleation of copper are incorporated into pre-nucleation sites on the surface used. The deposition of Cu / ITO has a high particle density and a more homogeneous distribution of germs.

### 4. Conclusion

This study confirms the possibility of obtaining metal deposition of copper on a semiconductor substrate in a solution of sulfate electrolyte at pH 5. Electrochemical methods show that the reaction of copper electroplating is controlled by the diffusion of electrochemical species. Also, it has been demonstrated by applying a theoretical model of nucleation-growth (3D) limited by the diffusion, the deposited layers follow a model of instantaneous nucleation. The morphological characterization carried out by AFM indicates an isotropic morphology (3D) extended over the entire surface with a homogeneous distribution of grains.

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# ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF $\text{CdSe}_x\text{Te}_{1-x}$

## MIXED CRYSTALS

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### Abstract

The band structure and optical properties of the  $\text{CdSe}_x\text{Te}_{1-x}$  ternary mixed crystals have been studied using the pseudopotential formalism under an improved virtual crystal approximation approach. Quantities such as, energy gaps, band-gap bowing parameters, electron effective mass and dielectric constants are calculated. Our results agree well with the available data in the literature. The composition dependence of all studied quantities has been expressed by quadratic polynomial forms.

### Introduction

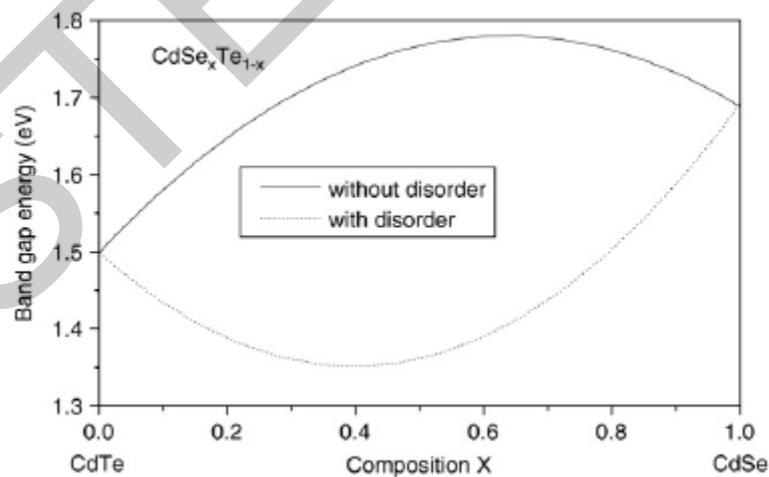
The II–VI ternary semiconductor alloys are used in optoelectronic devices ranging from blue to near-ultraviolet spectral region [1]. These materials are also used to fabricate X-ray and  $\gamma$ -ray detectors [2,3]. Cadmium chalcogenides CdTe, CdSe and their mixed ternary crystals  $\text{CdSe}_x\text{Te}_{1-x}$  have semiconducting properties, which are especially suitable for the conversion of solar energy to electrical energy in photovoltaic or photo electro-chemical devices. The materials are also be used for the photo-assisted decomposition of water [4,5]. In addition, Cd-based compounds such as CdSeTe/Si can be used as an alternative material for short and medium wavelength infrared focal plane arrays [6]. Besides,  $\text{CdSe}_x\text{Te}_{1-x}/\text{ZnSe}$  quantum dots structures have the large conduction-and valence-band offsets at an appropriate composition and are expected to be a highly efficient light-emitting material in green region [7]. CdTe and CdSe exhibit both hexagonal wurtzite and cubic zinc-blende structures. While the common form of CdTe is known to have the zinc-blende structure, it is possible to produce thin crystals with the zinc-blende phase for CdSe as well [8]. For  $\text{CdSe}_x\text{Te}_{1-x}$ , Uthanna and Reddy [9], Mangalhari et al. [10] and Islam et al. [11] have observed the presence of only cubic phase over the entire composition range, whereas a number of other investigations [12–15] have revealed that  $\text{CdSe}_x\text{Te}_{1-x}$  crystallizes in either cubic or hexagonal structure. In the present study, the crystal structures of CdTe and CdSe semiconductor compounds and their related ternary alloys  $\text{CdSe}_x\text{Te}_{1-x}$  are assumed to have the cubic zinc-blende structure. The electronic structure and optical properties of semiconductor alloys are important for guiding the successful design and fabrication of optoelectronic devices. Although some experimental and theoretical studies have been performed on  $\text{CdSe}_x\text{Te}_{1-x}$  mixed crystals [4–7,9–18], many fundamental properties of these materials remain to be determined precisely. To enhance the understanding of physical properties of  $\text{CdSe}_x\text{Te}_{1-x}$  for device applications, a theoretical study has been undertaken. The electronic structure and optical properties of  $\text{CdSe}_x\text{Te}_{1-x}$  alloys are calculated. The calculations are based on the empirical pseudopotential method (EPM) within the virtual crystal approximation (VCA). To include the compositional disorder, a correction to

the alloy potential has been introduced. Traditionally, because of its simplicity, the VCA is preferred to treat the chemical disorder in semiconductor alloys. Together with the VCA, the EPM is the one of the effective and accurate schemes to obtain the overall band structure of multi-component semiconducting alloys [19–22]. Besides, the method is capable of exploring insights and it may be used to calculate other ground state quantities for semiconductors [23–25]. The first principles calculations are technically involved and computationally difficult to perform for ternary and quaternary alloys. Moreover, these calculations give accurate results for some typical cases [26] but normally underestimate the band gaps [27–29] depending upon the species. Quasiparticle calculations need a complicated and CPU-intensive process [30]. Comparatively, the empirical calculations are simple, rapidly converging and estimate band gaps in good agreement with experimental results [31–34]. In addition, using empirical methods, it is possible to perform a large number of calculations.

## Results

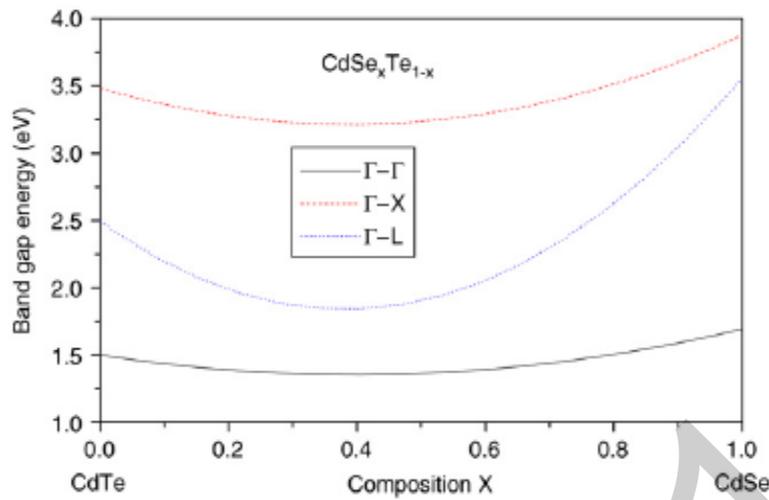
The variation of the direct band-gap energy  $E(\Gamma-\Gamma)$  as a function of Se content for  $\text{CdSe}_x\text{Te}_{1-x}$  using the VCA (without disorder) is shown in Fig. 1 (solid curve). Note that in case of VCA alone,  $E(\Gamma-\Gamma)$  varies nonlinearly with composition  $x$  suggesting an optical band-gap bowing parameter of  $-0.68$  eV. This is in disaccord with the experimental value;  $0.94$  eV reported by Poon et al. [20]. The discrepancy is mainly attributed to the use of the VCA that neglects the compositional disorder. In fact, the physical origin of the band gap bowing can be ascribed to disorder effects created by the presence of different cations (anions) [35,36]. A proportionality to the lattice mismatch between the end-point binaries has also been noted [36-38]. In the modified VCA which includes the compositional disorder into the effective potential, the alloy potential is:

$$V_{\text{CdSeTe}}(G) = xV_{\text{CdSe}}(G) + (1-x)V_{\text{CdTe}}(G) - p[x(1-x)]^{\frac{1}{2}}(V_{\text{CdSe}}(G) - V_{\text{CdTe}}(G))$$



**Fig. 1.** Direct band gap-energy,  $E$  in  $\text{CdSe}_x\text{Te}_{1-x}$  mixed crystals function of Se concentration without disorder (solid curve) and with disorder (dotted curve).

$$E_{\Gamma}^{\Gamma}(x) = 1.25 - 0.39x + 0.94x^2$$



**Fig. 2.** Direct  $E(\Gamma-\Gamma)$  (solid curve) and indirect  $E(X-\Gamma)$  (dashed curve) and  $E(\Gamma-L)$  (dotted curve) band gap energies in  $CdSe_xTe_{1-x}$  mixed crystals as a function of Se concentration at  $\Gamma$  point. Note that all band-gap energies exhibit a non-linear behavior with respect to  $x$  with different rate of variation. Using the same form of Eq. (1), the indirect band-gaps  $E(X-\Gamma)$  and  $E(\Gamma-L)$  have been expressed as:

$$E_{\Gamma}^X = 3.48 - 1.38x + 1.77x^2$$

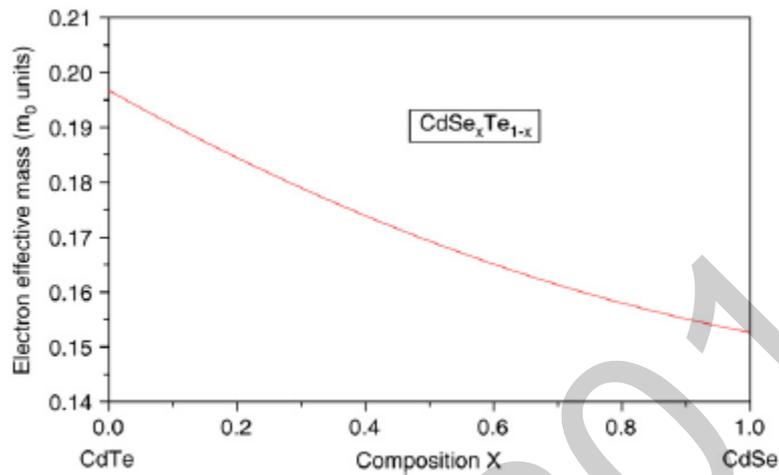
$$E_{\Gamma}^L = 2.47 - 3.29x + 4.43x^2$$

The quadratic terms in Eqs. (2) and (3) are referred to as band gap bowing parameters. Their values are too large as compared to that of  $E(\Gamma-\Gamma)$ . This indicates that the effect of disorder on  $E(X-\Gamma)$  and  $E(\Gamma-L)$  is more important than on  $E(\Gamma-\Gamma)$ . The effective mass is a necessary parameter for analyzing the electron transport in materials. It is also useful for the investigation of quantum well structures. In the present study, we adopt a parabolic fit to the conduction band dispersion in the vicinity of the minima. Thus, the electron effective mass is determined in the conduction band minimum at the  $\Gamma$  valley from the band curvature for different compositions  $x$  using the relation:

$$\frac{1}{m^*} = \frac{4\pi^2}{h^2} \frac{\partial^2 E(k)}{\partial k^2}$$

The second derivative of  $E$  with respect to  $k$  is obtained directly from the parabolic fit of  $E$  with  $k$ . Our results concerning the electron effective mass at the  $\Gamma$  high-symmetry point (in units of the free electron mass) for the compounds  $CdTe$  and  $CdSe$  in the zinc-blende structure are 0.20 and 0.15, respectively. Our result for  $CdSe$  is in good agreement with the theoretical value of 0.158 reported in Ref. [5], whereas for  $CdTe$ , our calculated value is larger than the experimental value of  $0.11 \pm 0.01$  reported by Marple [39]. Generally, the values of the electron effective mass thus obtained for III-V semiconductor compounds [40] are less supported by experiment than for II-VI semiconductor compounds. The reason is due to the fact that the energy band-gaps of III-V compounds are smaller than those of II-VI ones. As a matter of fact, the narrow gap between the conduction and valence bands in III-V compounds leads to a strong interaction between them which make the variation of the energy  $E$  with  $k$  non-parabolic. This makes the value of  $\partial^2 E(k) / \partial k^2$  obtained from a quadratic fit of  $E$

with  $k$  less accurate for III-V compounds as compared to II-VI ones. Fig. 3 shows the electron effective mass at the  $\Gamma$  valley plotted against the composition  $x$  for zinc-blende  $\text{CdSe}_x\text{Te}_{1-x}$  ternary alloys. Note that as one goes from pure CdTe ( $x = 0$ ) to pure CdSe ( $x = 1$ ), the electron effective mass decreases non-linearly.



**Fig 3.** Electron effective mass (in units of the free electron mass) in  $\text{CdSe}_x\text{Te}_{1-x}$  mixed crystals as a function of Se concentration

$$\frac{m_e^*}{m_0} = 5.17004 - 7.46699E_g + 3.63286E_g^2 - 0.57525E_g^3$$

The refractive index  $n$  of semi-conducting materials is very important in the determination of the optical and electric properties of the crystal. In the present work,  $n$  has been calculated using the Moss formula that is based on an atomic model [41]:

$$E_g n^4 = k$$

where  $k$  is a constant with a value of 108 eV. Our results concerning  $n$  for CdTe and CdSe are listed in Table 2 along with the known data reported in Refs. [42,43]. Our results are in good agreement with the known data to within 8% for CdTe and 14% for CdSe. The knowledge of  $n$  allowed us to calculate the high-frequency dielectric constant  $\epsilon_\infty$  using the expression:

$$\epsilon_\infty = n^2.$$

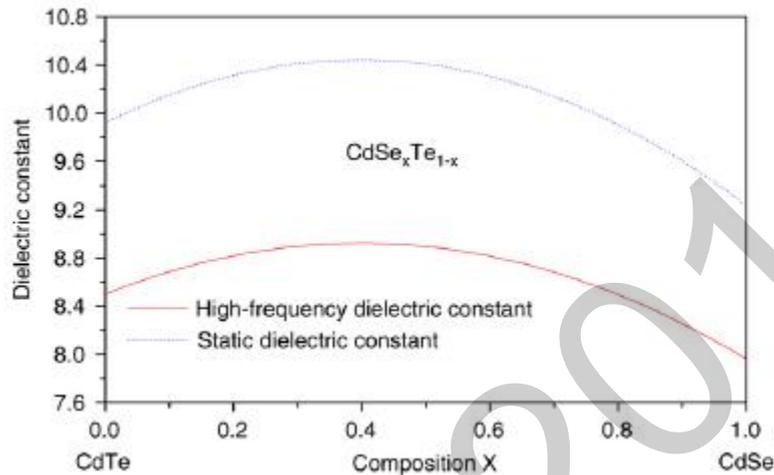
The variation of  $\epsilon_\infty$  as a function of composition  $x$  is shown in Fig. 4 (solid curve). Through Fig. 4, one may note that  $\epsilon_\infty$  varies non-linearly with  $x$ . Using a form similar to that used for the band-gap energy (i.e. Eq. (1)),  $\epsilon_\infty$  can be well described by the following:

$$\epsilon_\infty = 13.66 - 4.39E_g + 0.62E_g^2$$

The static dielectric constant  $\epsilon_0$  has also been calculated using a methodology similar to that used by Bouarissa [44].

The agreement between our results and the known data of 9.8 (CdTe) and 9.6 (CdSe) [45] is better than 4%. The variation of  $\epsilon_0$  as a function of composition  $x$  is depicted in Fig. 4 (dotted curve). One may note also that  $\epsilon_0$  varies non-linearly with  $x$ . The behavior seems to be qualitatively similar to that of  $\epsilon_\infty$ . Using a form similar to that of Eq. (1),  $\epsilon_0$  can be well written as:

$$\epsilon_0(x) = 9.92 + 2.63x - 3.32x^2$$



**Fig. 4.** High-frequency (solid curve) and static (dotted curve) dielectric constants in  $\text{CdSe}_x\text{Te}_{1-x}$  mixed crystals as a function of Se concentration. Known data reported in Ref. [45]

#### 4. Conclusion

The band-gap energies, electron effective mass and dielectric optical constants of  $\text{CdSe}_x\text{Te}_{1-x}$  ternary mixed crystals are reported using the pseudopotential scheme under the VCA including the effect of compositional disorder. The scheme combined with the Harrison bond-orbital model is employed to calculate  $\epsilon_0$ , while the Moss formula is to calculate  $\epsilon_\infty$ . Both the dielectric constants, namely  $\epsilon_0$  and  $\epsilon_\infty$  were found to vary non-linearly with respect to the composition  $x$  and overall good agreement of our results with the published data is found. The compositional disorder is found to improve the fundamental band-gap bowing parameter and related optical properties. The calculations suggested that  $\text{CdSe}_x\text{Te}_{1-x}$  alloys are direct gap semiconductors in the whole range of the Se concentration  $x$ . The variation of the electron effective mass versus the Se content was found to exhibit a weak bowing parameter. Quadratic polynomial forms were obtained to approximate all the studied quantities as a function of Se content.

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# ELIMINATION OF ORGANIC MICROPOLLUANTS BY ADSORPTION ON ACTIVATED CARBON PREPARED FROM AGRICULTURAL WASTE

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## 1. INTRODUCTION

Adsorption is often used to treat the waste water due to the efficient elimination of organic micropollutants and to the economic considerations (L.J. Kennedy et al., 2007; K.A. Krishnan, T.S. Anirudhan., 2008). The efficiency of this technique is mainly based on the quality of adsorbent materials. The activated charcoal was often used to treat the waste water (D. Kavitha, C. Namasivayam., 2007) and is an efficient adsorbent, particularly of organic pollutants, due to a high specific surface and the controlled chemical affinity (M. Sathishkumar et al., 2007). However, to lower the cost of the water treatment process, systematic studies are carried out to elaborate cheaper materials as alternative adsorbents (T.C. Chandra et al., 2007). Many researchers have recently studied the feasibility of converting by-products and agricultural wastes into activated carbon. In this paper we will focus on the investigation of the adsorptive properties of activated carbon, obtained by carbonization and chemical activation with H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> agricultural by-products: coffee grounds (CCG), orange peels (COP) towards phenolic micropollutants such o-nitrophenol

## 2. MATERIALS AND METHODS

### 2.1. Preparation of activated carbons

The peels orange and coffee grounds were abundantly washed with distilled water then dried in the oven at 120°C during 24 hours. Then they are grinded and filtered to retain only the fraction including between 150 and 250 µm. The retained grains are chemically pre-treated with H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> after carbonization. This chemical activation can also be done after carbonization. Before undertaking applications in adsorption tests of pollutants or others, carbon thus treated is dried in the oven at a temperature of 110 °C for at least 12 h

### 2.2. Characterization of the adsorbent

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of the raw materials were obtained on a TA Instruments model 2050 TGA V5.4A under nitrogen atmosphere, heated from room temperature up to 600 °C, and with an initial mass of approximately 10 to 30 mg of solid. Derivative thermogravimetric (DTG) curves were analyzed by derivative weight loss.

Scanning electron microscopy (SEM) was used to visualise the morphology of the elaborated materials. FEI-Quanta 200 microscope was used.

The raw material and the prepared activated carbon were analyzed by X-ray diffraction (XRD), using a Bruker D8 Advance diffraction system, with Cu K<sub>α</sub> 1 (λ = 1.5406 Å) radiation in theta/theta reflection geometry.

Infrared spectra were recorded with a spectrophotometer (Spectrum One FT-IR spectrometer) in the wave number range of 4000-650 cm<sup>-1</sup>. Infrared spectroscopy is used to obtain information on chemical structure and functional groups present in both the raw material and the prepared activated carbon.

### 2.3. Kinetics studies

The adsorption experiments were carried out by adding 0.030 g of activated carbon to 50 ml of aqueous solution at known concentration (20 mg/l) and at a pH of 4.9 for o-nitrophenol. The suspensions were shaken at room temperature using agitation speed 250 rpm. After, samples were withdrawn at desired time intervals and separated with 0.45 µm membrane. The residual concentrations were analyzed using Shimadzu UV- 1700 spectrophotometer at 273 nm wavelength for o-nitrophenol. The amount of organic compounds adsorbed per gram of adsorbent (q<sub>e</sub>, mg/g) at time (t) and the percent adsorption (R. %) is given by the following relations (Eqs. 1 and 2) (Carlos Escudero et al., 2008).

$$q_e = \frac{(C_i - C_e) \cdot V}{W} \quad (1)$$

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where W is the mass of adsorbent expressed in (g), V is the volume of the solution in (l) and C<sub>i</sub> and C<sub>e</sub> are the initial and at the equilibrium concentrations, respectively expressed in (mg/l).

### 2.4. Kinetic modeling

In order to investigate the kinetics of adsorption of o-nitrophenol on activated carbon prepared from; orange peel and coffee ground, the Lagergren pseudo-first-order model (Eq. (3)) (S. Lagergren et al., 1898).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (3)$$

Where  $q_e$  and  $q_t$  the quantities of o-nitrophenol adsorbed (mg/g) at equilibrium and at time t, respectively, and  $k_1$  is the rate constant for first-order adsorption ( $\text{min}^{-1}$ ).

Linear plots  $\log (q_e - q_t)$  versus t were plotted to evaluate this kinetic model and to determine rate constant and  $q_e$  from the slope and intercept, respectively. The equation of the second-order kinetic model is of the form Eq. (4):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

Where  $k_2$  is the equilibrium rate constant of pseudo-second order ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ). The integration of Eq. (5) in the initial conditions ( $t = 0, q_t = 0$ ) and ( $t = t, q = q_t$ ) gives Eq. (5):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{5}$$

This is the integrated rate law for a pseudo-second order reaction. Eq. (6) can be rearranged to obtain the linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

The straight-line plots of  $t/q_t$  ( $\text{min.g.mg}^{-1}$ ) against t have been tested to obtain rate parameters.

### 3. RESULTS AND DISCUSSION

#### 3.1. Thermogravimetric analyses

The TGA / DTG plot recorded from powdered orange peels (Fig.1a) shows three distinctive successive weight losses with 10.56 % due to the release of absorbed water molecules a weight loss of 42.87 % was recorded at 288.66 °C, while the last mass loss of 18.18 % observed at 385.43 °C.

The DTG curve of the coffee grounds (Fig. 1b) shows basically three main decompositions. A first mass loss at 121.28 °C is consistent with the elimination of physisorbed water (6.28 %). There is mass loss of 21.23 % and 52.26 % from 320.41 °C and 400.61 °C, respectively.

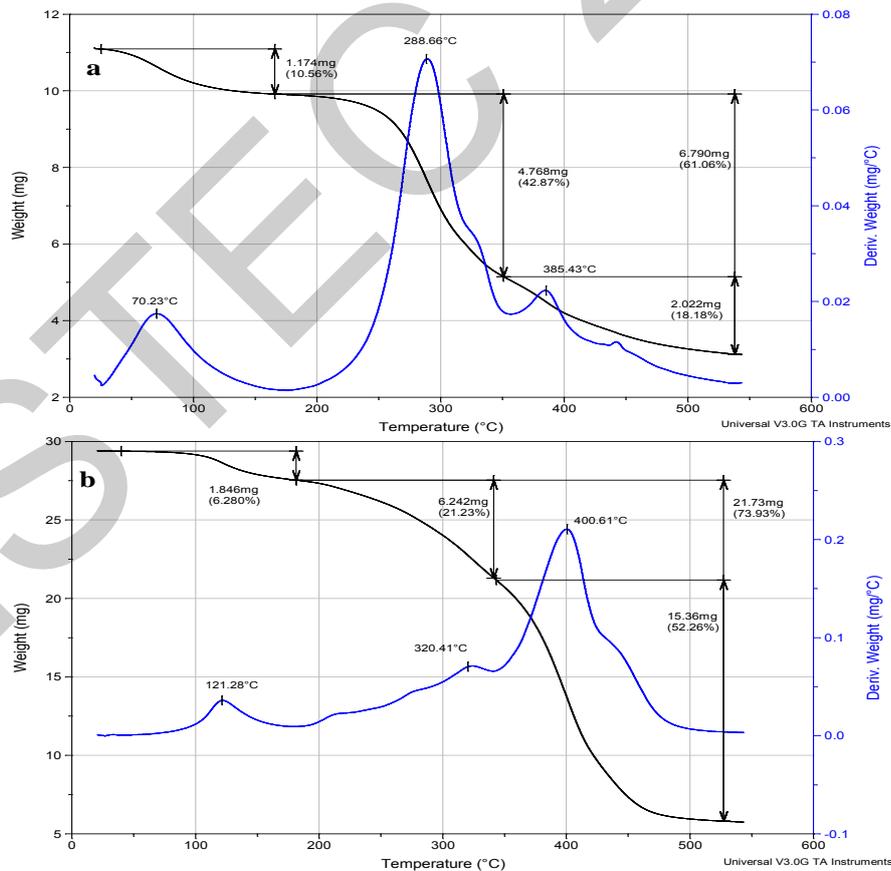
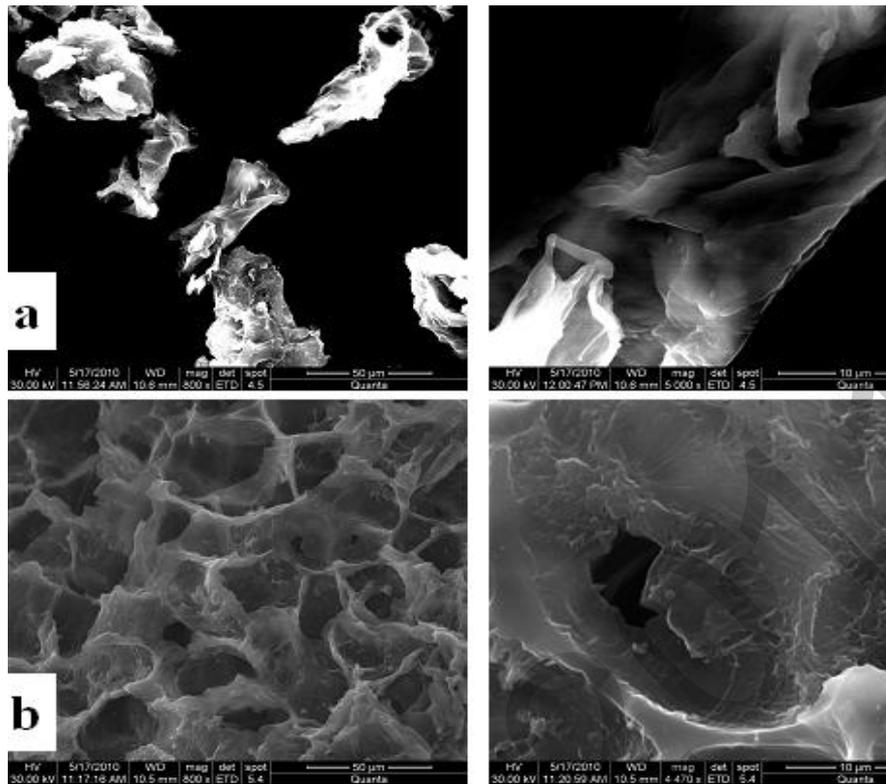


Fig. 1. TGA /DTG analysis of orange peels and coffee grounds.

#### 3.2. Scanning electron microscopy analysis

The SEM images of two activated carbons obtained with two magnifications are given at Fig. 2. Each material displays the specific surface morphology but all of the exhibit a highly developed porosity. Pore size and distribution (macropores and

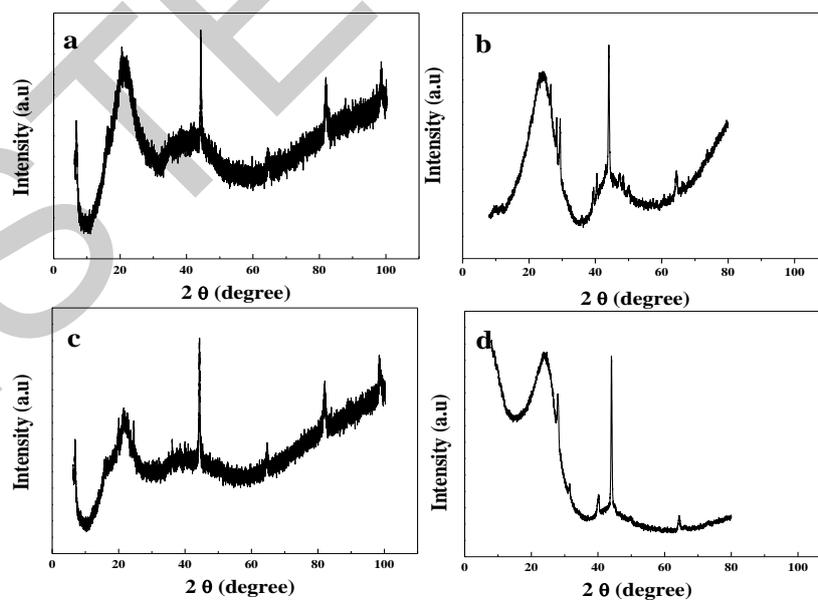
mesopores) are an individual property of every activated carbon. Over the entire surface of the samples with some heterogeneity, pore size varies from one carbon to another. Fine particles attached to the surface of the melon seed activated are probably impurities introduced during the preparation (S. Hazourli et al., 2009).



**Fig. 2.** SEM micrographs of activated carbon prepared from orange peels and coffee grounds at different magnifications.

### 3.3. X-ray diffraction studies

The results of X-ray diffraction obtained with three raw materials and corresponding activated carbons are presented in Fig. 3. All materials are mainly amorphous with small crystalline domains. The activation process does not change main characteristics of X-ray spectra.



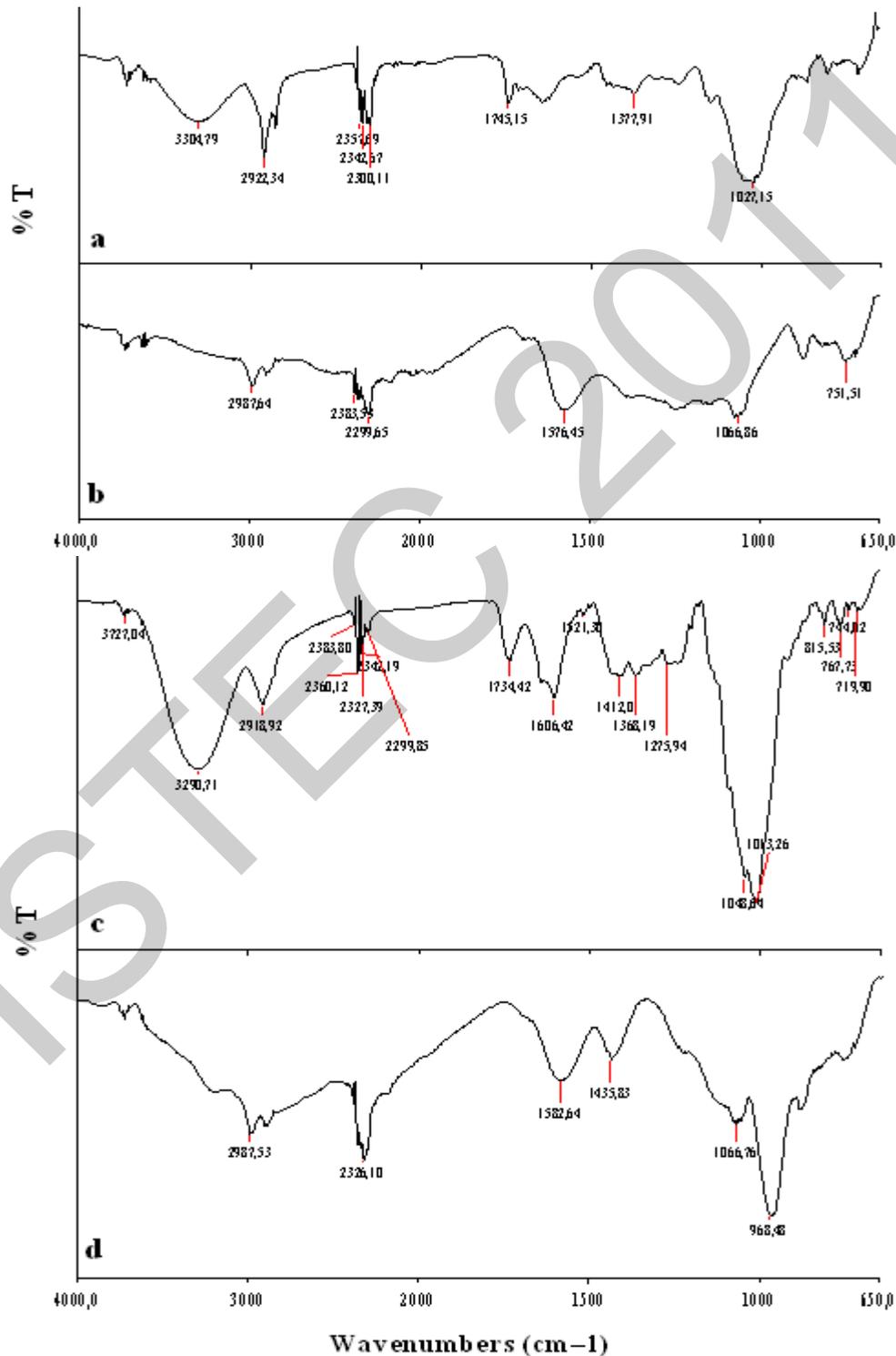
**Fig. 3.** XRD pattern of (a, c) orange peels and coffee grounds (b, d) activated carbon prepared from orange peels and coffee grounds.

### 3.4. Functional groups

The FTIR spectra of raw materials are shown in Fig. 4. These spectra are quite similar to other lignocellulosic materials (R. Baccar et al., 2009). All the spectra show the peaks typical for the groups  $\text{-OH}$  at ( $3304.79\text{--}3290.71\text{ cm}^{-1}$ ), confirming the presence of free hydroxyls groups of carboxylic acids, alcohols and phenols on the adsorbent surface (Ningchuan Feng et al., 2009).

Centered bands at ( $2922.34\text{--}2918.92\text{ cm}^{-1}$ ) are attributed to the symmetric and asymmetric C-H stretching vibration of aliphatic molecules and the bands located at ( $1745.15\text{--}1734.42\text{ cm}^{-1}$ ) correspond to the stretching vibrations of the carbonyl moiety  $\text{C=O}$  non-ionic of carboxylic acids ( $\text{-COOH}$ ) and esters ( $\text{-COOCH}_3$ ). Peaks at ( $1377.91\text{--}1368.19\text{ cm}^{-1}$ ) can be assigned to symmetric stretching of  $\text{-COO}^-$  and  $\text{C-O-C}$  ( $1027.15\text{--}1048.04\text{ cm}^{-1}$ ) (A.L. Ahmad, M.M. Loh, J.A. Aziz et al., 2007).

All these bands were shifted due to the carbonization and activation (Fig.4). Bands located at ( $3304.79\text{--}3290.71\text{ cm}^{-1}$ ), ( $1745.15\text{--}1734.42\text{ cm}^{-1}$ ) almost disappeared and the bands located at ( $2923.64$  and  $2854.29\text{ cm}^{-1}$ ) decrease in intensity, this indicates the fall of the quantity of water and aliphatic compounds due to the carbonization (R. Baccar et al., 2009).



**Fig. 4.** FTIR spectra of (a, c) orange peels and coffee grounds (b, d) activated carbon prepared from orange peels and coffee grounds.

### 3.5. Adsorption kinetics studies

Adsorption is a well known equilibrium separation process for treatment of water organic micropollutants. Fig. 5 shows the effect of time of treatment on the removal of o-nitrophenol with concentration of 20 mg/l by activated carbons. Data indicate that the removal of o-nitrophenol increase with time and attains equilibrium in 60 min. Organic adsorption increases sharply for a short time and slows gradually when equilibrium is approached. The plots show that the amounts of o-nitrophenol vary in a single smooth and continuous curve, leading to saturation. All the kinetics data agreed well with the pseudo-second-order kinetic model.

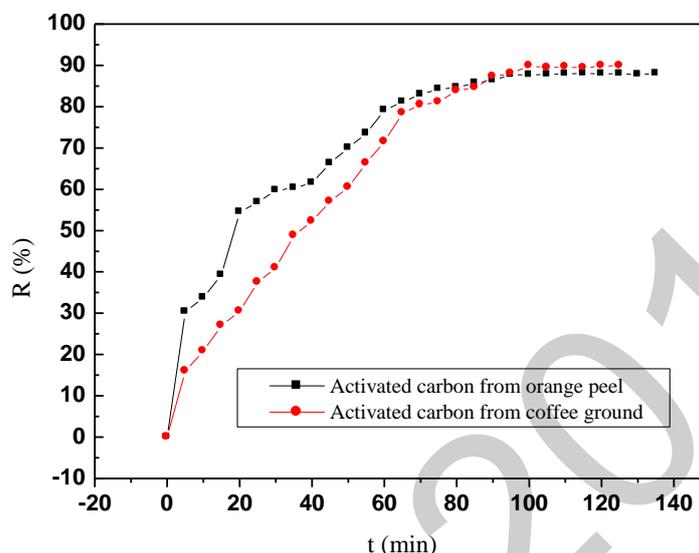


Fig. 5. Adsorption of o-nitrophenol onto different activated carbons.

## 4. CONCLUSION

This study was realized in two steps, the first is the production of an activated carbon from a lignocellulosic natural waste “orange peel and coffee ground”; the second step is the characterization of the obtained carbons and the adsorption efficiency of new materials was tested. The good preparation of the samples permit to obtain carbons with physicochemical and structural properties comparable with those found in the literature but from other materials.

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# EMOTIONAL EMBODIED CONVERSATIONAL AGENTS

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## Abstract

The study of multi-agent systems and on the modeling of artificial agents is based on many similar concepts. In this sense, the modeling of artificial agents has focused in these last years on the notion of expressiveness and developed new kinds of artificial agents. To this end, the architectures of agents have been developed to simulate the behavior of verbal and nonverbal communication. These agents can interact with users using voices, gestures, view and facial animation. The embodied conversational agents (ECA) are virtual characters that are capable of having a natural conversation with a user. Succeeding in integrating the emotional side into an agent means a new kind of artificial agents that we call emotional animated conversational agents. For a very long time, human emotion has been the source of many scientific researches regarding its definition and composition. Over time, several studies have shown that human activities are influenced a lot by the emotional state. This evidence leads to the birth of the idea of integrating the emotion side into the research of human daily activities, such as communicating, negotiating, learning, business activities, etc.

**Keywords:** Embodied conversational agents (ECA), emotion, (Situation Agent Intention Behavior Animation (SAIBA)).

## 1. INTRODUCTION

Humanoids inhabiting virtual environments have nowadays quality gestural animations. An emotional agent must have three features. Firstly, the ability to express a given emotion through various communication channels available to him, such as voice or facial representation in order to create a credible feedback for a human, the ability to perceive and recognize emotions that are transmitted by other agents or by a human contact. Finally, it must be able to model and reason about emotions in order to produce an appropriate response in relation with the emotional information available to him.

The objective is to improve agent's rationality by emotional artifacts that, in humans, seem necessary for an appropriate behavior and decision-making.

## 2. ANIMATED CONVERSATIONAL AGENTS

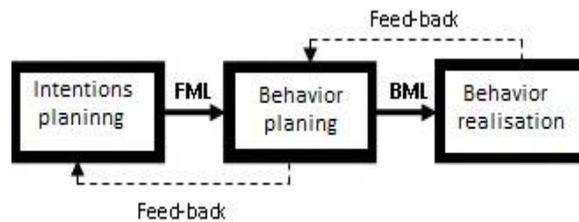
Recent technological advances make it possible to create expressive and interactive virtual humans. Embodied Conversational Agents (ECAs) are animated virtual beings who are capable of having a natural conversation with a user. To this end, architectures of agents have been developed to simulate verbal and nonverbal communication behaviors. ECAs can interact with users using voices, gestures, view and facial animation.

Building an ECA requires the involvement of several areas of research. Problems such as speech recognition, motion capture, and dialogue management require different skills from their designers.

This kind of complexity makes it difficult to create an ECA by a single research group. It quickly became obvious that it was necessary to share expertise and ECA's modules among researchers. It is therefore important to develop standards that will allow inter-operability between the different modules of an ECA (Rickels et al., 2002). Standardization ensures both the interchangeability of modules and the extent of ECA (Kopp et al., 2006), and finally gives the opportunity to compare different agent technologies (Marriott et al., 2002). Architectures, which are built on a common structure and use standardized protocols for communication, can be easily extended in order to develop a wide variety of applications (Thiébaux et al., 2008). One can also imagine that the modules (e.g. animation engine) can be replaced by others. Finally, the usage of the same standard input makes possible the evaluation and comparison of different agents.

## 3. STANDARDIZED ARCHITECTURE - SAIBA

SAIBA (Situation Agent Intention Behavior Animation) (Vilhjálmsson et al., 2007) is an international research initiative whose primary goal is to define a standard architecture for generating interactive behaviors of animated virtual agents. It defines a number of abstract levels (see Fig 1) of the agent's communicative intentions planning in the planning of their behavior and of their generation.



**Figure1:** Standardized architecture -SAIBA

The Intentions planning module defines the current goals, emotional state and beliefs of the agent. It encodes them in FML (Function Markup Language) which is a mark-up language for specifying communicative intentions (Heylen et al., 2008).

In order to transmit the communicative intentions of the agent, the planning behavior module determines from the FML a number of communicative signals (e.g. speech, facial expressions, and gestures) that are encoded in BML (Behavior Markup Language). This standard markup language can specify nonverbal behaviors of ECA (Vilhjálmsón et al., 2007). Finally, the function of the third module of the SAIBA architecture, behavior generation, is to create behaviors generated by the planning behavior module. It receives data input in BML format and calculates animation files of the virtual agent.

#### 4. THE EMOTION

In 1872, Darwin (Darwin, 1872) shows that emotions are useful, scalable and universal behavioral mechanisms, thus breaking with the previous trend that used to see them as useless parasites. The term "Affective Computing" designating computer systems that process, manipulate and influence the emotions appears in 1995 (Picard et al., 1995). Emotion psychologists define it as an episode in time which implies a visible change in the functioning of the body triggered by a specific event that can be external (such as: the behaviors of others, a change in the course of things or meeting with new stimuli) or internal (such as thoughts, memories or feelings). Emotion includes cognitive processes, physiological activation, a motion expression, a subjective feeling and the tendencies to action.

#### 5. EVALUATION THEORY

Since 1970, numerous researches have been conducted in order to specify all the criteria involved in the differentiation of emotions. The theory of cognitive assessment (appraisal) tend to explain what distinguishes an emotional experience from a different type of experience and what differentiates an emotional experience, such as fear from another, such as sadness. According to this theory, situational, cultural factors and personality, determine the nature of that emotion.

Elliott explains that what triggers an emotion is the appraisal, which means the evaluation of an event, action or object. Lazarus has defined evaluation as an adaptive process used to maintain or modify the relationship between the agent and his goals, the world and its constraints in order to maintain balance.

##### 5.1 Roseman's Cognitive Evaluation Model

Roseman and his colleagues (Roseman et al., 1990) have proposed a model of cognitive assessment that generates emotions according to an evaluation process of an event and a small number of criteria of cognitive assessments interact to give birth to 17 emotions.

They divide events into two categories:

- *Motive-consistent events*, events that are consistent with one of the goals of the individual,
- *Motive-inconsistent events*, in the contrary, these are events that threaten one of the goals of the individual.

Their model is based on several cognitive assessment criteria (Picard, 1998). For example, an event may be motivated by the desire for reward or, in the contrary, by the escape for punishment. Roseman's model is thus interesting to its simplicity and the foundation it lays in the study of cognitive assessment.

##### 5.2 The model of Ortony Clore and Collins (OCC)

Ortony, Clore and Collins (Ortony et al. 1988) have developed another model based on the theory of appraisal, which is similar to that presented by Roseman, but this one uses a more refined notion of goals.

Instead of trying to describe every possible emotion, the OCC model places itself at the level of types of emotions. Therefore, it provides a classification scheme for common emotional reaction based on a valence feedback to events and objects in the light of goals, standards and attitudes of an agent (Reilly et al. 1992).

This model became popular very quickly because of its success in the simplification made to the representation of emotional states, while providing clear and distinct emotional parameters.

However, this model, as well as the model of cognitive assessment of Roseman, does not provide a complete emotional process (Bartneck et al. 2002) (El-Nasr et al. 2000). In fact, the model can't provide the simple management of mixed emotions as is often the case in reality. It does not show how to filter the mix of triggered emotions to obtain a consistent emotional state. In addition, the model was initially created in order to understand the emotions and not to simulate them. Therefore, the links between emotions and intensity, including the different levels of intensity for each emotion, are not described in the model.

### 5.3 Evaluation criteria according to Scherer

Scherer (1993), member of an emotions research group in Geneva, built and implemented a model based on the appraisal theory, the theory of the components process. The general idea is that the evaluation of an event or a stimulus, based on the evaluation criteria defined by Scherer, determines the nature (both the quality and intensity) of the emotional reaction (Scherer et al. 1996).

His model is essentially a knowledge-based system that takes as input a description of the situation in terms of 15 criteria of cognitive assessment and matches them to an emotion characterized by 14 components.

## 6. THE EMOTION IN EMBODIED CONVERSATIONAL AGENTS

Nowadays, acting virtual agents exist in different forms in order to entertain users. These agents must be credible in their actions, their environment and their interactions with other characters in the simulation. In order to offer them this credible behavior, which resemble to some extent to the reality, we believe it is important to build cognitive models based on those ones developed in psychology.

In this application context, emotions have an important role to play by what they bring to the learning process. This integration is consistent with the work in the field of neuroscience in order to explain on one hand the emotional functioning of man and on other hand to propose the modeling. In our case, we are interested in a particular class of emotions. These emotions come within the reasoning of the agent, as shown by the theories of evaluation (Klaus et al. 2001), (Aaron et al. 2001).

If we take the emotion 'shame', this is a mixed emotion, that is to say a mixture of simple emotions (fear, anger, sadness). This is a more archaic emotion than guilt in the sense which it is often less verbal and more sensory than this one. It manifests emotional (embarrassment, discomfort, fear, or ... exuberance, aggression ...), physically (looking down, head down, blushing ... or head up ...), cognitively (demeaning or aggressive internal discourse...) and behaviorally (inhibition, paralysis or ambition, exhibitionism ...).

Emotions are used as means to regulate the behavior in the environment. Modeling the emotions for an agent is not an obstacle free process, both in assessing the events from the environment and from other agents, and in the expression and use of emotional states of the agent.

The aim of our work is to incorporate some complex emotions such as: regret, disappointment, guilt, blame, satisfaction ... The integration of these emotions is based on the work of (Rivière et al. ,2010), who were able to identify the relationship between the conversation acts and emotions. This link is obtained from the study of the theory of speech acts, such as the act of conversation 'Apologize' is expressed by the emotion of regret, by the sincerity condition of the act, which is the minimum that the speaker is sincere.

Given the difficulty to achieve an ACA, we have chosen to work with the ECA from Embodied Agents Research Group (EMBOTS) (Heloir et al. ,2010). This ACA is based on the SAIBA architecture, and its originality lies in the precision of movement. As for the emotions, it contains only basic emotions such as joy or sadness.

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# EVALUATION OF THE NUMBER OF TRANSFER UNITS(NTU) AND THE COLUMN HEIGHT BY USING ON-LINE TEMPERATURE MEASUREMENTS FOR A PILOT SCALE PACKED BATCH DISTILLATION COLUMN

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## ABSTRACT

There have been relatively few experimental attempts at evaluating the column height and comparing experimental results obtained from a pilot scale packed batch distillation column with theoretical ones.

In the present study, the pilot plant packed batch distillation column was used to distillate the binary methanol-water mixture, and to obtain on-line temperature values. The top temperature changes with time were observed at steady-state and dynamic conditions. The column was operated initially for approximately one hour at the total reflux. In this case, There were no feed and product flows. Temperature samples were taken on-line from the top and bottom of the column. Temperature profiles observed on the computer were recorded. Refractive index of the samples were determined. When the temperatures were constant, the system was at a steady-state condition for total reflux. After the system reached the steady-state condition the reflux ratio was adjusted to a certain level. From experimental top and bottom temperature values, two models were obtained between mol fraction and temperature. The mass transfer coefficient was calculated, and the final mol fraction of reboiler was determined. The column height was calculated and compared with the real packed height. It is noted that the equation used for mass transfer coefficient is considerable well.

**Keywords:** batch distillation, packed column, packed height, mass transfer coefficient

## INTRODUCTION

The investigation of distillation columns is mainly based on two different approaches: fundamental studies, for example concerning mass transfer behaviour of packed sections, etc. and alternatively, integral studies on columns provided with trays or packing (Elgue, Prat, Cabassud, Lann and Cezerac, 2004; Zuiderweg, 1999). There has been many articles to produce a certain amount of product at desired composition either in minimal production time or with maximal economic profit (Betlem, Krijnsen and Huijnen, 1998; Muddu, Narang and Patwardhan, 2010). The investigation of column performance can be identified by studying the liquid composition profile.

The batch distillation have been widely used in the separation processes because of its easy operation and maintenance. Noda, Kato, Chida, Hasebe and Hashimoto (2001) discussed the optimal structure and operation of a batch distillation column separating ternary mixture from the viewpoint of energy conservation, and derived the optimal reflux operation for three types of batch distillation columns; rectifying, stripping and total reflux columns. They noted that the energy consumption of the total reflux column is reduced when the optimal operation is used. Kim and Han (1999) showed that the dynamic model gives an accurate design for the operation of a batch distillation column. The variations of reflux ratio and top product composition are obtained.

Sadeghifar and Kadri (2011) developed a general and accurate method for efficiency calculation of the distillation columns packed with structured packings. They noted that for distillation columns with a large number of components (except for total reflux conditions), it is too difficult to obtain the realistic value of the experimental efficiency. An approximate estimation of the experimental efficiency is also sometimes impossible. Senol (2001) suggested that the increased amount of effective area in randomly packed distillation column, as compared with the wetted one, is due to tendency toward rippling, wave and droplet formation in the falling liquid film. It is shown that the observed and predicted behaviors of the relative proportion of effective interfacial area are overly sensitive to the vapor and liquid loads, as well as to the packing properties.

Rejl et. al. (2006) measured volumetric mass transfer coefficients in liquid and vapour phases in distillation column by the method consisting of a fitting of the concentration profile of liquid phase along the column obtained by the integration of a differential model to the experimental one. It is noted that the concentration profiles obtained by the integration of the differential model of the distillation column using the coefficients from absorption correlation are differed from the experimental profiles. Liu, Yu, Yuan and Liu (2009) proposed a numerical method for modeling the distillation process in a randomly packed column. They showed that the predicted height equivalent of theoretical plate of the distillation column concerned is in satisfactory agreement with the reported experimental data.

In the present study, it is shown that mass transfer coefficient and the column height can be predicted much more simply using experimental top and bottom temperature data while being able to achieve the required separation in a pilot scale packed batch distillation column.

**METHODS AND PROCEDURES**

Distillation system consists of a glass flask (100 L), a heating mantle (2000 W), a packed 80 mm internal diameter column filled with 1 in Rasching rings, a valve adjusting reflux ratio at the top of the column and a condenser. System has two thermocouples to measure the temperature of top product and the boiler (See Figure 1).

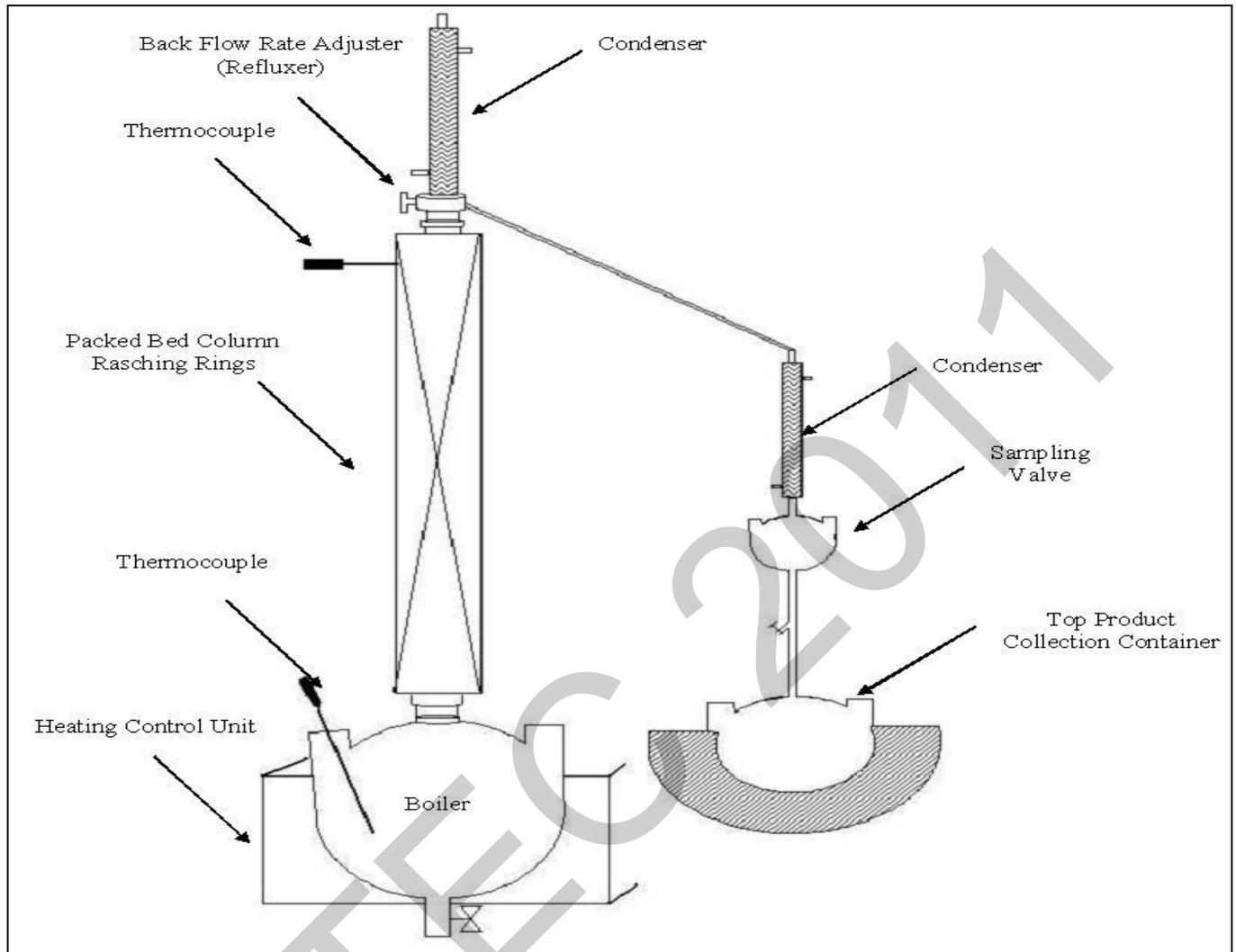


Figure 1. Experimental system

To operate the experimental system, certain volume and concentration of methanol-water mixture is filled into boiler. Cooling water inlet valve opening is provided for condenser. The button on the distillation column control panel that gives energy to the system is turned on. Thus, heating mantle begins to heat the mixture in the vessel. Batch distillation is operated at the total reflux until the steady state condition occurs. When the steady-state condition is reached in the column, reflux valve is adjusted to a desired value and the top product is obtained by batch distillation. Experimental data for the distillation column is given in Table 1.

Table 1 Experimental data for distillation column

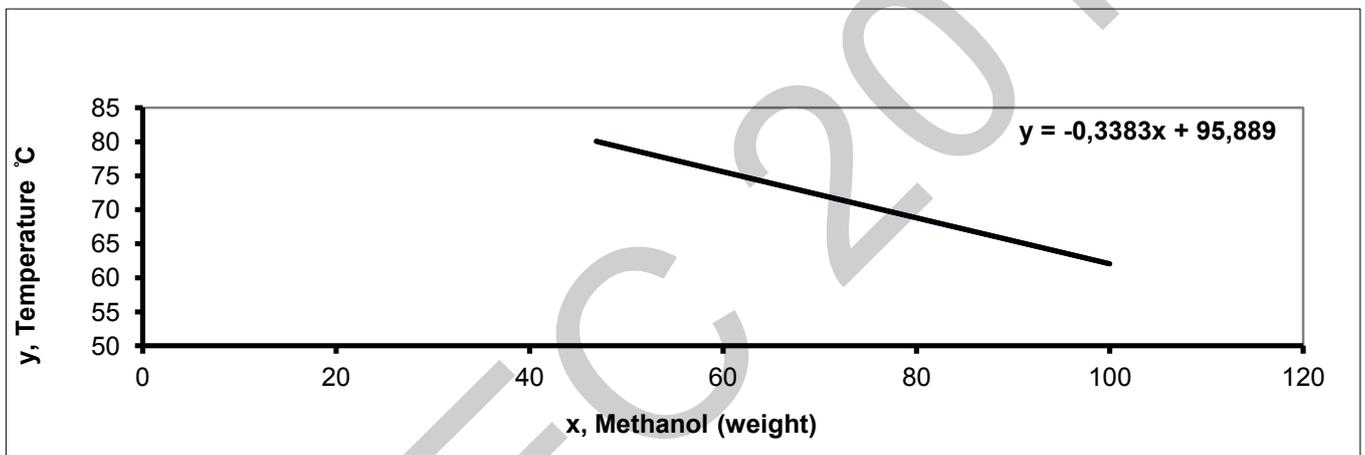
Initial reboiler amount (F)	55 L
Initial reboiler methanol mol fraction ( $X_{s1}$ )	0.222
Reboiler temperature	81.7 °C
Top product flow rate (D)	0.14 mL/s
Total top product amount (d)	2.726 L
Vapour flow rate (V)	0.24 mL/s
Liquid flow rate (L)	0.10 mL/s
Average top product temperature	67.8 °C
Average top product density ( $\rho_{ort}$ )	910.407 kg / m <sup>3</sup>
Average top product molecular weight ( $M_w$ )	21.559 kg / kmol
Reflux ratio	0.682

RESULTS

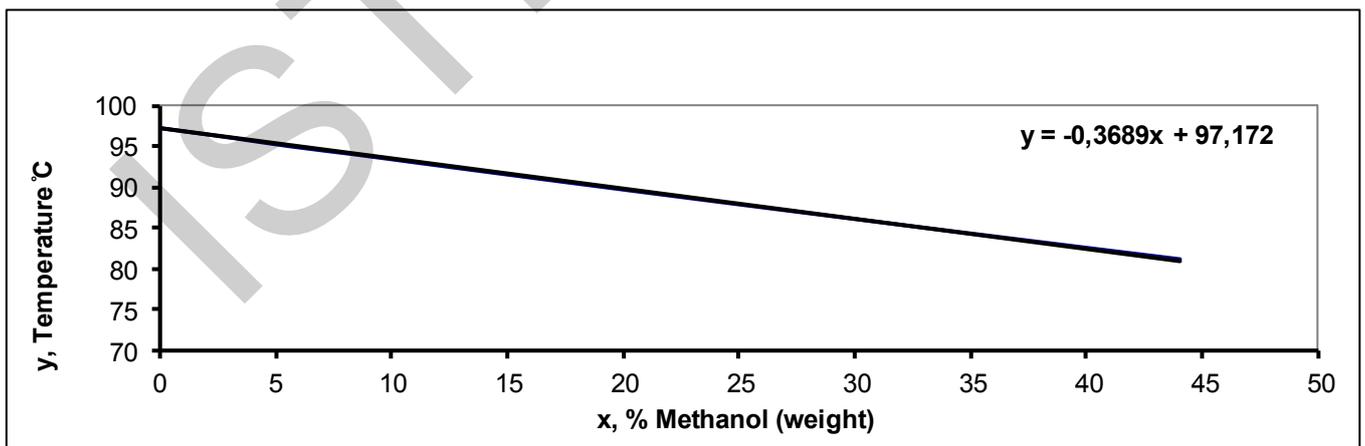
55 L mixture with 22% methanol concentration is fed to boiler. The temperature change is monitored during the distillation (Table 2). Samples are taken from the product collection container at a certain time intervals (10 min). The sample concentrations are determined by reading the indices of refraction from refractometer (see Figure 2 and Table 2). At the same time the top product is read on the temperature indicator.

Table 2 Experimental temperature data and calculated methanol mole fractions

Time (min)	Top Product Temperature (°C)	Reboiler Temperature (°C)	Calculated Top Product Methanol Mole Fractions $X_D$ (See Figure2-b )	Intercept: $\frac{X_D}{R+1}$	Calculated Reboiler Methanol Mole Fractions $X_S$ (See Figure2-a)	$\frac{1}{X_D - X_S}$
0	60.4	81.7	0,994	0,591	0,530	2,155
10	60.9	82.0	0,971	0,577	0,400	1,751
20	63.2	82.4	0,868	0,516	0,220	1,543
30	66.3	82.5	0,743	0,442	0,150	1,686
40	71.9	82.6	0,550	0,327	0,080	2,128
50	72.6	82.7	0,529	0,315	0,070	2,179
60	73.0	82.7	0,517	0,307	0,065	2,212



(a)



(b)

Figure 2 : Calibration plots a) for reboiler b) for top product

At the end of a certain operating time, to measure the flow rate of steam, refluxer is fully opened and the top of the product volume collected per unit time is measured in container. The concentration of the bottom product is determined by reading reflective index. Total top product volume is measured at the end of the distillation time.

Equations used to calculate top product and reboiler methanol mole fractions ( $X_D$  and  $X_S$ ) are given as follows:

Calibration Equation for Top Product :  $Y = -0.3689 * X + 97.172$  (3.1)

$$X_D = \frac{(X_A/M_A)}{\left(\frac{X_A}{M_A}\right) + \left(\frac{100 - X_A}{M_B}\right)}$$
 (3.2)

Calibration Equation for Reboiler :  $Y = -0.3383 * X + 95.889$  (3.3)

$$X_S = \frac{(X_A/M_A)}{\left(\frac{X_A}{M_A}\right) + \left(\frac{100 - X_A}{M_B}\right)}$$
 (3.4)

Initial methanol amount ( $S_1$ ) in the reboiler before the distillation is determined as:

$t = 0$   $\rho_{\text{methanol}} = 721.6 \text{ kg/m}^3$ ,  $\rho_{\text{water}} = 970.2 \text{ kg/m}^3$   
 Average Molecular Weight (Mw) =  $0.283 * 32.04 + 0.717 * 18.02 = 21.986 \text{ kg / kmol}$  (3.5)

Average Density ( $\rho_{\text{av}}$ ) =  $0.283 * 721.6 + 0.717 * 970.2 = 899.871 \text{ kg/m}^3$  (3.6)

$$S_1 = \frac{\rho_{\text{av}} * V}{M_w} \Rightarrow S_1 = \frac{\left(899.871 \frac{\text{kg}}{\text{m}^3}\right) * (55 * 10^{-3} \text{m}^3)}{(21.986 \text{ kg/kmol})} = 2.251 \text{ kmol}$$
 (3.7)

Methanol amount( $S_2$ ) in the reboiler after the distillation is evaluated as below:

Amount of mixture in the boiler ;  $V = F - D$   $V = 55 - 2.726 = 52.274 \text{ L}$  (3.8)

$t = \infty$   $\rho_{\text{methanol}} = 741.3 \text{ kg/m}^3$ ,  $\rho_{\text{water}} = 967.5 \text{ kg/m}^3$   
 Average Molecular Weight (Mw) =  $0.2524 * 32.04 + 0.7476 * 18.02 = 21.559 \text{ kg / kmol}$  (3.9)

Average Density ( $\rho_{\text{av}}$ ) =  $0.252 * 741.3 + 0.748 * 967.5 = 910.407 \text{ kg/m}^3$  (3.10)

$$S_2 = \frac{\rho_{\text{av}} * V}{M_w} \Rightarrow S_2 = \frac{\left(910.407 \frac{\text{kg}}{\text{m}^3}\right) * (52.274 * 10^{-3} \text{m}^3)}{(21.559 \text{ kg/kmol})} = 2.207 \text{ kmol}$$
 (3.11)

$$V = 0.24 \frac{\text{ml}}{\text{s}} * 3600 \frac{\text{s}}{\text{hr}} * 910.407 \frac{\text{kg}}{\text{m}^3} * \frac{1 \text{m}^3}{10^6 \text{ml}} * \frac{1 \text{ kmol}}{21.559 \text{ kg}} = 0.037 \frac{\text{kmol}}{\text{hr}}$$
 (3.12)

$$L = 0.10 \frac{\text{ml}}{\text{s}} * 3600 \frac{\text{s}}{\text{hr}} * 910.407 \frac{\text{kg}}{\text{m}^3} * \frac{1 \text{m}^3}{10^6 \text{ml}} * \frac{1 \text{ kmol}}{21.559 \text{ kg}} = 0.015 \frac{\text{kmol}}{\text{hr}}$$
 (3.13)

$D = V - L = 0.037 - 0.015 = 0.022 \text{ kmol / hr}$  (3.14)

Column Cross-sectional Area=  $S = \pi * (0.08)^2 / 4 = 0,005 \text{ m}^2$  (3.15)

$$G_y = \frac{V}{S} = \frac{0.037}{0.005} = 7.4 \frac{\text{kmol}}{\text{m}^2 \cdot \text{hr}} \quad \text{and} \quad G_x = \frac{L}{S} = \frac{0.015}{0.005} = 3.0 \frac{\text{kmol}}{\text{m}^2 \cdot \text{hr}}$$
 (3.16)

Mass transfer coefficient is written as follows (Sahay and Sharma,1973; Karacan, Hapoğlu, Cabbar, and Alpbaz, 1997)

$$K_y a = 1.28 * 10^{-5} * (V)^{0.64} * (L)^{0.48}$$
 (3.17)

$$K_y a = 1.28 * 10^{-5} * (7.4 * 10^3)^{0.64} * (3.0 * 10^3)^{0.48} = 0.179 \frac{\text{kmol}}{\text{m}^2 \cdot \text{hr}}$$
 (3.18)

To determine Height of Transfer Units ( $H_{\text{Theo}}$ ) and Number of Transfer Units ( $N_{\text{Theo}}$ ) for multistage batch distillation, the equations given below and Table 3 and 4 are utilized.

$$\ln \frac{S_1}{S_2} = \int_{X_{S2}}^{X_{S1}} \frac{dX_S}{X_D - X_S} = (1|X_D - X_S)_{\text{average}} * (X_{S1} - X_{S2}) \Rightarrow 0.01974 = 1.54 * (0.222 - X_{S2})$$
 (3.19)

$$S_1/S_2 = 0.014, \quad X_{S1} = 0.222, \quad X_{S2} = 0.209$$

$$y_{average} = \frac{S_1 * X_{S1} - S_2 X_{S2}}{S_1 - S_2} \Rightarrow y_{average} = 0.874 \tag{3.20}$$

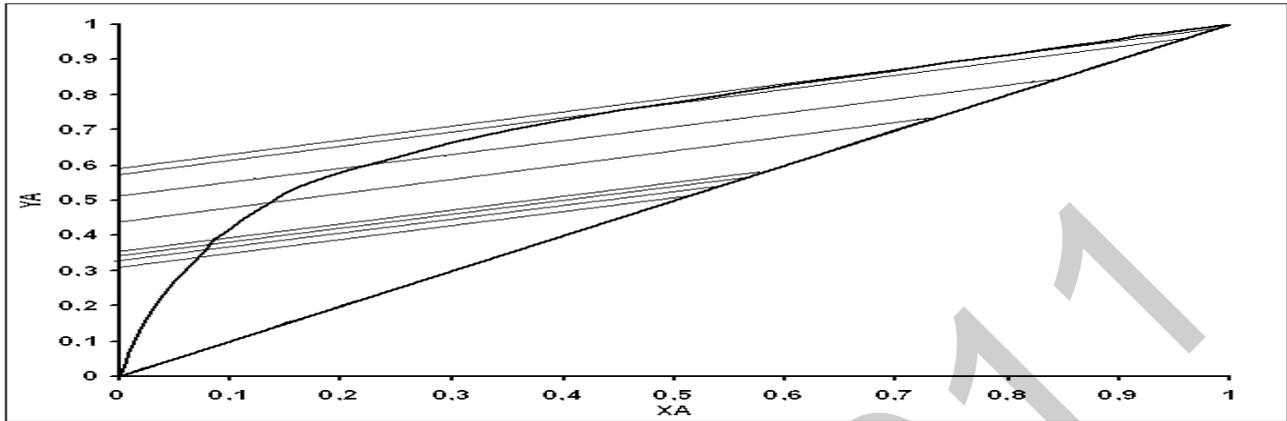


Figure 3. Equilibrium curve and Operation lines for the case studied

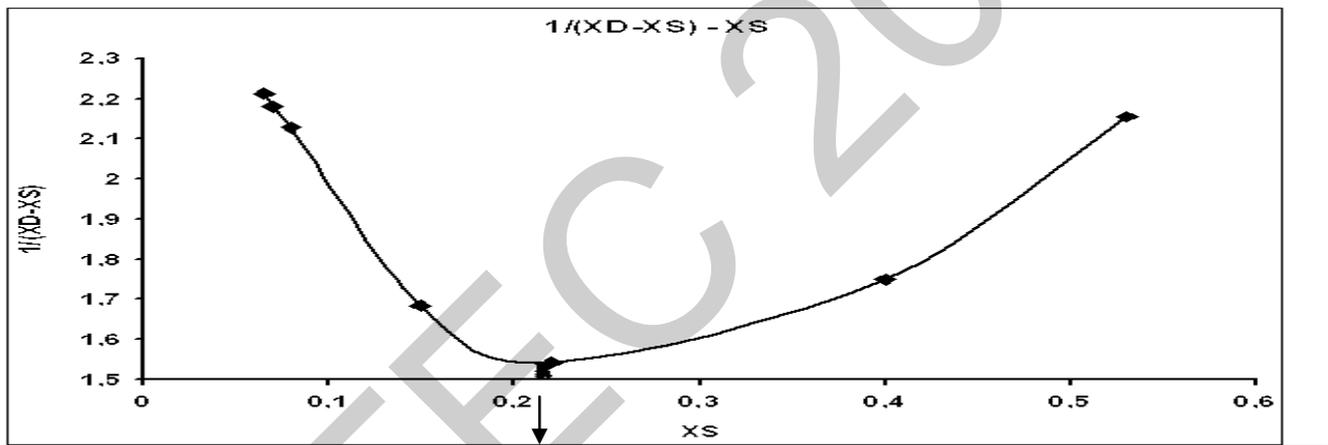


Figure 4. Relationship between  $1/(X_D - X_S)$  and  $X_S$  values.

$$H_{Theo} = \frac{G_y}{K_y a} = \frac{7.4}{0.179} = 41.37 \tag{3.21}$$

$$N_{Theo} = \int_{y_1}^{y_2} \frac{dy}{y - y^*} = \frac{y_2 - y_1}{\Delta y_L} = N_{Theo} = \frac{(y_w - y_F)}{\Delta y_L} = \frac{(0.209 - 0.222)}{-0.379} = 0.0343 \tag{3.22}$$

$$\Delta y_L = \frac{(y_2 - y_2^*) - (y_1 - y_1^*)}{\ln \frac{(y_2 - y_2^*)}{(y_1 - y_1^*)}} = \Delta y_L = \frac{(0.209 - 0.59) - (0.222 - 0.60)}{\ln \frac{(0.209 - 0.59)}{(0.222 - 0.60)}} = -0.38 \tag{3.23}$$

Column Height (Z) is determined as follows:

$$Z_{Theo} = H_{Theo} * N_{Theo} \Rightarrow Z_{Theo} = 41.37 * 0.0343 = 1.42 \text{ m} \tag{3.24}$$

The column height is evaluated as 1.42 m and by comparing with the real packed height of 1.25 m, correction factor (e) is calculated for the column studied as follows:

$$Z_{Real} = Z_{Theo} * e \Rightarrow e = \frac{Z_{Real}}{Z_{Theo}} = 0.88 \quad (3.25)$$

it is shown that the equation used for mass transfer coefficient can be written as follows:

$$K_y a = e^{-1} * 1.28 * 10^{-5} * (V)^{0.64} (L)^{0.48} \quad (3.26)$$

## CONCLUSION

The evaluated packed distillation column height is in satisfactory agreement with the real one. The separation efficiency of packed column is generally expressed in terms of height equivalent of theoretical plate (HETP). For distillation at total reflux, HETP may be calculated by the following equation:

$$HETP = H_{Theo} * e = (Z_{Theo} * e) / N_{Theo} = Z_{Real} / N_{Theo} \quad (3.27)$$

This work provides a new tool for those concerned with the design or batch performance of packed distillation columns. It gives a simple method to assess the sensitivity of a packed bed to batch distillation.

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# EXPERIMENTAL AND NUMERICAL MODAL ANALYSIS OF A CRACKED CANTILEVER BEAM

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## Abstract:

Structural damage detection using non-destructive methods is a research area of great interest for structural systems and their analysis. Information about the existence, location and extension of the cracks by non-destructive test data can be used to plan the next steps of the engineering design problems. In this study, vibration analysis of a cracked cantilever beam (CCB) is performed in order to identify the existence of the crack in the cantilever beam. An experimental set up and numerical analysis is carried out to calculate the mode shapes and natural frequencies of the CCB. The experimental and numerical results are compared with each other. Some interesting correlations are found between experimental and numerical natural frequency values.

Keywords: Modal analysis; crack; mode shapes; natural frequencies.

## 1. INTRODUCTION

Most of the structural failures are due to the presence of cracks. Several different approaches have been developed for early detection and localization of cracks. As a result, a variety of analytical, numerical and experimental investigations now exist.

A crack in a structure induces a local flexibility which significantly affects the dynamic behavior of the whole structure. It causes a change in the natural frequency of vibration associated with the mode which prevails in the vicinity of this location.

A review of vibration based methods for testing cracked structures has been published by Dimarogonas (1996).

The crack was modeled as a local flexibility and the equivalent stiffness using fracture mechanics methods by Dimarogonas (1976) and Paipetis and Dimarogonas (1983).

Adams and Cawley (1979) developed an experimental technique to estimate the location and depth of a crack using changes in natural frequencies.

Rizos and Aspragathos (1990) proposed a method used to identify cracks in structures by measuring its modal characteristics.

Ostachowitz and Krawczuk (1991) replaced the crack section with a spring and done model analysis for each part of the beam using appropriate matching conditions at the spring location.

Chati et al. (1997) are utilized bilinear frequency in order to define effective natural frequencies for the piecewise linear system analysis.

## 2. OBJECTIVES

In this study structural crack identification has been carried out by comparing measured natural frequencies and mode shapes. One specific objective of the present study is to determine if the crack locations could be identified from changes in the mode shapes and eigenfrequencies of vibration of the structure. To accomplish the objectives, a numerical and experimental study of a CCB was carried out. The results for an uncracked cantilever beam (UCB) are compared with dynamic response, like frequencies and mode shapes of vibration for a CCB with specific crack location and depth experimentally and numerically.

## 3. NUMERICAL ANALYSIS

Various numerical methods have been developed to derive important fracture parameters like Stress Intensity Factor (SIF), Energy Release Rate (ERR), Crack Tip Opening Displacement (CTOD) and J-integral in Fracture Mechanics. Finite Difference Method (FDM), Finite Element Method (FEM), Finite Volume Method (FVM) and Boundary Element Method (BEM) are some of commonly used numerical methods to determine the fracture parameters.

FEM has been widely employed for the solution of problems in linear elastic and elasto-plastic fracture problems. However, the high stress and strain gradients near the crack tip require very refined meshes and special elements at the crack tip. This has to be done in order to obtain accurate stress values near crack tip. Thus, numerical modeling of CCB has been performed using the Finite Element (FE) procedure with special FEs at the crack tip. An example of standard and crack tip eight-node elements used in numerical analysis can be seen in Figure 1.

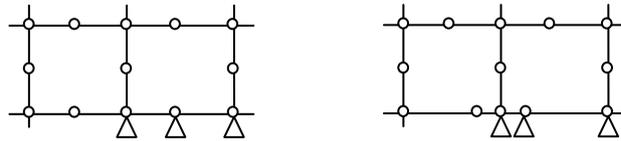


Figure 1. Standard and crack tip eight-node isoparametric elements

The commercial FE package ANSYS was used to obtain the numerical results. The CCB has been modeled as in Figure 2.

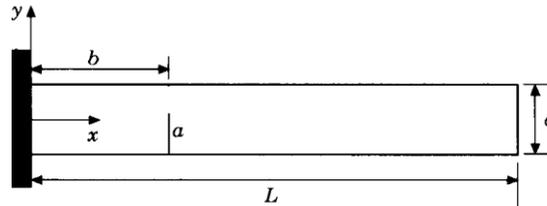


Figure 2. Cracked Cantilever Beam (CCB) geometry

The test rig comprises a cantilever aluminum beam,  $L=440$  mm long,  $d=40$  mm wide and  $h=0.28$  mm thick with a crack  $b=83$  mm away from the clamped edge. The mechanical and electrical material properties of the aluminum CCB beam are defined in Table 1.

Table 1. Material properties of the CCB

Aluminum	
$E[N\ m^{-2}]$	$70*10^9$
$G[N\ m^{-2}]$	$26.92*10^9$
$\rho\ [kg\ m^{-3}]$	2710

In analysis of the CCB and UCB; 14115 nodes, 8938 SOLID45 elements are used in ANSYS (Figure 3). Block Lanczos method is used for the mode extraction from the reduced solution.

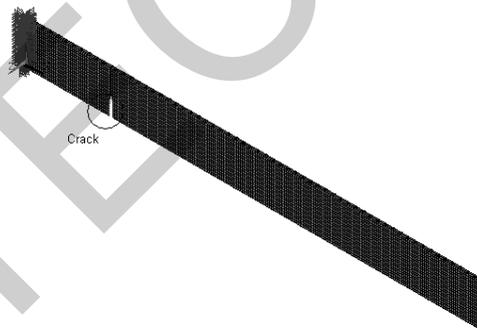
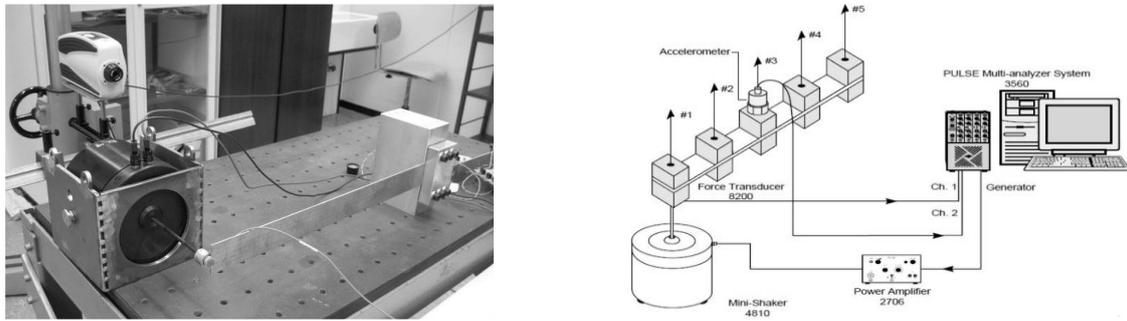


Figure 3. CCB ANSYS model

#### 4. EXPERIMENTAL ANALYSIS

Besides the numerical modal analysis with the standard FE software ANSYS, the experimental modal analysis was performed in order to find a correlation between cracked and uncracked beam natural frequency results.

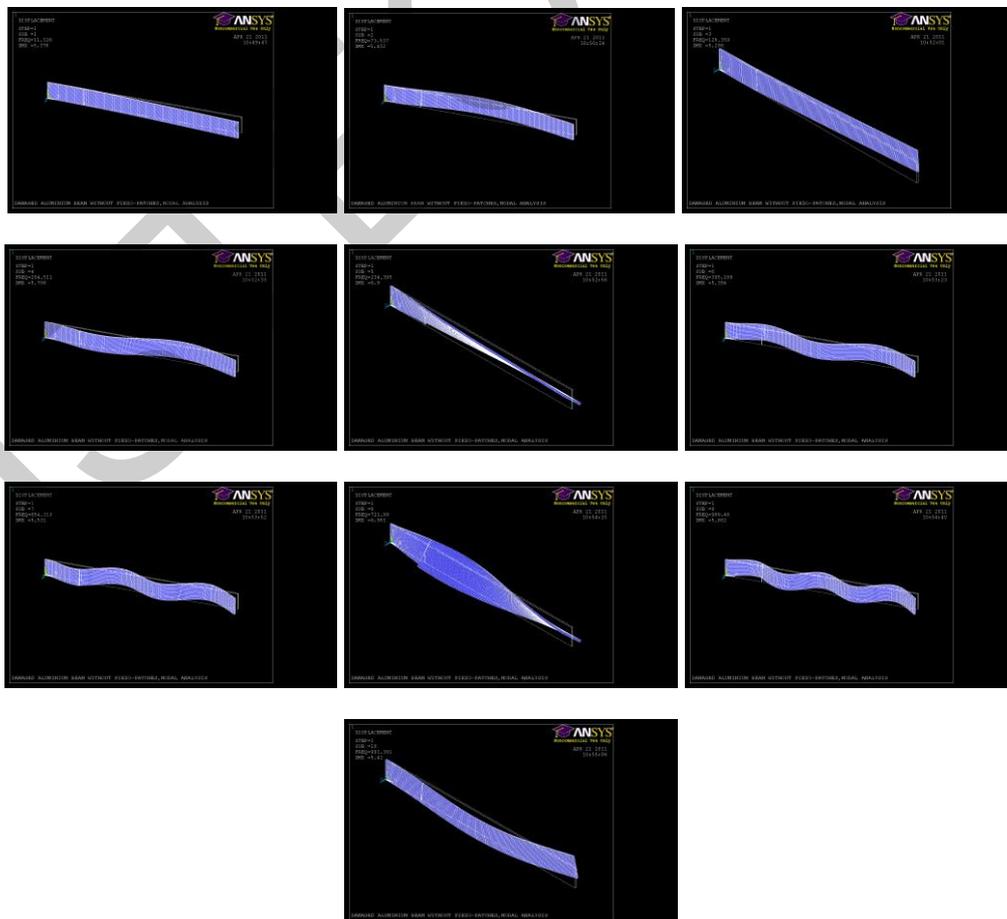
In experimental implementation, the real dynamic behavior of the beam has been represented using a laser Doppler vibrometer, accelerometer and PULSE package program to measure the velocity at special points marked on the beam. A dynamic signal analyzer Brüel & Kjaer 2035 with two channels and a generator module was utilized for the data acquisition. The experimental setup and utilized equipment are presented in figure 4. The free-vibration excitation is considered using a shaker applied at the free end of the beam. The signal data obtained from the PULSE program have been imported to the MATLAB program for obtaining the frequency response function values and the mode shapes.



**Figure 4.** Experimental setup for modal analysis with PULSE system a) experimental setup at Ruhr- Universitat Bochum[8], b) scheme of the experimental setup according to [9].

**CONCLUSIONS AND RESULTS**

The numerical results were obtained from a dynamic analysis using a FE modeling of the CCB. Ten numerical modes are given in Figure 5. The 3<sup>rd</sup>, 5<sup>th</sup>, 8<sup>th</sup> and 9<sup>th</sup> modes are the torsional numerical modes and the other modes are bending modes. The comparison of the results confirms the expected difference between the eigenfrequencies of the beam with and without crack. In this way it has been confirmed that the crack existence can be detected by performing the modal analysis and determining the eigenfrequencies of a structure under investigation. Experimental modal analysis involves only the bending mode shapes, since due to the implementation of the uniaxial accelerometer only the measurement of acceleration in direction perpendicular to the longitudinal axis of the beam could be performed. In this way the bending mode shapes were determined experimentally. Additional information is acquired by performing the numerical analysis, which also provides information about the torsional modes. As expected, higher influence of the crack existence is recorded with the torsional eigen modes, which is observed through a remarkable difference between the torsional modes eigenfrequencies of the UCB and CCB. Table 3 shows a remarkable value of the third (torsional) eigenfrequency determined numerically. Another observation of interest is agreement between the numerically and experimentally determined eigenfrequencies. On the other hand the measurement of the free-vibration mode-shapes and their corresponding eigenfrequencies can not indicate the exact crack location although it can be used to indicate the crack existence through differences in determined eigenfrequencies. Additional research is required to develop non-destructive testing technique to evaluate the crack location which is a topic of the ongoing and further investigations.



**Figure 5.** CCB Bending and Torsional Mode Shapes

In Table 3, 4, 5 and 6 natural frequencies are compared for CCB and UCB models. It can be clearly seen from the tables that the most remarkable results are obtained for the first mode.

In Table 3 the 3<sup>rd</sup> numerical natural frequency value is remarkable.

The experimental results are mostly affected by material properties and environmental conditions. Mesh structure and the crack tip element are the most important parameters for the numerical analysis.

**Table 3 Numerical natural frequencies of CCB and UCB**

Modes	without crack	with crack	Percentage difference
1	11,765	11,326	3,88
2	73,701	73,537	0,22
3	164,812	128,359	28,40
4	206,475	204,511	0,96
5	244,839	234,395	4,46
6	405,097	395,189	2,51
7	670,759	654,319	2,51
8	737,907	721,99	2,20
9	995,835	989,48	0,64
10	1004	991,391	1,27

**Table 4 Experimental natural frequencies of CCB and UCB**

Modes	without crack	with crack	Percentage difference
1	14,65	13,803	6,14
2	73,24	74,992	2,34
4	205,1	204,12	0,48
6	405,3	400,32	1,24
7	668,9	658,21	1,62
10	1025	1003,6	2,13

**Table 5 Numerical and experimental natural frequencies of UCB**

Modes	Numerical- without crack	Experimental- without crack	Percentage difference
1	11,765	14,65	19,69
2	73,701	73,24	0,63
4	206,475	205,1	0,67
6	405,097	405,3	0,05
7	670,759	668,9	0,28
10	1004	1025	2,05

**Table 6 Numerical and experimental natural frequencies of CCB**

Modes	Numerical- with crack	Experimental- with crack	Percentage difference
1	11,326	13,803	17,95
2	73,537	74,992	1,94
4	204,511	204,12	0,19
6	395,189	400,32	1,28
7	654,319	658,21	0,59
10	991,391	1003,6	1,22

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# EXPERIMENTAL CHARACTERICS OF A PIEZOELECTRIC FAN SYSTEM

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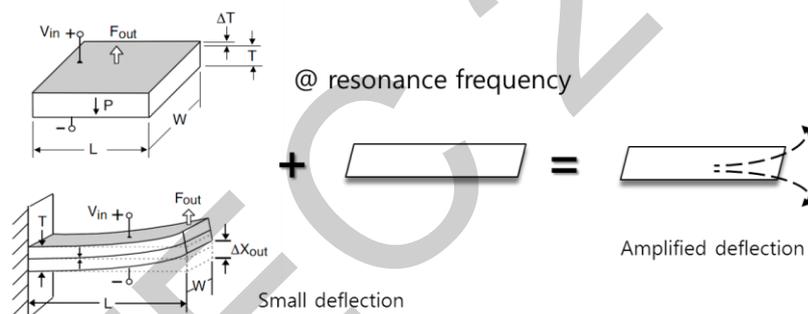
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## ABSTRACT

In this study, a heat sink design for a piezoelectric fan system is investigated. In order to find the proper geometry of the heat sink that improves the cooling performance of a piezoelectric fan system, experimental models were used for heat transfer predictions. The results give several concepts of heat sink design for a piezoelectric fan system. Experimental results verifies numerical model and new design of a piezoelectric fan fin shows enhanced heat transfer performance.

## 1. INTRODUCTION

As the advancement of semiconductor technology, high performance devices became smaller. However, a small device has limits on its heat transfer area thus maintaining safe surface temperature is become challenging. Therefore, forced convection effects are required but the conventional methods such as fins with a motor powered fan are challenged by space, noise and minimal energy issues. A piezoelectric fan shows possibilities on alternative for conventional cooling methods that because of the low power consumption and compact dimension. [1], [2] Chips on mobile devices and LED lights are viable implementation of piezoelectric fan system.

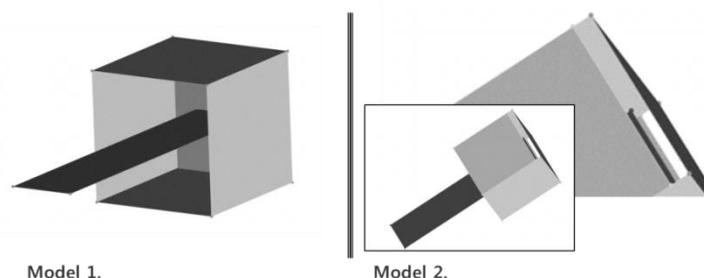


**Figure 1** Schematic of a piezoelectric fan.

Fig. 1 shows schematic of piezoelectric fan. A piezoelectric fan composed by two layers of piezoelectric material that contracts and expands when electric current applied. This piezoelectric patch produces curvature when one expands while another contracts. Under an alternating voltage, the piezo patch expands and contract alternately at the same frequency as the input signal. Normally, this effect is too small to use. However, when the flexible blade attached and this thin blade flipping with piezoelectric patch at the resonance frequency, folding displacement is greatly amplified.

## 2. MODELS FOR HEAT SINK GEOMETRIES

In this study, the tip is confined not only perpendicularly but also adjacently. This is the basis for the models shown in Fig 2.



**Figure 2** Two models of heat sink designs in a piezo fan system

Model 1 is the simple rectangular shape design to induce confining-flow concept when a piezo fan is active. This model simply blocks flow around a piezoelectric fan tip. It increases flow velocity and heat transfer area. However, the expected flow in this model has a stagnation problem. Model 2 shows a new model to avoid a stagnation problem in Model 1. Model 2 has narrow slits on the heat surface perpendicular to piezoelectric fan tip.

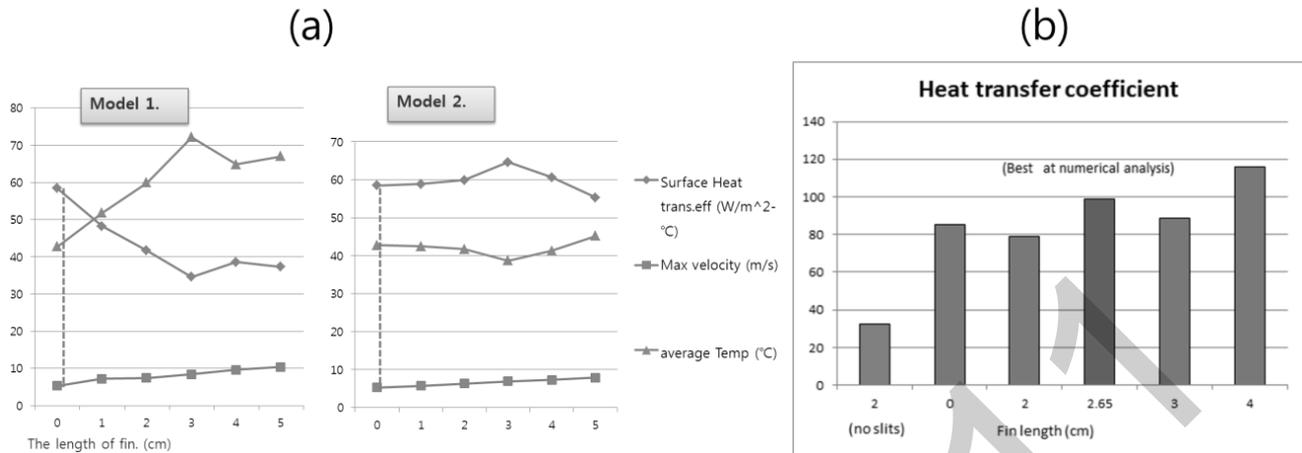


Figure 3 Results of previous study

Figure 3 is this two earlier model's numerical and experimental results. Model 1 shows a little bit higher flow velocities than model 2. However, the overall heat transfer rate is lower than the original fin model. This is because of the fin blocks flow interchanging between heated air with cool ambient air. Model 2 shows better heat transfer performance with a little smaller flow velocities. A slit on model 2 decreases the flow stagnation and improves the cooling effect. In the model 2, 3 cm-60% of piezo fan's length)-shows the best results. The implementation of fins is effective until 4 cm. By the time it reaches 5 cm, the cooling effect is worse than the beginning.

To find an appropriate heat-sink design for piezoelectric fan which enhances effectiveness of induced flow of piezoelectric fan and heat transfer, four models are shown below. As shown by Figures 1~4, Model 0 is only-fan model which compared by another 'finned' models. This model represents plain setting of normal a piezofan cooling system. Model 1 is 'narrowed' model. Model 1's fin is shrunk both horizontally and vertically compared to original fins with the slit Model. Also, another two models (Model 2, Model 3) were shrunk only horizontal or vertical direction of the previous fin-slit model.

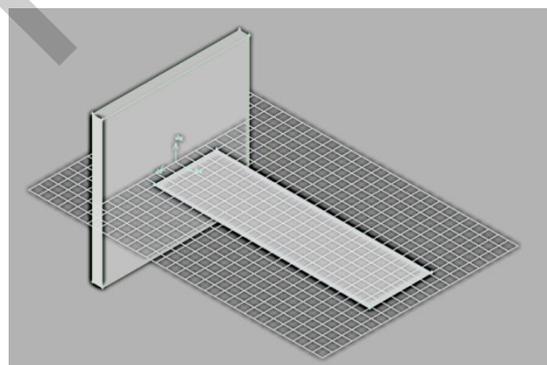
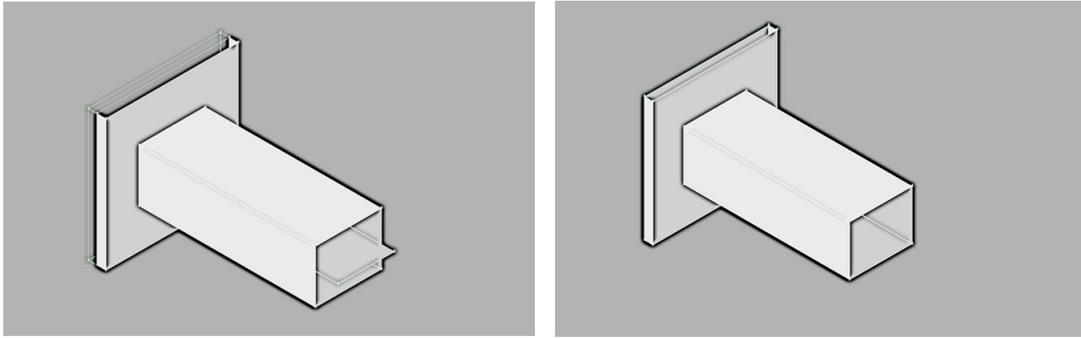
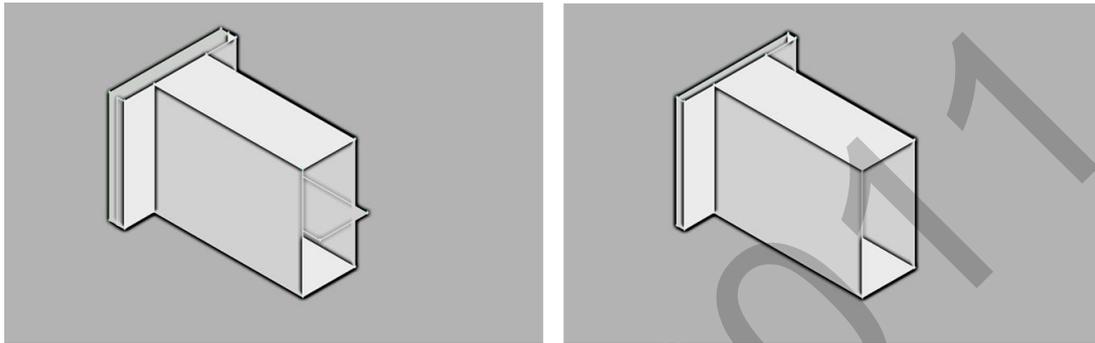


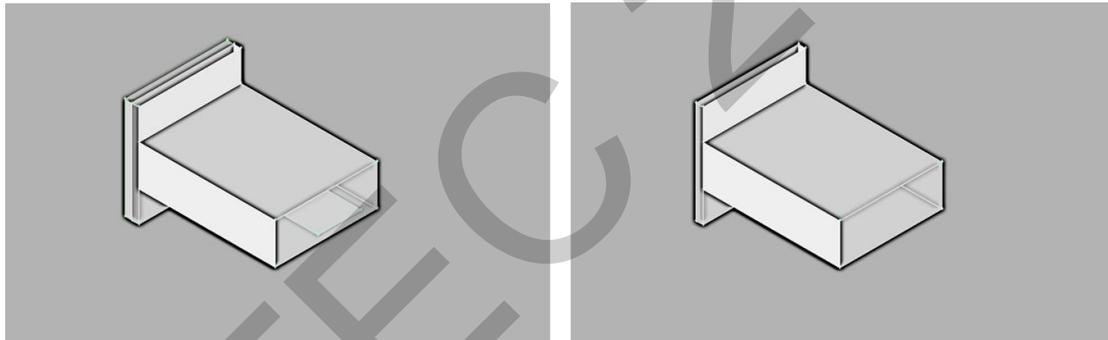
Figure 4 Model 0 no fin with 2mm fan-tip distance.



**Figure 5** Schematics of model 1



**Figure 6** Schematics of model 2



**Figure 7** Schematics of Model 3

### **3. EXPERIMENTAL METHODS**

Figure 8 shows a schematic of an experimental system. In this experiment, the low voltage piezoelectric fan kit was used. This piezofan operates at 115Hz and 15V of maximum operating voltage. The heat source is 12W white LED lamp. This LED lamp is attached on the 3 cm x 3 cm thermal conductive circuit. Thermal resistance of LED lamp to thermal tape junction is lower than 0.13 °C/W. LED Lamp and piezo fan are operated by each DC power supplies. The mini piezo fan drives board which coupled with small piezo fan.

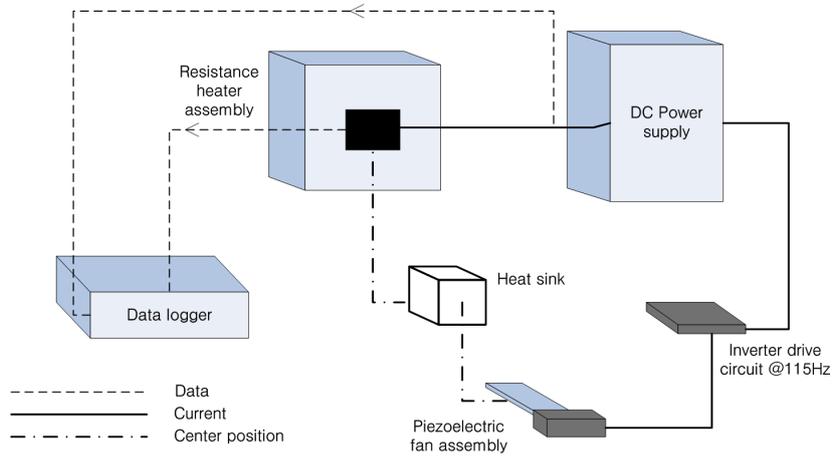


Figure 8 Schematic of experimental system.

4. EXPERIMENTAL RESULTS

Figure 9 shows the temperature variation of the each model with various outputs. Figure 9(a) shows the temperature profiles of the circuit board and Figure 9(b) shows the temperature difference between the surface and ambient air. All models of heat sinks show better cooling performance than no heat sink model. Model 1 shows best results with quite lower temperature compared to other heat sink models.

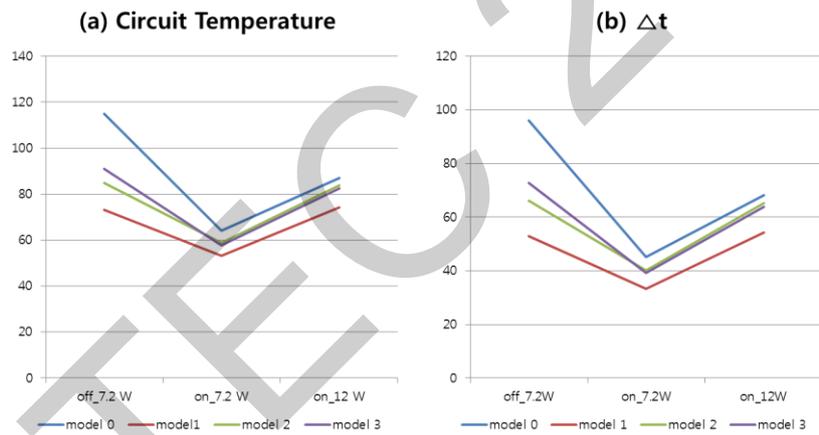


Figure 9 Temperature of LED circuit board of each setting

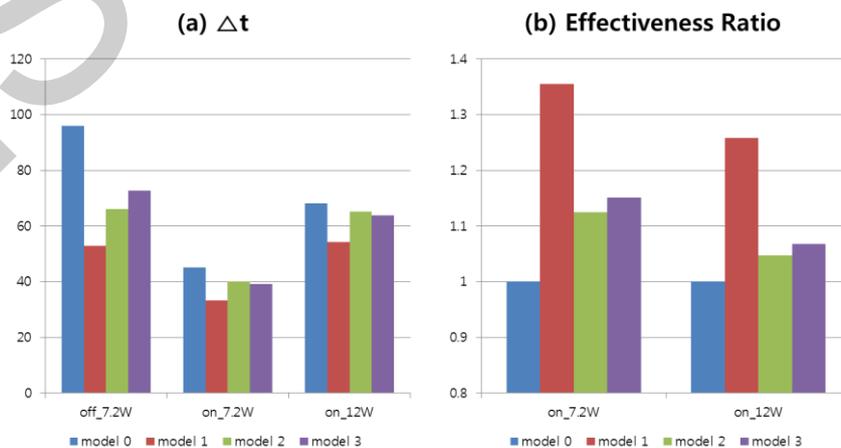


Figure 2 Comparison of each model.

Figure 10 shows the temperature differences and the rate of performance increase of each model, respectively. According to the results, Model 1 shows best performance. Nevertheless, it has smaller heat sink surface than the other models. Also, Model 2 shows better cooling performance than Model 3. This is caused by Model 2's vertical arrangement. This has slightly bigger surface than that of Model 3. But the tendency had reversed when the piezo fan is operated. Figure 10(b) shows the performance of each heat sink model with a piezo fan system. The best result is the case of Model 1. As we discussed earlier, this is caused by the vertical surface of heat sink. Heat sink Model 1 shows 35.5% enhancement of cooling performance.

## 5. CONCLUSIONS

Experimental models for a piezoelectric fan are studied. Heat sink design parameters of confining geometry models are suggested. Experimental analysis suggest the new design of heat sink model optimally. Among Models, Model 1 shows best performance. This is caused by the vertical surface of heat sink. Heat sink Model 1 shows 35.5% overall enhancement of cooling performance.

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# EXPERIMENTAL STUDY ON FLOW CONDENSATION HEAT TRANSFER CHARACTERISTICS OF PURE R134A VAPOR INSIDE A VERTICAL SMOOTH TUBE

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## ABSTRACT

In this study, condensation of pure refrigerant R134a vapor inside a smooth vertical tube was experimentally investigated. The test section was made of a copper tube with the outside diameter of 9.52 mm and 1 m. length. The experimental tests were carried out at a fixed mass flux of 50 kg/m<sup>2</sup>s with saturation pressure ranging between 5.9 and 6.7 bar. The effects of vapor quality change ( $\Delta x$ ), saturation pressure, temperature difference between the refrigerant and tube wall ( $\Delta T$ ) on the heat transfer performance were analyzed throughout experimental data. Obtained results showed that average Nusselt number decreases as the saturation pressure increases. Besides that, heat can be removed from the refrigerant at a higher rate at relatively low pressure values at the same temperature difference,  $\Delta T$ . Finally, most widely used condensation heat transfer coefficient correlations for condensation in smooth tubes at various position such as Shah (1979-2009), Cavallini and Zecchin (1971), Dobson (1994), Haraguchi (1994), Traviss (1973) were analyzed through the experimental data. Best fit was obtained with Dobson (1994) correlation with an absolute deviation of 22 %.

## Nomenclature

A	: Heat transfer area, $\pi dL$ , [m <sup>2</sup> ]
$c_p$	: Specific heat capacity [Jkg <sup>-1</sup> K <sup>-1</sup> ]
d	: Tube diameter [m]
g	: Acceleration of gravity [m/s <sup>2</sup> ]
$h_{avg}$	: Average heat transfer coefficient [W/m <sup>2</sup> K]
$h_{LG}$	: Latent heat [Jkg <sup>-1</sup> ]
k	: Thermal conductivity [W/mK]
l	: Characteristic length [m]
L	: Length of the test section [m]
m	: Mass flow rate [kg/s]
$q''$	: Heat flux [W/m <sup>2</sup> ]
Q	: Heat removal rate [W]
T	: Temperature [°C]
$\Delta x$	: Vapor quality change

## Subscripts

avg	: average
i	: inlet
o	: outlet
R	: R134a
sat	: saturated
w	: water

## INTRODUCTION

Condensation, which is generally observed in refrigeration systems, is an important multiphase phenomenon. Accurate design of this type refrigeration system is required for better performance with less energy usage. Nevertheless, due to the physical complexity of the multiphase flow, theoretical studies are restricted with certain flow patterns. Therefore, most of the researchers have focused on experimental studies. **Cavallini et al. (2001)** have investigated flow condensation of refrigerants (R134a, R125, R32, R410A, R236ea) inside a smooth horizontal tube experimentally. Experiments were conducted at 30-50 °C saturation temperature with mass flux ranging between 100-750 kg/m<sup>2</sup>s. Test section was made of a copper tube with 8 mm outside diameter and 1 m length. The effects of vapor quality, mass flux, saturation temperature and the temperature difference between the tube wall and the saturated refrigerant, on heat transfer coefficient were analyzed. Similar to that study, **Jung et al. (2003)** have done experiments for flow condensation of different refrigerants (R12, R22, R32, R123, R125, R134a, R142b) inside a horizontal smooth tube. For those experiments, saturation temperature was 40 °C and mass flux ranged between 100-300 kg/m<sup>2</sup>s. Test section was made of a copper tube with 9.52 mm outside diameter and 1 m length. **Dalkilic et al. (2009)** have investigated laminar film condensation of R134a inside a vertical tube. Test section was made of a copper tube with 7.1-8 mm outside diameter and 0.5 m length. Experiments were conducted at 29-263 kg/m<sup>2</sup>s mass flux and 0.77-0.1 MPa saturation

pressure. **Oh et al. (2005)** researched complete condensation of water vapor inside a vertical smooth tube passive condenser. Test section was made of stainless steel tube with 2.4 m in length and 26.6 mm in outside diameter. The aim of these experimental studies is to obtain experimental data under different operating conditions. By using these data, correlations are suggested to define the heat transfer performance of the system. Moreover, obtained data is used to check validity range of heat transfer coefficient correlations. **Valladares (2003)** summarized the correlations published in literature.

In this study, condensation of R134a vapor inside a smooth vertical tube was investigated through experimental analysis. Obtained results were compared with **Shah (1979-2009)**, **Cavallini and Zecchin (1971)**, **Dobson (1994)**, **Haraguchi (1994)**, **Traviss (1973)** heat transfer coefficient correlations.

## METHODS AND PROCEDURES

An experimental set up is built to investigate heat transfer characteristics of R134a vapor condensing in a vertical tube (Fig. 1). It consists of two main subsystems; the vapor compression and water loops. The vapor compression loop consisted of a storage tank, pump, flow meter, evaporator and condenser. Test section was designed as tube-in-tube type heat exchanger with refrigerant flowing in the inner tube and water flowing in a counter flow direction in the annulus. Outside diameter of this section is 9.52 mm and the condenser length is 1 m. At the inlet and exit of the test section, pressure and temperature sensors were mounted. At these points, sight glasses were used to observe the R134a flow. Surface temperatures of the test tube were measured at six different points. At the exit of the test section, a liquid-vapor separator mounted. In that way, vapor quality change at the test section can be measured throughout the experiments.



**Figure 1:** Experimental Set up

At the inlet of the test condenser, R134a vapor is obtained by supplying hot water to the evaporator. Evaporator is a plate type heat exchanger. Condenser and the storage tank are conditionalized by using cold water in order to control the liquid level in the storage tank. Temperatures of the R134a and water are measured with thermocouples. Uncertainties for the sensors used in experiments are given in Table 1.

**Table 1:** Uncertainties for the sensors

Sensor	Uncertainty
Thermocouples	0.05 °C
Pressure transmitter	0.5 %
Flow meter (R134a)	0.25 %
Flow meter (Water)	4 %

Heat removed from the test section is calculated by measuring the mass flow rate ( $\dot{m}_w$ ) and temperature difference of the cooling water at the inlet and outlet.

$$\dot{Q} = \dot{m}_w c_{p,w} (T_{w,i} - T_{w,e})$$

Vapor quality change of R134a along the test section is calculated by using the heat removal rate (Q).

$$\Delta x = \frac{\dot{Q}}{\dot{m}_R h_{LG}}$$

Average heat transfer coefficient and average Nusselt number were defined as follows.

$$h_{avg} = \frac{\dot{Q}}{A(T_{sat} - T_{wall,avg})}$$

$$Nu_{avg} = \frac{h_{avg} l}{k}$$

Here, 'l' is defined as the characteristic length for film condensation inside tubes.

$$l = \sqrt[3]{\frac{V_L}{g}}$$

Required thermodynamic and transport properties of refrigerant were obtained by REFPROP program.

### RESULTS

Experiments were conducted at 50 kg/m<sup>2</sup>s mass flux. Firstly, effect of saturation pressure on condensation heat transfer performance was investigated. In Figure 2, change of average Nusselt number for different saturation pressure is given.

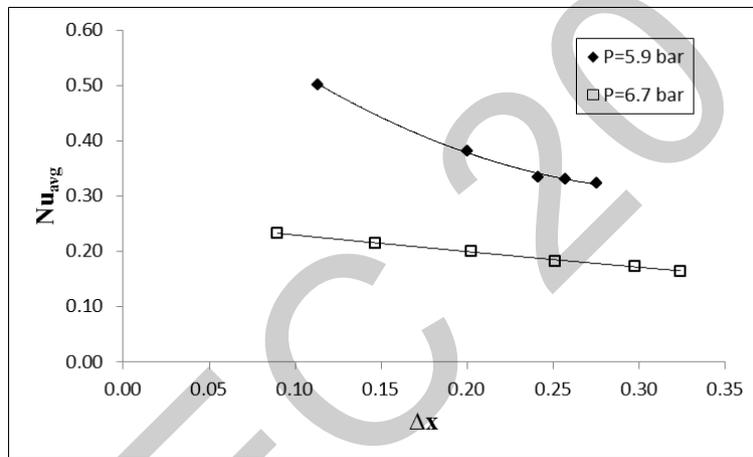


Figure 2: Effect of saturation pressure on average Nusselt number.

It is clearly seen that increasing saturation pressure causes a decrease in average Nusselt number. Moreover, increasing vapor quality change along the test section causes a decrease in average Nusselt number for each saturation pressure. Increase in vapor quality change is obtained by increasing the difference between saturation temperature and tube wall temperature (ΔT). In Figure 3, change in heat removal rate (Q) at test section according to ΔT is given.

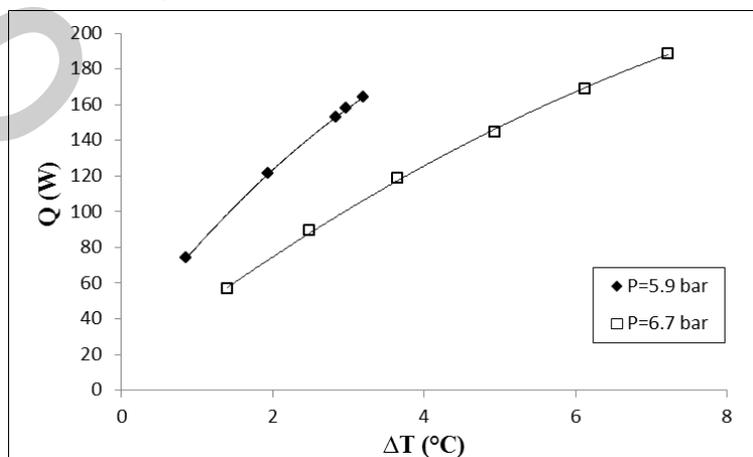
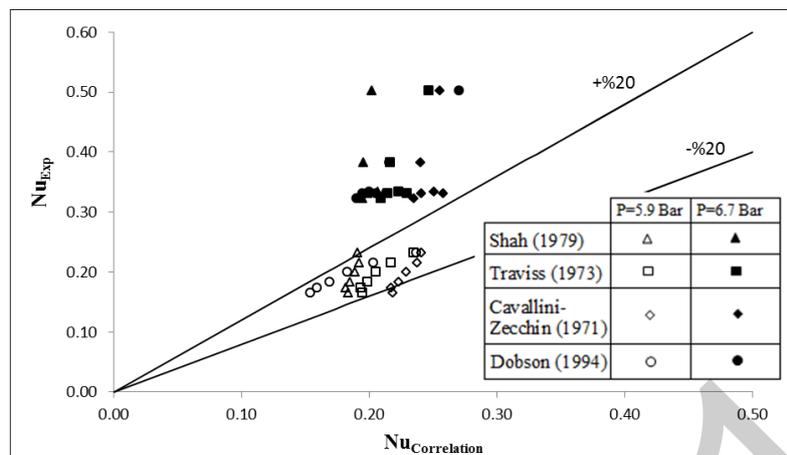


Figure 3: Change in heat removal rate (Q) according to ΔT

In Figure 3, it is clearly seen that heat removal rate at the test section is higher at low saturation pressure. As expected, heat removal rate has increased with increasing ΔT. To remove the same amount of heat from test section under different saturation

pressures, low temperature difference has been obtained at low saturation pressure. This is very important for efficient condenser design.

Finally, heat transfer coefficient correlations published in literature were analyzed. In Figure 4, comparison of correlation Nusselt number with experimental data is given.



**Figure 4:** Comparison of correlations with experimental data

In Figure 4, it is seen that the results obtained from correlations for low saturation pressure deviate within a range of -20% to +20%. Due to the uncertainty of the experimental data estimated as  $\pm 7-14\%$ , obtained results show good agreement. As the saturation pressure of the refrigerant increases, the experimental data shows that correlations overestimate the heat transfer coefficient. As mentioned before, correlations were obtained for certain experimental data. For that reason, an improvement is required for the given correlations. The best result is obtained from **Dobson (1994)** correlation. The absolute mean deviation and standard deviation are obtained as 24%, 19%, respectively.

## CONCLUSION

In that study, condensation of R134a vapor inside a vertical smooth tube investigated experimentally. Experiments were carried out to measure the heat transfer coefficient via Nusselt number under different operating conditions. Under constant mass flux, effects of different saturation pressure and temperature difference ( $\Delta T$ ) to condensation heat transfer coefficient were analyzed. It is presented that saturation pressure has an important effect on condensation heat transfer in tube. At low saturation pressure, higher heat removal rate has been obtained. Another important parameter is the temperature difference between tube wall and the saturated refrigerant ( $\Delta T$ ). Under different  $\Delta T$  values, experiments were conducted and heat transfer coefficients were measured. Obtained results showed that for high  $\Delta T$  values, heat removal rate is higher. Finally, comparison of the heat transfer coefficient correlations has been done. The best result is obtained from **Dobson (1994)** correlation. The success of the correlations to predict the experimental data may differ according to the operating conditions.

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# EXPERT IDEA ON LIQUID LIMIT AND PLASTIC LIMIT ESTIMATION WITH SOIL RESISTIVITY PROFILE

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**Abstract**— This paper presents the idea on determination of liquid limit and plastic limit with soil electrical resistivity in geotechnical investigations. Depending on the moisture contents, the soil behavior is revealed as solid, semisolid, plastic and liquid states in geotechnical engineering and other division of civil engineering. Determination of liquid limit and plastic limit of soil in conventional laboratory test is very tedious, slower and costly for the laboratory testing example as fall cone testing with a lot of collected soil sample. In this work, a method of soil liquid limit and plastic limit determination with electrical resistivity is revealed to define the state of soil as well as the relationship of soil particle distribution in the soil site investigations of geotechnical engineering. In addition, soil resistivity measurements with moisture contents and conventional laboratory test as fall cone test are performed whereas experimental results in laboratory and results from the available literature review are considered. A good correlation of soil electrical resistivity and moisture contents is demonstrated in results to determine the liquid limit, LL and plastic limit, PL in soil behavior. The research is most significant to obtain faster, cost-effective and consistent performance in soil liquid limit and plastic limit determination through electrical signal for a wide range of applications in geotechnical engineering.

**Keywords-** *Liquid limit, Plastic limit, Fall cone test, Electrical resistivity profile*

## 1. Introduction

Observations of soil state behaviors and determinations of soil strength are prerequisite in highway and road engineering including construction of highway embankments, earth dams, geotechnical engineering, and other divisions of civil engineering (Benson and Trast, 1995). The behaviors of soil can be divided into the basic states of solid, semisolid, plastic and liquid depending on the moisture contents. The change from one state to the next is measured with increasing of moisture contents. These smooth transitions are considered for introducing LL, PL in geotechnical investigations. The moisture content between PL and LL is defined as the plasticity index, PI where PI is a measure of the plasticity of soil.

General techniques for the determination of this soil LL and PL were conducted through the laboratory tests, in-situ tests and geophysical methods (Avnimelech et al., 2001; Sridharan and Nagaraj, 2005). The laboratory test is generally conducted to obtain the moisture contents for changing the behaviors of soil states in soil investigations (Elshorbagy and Mohamed, 2000). As an example, in fall cone test, moisture contents are obtained corresponding to the empirical cone penetration to determine LL and PL of soil. Determination of LL and PL in soil is also tedious, slower and costly using conventional laboratory testing

based on the procedure of testing. In addition, conventional methods are usually in difficulties during the collecting of dry sample and soil sampling processes, which may change the original value of the testing results.

Determination of soil LL and PL with electrical resistivity shows the important role in the construction of highway embankments, structural engineering and others geotechnical engineering (Osella and Favetto, 2000; Yoon and Park, 2001 ). The electrical resistivity of the soil is manipulated by soil type, degree of saturation, concentration of ions, water contents and temperature of pore water. Transport properties such as electrical conductivity (Friedman, 2005), soil resistivity (Huang and Fraser, 2002), thermal conductivity, and hydraulic conductivity show associations with the porosity, water saturations, composition, salinity of the pore water, grain size distribution, and particle shape and orientation (Samouelian et al., 2005 ).

The fall cone test for determination of liquid limit and plastic limit is performed in this work to get the empirical relationship with soil resistivity profile for the collected sample of different type soil. The resistivity of the collected soil is measured with the high resistance meter for each sample of the estimation of LL and PL. The relationship is shown to determine the soil state behaviors with the measurement of soil resistivity corresponding to the different moisture contents in collected soil. Experimental results and study from the available literature are considered to justify the measurements of LL and PL with electrical properties in geotechnical investigations. Background and objective of this study intends the relationships between electrical resistivity and determination of LL and PL in context of electrical properties of collected soils. The aim of the research is to obtain a set of consistent measurements of LL and PL which is used to yield an equivalent model with the electrical performance in geotechnical investigation system.

## 2. Methodology

The research work on determination of LL and PL of soil through electrical resistivity is conducted at University Kebangsaan Malaysia with the cooperation of Ministry of Science, Technology and Innovation of Malaysia. The fall cone test for the different type of soil sample is done in the geotechnical laboratory of Civil and Structural Department, UKM. The data collection for soil resistivity measurement is carried out using digital precision multimeter, model 8846A, Fluke at construction site of University Kebangsaan Malaysia (UKM) in Bangi, Selangor, Malaysia shown in Fig. 1. The study on the relationship development between soil electrical resistivity and LL, PL of soil is done and the analysis is performed using MATLAB 2009 in Geotechnical Laboratory, Faculty of Engineering and Built Environment, UKM.



Figure 1. Soil electrical resistivity measurement for soil state determination

Conventionally, LL and PL estimation of soil is estimated with fall cone test as moisture contents of soil corresponding to the cone penetration in soil considering the specifications of penetration depth and size of cone in the test (Sridharan and Gurtug, 2004). As an example, moisture contents corresponding to the 20 mm cone penetration for 0.75 N cone weight reveals the LL of the soil sample in fall cone test.

In the research, soil resistivity is taken considering the increasing of moisture contents to get the soil state behaviors. Decreasing of the resistivity of surface soil is dependable on the increasing of water contents of soil in geotechnical field. Thus, the relation of soil water content with soil resistivity at the time of measurement clearly is major factors contributing to soil EC surveys. The resistance,  $R$  in unit of Ohm ( $\Omega$ ) of soil sample is defined with fundamental equation of electrical engineering called as Ohm's law.

$$R = \frac{V}{I} \quad (1)$$

Where  $V$  is the potential difference in volt (V) and  $I$  is the supplied current in ampere (A) of electrical measurements. The resistivity,  $\rho$  of compacted soil is defined from the measured resistance including probe space and area of the soil sample.

$$\rho = \frac{R \times A}{l} \quad (2)$$

Where  $R$  is the resistance ( $\Omega$ ) of the material,  $l$  is the length of the conductor (m), and  $A$  is the cross sectional area ( $m^2$ ).

When a constant voltage is applied to one of the two probes placed in the soil, the current that flows between the probes is inversely relative with the resistance of the soil (Doolittle et al., 1994; Kelleners et al., 2005). Electrical resistivity shows indeed strong variations that principally depend on variations of water contents in soil (McNeill, 1980; Saarenketo, 1998). The electric current passed through the soil between two steel probes makes an electric field in surface soil investigations. The voltage difference as well as electric field strength in geo-electric field is obtained for soil resistivity measurements. The analog electrical signal is converted into a digital value for getting robust performances using criteria of Analog to Digital Converter (ADC) in soil resistivity observations.

The soil resistivity measurements for determination of LL and PL of soil are done in this work using precision digital multimeter of Fluke Company, model 8846A with accurate measurements and Kilo-Ohm scale for easier reading. The specifications and functions of digital multimeter shown in Table 1 for soil resistivity calculations include 100  $\mu A$  to 10 A current ranges, with up to 100 pA resolutions for the measurements techniques. High resistance meter with digital and analog configurations are used in our research to measure soil resistance with consistency.

Table 1 Specifications of insulation tester used in soil resistance measurements

	Specifications	Functions
Insulation Resistance Tester-Digital	Test Voltage	1000 V and 600 V
	Measuring ohms Ranges	10 $\Omega$ to 1 G $\Omega$ with up to 10 $\mu\Omega$ resolution
	Measuring current ranges	100 $\mu A$ to 10 A current range, with up to 100 pA resolution
	Measurement technique	2 x 4 ohms 4-wire

### 3. Results and Discussions

Modern research and innovations in geo-electric and system engineering have improved the ability to collect and process data with manifesting reliable subsurface soil properties of near surface soil profile. Usually, soil LL and PL is determined through the laboratory testing with demonstration of soil moisture contents corresponding to the reading of specified tools (Sridharan and Gurtug, 2004) in geotechnical characterizations. As an example, soil moisture contents corresponding to the specified cone penetration depth in millimeter is considered as LL for particular size of cone for the fall cone test method. PL can be estimated with another size of cone considering the moisture contents for specified cone penetration depth in millimeter. The laboratory tests of different soil sample are also costly and tedious to obtain the criteria of estimation of cone penetration, moisture contents in soil for geotechnical investigations (Sridharan and Nagaraj, 2005). The previous soil LL and PL estimation in laboratory is also time consuming system due to the collecting sample with fall cone test as well as obtaining dry sample of soil.

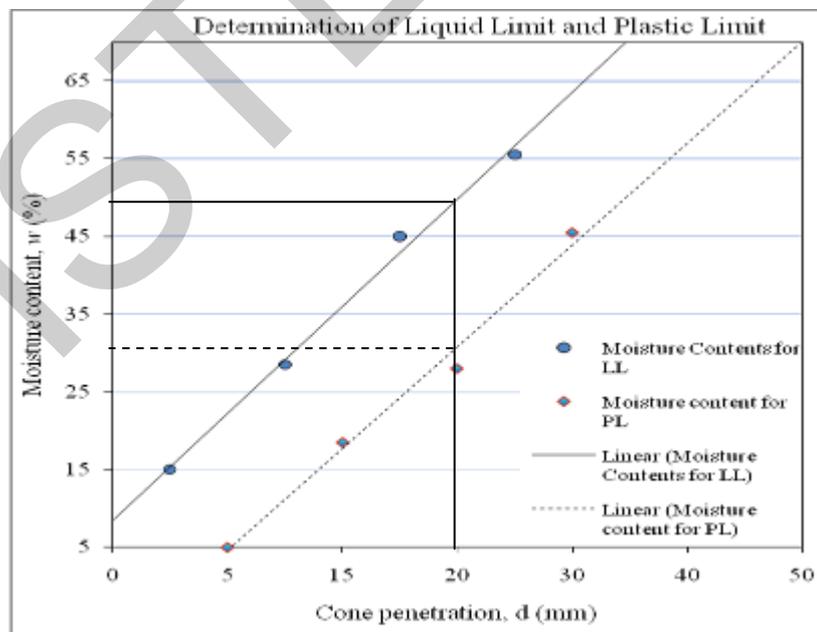


Figure 2. Fall cone test for liquid limit and plastic limit

In this research, fall cone test is performed and cone penetration size is obtained with increasing of water contents for determining LL and PL shown in Fig. 2. The LL of soil is observed using with the weight of cone as 0.75 N whereas the PL of soil is determined with 2.35 N as cone weight in the fall cone test. In both cases, the moisture contents are taken as LL and PL at the empirical cone penetration depth of 20mm. Figure 2 shows that about 49.5 % of moisture contents are considered as LL of soil according to the criteria of fall cone test in the investigated soil sample. Hence, PL is shown as about 30.75 percent moisture contents in soil including cone penetration of 20 mm in the convention laboratory test.

In this study, the resistivity of collected soil sample is determined according to the increasing of moisture contents in soil identifications. Figure 3 shows the soil resistivity decreases exponentially with increasing of moisture content in soil sample. Thus, the resistivity of soil sample is shown about 38 Kilo Ohm-meter ( $k \Omega\cdot m$ ) for 50 percent water contents in soil resistivity estimation.

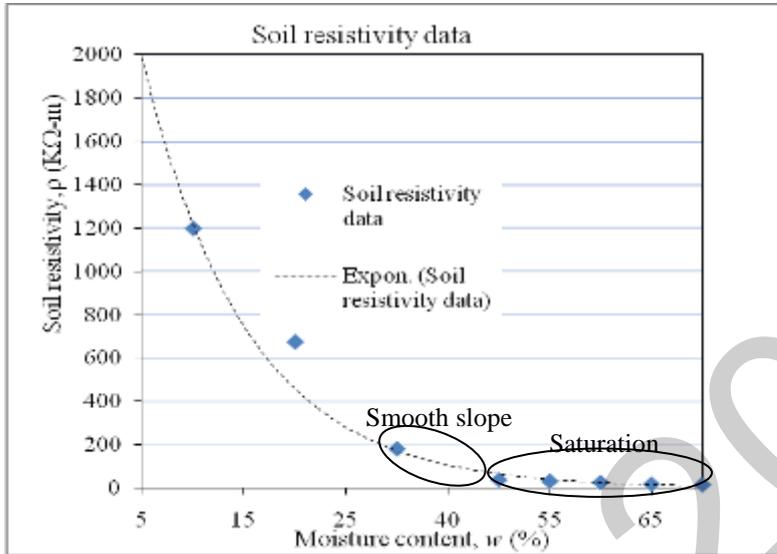


Figure 3. Soil resistivity observations with moisture contents

The resistivity of soil goes into the saturation state with increasing the moisture contents after 50 percent in the soil sample. Moreover, the smooth slope of resistivity data is observed in the range of 30 percent to 50 percent water contents shown in Fig. 3. The moisture content of the starting point of the saturation state is revealed as the LL of soil sample in the research criteria with soil resistivity profile. In addition, the initial moisture content of the smooth slope of soil resistivity data is demonstrated as the PL of soil state behavior observations.

The method of soil LL and PL determination through soil resistivity is faster, easier and more cost-effective than the conventional laboratory test in soil investigations. The soil resistivity measurements manifest better and robust performance in geotechnical monitoring systems. There is no criteria of collecting dry sample with certain temperature in geotechnical laboratory which is tedious, time consuming and labor intensive for soil type identification system. In this study, expert idea of soil LL and PL determination are taken from the measured resistivity data of collected soil sample through high resistance meter. Table 2 shows the data of obtaining empirical relationships of LL and PL with soil resistivity in geotechnical characterizations. This system is also consistent for data acquisition and analysis to estimate soil properties with non-destructive performance for roads and highway engineering, geotechnical and many other engineering structures.

Table 2 Soil LL and PL determination with resistivity profile

Sample No.	Sand (%)	Silt (%)	Clay (%)	Soil LL	Soil PL	Soil resistivity, K $\Omega\cdot m$
A	33.5	38.5	26.0	37.0	20.0	150
B	36.5	58.5	5.0	39.0	26.0	123
C	3.5	56.0	40.5	55.4	31.0	76
D	13.0	35.5	51.5	70.5	35.6	29

#### 4. Conclusions

A technique of soil LL and PL determination with electrical resistivity is revealed with the aim of achieving better performance in sensing of soil properties for geotechnical engineering. The empirical relationship is demonstrated to get the soil state behaviors through resistivity measurement in soil profile. The saturated state of resistivity with increasing of soil moisture contents is shown as LL of soil whereas the smooth slope in resistivity data before the saturation state is considered as PL of soil in this research work. The resistivity measurement of collected soil sample is able to obtain the better, faster and cost-effective performance in soil type estimation system. The analysis used in this study incorporates collected data with high resistance meter for soil sample in geotechnical characterizations. In addition, laboratory testing also verifies the idea for obtaining soil condition with soil electrical properties as reliable and consistent investigations in geotechnical profile. There will be future studies including more test data for different type of soil on refining this method to estimate earth parameters in particular applications of geotechnical engineering.

#### Acknowledgements

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# EXTRU-SPIN PROCESS OF EXTRUDED PART WITH HELICAL FINS

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## ABSTRACT

An extru-spin process of extruded part with helical fins could be developed by using rotating extrusion die. Twisting of extruded product is caused by the twisted conical helical die cavity. But, until now, because the process has used fixed extrusion die, it needs high load in order to twist billet and form fin shape on the surface of extruded part. So, during extruding part, in order not to twist part, the extrusion die is needed to rotate itself instead of twisting of part. It was known that it is possible to reduce extrusion load of part with helical fins through forming analysis of extru-spin process using rotating die. And it was known that, through the extrusion load analysis by DEFORM<sup>TM</sup>-3D software, optimal rotational velocity of rotating die can be founded according to reduction ratio of area and twisted angle of rotating die.

## 1. INTRODUCTION

It has been known that twisted angle of extrusion die can be primary reason of twisting phenomena of extruded product. In order to solve twisting problems in extrusion process, some researches by Yang and Kiuchi have been reported that the kinematical admissible velocity fields are proposed and they are analyzed with upper-bound theorem.<sup>1)-3)</sup>

But, when the helical fins are extruded by fixed helical extrusion dies, there are some problems such that it demands high forming loads combined by the two loads of forming fins and rotating extruded part.<sup>4)-6)</sup> In order to improve this problem, in this paper, it is proposed that the load could be reduced during extruding helical fins by using rotating twisted conical extrusion die.

When helical fins are extruded, if the rotating direction of rotating die could be opposite to the rotating direction of material due to the shape of helical dies, it can form the helical fins on the product surface without rotating of extrusion material. For computer simulation of extru-spin process with rotating extrusion die, DEFORM-3D software was used, and it was known that the extru-spin process using rotating die can make helical fins without twisting of material, and reduce extrusion load, and increase durability of dies.

## 2. EXTRU-SPIN PROCESS<sup>7)</sup>

### 2.1 Method and device of extru-spin process

Fig.1 shows a simple figure of extru-spin process device. This figure explains how it can be operated by pinion gear connected with a rack gear. Extrusion dies is rotated by pinion gear attached on dies and is slid with an extrusion container and they are moved separately. And, the pinion gear is rotated by linear motion of rack gear connected to hydraulic cylinder.

When material in container is pushed by extrusion stem, the helical fins on surface of product can be formed and extruded by rotating extrusion dies, without rotating of material.

### 2.2 The rotating extrusion die assembly and structure

Fig.2 shows the inside of structure of rotating extrusion die, the rotating extrusion die with pinion gear is located at front of container.

So, the die can be rotated by the pinion gear with linear motion of rack gear, but the container is fixed to the housing of extrusion device.

Fig.3 is the helical rotating extrusion die used at the computer simulation. It has 8 helical fins with square sections. The left picture is the solid modeling of extrusion die and the right picture is wire frame model.

And, the characteristics of shape of rotating extrusion die is a twisted and curved plane on the inclined ruled surface with same angle, connecting circle section of entrance part to same fin section as exit part of conical extrusion dies.

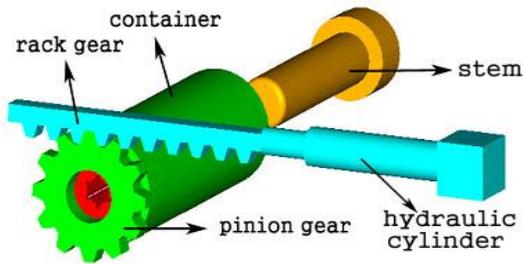


Fig.1 Extrusion process using rotated die

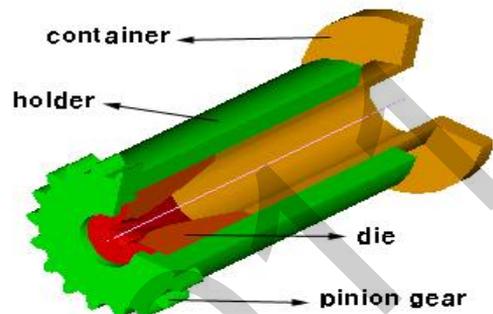


Fig. 2 Rotating extrusion die assembly

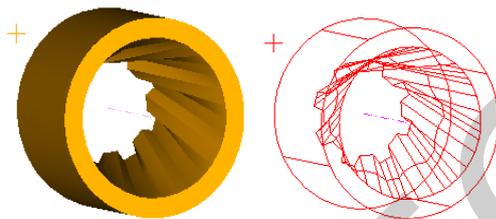


Fig. 3 Twisted extrusion die with 8fins

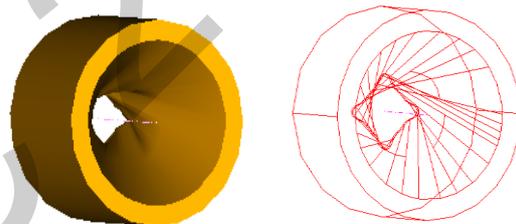
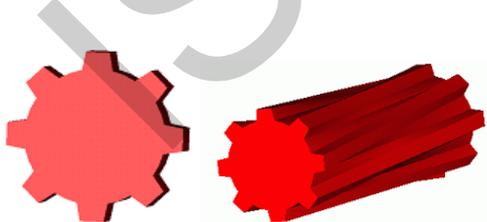


Fig. 4 Twisted extrusion die with 4fins

2.3 Forming analysis of extru-spin process

2.3.1 Results and discussion of forming analysis

Fig.5(a)(b) is s cylindrical rod with square section helical fins and it has 8 fins.



(a) Section of product (b) Shape of product

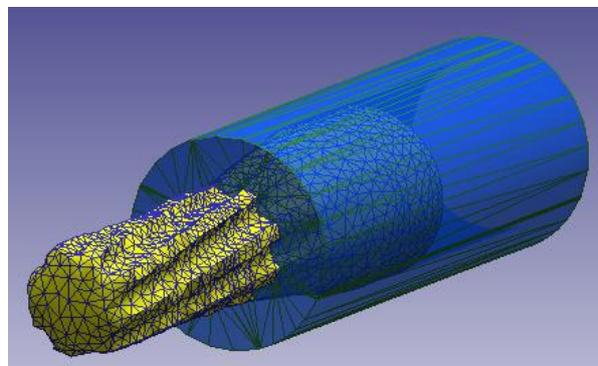
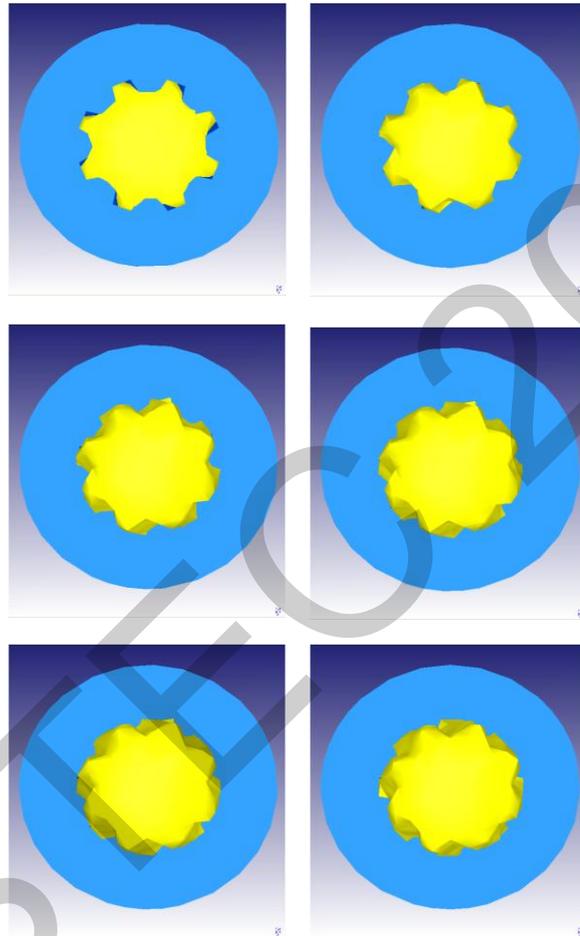


Fig. 5 Section and shape of extruded product Fig. 6 Simulation results of analysis of extru-spin process

Fig.6 shows the result of analysis by DEFORM-3D. In constraint condition of material for analysis, if the rotating extrusion die with helical fin cavity is moved in direction of center axis and rotated simultaneously, it shows that the twisted part with helical fins become to be extruded

At that time, the used material type is aluminum 1100 and extrusion velocity for analysis is 1mm/sec and angular velocity of die is 0.1 rad/sec. The number of mesh for modeling is about 50,000 mesh.

The material is not rotated in spite of rotating of extrusion die because of the helical shape of cavity of extrusion die, and only helical fins become to be formed on rod surface.



**Fig. 7 Front view of extru-spin process using rotated die with 8 fins**

Fig.7 shows the analysis results of extru-spin process, they are front views looking at the front side of extruded rod. In spite that extrusion dies begins to be rotated to opposite direction of helical direction, the extruded rod doesn't rotate but fins can be extruded in helical type on rod surface.

### 2.3.2 Extrusion loads of fixed helical die and the rotating helical die

According to Fig.8 and Fig.9, the extrusion load is 141 KN in case of using the fixed die. But in case of using the rotating die, the extrusion load is 120 KN. It is known that the extrusion load in the case of using the rotating die is less than that of fixed die.

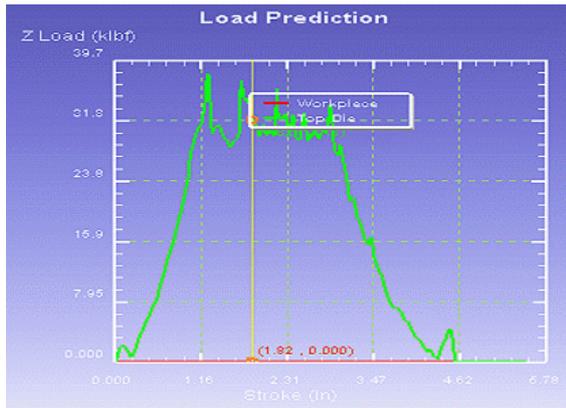


Fig. 8 Extrusion load and stroke in case of using fixed die

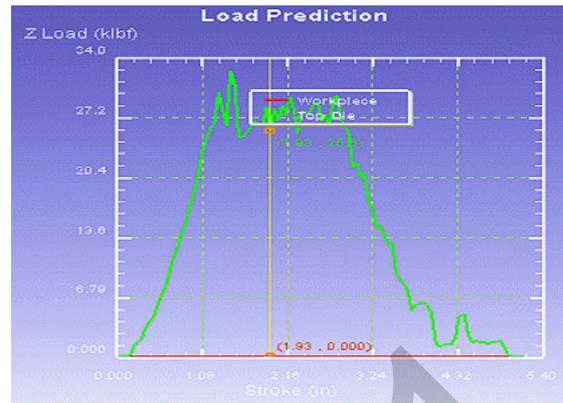


Fig. 9 Extrusion load and stroke using rotated die

When helical fins on the material surface are extruded by the extru-spin process, the reduction of load are shown in second figure, Fig 9, in case of using rotating dies.

### 2.3.3 Extrusion load and twisted angle

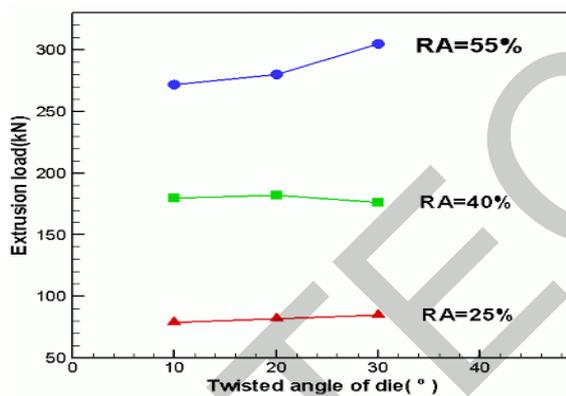


Fig.10 Extrusion load using fixed die

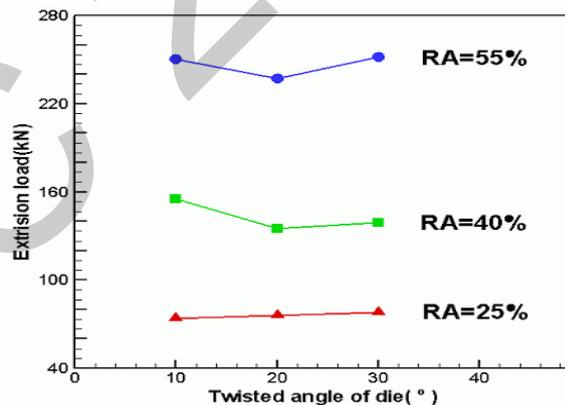


Fig.11 Extrusion load using rotated die

Fig.10 is a result of analysis in fixed helical die by DEFORM-3D, and Fig.11 shows the extrusion load when rotating die is used. When the helical die rotates opposite direction to material rotating direction, the extrusion load is less than load using the fixed die through the Fig.11 and Fig.10.

And, in case of die without rotating, if the twisted angle increases, the load of extrusion increases together. It is showing through the Fig.10. In case of using the rotating die, the extrusion load is lower than fixed extrusion die according to twisted angle of die in Fig.11

### 2.3.4 Twisted angle of part and twisted angle of die

Fig.12, Fig.13 are analysis result in the case of the fixed die and the rotating die by DEFORM-3D. And they show that they have different loads according to reduction ratio of area and twisted angle of die. When reduction ratio of area is constant, if the twisted angle of dies increases, the twisted angle of extrusion part also increases together. As shown in Fig.12 and Fig.13, the twisted angle of product rod, twisted angle of part twisted by using the rotating die is bigger than that of part twisted by using the fixed die. From the results, it was known that using the rotating die is much more effective.

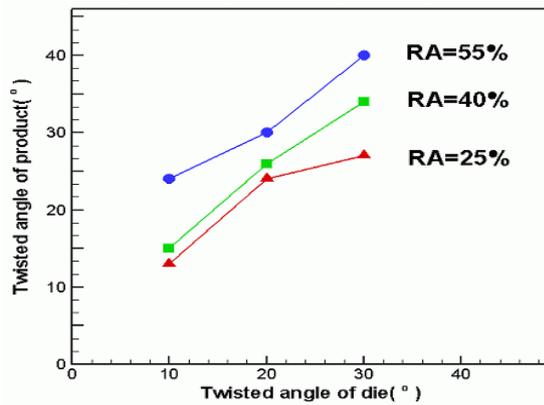


Fig.12 Twisted angle of product using fixed die

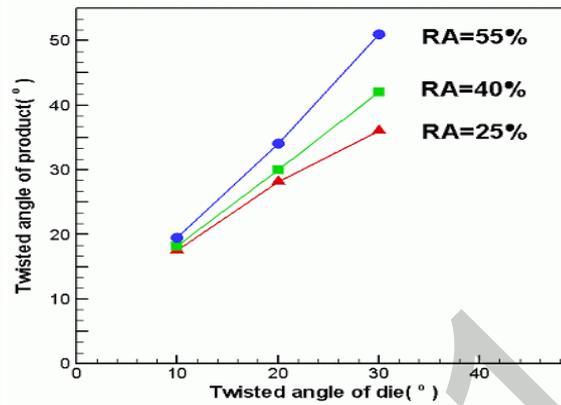


Fig.13 Twisted angle of product using rotated die

### 2.3.5 The optimized rotating-velocity analysis

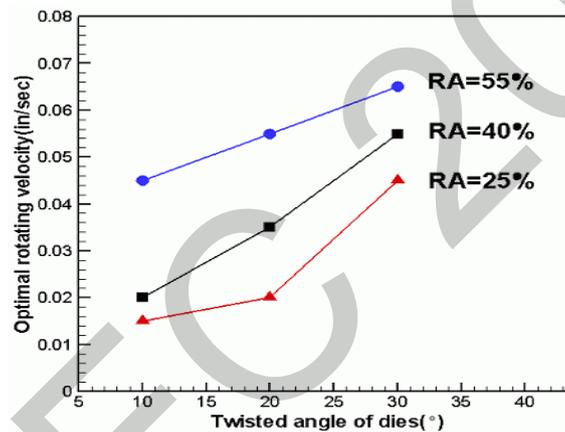


Fig.14 Result of optimal rotating velocity

Fig.14 shows that optimized rotating velocity can be founded, according to each reduction ratio of area, in order to minimize extrusion load during the extrusion process.

When reduction ratio of area is increasing and the twisted angle of die is increasing, it was shown that the optimized rotating velocity is increasing.

## 3. CONCLUSION

It was known that, through analysis of extru-spin process, extrusion load can be reduced by using the rotating extrusion die with helical and conical type cavity,

(1) It was known through the analysis results by DEFORM-3D software that metal forming load of helical fins in extru-spin process using fixed extrusion die is higher than the forming load in the extrusion process using rotating extrusion dies, because that forming load of helical fin and rotating load of used material are added to each other in the case of using fixed dies.

(2) In case of using the rotating extrusion die, the twisted helical die cavity makes helical fins without rotating material, because rotating direction of die is opposite to material rotating direction.

At that time, because this rotation of die can make extrusion load minimize, an optimized rotating-velocity can be found through the forming analysis of the helical fins of square type.

In case of using the rotating die, extrusion load used to form helical fins on surface of rod can be reduced by applying the optimized rotating-velocity, according to each different extrusion process conditions. So, the durability of die can be extended and the extrusion product quality can be improved.

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# FARKLI MALZEMELERİN AŞINDIRICILI SUJETİ (ABRASIVE WATERJET) İLE İŞLENEBİLİRLİĞİNİN ARAŞTIRILMASI

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## ÖZET

Suyun aşındırma etkisiyle oluşturduğu akarsuları, vadileri gören araştırmacılar bu gücü kontrol altına alarak endüstride kullanma yollarını araştırmışlardır. 70'li yıllarda kullanılmaya başlanan bu sistem başlangıçta pahallı, gürültülü çalışan, ortamı kirleten, karmaşık bir kesme sistemi iken; teknolojinin gelişmesiyle her alanda tercih edilen bir sistem haline gelmiştir. Geleneksel olmayan imalat yöntemlerinden biri olan su jetiyle kesme, diğer kesme yöntemlerine göre üstün yönlerinin olması nedeniyle tercih edildiği alanlar sürekli artmaktadır. Sistemin en belirgin özelliği kesim işlemi esnasında işlem gören yüzeyin ısıdan etkilenmemesidir. Bu çalışmada, su jetinin farklı malzemelerde ve farklı parametrelerde kesme özellikleri araştırılmıştır. Çalışmada; 10 mm kalınlıkta Granit, Cam, Seramik, St37, Paslanmaz Çelik ve Alüminyum malzeme kullanılmıştır. İşleme parametreleri olarak iki farklı nozzle yüksekliğinde (5 ve 10 mm), iki farklı basınçta (180 ve 280MPa) ve üç farklı ilerleme hızında (60,120,240 mm/dak) suyla kesme işlemleri yapılmıştır. Suyla kesme yönteminde uygulanması sonucunda hangi malzemelerin ve hangi parametrelerin suyla kesme yöntemiyle daha verimli olduğu araştırılmıştır.

**Anahtar Kelimeler:** Aşındırıcılı (Abrasive) Su jeti, Su jeti ile işlenebilirlik, Su jeti ile kesme, İleri işleme-kesme yöntemleri,

## INVESTIGATION OF MACHINABILITY DIFFERENT MATERIALS BY ABRASIVE WATERJET

### ABSTRACT

Researchers, who realized the effect of erosion on shaping of nature, investigated ways to use this power by controlling the industry. When the system was originally introduced - in the '70s-, it was working in a noisy, polluting the environment, expensive and had complex cutting system. Thanks to the development of technology, today, it has become a preferred system in all areas. One of the non-traditional methods of manufacturing the water-jet cutting, superior to other cutting methods are preferred aspects of the fields due to the constantly increasing. The most prominent feature of the system is traded on the surface during the cutting process is not affected by heat. In this study, waterjet machining parameters of different materials and different cutting properties were investigated. In this study, with 10 mm thickness granite, glass, ceramic, St37, Stainless Steel and Aluminum materials are used. Machining parameters in two different nozzle height (5 and 10 mm), two different pressures (180 and 280MPa) and three different feed rates (60,120,240 mm/min) were made waterjet cutting operations. A result the implementation of waterjet machining method, which is a more efficient method of cutting water supplies, and what parameters were investigated.

**Keywords:** Abrasive Waterjet, Machining with Waterjet, Abrasive Cutting with Waterjet, Advanced Machining Method,

### 1.Giriş

Suyun aşındırma etkisini gören araştırmacılar, çakıl taşlarını topraktan ayırmak için kullanılan ilk sistemin ardından, 1930' lu yıllarda suyun kuvvetini kömür, taş ve toprağın birbirinden ayrılması için kullanmışlardır. Su jeti haline gelmesi 1970' li yıllarda olmuştur. Yaygın kullanımı ise 1990' lı yılları bulmuştur. Geleneksel işleme sistemlerine göre üstünlüklerinin olması nedeniyle, kullanımı hızla artmaktadır. Kesilecek ürünün metale yapışıp deforme olmaması yönüyle gıda sektöründe ([www.ttconsultant.com](http://www.ttconsultant.com), 2010) ; buruşma kenar yırtıkları ve katların açılmaması yönüyle kağıt ve mukavva sanayinde ([www.waterjettingdirectory.com](http://www.waterjettingdirectory.com), 2010) ; kesici bıçak ile zor kesilen kumaşı basitçe kesmesi yönüyle tekstil ve giyim sektöründe ([www.ttconsultant.com](http://www.ttconsultant.com), 2010) ; pvc, plastik, kauçuk, sünger gibi malzemeleri hızlı kesmesi yönüyle plastik sanayinde ([www.waterjettingdirectory.com](http://www.waterjettingdirectory.com), 2010); malzeme sarfiyatını azaltması yönüyle ayakkabı sektöründe ([www.ttconsultant.com](http://www.ttconsultant.com), 2010) ; metallerin işlenmesinde ortaya ısı çıkmaması nedeniyle özellikle metal işleme sanayinde ([www.waterjettingdirectory.com](http://www.waterjettingdirectory.com), 2010); kırılğan olan cam, mermer, granit ve seramik malzemeleri deforme olmadan ve

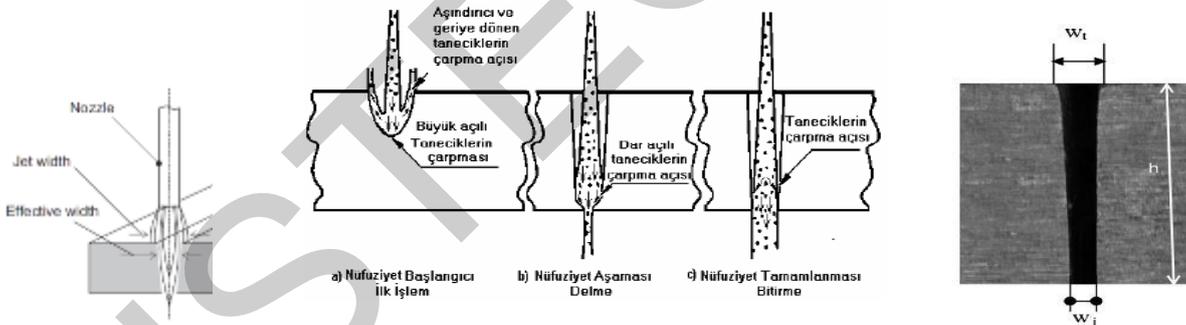
malzeme kaybını önleyerek kesmesi nedeniyle cam-mermer-granit ve seramik sanayinde kullanılmaktadır (www.waterjets.org, 2010) ASJ ile kesmede ısıdan etkilenen bölgenin oluşmaması (soğuk kesme), malzemelerde sertleşmenin gözlenmemesi, başlangıç deliğinin açılmasına ihtiyaç duyulmadan çok sayıda malzemenin çok yönlü kesilmesi, her türlü malzeme kesiminde kullanılması, ikinci bir işlem gerekmeden imalatın gerçekleşmesi, işleme için az sayıda aparat gereksinimi, çevre dostu olması, kesme sonunda gerilmenin söz konusu olmaması ve soğuk kesme ile ulaşılan kalite, ASJ ile kesme yönteminin tercih edilme nedenleridir (www.formingfabricating.com). Bu çalışmada geleneksel olmayan bu işleme teknolojisini; farklı parametrelerde uygulamalı çalışması yapılarak, en verimli sonucu hangi malzeme ve kesim değişkeni üzerinde verdiğini bulmak amaçlanmıştır.

## 2. Aşındırıcılı Su Jeti

Su jeti ile kesme işleminde, basınç yükselticiden çıkan su dar bir boru içerisinde yüksek basınçta ilerler ve meme ağzına yaklaştıkça daralan kısımlarda hızını daha da arttırarak malzeme yüzeyine püskürtülür. İşlem sırasında yüzeye çarpan su jeti huzmesi ile oluşturulan kesme kuvveti, malzeme yüzeyinden parçacık kopararak kesme işlemini gerçekleştirir. Yüzeyden aşındırma ile uzaklaştırılan parçacık oranı; jet basıncına, yanıl ilerleme hızına, kesilen malzemenin özelliğine, su jeti içerisindeki katkı maddesi (aşındırıcı malzeme) ve oranına bağlı olarak değişir (Wakuda vd., 2003; Karakurt, 2007; Hasçalık vd., 2007).

Su jeti kesme teknolojisinde kesici eleman yüksek basınç ve hızla sahip su demetidir. Yöntem, su demetini bir kesme aracı olarak kullanarak çeşitli malzemelerde aşındırma etkisiyle kesme ve işlemeyi kapsamaktadır (Engin, 2006). Su jeti ile kesilen malzemenin yüzeyine bakıldığında, düzgün olan üst kısım ve onu takip eden çizgili, dalgalı bir bölge görülür. Düzgün görülen üst kısım kesme aşınma bölgesi olarak adlandırılırken daha çok çizgili ya da dalgalı görünen alt kısım deformasyon aşınma bölgesi olarak adlandırılır. Birinci bölge daha düzgün bir yüzey olup, malzeme pürüzlülük kalitesinin belirlendiği bölgedir. Bu bölgenin yüzey kalitesi, başlıca aşındırıcı tanelerin malzeme yüzeyine dik açıyla çarpmasının bir sonucudur. İkinci bölge ise, aşındırıcı parçacıklarının malzeme yüzeyine geniş açılarda çarpmasıyla oluştuğu bölgedir. Şekil 1'de aşındırıcılı su jeti ile işlenmiş yüzeylerde meydana gelen kesme aşınması ve deformasyon bölgelerinde oluşan aşınmalar görülmektedir (Liu ve Chen, 2004; Akkurt, 2009).

Su Jeti Kesme Kalitesi incelendiğinde; Su jeti ile kesme sistemlerinde, kesme yüzeylerinin kalitesi, suyun basıncı, aşındırıcı miktarı ve akışı, ilerleme hızı, malzeme kalınlığı ve meme titreşiminin bir fonksiyonu olarak değişim gösterir. Yüzeyin kalitesi (pürüzlülüğü) ilerleme hızının artması ile azalmaktadır (www.sharplesdie.com, 2009). Şekil.1.a'da işlenecek olan malzeme üzerine su jetinin ilerlemesi, Şekil.1.b'de kesme sırasında meydana gelen kesme aşınma bölgesi ve daha çok çizgili ya da dalgalı görünen alt kısımda bulunan deformasyon aşınma bölgesi, Şekil.1.c'de malzeme kalınlığına bağlı olarak aşınma sonucu oluşan ölçü değişimi görülmektedir.



Şekil.1 a) Suyla Kesme b) Kesme ve Deformasyon Aşınması (Akkurt,2006) c) Ölçü değişimi( Hasçalık ve ark., 2007)

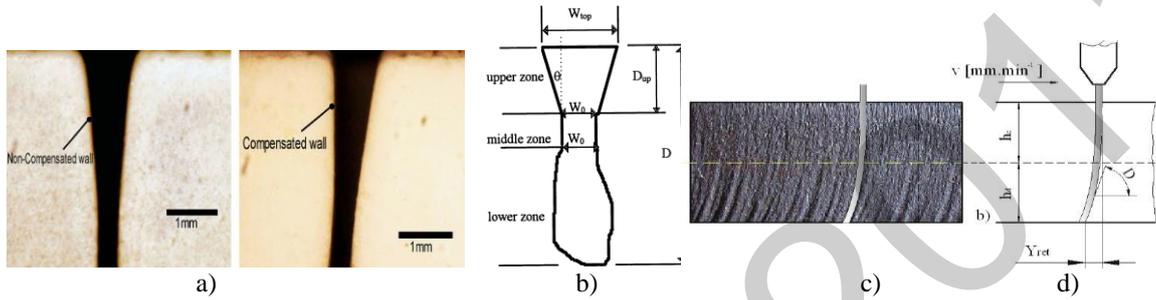
## 3. Deneysel Çalışma

Yapılan deneysel çalışmada 10 mm sabit kalınlıklarda altı farklı malzeme kullanılmıştır. Bu malzemeler metal grubu olarak; alüminyum, St37 ve çeliktir. Diğer grup malzemeler ; cam, granit ve seramik (granit seramik) tir. Çalışmada nozul yüksekliği 5 ve 10 mm olarak sabit tutulmuştur. Sırasıyla bu altı farklı malzeme üzerinde 180MPa ve 280MPa basınçlarda 60, 120 ve 240 mm/dak ilerleme hızlarında, her numuneden 10x10mm ölçülerinde kesme işlemi yapılmıştır. Kesme işleminde seçilen parametrelere bağlı olarak malzemelerden kare biçimde numuneler elde edilmiştir. Aşındırıcı su jetiyle kesilerek elde edilen bu numuneler üzerinde kesme ve deformasyon aşınma bölgeleri incelenmiştir. Deneysel çalışmada numune yüzeyleri ve ölçümler Nikon Epiphot 200 marka optik mikroskopta gerçekleştirilmiştir. Elde edilen veriler grafiklere dönüştürülmüştür. Deneysel çalışmada işleme parametreleri Tablo 1.'de görülmektedir.

**Tablo.1 İşleme Parametreleri**

Değişkenler	
Basınç (MPa)	180, 280
İlerleme Hızı (mm/ dak)	60, 120, 240
Nozul Yüksekliği (mm)	5, 10
Malzemeler	Granit, seramik,cam,St37, Al., Çelik
Malzeme Kalınlığı (mm)	10

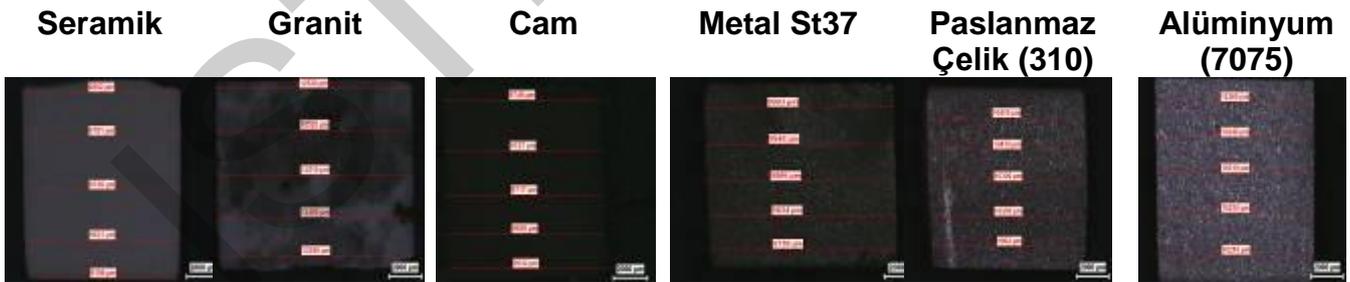
Aşındırıcılı su jeti ile kesme malzeme yüzeyinde çizikli bir yapı (kerf) oluşturmaktadır ve bu da kesme sisteminin kullanımını sınırlayan bir durumdur (Chen ve Siores, 2003). Şekil.2 a ve b de kesme ve deformasyon aşınması ve Şekil 2 c ve d'de deformasyon bölgesinden itibaren oluşan çizikli yapı (kerf) görülmektedir. Kesilen numuneler üzerinde kesmeye başlama yüzeyi ile sujetinin kesme işlemi parça kalınlığını tamamlayarak çıktığı alt yüzey arasında ölçü farkları nozul üst den bu şekilde ölçümle elde edilen rakamsal değerlere göre çalışma yorumlanacaktır.



Şekil 2. a-b) Kesme ve Deformasyon Aşınması

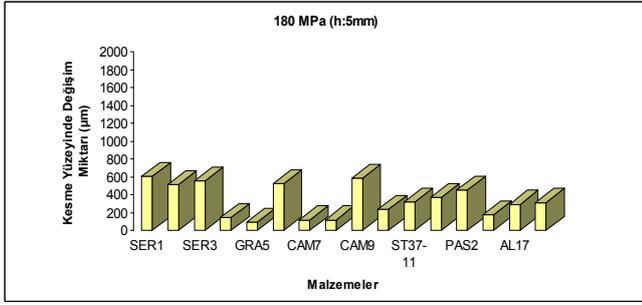
c-d) Deformasyon bölgesinde oluşan çizikli yapı (kerf)

Malzemelerin sujetinin (waterjetin) kesmeye başladığı (malzemeyi delmeye başladığı) üst yüzey ile alt kenar arasında meydana gelen ölçü farklılıkları ve kerf oluşumu araştırılarak, seçilen parametrelere göre kesilen numuneler üzerindeki değişimler incelenmiştir. Şekil.3'te su jetinin kestiği yüzeyler üzerinde beş farklı noktadan (kesme ve deformasyon bölgelerinde) yapılan ölçümlere ilişkin fotoğraflar görülmektedir. Kesilen numuneler üzerinde kesmeye başlama yüzeyi ile sujetinin kesme işlemi parça kalınlığını tamamlayarak çıktığı alt yüzey arasında ölçü farkları belirlenerek bu şekilde elde edilen rakamsal değerler incelenmiştir. Elektron mikroskobunda yapılan ölçümlerden elde edilen değerler grafikler halinde düzenlenmiştir.

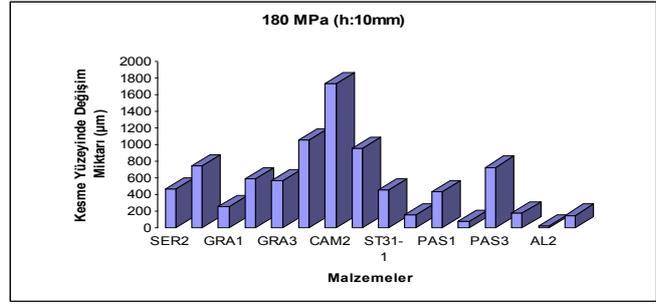


Şekil.3 Malzemelerin Su jetiyle Kesilmesi sonucu oluşan aşınma görüntüleri

Su jeti ile kesme işleminde kesme parametrelerine ve malzemelere göre, kesilen yüzeyde meydana gelen değişikliklerin grafikleri aşağıdaki gibidir (Şekil.4). Grafikte görüldüğü gibi, 180 MPa basınç ve 5 mm nozul yüksekliğinde kesilen malzemelerin yüzeyinde meydana gelen dalgalanmaların sonucunda, kesim genişlik mesafelerinde oluşan farklılıkları ifade etmektedir. Suyun girdiği ve kesim işlemi bitirdiği noktalar arasındaki bu farklılıklara göre SER1 kodlu seramik malzeme en fazla farka sahip olan numunedir. SER1'in ilerleme hızı 60 mm/dak'dır. Seramik malzemedan 120 mm/dak ve 240 mm/dak ilerleme hızlarında kesilen diğer parçalara bakıldığında, aynı şekilde sapmalarının grafikte üst sıralarda aldığı görülmektedir. Şekil 4 b'de, 180 MPa basınçta fakat 10 mm nozul yüksekliğinde kesilen parçaların kesim yüzeyi sapmalarını ise en büyük ölçü farklılığın CAM2 kodlu malzemede olduğu görülmektedir. Buradan seramik malzemenin nozul yüksekliğinin artışına bağlı olarak daha az yüzey sapması ile kesildiği görülmektedir. Akkurt ve arkadaşları tarafından yapılan çalışmada (2004), örnek kalınlığına yakın kesme derinliklerinde yüzey pürüzlülüğünün giderek en yüksek değere ulaştığını rapor etmişlerdir.



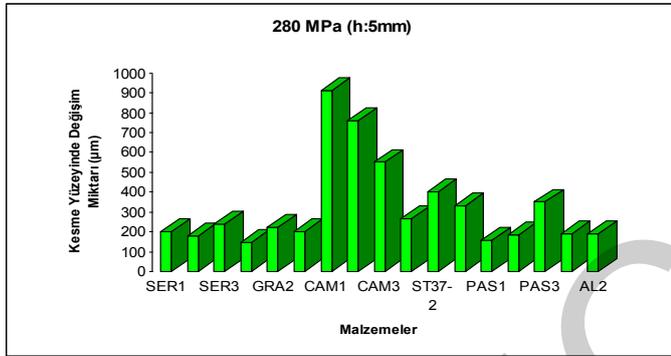
a)



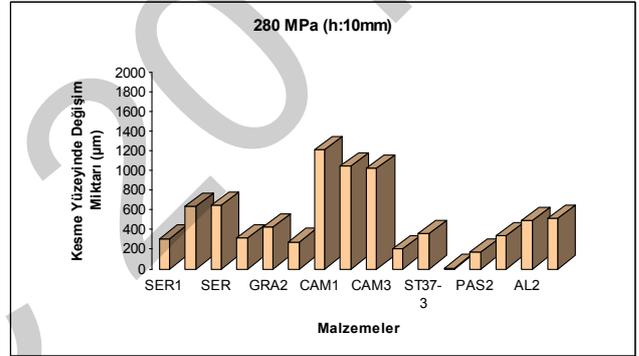
b)

Şekil.4: Suyla Kesme (Waterjet) Malzemelerde Kesme Sırasında Meydana Gelen Aşınma Miktarı (180Mpa basınç, İlerleme Hızı sırasıyla, 60,120 ve 240 mm/dak)

Şekil. 5 a'da görülen grafikte, 280 MPa basınç ve 5 mm nozul yüksekliğinde kesilen malzemelerin yüzeyinde meydana gelen dalgalanmaların sonucunda, kesim genişlik mesafelerinde oluşan farklılıkları ifade etmektedir. Malzeme kesitinde en çok sapmanın görüldüğü CAM1 kodlu numunedir. CAM1'i, CAM2 ve CAM3 kodlu numune takip etmektedir. Bu numunelerin kesim hızları sırasıyla 60 mm/dak, 120 mm/dak ve 240 mm/dak'dır. Buradan kırılma yapıya sahip olan cam malzemenin hızı arttıkça ölçü sapmasının ters yönlü olarak azaldığı sonuca varıyoruz. Şekil.9.b'de 280 MPa ve 10 mm nozul yüksekliğinde yapılan kesimlerde de en fazla ölçü sapmasının cam malzemede olduğunu görüyoruz. Nozul yüksekliği arttıkça cam malzemenin ölçü sapmaları da artmıştır.



a)



b)

Şekil. 5: Suyla Kesme (Waterjet) Malzemelerde Kesme Sırasında Meydana Gelen Aşınma Miktarı (280Mpa basınç, İlerleme Hızı sırasıyla, 60,120 ve 240 mm/dak, Nozul Yüksekliği 10 mm)

#### 4.Sonuçlar

Deneysel sonuçlar;

Kesme aşınması ve deformasyon bölgelerinin Malzemelere göre değiştiği,

Kesme aşınması ve deformasyon bölgelerinin ilerleme hızı, basınç ve nozul yüksekliğine bağlı olarak değiştiği ve bunun yüzey kalitesini etkilediği,

Kesme kalınlığına ve malzeme özellikleri ve işleme parametrelerine bağlı olarak kerf oluşumun ve kesme aşınması ve deformasyon bölgelerinin değiştiği,

İlerleme hızının yüzey pürüzlülüğümü etkileyen önemli parametrelerden biri olduğu, İlerleme hızın artmasına bağlı olarak Yüzey pürüzlülüğünün arttığı,

Yüksek kesme hızı ve düşük ilerleme hızlarında kesme aşınması bölgelerinde yüzey pürüzlülüğünün azaldığı,

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# FATE OF FLUOMETURON DISSOLVED IN NATURAL WATERS AND EXPOSED TO SOLAR LIGHT

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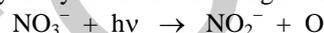
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**Abstract** - To predict the fate of pollutants in the aquatic environment and to assess the risk they may pose, it is necessary to improve our knowledge on their chemical reactions under environmental conditions. Photochemical reactions are a route for the attenuation of organic pollutants present in surface waters. This work was devoted to herbicide fluometuron which is used to control weeds in cotton. Phototransformation of fluometuron (1  $\mu\text{M}$ ) in natural sunlight was investigated in synthetic waters containing either natural organic matter, nitrate ions or both in order to mimic reactions taking place in aquatic environments. Fluometuron underwent photolysis and its degradation was faster in the presence of fulvic acids (10  $\text{mg l}^{-1}$ , factor 2.5) or nitrates (25  $\text{mg l}^{-1}$ , factor 15) than in Milli-Q water showing the importance of natural waters constituents. Identification of major photoproducts was conducted under laboratory conditions. Hydroxylation of the aromatic ring with or without hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$  and oxidation of the urea chain leading to demethylation were observed.

**Keywords:** photodegradation, phenylureas herbicides, solar light, naturel waters.

## INTRODUCTION

Photochemistry is one of the main abiotic degradation pathway of organic pollutants occurring in surface waters. This is a route for attenuation of organic pollutants. Several types of reactions may occur depending on the medium composition. Direct photolysis is possible if the considered pollutant absorbs solar light. In addition, photoinduced or photosensitized transformations mediated by components of the aquatic medium can also take place. In particular, dissolved natural organic matter (DOM) which absorbs a large portion of photons is a potential photosensitizer. Singlet oxygen, superoxide ion/hydroperoxyl radicals, hydroxyl radicals, excited triplet states and alkylperoxyl radicals were proved or proposed to be generated in natural waters under the influence of sunlight (Vaughan and *al.*, 1998; Canonica and *al.* 1995; Halladja and *al.* 2007). However, a part of these species are trapped by DOM itself. Nitrate ions that are present in surface waters at level varying from 0.2 to 25  $\text{mg.L}^{-1}$  generate the highly oxidizing hydroxyl radicals under light excitation (Boule and *al.*, 1999).



The percentage of hydroxyl radicals trapped by pollutants is thus strongly dependent on the medium composition. In the present work, we focused on the phototransformation of the phenylurea herbicide fluometuron (FM). This compound is widely used for pre- and post-emergence control of weeds in fields of conventional cotton cultivars. It is persistent (Stoeckel and *al.*, 1997) and may pose some risks to aquatic organisms (Muschal and *al.*, 2003). FM poorly absorbs solar light (*see Fig. 1*) but indeed its direct photolysis in simulated solar light ( $k > 290 \text{ nm}$ ) was reported (Lam and *al.*, 2005). The  $\text{CF}_3$  group undergoes photohydrolysis into  $\text{CO}_2\text{H}$ .

The objective of the present work was to investigate the photolysis of FM in conditions approaching real ones. FM in the micromolar range was irradiated in natural solar light. The influence of DOM or/and nitrates on the phototransformation was assessed. In parallel, laboratory experiments were conducted to identify the main photoproducts on the basis of HPLC-ESI-MS analyses.

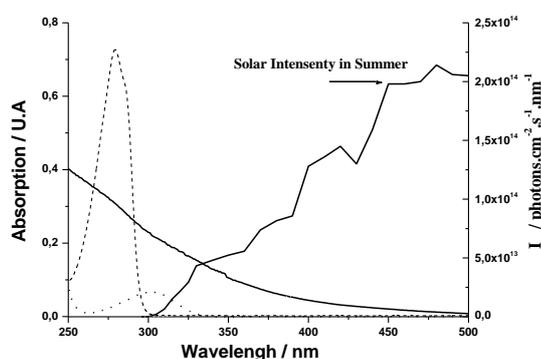


Fig. 1: Absorption spectrum of (---) FM at  $3.10^{-4} \text{ M}$ , (—) FA at  $10 \text{ mg.L}^{-1}$ , (.....) nitrates at  $0.01 \text{ M}$  and solar light emission reaching the earth surface in summer (Zepp and *al.*, 1977)

## METHODS AND PROCEDURES

### Photoreaction setup

For kinetic purpose, FM ( $1 \mu\text{M}$ ) was irradiated (1) in Milli-Q water, (2) in water containing fulvic acids ( $10 \text{ mg.L}^{-1}$ ) used as a surrogate of DOM, (3) in water containing nitrate ions ( $25 \text{ mg.L}^{-1}$ ) or  $3.10^{-4} \text{ M}$ ) and (4) in water containing both fulvic acids ( $10 \text{ mg.L}^{-1}$ ) and nitrate ions ( $3.10^{-4} \text{ M}$ ). Irradiation experiments in natural sunlight were performed at Clermont-Ferrand ( $46^\circ \text{ N}$ ,  $3^\circ \text{ E}$ ) in June 2006. Cylindrical quartz glass reactors (14 mm internal diameter) were filled with 14 ml of solutions. Reactors were closed by a septum, attached on a rack inclined by about  $15^\circ$  from horizontal and exposed to solar light. Samples received 13 h of sunshine per day. Aliquots of 0.5 ml were removed simultaneously from all the solutions at selected intervals. Samples were immediately analyzed by HPLC. Irradiations under laboratory conditions were also carried out for photoproducts identification. Irradiations were performed in a device equipped with six TLAD 15W/05 fluorescent tubes emitting within the wavelength range 300–450 nm with a maximum of emission at 365 nm and in a Pyrex glass reactor (14 mm i.d). The device was cylindrical and equipped with reflecting inner walls. A ventilator was used as a cooling system. The reactor was placed in the centre of the device and was surrounded by the six fluorescent tubes. Light intensity was measured using p-nitroanisole/pyridine as a chemical actinometer. PNA ( $10^{-5} \text{ M}$ ) and pyridine ( $10^{-4} \text{ M}$ ) were irradiated in the same conditions as samples in the polychromatic device and in solar light. In the polychromatic device, PNA loss was 12% after 1 h and 63% after 5 h. In solar light, 56% of PNA had disappeared after 4 h of exposure between 10 am and 2 pm. It can be deduced that the average light intensity delivered by the tubes of the polychromatic device was of the same magnitude order as that of solar light within the wavelength range 300–400 nm (limit of PNA absorption).

### Analytical procedures

Loss of fluometuron and formation of photoproducts were monitored by HPLC–UV using a Waters apparatus equipped with two pumps (model 510), an autosampler, a photodiode array detector (model 996), a detector W2487 and a C18 reverse-phase column (4.6 mm, 250 mm, Spherisorb S5 ODS2, 5  $\mu\text{m}$ , Waters). Eluent was a mixture of water acidified with 0.1% of orthophosphoric acid and methanol (50%/50%) delivered at a constant flow of  $1 \text{ mL.min}^{-1}$ .

The HPLC–UV–MS analyses were performed using a Waters/Micromass LC/QTOF (Micromass, Manchester, UK). For the HPLC conditions, a Waters Alliance 2695 HPLC equipped with a photodiode array detector (DAD) was used. A reversed-phase column (C18 Hypersil ODS, 5  $\mu\text{m}$ , 100 mm, 2.1 mm; Interchim, Montluc, on, France) was used at a flow rate of  $0.3 \text{ mL.min}^{-1}$ . The mobile phase was composed of acetonitrile (solvent A) and acidified water (formic acid, 0.4% v/v; pH 2.6) (solvent B). Gradient: 0–5 min, 5% A; 5–30 min, 5–95% A (linear); 30–34 min, 95% A; 34–35 min, 95–5% A; 35–40 min, 5% B equilibrium period). The injection volume was 30  $\mu\text{l}$ . The LC–ESI–MS worked both in positive and negative mode.

UV spectra were recorded on a Cary 3 (Varian) spectrophotometer. A 1-cm path quartz cell was used for all the experiments. The reference beam blank was always Milli-Q water.

## RESULTS

### Kinetics of phototransformation in solar light

We first compared the profiles of FM loss in various conditions (Fig. 2). In the absence of fulvic acids (FA) and nitrate ions, the consumption of FM ( $1 \mu\text{M}$ ) in solar light was very slow: less than 30% had disappeared after 6.7 d. The addition of fulvic acids ( $10 \text{ mg.L}^{-1}$ ) significantly increased the rate of FM consumption: about 50% of FM had disappeared after 6.7 d. A larger enhancement of the reaction rate was observed in the presence of nitrate ions ( $25 \text{ mg.L}^{-1}$ ): a complete FM loss was obtained after 3.3 d. In the presence of both fulvic acids ( $10 \text{ mg.L}^{-1}$ ) and nitrate ions ( $25 \text{ mg.L}^{-1}$ ), FM disappeared more slowly than in the presence of nitrates alone. To determine rate constants, we plotted  $\ln C_0/C$  vs irradiation time, where  $C_0$  is the initial FM concentration and  $C$  the concentration at  $t$ . In all cases, FM consumption followed pseudo first order kinetics. The rate coefficients,  $k$ , and  $R^2$  values are reported in Table 1.

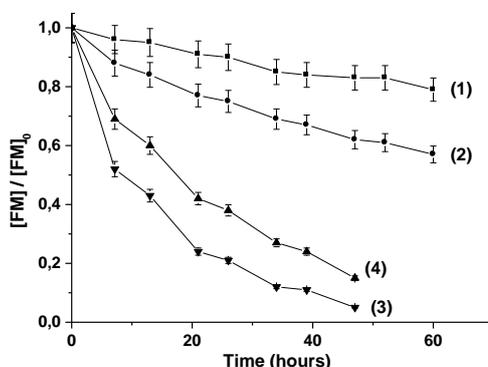


Fig. 2. Kinetics of FM ( $10^{-6} \text{ M}$ ) phototransformation in solar light in various aqueous media.

(1): in pH 6.5 Milli-Q purified water; (2): in water containing FA ( $10 \text{ mg.L}^{-1}$ );

(3): in water containing FA ( $10 \text{ mg.L}^{-1}$ ) and nitrates ( $3.10^{-4} \text{ M}$ );

(4): in water containing nitrates ( $3.10^{-4} \text{ M}$ ).

Table 1: Phototransformation of FM ( $10^{-6}$  M) in solar light

Medium	k (s <sup>-1</sup> )	R <sup>2</sup>	t <sub>1/2</sub> (days)
1	$6.4 \times 10^{-7}$	0.974	12.5
2	$1.6 \times 10^{-6}$	0.964	5.0
3	$9.8 \times 10^{-6}$	0.948	0.82
4	$6.2 \times 10^{-6}$	0.959	1.3

These kinetic results bring insight into the photodegradability of FM in solar light. FM is hardly transformed in pure water due to the poor absorption of solar radiations. Using the rate coefficient given in *Table 1*, one computes a half-life of 175 h. The chromophoric constituents of water (nitrate and fulvic acids) promoted FM phototransformation. The effect of fulvic acids was quite moderate. In the presence of fulvic acids ( $10 \text{ mg.L}^{-1}$ ), the rate coefficient was increased by a factor of 2.5 and the half-life reduced by the same factor. Nitrate ions ( $25 \text{ mg.L}^{-1}$ ) had a more pronounced influence increasing the rate coefficient and reducing the half-life by a factor of 15. In the presence of fulvic acids and nitrate ions, the rate of FM photodegradation was smaller by about 40% than in the presence of nitrate ions alone. At the considered concentrations, the absorbance of nitrates is very small (around 0.002) while that of FA bigger (around 0.22) (*see Fig. 1*). The inhibiting effect of FA on nitrate photolysis through screen effect is difficult to evaluate due to the cylindrical shape of reactors. Based on a mean path-length of 0.7 cm, one would compute a rate reduction between 15% and 20%. It represents 50% of the measured inhibition. The remaining 50% of inhibition are likely to be due to the scavenging of hydroxyl radicals by FA (Brezonik and al., 1998; ter Halle and al. 2006). In an attempt to delineate the role of hydroxyl radicals in the fulvic acids mediated phototransformation of FM, we studied the influence of 2-propanol added as a hydroxyl radical scavenger on the reaction ( $k = 1.9 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , Buxton and al., 1988). These experiments were undertaken in laboratory conditions. In the absence of fulvic acids, the initial rate of FM phototransformation was equal to  $2 \cdot 10^{-8} \text{ M.h}^{-1}$ . In the presence of fulvic acids ( $5 \text{ mg.L}^{-1}$ ), it raised to  $5.2 \cdot 10^{-8} \text{ M.h}^{-1}$ . The addition of 2-propanol (0.015 M) reduced the latter rate by a factor comprised between 1.5 and 2, suggesting the involvement of hydroxyl radicals in the phototransformation reaction and showing the ability of FA to produce them under irradiation. We also studied the influence of oxygen on the reaction (*see Fig.3*).

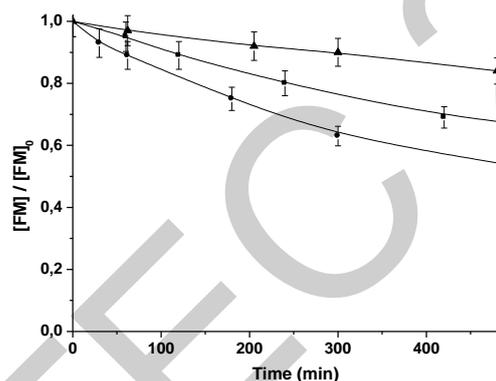


Fig. 3. Kinetics a neutral solution of FM ( $3 \cdot 10^{-5}$  M) phototransformation containing fulvic acids ( $25 \text{ mg.L}^{-1}$ ) at 365 nm in various aqueous medias: air-saturated medium (■); oxygen-free medium (●); oxygen-saturated medium (▲)

After 5 h of irradiation, FM consumption was twice faster in air-saturated than in oxygen-saturated medium and 3-fold faster in nitrogen-saturated medium than in air-saturated medium. Thus, oxygen clearly inhibited the reaction.

### Photoproducts identification

To achieve photoproducts characterization, we irradiated more highly concentrated FM solutions under laboratory conditions. The photolysis of FM ( $3 \cdot 10^{-5}$  M) in Milli-Q water yielded the acidic compound resulting from the hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$  as previously reported (Lam and al., 2005). Its UV absorption spectrum differs from that of FM: the far UV absorption band ( $k_{\text{max}} = 224 \text{ nm}$ ) shows a shoulder and the second maximum of absorption is located at 297 nm instead of 275 nm in the case of FM.

The irradiation of FM ( $3 \cdot 10^{-5}$  M) in the presence of fulvic acids ( $25 \text{ mg.L}^{-1}$ ) yielded two HPLC–UV detectable photoproducts, **I** and **II** (*Fig. 4a*).

The UV spectrum of **I** exhibited the same shoulder as that of the acidic product and a second maximum red-shifted by 27 nm ( $\lambda_{\text{max}} = 297 \text{ nm}$ ). The UV spectrum of **II** resembled that of FM but the second maximum was red-shifted by 20 nm compared to it ( $k_{\text{max}} = 295 \text{ nm}$ ).

The HPLC–mass analysis of **I** gave a first molecular ion at  $m/z = 223$  in  $\text{ES}^-$  mode and at  $m/z = 225$  in  $\text{ES}^+$  mode corresponding to the loss of 9 amu that may be explained by the hydrolysis of  $\text{CF}_3$  into  $\text{CO}_2\text{H}$  and the addition of an oxygen atom. Fragments at  $m/z = 179$  [M-44] and at  $m/z = 134$  [M-89] were obtained in  $\text{ES}^-$  mode. These data are compatible with the structure proposed in *Table 2*. The first fragment would correspond to the loss of the carboxylic group and the second to the cleavage of the terminal amine group  $-\text{N}(\text{CH}_3)_2$  followed by loss of an H atom to yield an isocyanate. Photoproduct **II** gave molecular ions at  $m/z = 247$  and  $249$  in  $\text{ES}^-$  and  $\text{ES}^+$  modes, respectively, corresponding to the addition of an oxygen atom to FM. A fragment at  $m/z = 202$  corresponding to M-45 was observed in  $\text{ES}^-$  mode. The loss of 45 amu is likely to result from the

departure of  $N(CH_3)_2$  by cleavage of the terminal urea C–N bond and the elimination of H to form the isocyanate. It is compatible with structure given in Table 2.

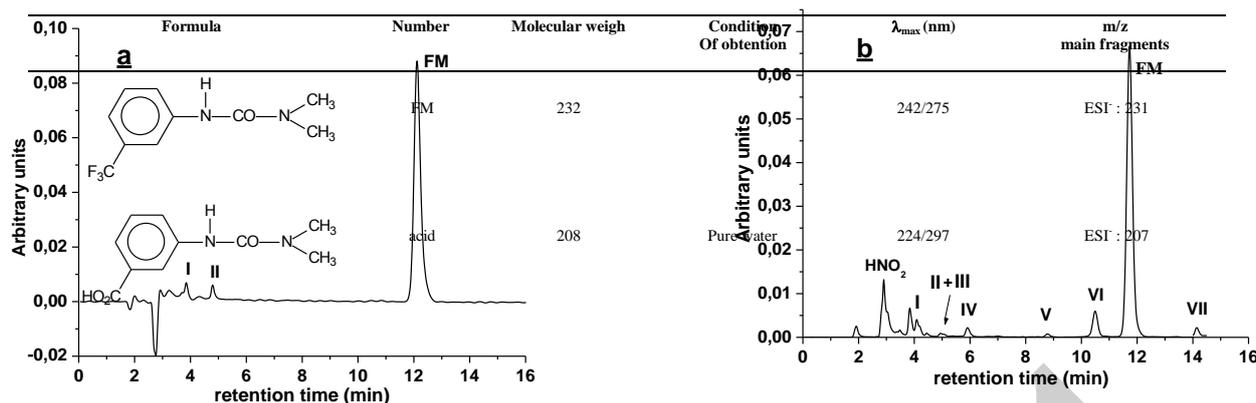


Fig.

HPLC chromatogram of (a) a neutral solution of FM ( $3.10^{-5}M$ ) containing fulvic acids ( $mg.L^{-1}$ ) at a conversion extent of 20% and (b) a neutral solution of FM ( $3.10^{-5}$ ) containing nitrate ions ( $25 mg.L^{-1}$ ) at a conversion extent of 46%. Both solutions were irradiated in simulated solar light. Photoproducts are numbered as indicated in Table 2.

The irradiation of FM ( $3.10^{-5} M$ ) in the presence of nitrate ions ( $25 mg.L^{-1}$ ) yielded seven photoproducts detectable by HPLC–UV (see Fig. 4b). Based on HPLC retention times, UV absorption spectra and mass data, we could conclude that photoproducts I and II were present among the seven photoproducts. Two other compounds III and IV with a molecular ion at  $m/z = 223$  in  $ES^-$  mode were also detected. As they showed distinct retention times and UV maxima, but similar fragmentation at  $m/z = 179$  and  $134$  with different percentages of fragments, they are likely to be isomers of I. Photoproducts I, III and IV should differ from each other in the position of the hydroxyl group on the ring. The photoproducts V and VI that were eluted just before FM showed similar absorption spectra. One of them, V, gave a molecular ion at  $m/z = 203$  in  $ES^-$  mode corresponding to the loss of 28 amu and a fragment at  $m/z = 160$ . The other one, VI, gave a molecular ion at  $m/z = 217$  in  $ES^-$  mode and the same fragment at  $m/z = 160$ . These compounds could be assigned to demethylated products; VI would be the monodemethylated derivative and V the didemethylated derivative (see Table 2).

A molecular ion at  $m/z = 245$  in  $ES^-$  mode was also detected at a retention time longer than that of FM. This mass corresponds to the addition of 14 amu. Three fragments were observed at  $m/z = 217$  [M-28], 188 [M-28-29] and 160 [M-28-29-28]. This fragmentation indicates that the aromatic ring was not altered. It is in favour of photoproduct VII that bears a carbonyl group and for which successive losses of CO,  $NCH_3$  and CO are again possible.

Finally, we used the selected peak method to detect some specific photoproducts formation of which was expected. In the case of nitrate ions, we could find nitro derivatives at  $m/z = 276$  in  $ES^-$  mode corresponding to the addition of 45 amu ( $+NO_2-H$ ). In the case of fulvic acids, careful examination of chromatograms revealed the presence of peaks at  $m/z = 217$  and 245 in  $ES^-$  mode and  $m/z = 219$  in  $ES^+$  mode, showing that fulvic acids photosensitized transformation also yielded FM demethylation, but this pathway was very minor.

## CONCLUSION

Direct photolysis of aqueous FM is slow but photosensitizing processes may promote its transformation in surface waters. In the presence of hydroxyl radicals, both the lateral chain and the ring of FM are oxidized. Photoreactants deriving from fulvic acids privilege oxidation of the aromatic ring. Photoproducts of hydrolysis or hydroxylation of the aromatic ring absorb solar light better than FM itself. They are thus susceptible to undergo photolysis faster than FM. Photoproducts resulting from oxidation of lateral urea chain are more photostable. It would be now necessary to test the toxicity of each individual compound or that of the irradiated mixtures toward reference organisms in order to access the risk that may pose FM.

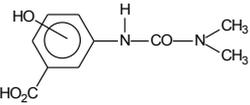
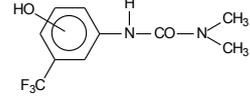
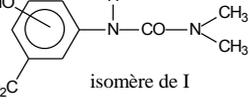
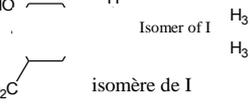
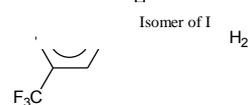
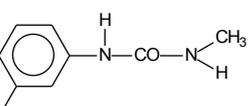
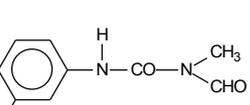
	<b>I</b>	224	FA or nitrates	222/324	ESI <sup>+</sup> : 223 (179, 134) ESI <sup>-</sup> : 225
	<b>II</b>	248	FA or nitrates	242/295	ESI <sup>+</sup> : 247 (202) ESI <sup>-</sup> : 249
	<b>III</b>	224	Nitrates	230/311	ESI <sup>+</sup> : 223 (179, 134)
	<b>IV</b>	224	Nitrates	224/315	ESI <sup>+</sup> : 223 (179, 134)
	<b>V</b>	204	Nitrates	241/280	ESI <sup>+</sup> : 203 (160)
	<b>VI</b>	218	Nitrates or FA (minor)	243/279	ESI <sup>+</sup> : 217 (160)
	<b>VII</b>	246	Nitrates or AF (minor)	245 and shoulder at 280	ESI <sup>+</sup> : 245 (217, 188, 160)

Table 2: Structure of detected photoproducts, molecular weigh, maxima of absorption, molecular ions and main fragments detected by LC-ESI-MS

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# FATİH PROJESİNE UYGUN ÖĞRETİM SİSTEMLERİ GELİŞTİRİLMESİ (SORU-CEVAP TEKNİĞİNİN YENİDEN YORUMLANMASI)

## DEVELOPING INSTRUCTIONAL SYSTEMS FOR FATİH PROJECT (RE-INTERPRETATION OF QUESTION-ANSWER TECHNIQUE)

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### ÖZET

Milli Eğitim Bakanlığı 2010 yılı kasım ayında Fırsatları Arttırma ve Teknolojiyi İyileştirme Hareketi olarak adlandırdığı FATİH projesini duyurmuştur. Proje 3 yıl içerisinde, 40 bin okuldaki 500 binden fazla dersliğe projeksiyon, akıllı tahta , öğretmen bilgisayarı ve öğrenci tabletleri dağıtılmasını öngörüyor. Şüphesiz ki eğitim araç gereçlerini yalnızca sınıflarımıza yerleştirmek eğitim amaçlarımız bakımından bir katkı sağlamayacaktır. Yeni teknoloji beraberinde yeni bir öğretim sistemi getirmeli ve eski anlayışlarımızda da farklılıklar yaratmalıdır. Bu noktadan hareketle sınıf içi öğretim tekniklerinden soru cevap tekniğini FATİH projesine uygun şekilde yeniden ele aldık. Öğrenci tabletlerinin akıllı tahta ve öğretmen bilgisayarı ile bağlantı kurabilecekleri online bir değerlendirme sistemi geliştirilerek ,bu sistemin öğrenci, öğretmen ve eğitim ortamında yarattığı farklılıkları inceledik.

**Anahtar Kelimeler:** Fatih Projesi, Soru Cevap Tekniği, Ölçme ve Değerlendirme, Tablet PC, Akıllı Tahta

### ABSTRACT

In November of 2010, the Ministry of Education, announced Enhancement Opportunities, and Technology Improvement Movement which called as Fatih project The project aims to deliver projectors, smart boards, tablet pcs and teacher computers to more than 500 thousand classrooms in 40 thousand schools within 3 years..Surely just contributing educational materials don't help us in our educational purposes. New Technologies should bring a new education system with itself and change our old understandings. From this point we considered again the question and answer technique in using Fatih Project. By developing a new assessment system , we focus on the impact of the system on educational environment.

**Keywords:** Fatih Project, Question-Answer Technique, Measurement and Evaluation, Tablet PC, Smart Board

### Giriş

FATİH projesiyle 3 yıl içerisinde, 40 bin okuldaki 500 binden fazla dersliğe 614 bin 364 adet dizüstü bilgisayar ve projeksiyon cihazı ile 38 bin 688 çok amaçlı fotokopi makinesi ve akıllı tahta sağlanacaktır. Ayrıca projeye tablet bilgisayarların da eklenmesi düşünülmektedir. Projenin ortaöğretim kurumlarından başlayarak kademe kademe okulöncesi seviyesindeki kurumlara kadar inmesi planlanmaktadır. Üzerine çok konuşulan bir konu olmakla birlikte projenin hayata geçmesinin ardından eğitim ortamlarına yapacağı katkı konusunda bir belirsizlik mevcuttur.

Öte yandan eğitimde bilişimin kullanılmasıyla ilgili geçmiş başarısızlıklar ve öğretmenlerimizin bilişim teknolojilerini kullanma yeterlilikleri proje başarısı açısından soru işaretleri oluşturmaktadır. Eğitimde FATİH Projesinin Öğretmenlerin Yeterlik Durumları Açısından İncelenmesi ‘ çalışmada bu durum şöyle ifade edilmektedir.” Çalışmada gerçekleştirilen uygulama sınavı sonuçlarına göre; başarı ortalamasının en yüksek olduğu kelime işlemciler uygulamasında, öğretmenlerin %80’inin satır aralığını değiştirebilme, %55’inin sayfa kenar boşluklarını ayarlayabilme ve sayfa numarası ekleyebilme davranışlarını gerçekleştiremedikleri gözlenmiştir. “ ( Kayaduman, Sırakaya, Seferoğlu, 2011, 3 )

Eğitim dünyasında pek çok fikrin ve ön kabulün bulunduğu bir ortamda projenin getirileri ile ilgili sağlıklı bir değerlendirme yapma imkanı bulunmamaktadır. Bu noktadan hareketle FATİH Projesinin eğitim dünyamıza katkılarını anlayabilmek için geleneksel öğretim tekniklerini proje kapsamında yeniden ele almak gereği duyulmuştur. Öğretim teknikleri içerisinde bulunan soru cevap tekniği yeterince bilinen ve uygulanan bir teknik olmasından dolayı çalışma kapsamına dahil edilmiştir. Soru cevap tekniğine yönelik bir yazılım oluşturularak geleneksel soru cevap tekniği ile karşılaştırılmıştır.

### Geleneksel Soru Cevap Tekniği

Soru cevap tekniği her dersin öğretiminde yararlanılabilecek eski fakat kullanışlı bir teknik olarak bilinmektedir. Teknik, öğretmenin sözel olarak sorduğu sorulara sınıf içerisinde seçilecek bir öğrencinin yine sözel olarak cevap vermesine dayanır. İhtiyaca göre ders içerisinde dikkat çekme , öğretilen konunun pekiştirilmesi veya eksik öğrenmelerin tespit edilmesi gibi pek çok amaçla ilişkili olarak kullanılabilir. Biz çalışmamızda soru cevap tekniğini bir değerlendirme aracı olarak ele alacağız.

Yapılan pek çok çalışma soru cevap tekniğinin öğretim teknikleri arasında en çok kullanılan teknik olduğunu ortaya koymaktadır.( Fidan,1997 ;Saracaloğlu , Karasakaloğlu,2011) Aynı şekilde güncel bazı çalışmalardan da benzer sonuçlar elde edilmiştir.

Öğretmenlerin derste en fazla kullanmış olduğu geleneksel ölçme değerlendirme tekniğinin soru-cevap tekniği olduğu görülmüştür. Öğretmenlerin soru cevap tekniği ile dersi işleminin nedeni sürekli sorular sorarak öğrencileri derse aktif şekilde katmak istemesi ile ilişkilendirilebilir. Buradan ister alternatif ister geleneksel ölçme değerlendirme teknikleri olsun öğretmenlerin her ikisinde de vazgeçemediği tekniğin soru-cevap tekniği olduğu görülmüştür.( Çepni, Çoruhlu, 2010 )

### Teknoloji Destekli Soru Cevap Uygulaması

Bahsedildiği üzere FATİH projesinin taşımakta olduğu potansiyeli görebilmek için proje imkanları dahilinde kullanılmaya uygun online bir soru-cevap sistemi tasarlanmıştır. Sistemin işleyişi Şekil 1 de görülmektedir.



Şekil 1

Sistem soruların kaydedildiği bir soru havuzu, öğrenci kayıtları ve istatistik modülünden oluşmaktadır. Sistemin kullanımı şu aşamalardan oluşmaktadır.

#### A - Öğrenci Kayıtlarının Yapılması

Öğretmen öğrenci kayıt modülünü kullanarak sınıfında bulunan öğrencileri sisteme kayıt edecek. Bu işlem için öğrencinin numarası, sınıfı ve adı 'nın bir kez kaydedilmesi yeterlidir.

#### B - Soru Havuzunun Oluşturulması

Öğretmen istediği ders ve konu için soru-cevap uygulamasında kullanmayı düşündüğü soruları sisteme kaydedecek.

#### C - Soru Cevap Uygulamasının Sınıfta Kullanımı

Yazılımın sınıftaki uygulamasında şu aşamalar izlenir.

- Öğretmen kendi şifresi ile sisteme giriş yapar.
- Havuzda ders ve konuya göre filtreleme yaparak sormak istediği soruya ulaşır.
- Öğrenciler sisteme öğrenci numaraları ile girerek soruyu beklemeye başlarlar.
- Öğretmen soruyu aktif hale getirir, isterse zaman sınırlaması koyar.
- Soru öğrenci bilgisayarlarında/tablet bilgisayarlarında görüntülenir.
- Öğrenciler soruya uygulama arayüzünü kullanarak cevap verirler.
- Cevaplar uygulamanın kurulu olduğu öğretmen bilgisayarında toplanır.
- Gerekli istatistikler ekrana yansır.

### Sistemin Teknik Alt Yapısı

Sistemin çalışması için ihtiyaç duyulan cihazlar; öğrenci bilgisayarları ( tablet bilgisayar, dizüstü bilgisayar ya da pc ), projeksiyon (ya da akıllı tahta), öğretmen bilgisayarları, modem (tablet bilgisayarlar için kablosuz modem) den oluşmaktadır. Uygulama yerel ağ üzerinde çalışacağı için internet gerekmemekte fakat öğrenci bilgisayarları yerel ağa bağlı olmalıdır.

Sistemin geliştirilmesi aşamasında mümkün olduğunca esnek araçlardan yararlanılarak henüz pilot uygulamaları yapılmakta olan Fatih projesinin son halinde dahi çalışabilmesi hedeflenmiştir. Kullanılan uygulama geliştirme dili açık kaynak bir web programlama dili olan PHP dir. Verilerin depolanması amacıyla kullanılacak veritabanı MySQL (MyOracle) olarak belirlenmiştir. Uygulamaları çalıştırmakta kullanılan web server programı Apache'dir. Seçilen bu öğelerin en önemli

özellikleri hem Linux ,hem de Windows platformlarında çalışabilmeleridir. Ayrıca bahsi geçen uygulamalar ücretsizdir.

Fatih projesi kapsamında seçilen akıllı tahta, uygulama yüklenmesine izin verirse, sistemin çalıştırılacağı ana bilgisayar olarak tercihen akıllı tahtanın kendisi de seçilebilir. Bu seçim aynı sınıfta birden fazla öğretmenin ders vermesi halinde tercih edilebilir. Fakat tavsiye edilen ana bilgisayar olarak öğretmen bilgisayarının kullanılmasıdır. Bu sayede öğretmen havuza eklemesi gereken soruları okul dışında da ekleyebilir. Uygulamanın çalıştırılacağı bilgisayara Web Server ve veritabanı ve php kurulumunun ardından bu öğrenci pelerinin ana bilgisayara erişebilmesi için bu bilgisayara sabit bir yerel IP numarası atanmalıdır.Bu ayarlama Windows üzerinde Kontrol Paneli > Ağ ve İnternet > Ağ ve Paylaşım Merkezi > Ağ Bağlantısı > Bağlantı Ayarları yolu ile ulaşılabilir.IP'ye verilecek değer şu şekilde olabilmektedir: 192.168.1.X

Obtain an IP address automatically

Use the following IP address:

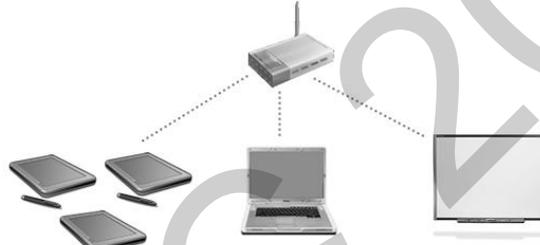
IP address:

Subnet mask:

Default gateway:

Şekil 2

Uygulamada kullanılan kodlama bildiri kapsamı dışında kalmakla birlikte htdocs ya da wwwroot klasörüne yerleştirilmelidir.Bu noktadan sonra öğrenci bilgisayarları <http://tanımlanan-ip-adresi> ni adres satırına yazarak uygulamaya ulaşabilir hale geleceklerdir.Öğretmen bilgisayarında ise erişim için <http://localhost> kullanılması yeterlidir.



Şekil 3

### Sistemin Avantajları

- Ders etkinliklerinden yararlanma derecesinin tespiti için kullanılan soru cevap tekniğinde öğretmen soruyu tüm sınıfa yöneltmekle beraber sorunun yanıtlanması için birkaç öğrenciye söz hakkı tanır. Bu aşamada öğretmenler çoğunlukla yeterli sayıda öğrenciye soru yöneltmezler. Bu durum izleme değerlendirmesinin gerçekçi olmayan sonuçlar vermesine neden olur. Özellikle tam öğrenme modeli kullanılan etkinliklerde öğretmen öğrencilerin bir sonraki konu için gerekli ön öğrenme seviyesi konusunda yanılabilir. Eksik öğrenmelerin tamamlanması için gerekli etkinlikler ihmal edilecektir. Sistemimizde soruların tüm sınıfa yöneltilmesi ve cevaplar üzerinden doğru yanlış istatistikleri çıkarılması tam öğrenme modeli'nin ihtiyaç duyduğu değerlendirmenin daha başarılı yapılmasını sağlayacaktır.
- Geleneksel soru cevap tekniğinde öğretmenin birkaç öğrenciyi cevabı vermeleri için seçiyor olması esasında büyük bir sorunun kaynağını oluşturmaktadır. Öğrenci algıları bu seçimi dikkatle takip eder ve çıkarsama yapar. Sonuç sıklıkla öğretmenin sınıf içerisinde bazı öğrencilere özel bir ilgi gösterdiği şeklinde gelişir. Kimi zaman da öğretmen bu seçimi bilinçli yapar.Bu durum sınıf içerisinde eşitsizlik ve dışlanmışlık duygusu oluşturur.Zamanla öğrenciler soru cevap tekniğinin amacına zıt şekilde ders etkinliğine ilgilerini kaybederler.Bu sorun aynı öğretmenin diğer derslerine de yayılacaktır.Sistemimizde öğretmen soruları sınıfın tamamına yönelttiği için bu algı oluşmayacaktır.Soru cevap etkinliğine öğrencide oluşması muhtemel dışlanmışlık duygusu yerini her soruya hazır olabilmek amaçlı dikkate bırakacaktır.
- Soru cevap etkinlikleri sırasında ifade gücü çeken ya da sosyal fobilere sahip öğrenciler etkinliğe katılmakta çekingen davranabilirler. Cevap vermeleri de zaman alıcıdır. Öğretmenler etkinliği yavaşlatacağından bu öğrencileri

etkinliğe katmak istemeyebilirler. Uygulamamız bu ve benzer sıkıntılar yaşamakta olan öğrencilerde ve özel öğretimde kullanılmaya elverişlidir.

- İstenirse soruya doğru yanıt verenler arasında en hızlı cevap verenler sıralaması yapılarak rekabetçi bir sınıf etkinliği oluşturulabilir.
- Doğru yanıtlara puan verilerek (sembolik ödül yoluyla) kanaat notuna gerçekçi ve objektif bir dayanak oluşturur.
- Soru cevap tekniğinde sınıfta oluşabilecek karmaşayı önler.
- Ayrıntılı istatistiksel veriler elde edilebilir. Bu veriler;en çabuk cevaplayan öğrenciler, bir ders etkinliği boyunca etkinliklerden en fazla ve en az yararlanan öğrenciler, aynı konuyu en iyi öğrenen sınıfı tespit etmek ,okul çapında en az öğrenilen konu vb. olabilir.
- Diğer avantajlar Tablo1’de geleneksel soru cevap sistemi ile karşılaştırmalı olarak gösterilmiştir.

Geleneksel Soru Cevap Tekniği	Teknoloji Destekli Soru Cevap Sistemi
Öğretmen soruları sözel olarak iletir.	Öğretmen soruları sözel ve görsel olarak iletebilir.
Soru öğretmenin seçtiği bir ya da bir kaç öğrenci tarafından cevaplanır.	Soru tüm öğrenciler tarafından cevaplanır.
Kalabalık sınıflarda uygulanması zordur.	Kalabalık sınıflarda da rahatlıkla uygulanabilir.
Tüm konu alanı değerlendirilmeye çalışıldığında uzun zaman alır.	Tüm konu alanı değerlendirildiğinde nispeten kısa bir süreye ihtiyaç duyulur.
Öğrenci yanlış yapma korkusuyla cevap vermeye çekinir.	-
İfade sıkıntısı çeken öğrencilerin katılımını sağlamak zordur.	-
Rekabetçi ortam oluşturulmaya çalışıldığında sınıfta kargaşaya sebep olur.	-
Sözlü değerlendirme olduğu algısına kapılan öğrencide heyecan ve tedirginlik yaratır.	-

Tablo 1

Sistemin en önemli dezavantajı; soru cevap tekniğinde öğrencinin kendini ifade kabiliyeti gelişirken sistemimizde bunun mümkün olmamasıdır. Bu yüzden sistem ilköğretim ilk kademe için tavsiye edilmemektedir.

## Sonuç

Tablo1’de de görüldüğü üzere geleneksel öğretim tekniklerinde eğitim teknolojisinin işe koşulması ciddi farklılıklar yaratmaktadır. Özellikle öğrenme ortamında istenmeyen durumların kontrolü konusunda oldukça etkilidir. FATİH projesi kapsamında düşünüldüğünde öğrenci merkezli etkinliklerde olumlu sonuçların elde edilmesi beklenmektedir. Bu beklenti ancak FATİH projesi kapsamında alınacak donanımların salt fiziksel araç gereçler olmadığını insan psikolojisi ve davranışları üzerinde etkileri olacak öğeler olduklarını kavramamız sayesinde gerçekleşecektir. Geçmişte yaşanmış olduğu gibi eğitim ortamında modern eğitim araç gereçleri bulunduğu halde öğretmenlerin eski anlayışlarla öğretimi yürütmeye çalışmaları kabul edilemez. Kamuran Çilenti , Eğitim Teknolojisi ve Öğretim adlı kitabında durumu şöyle ifade etmektedir.

Şüphesiz ki bu teknolojiler,fiziksel bilimlerin teknolojik ürünü olan sesli, sessiz elektronik araçlarla , projektör ve mekanik araçlar kullanılmaktadır, fakat bu kullanımda önemli olan araçlarla insanların fizyolojik psikolojileri arasındaki ilişkilerin insan davranışlarında yaptığı değişikliklerin ön planda tutulmasıdır.(Çilenti, 1988, 30)

Bölümü bitirirken söylenecek son söz, bilgisayarın bütün eğitim problemlerini çözebilecek sihirli araçlar olduğunu düşünmemek gereğidir. Onların insan yapısı programlarla çalıştığı hiç hatırdan çıkarılmamalıdır. Eğitimde yararlı olacak eğitim programlarının ise , eğitimi yapılacak konu alanını iyi bilen uzmanlar ile, eğitimde program geliştirme yöntemlerini ve programlı öğretim ilke ve tekniklerini iyi bilen ve uygulayabilen uzmanların bir arada çalışmasıyla ortaya konulabileceğini unutmamak gerekir.(Çilenti,1988,123)

Salt yapılabirlik bir öğretim sistemi geliştirilmesi için yeterli kıstas değildir. FATİH projesi için öğretim sistemleri geliştirilirken bunun öğretme ortamında yol açacağı değişiklikler dikkatlice incelenmelidir. Bu incelemelerle içerik tasarımı da birlikte düşünülmelidir.Kolay ulaşılabilir,maliyetsiz ve işlevsel içerik ve sistemlerin tasarımı FATİH projesinin amaçlarına ulaşma derecesi üzerinde etkili olacaktır. Proje üzerindeki tartışmaları da göz önüne alarak diyebiliriz ki ; bir yanlış yaparsak hiç olmazsa onu doğru yapalım. Bunun da yolu kaliteli öğretim sistemleri tasarlamaktan geçmektedir.

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# FIELD APPLICATIONS OF PREAERATION AND CHEMICAL PRECIPITATION FOR WASTEWATER TREATMENT

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## ABSTRACT

Chemical coagulation of wastewater proceeded by bioadsorption of soluble fraction is the main aim of the prevailing study. Chemical precipitation process was investigated to remove the colloidal and coarse-suspended solids COD fractions of domestic sewage whereas the soluble COD fraction was reduced by the preaeration process. The semi-technical scale field installation has been run in "Suez Wastewater Treatment Plant" that receives domestic wastewater produced from Suez Governorate.

The field-scale updated installation could be designed to investigate the treatment scheme on real ground (continuous flow configuration). The preaeration has been processed using pressurized diffused air at concentration range of 2.0-3.0 mg O<sub>2</sub> /lit. Two runs depending on the aeration period of the preaeration process have been investigated to evaluate the system set-up for which each run has been continued for six days. The flow rates of these runs were 0.5 & 0.35 l/min as a result of using aeration time one hour & one and half hour respectively. Ferric chloride has been added to the aerated wastewater in the rapid mixing vessel with dose 60 mg/ l (this dose was determined previously by using Jar Test in the laboratory with different types of coagulants and different doses for each). The degree of concentration was 10% so the rates of the solution which have been added through the two runs were 17.7, 12.4 ml/hr respectively. Mixing and flocculation processes have been carried out by using pressurized diffused air. Sedimentation process has been carried out to remove readily settleable solids and floating material of sewage coming from the flocculation basin and thus reduce the suspended solids content.

The treatment system using preaeration and chemical precipitation induces a good performance for removal of colloidal and coarse suspended solids fractions. The removal of soluble fraction is not high enough to permit for final effluent for disposal into waterways. Post treatment using activated sludge is suggested to reduce the residual soluble fraction so as the final effluent characteristics can comply with the regular standards for disposal into waterways.

## Key Words

COD-fractions; flash mixing; chemical precipitation; preaeration; coagulation; flocculation; complete treatment.

## 1. INTRODUCTION

Sewage discharge has a highly important effect on human health because it can spread disease-causing bacteria and viruses. Initial efforts to control human wastes evolved from the need to prevent the spread of diseases. Although untreated wastewater contains many billions of bacteria per liter, most of these are not harmful to humans, and some are even helpful in wastewater treatment processes. The goal is to reduce or remove organic matter, solids, nutrients, disease-causing organisms and other pollutants from wastewater. Therefore, all sewage treatment plants must hold a permit listing the

allowable levels of biological oxygen demand ( $BOD_5$ ), chemical oxygen demand (COD), suspended solids, coliform bacteria and other pollutants.

Wastewater solids that include all types of pollutants can be categorized into three different fractions based on particle size. On the chemical oxygen demand (COD) basis, these fractions include the soluble fraction ( $COD_{sol}$ ), the colloidal fraction ( $COD_{col}$ ), and the coarse suspended solids fraction ( $COD_{ss}$ ).

Preaeration process for the raw sewage plays an important role in the activation of the microorganisms that already are there in it and gives them a choice to use the organic soluble fraction in the sewage as a source of food, partly to maintain life and partly to synthesis new cell material whereas the addition of chemicals to the preaerated sewage removes the other two fractions of the sewage by processes including coagulation, flocculation and precipitation. As a result of addition of certain reactants, flocs of considerable dimensions can form and be removed by sedimentation or filtration processes.

The two basic methods of aerating wastewater include the Introducing air or pure oxygen into the wastewater with submerged diffusers or other aeration devices and the agitation of wastewater mechanically to promote solution of air from the atmosphere. The air mixing may be considered better than the mechanical paddles because paddles cause vortex action, destroy flocs and cost much for maintenance and handling.

This study involves the investigation of the continuous flow semi-technical installation incorporated both preaeration and chemical precipitation processes for complete removal of all fractions ( $COD_{ss}$ ,  $COD_{col}$  &  $COD_{sol}$ ) according to the results of the preliminary investigation which used laboratory installation (jar-test simulator) to determine the most effective coagulant and the optimum dosage can be used for full treatment of a preaerated sewage sample coagulated and flocculated using air-mixing diffusers as shown in Fig.1.

## 2. MATERIALS & METHODS

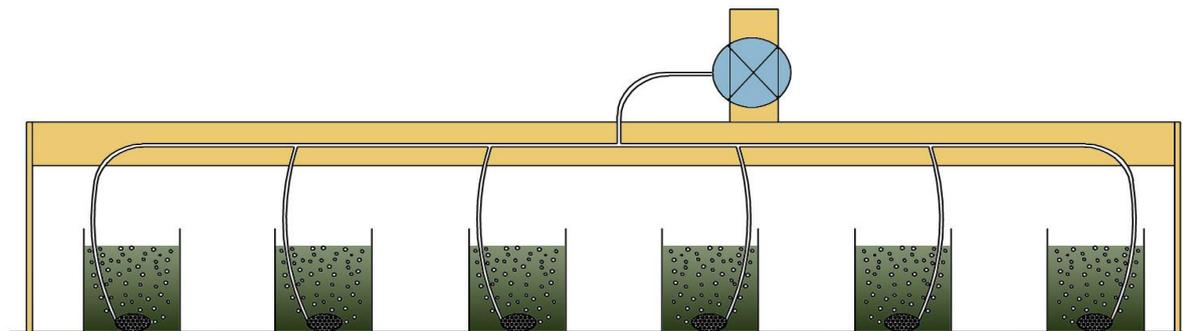
### 2.1 Semi-Technical Scale Pilot Plant

The semi-technical scale field installation is constructed according to the basic flow line as shown in Fig.2. This system is consisted of three separate spiro-plastic basins (6 mm thickness), which were connected by plastic pipes and fittings like elbows and tees. The first one is a rectangular aeration basin and its internal dimensions are 40 cm in length, 25 cm in width and 31 cm in height at the influent and effluent. The second one is the chemical feeding unit, which is a small circular tank, its diameter is 8 cm and its height is 20 cm as well as a flash-mixing basin attached by a rectangular flocculation basin. The internal dimensions of the flash-mixing basin are 15 cm in length, 15 cm in width and 23 cm in height at the influent and effluent. The internal dimensions of the flocculation basin are 40 cm in length, 25 cm in width and 33 cm in height at the influent and effluent. The third one is a rectangular sedimentation basin with inclined plates at the bottom and its internal dimensions are 25 cm in length, 25 cm in width and 60 cm in height. The height of the influent is 30 cm but the height of the effluent is 50 cm. The sludge effluent is at the bottom of the basin. The heights of the basins to achieve the required balance are 90, 73, 41 cm respectively. The details of the semi-technical scale pilot plant are shown in Fig.3and Fig.4.

### 2.2 Source of Wastewater

The semi-technical field system was constructed at the inlet of “Suez Wastewater Treatment Plant”, after the grit removal chambers. The raw wastewater was lifted to the system by using a submerged pump. The collected samples were transmitted and analyzed within one hour from collection. The analysis work was carried out in the laboratory of this plant.

Figure 1: The Jar Test Laboratory Installation Set-up



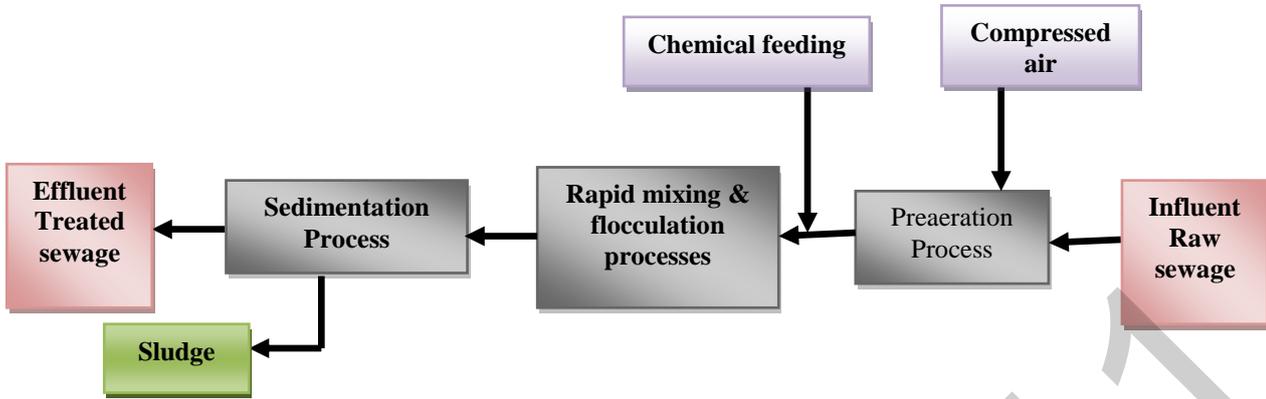


Figure 2: The Flow line of Sewage Treatment

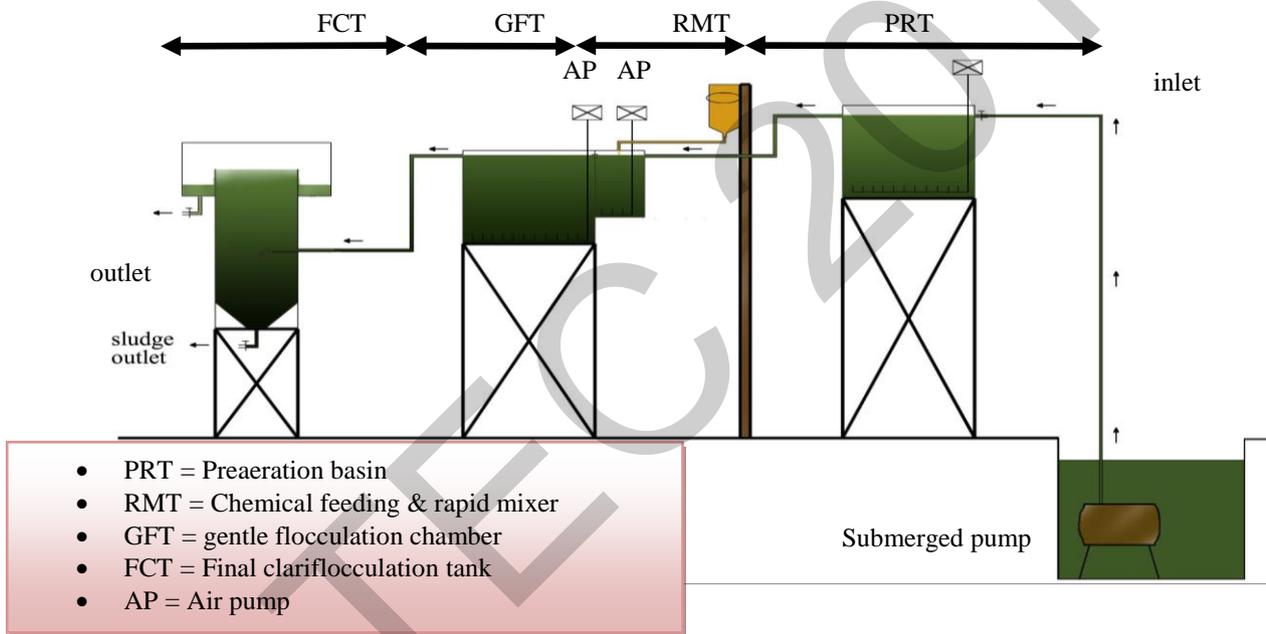


Figure 3: The semi-technical field installation treatment



Figure 4: The semi-technical field system

### 2.3 Characteristics of Wastewater

The characteristics of raw sewage used during the investigation are presented in Table.1. The wastewater is categorized as low strength complex wastewater as the total chemical oxygen demand ( $COD_{tot}$ ) is less than 2000 mg/l.

Table 1: The Physico-Chemical Characteristics Of Raw Domestic Wastewater

Parameter	Value	Parameter	Value
Total chemical oxygen demand ( $COD_{tot}$ )	190 mg/l	Temperature	21 C°
Coarse suspended solids COD ( $COD_{ss}$ )	63 mg/l	PH-value	7.50
Colloidal solids COD ( $COD_{col}$ )	39 mg/l	Dissolved oxygen (DO)	0.81 mg/l
Soluble solids COD ( $COD_{sol}$ )	79 mg/l	Turbidity	37 Btu
Total total solids ( $TS_{tot}$ )	3487 mg/l	Ammonia Nitrogen (Total N)	40 mg/l
Coarse suspended solids TS ( $TS_{ss}$ )	193 mg/l	Phosphorus (Total P)	9 mg/l
Colloidal solids TS ( $TS_{col}$ )	63 mg/l	Biological Oxygen Demand (BOD)	139 mg/l
Soluble solids TS ( $TS_{sol}$ )	3231 mg/l	Dissolved oxygen (DO)	0.81 mg/l

### 2.4 Experimental Set-up

Two runs were carried out depending on the preaeration time. The flow rates of these runs were 0.5, 0.35 l/min as a result of using detention time one hour & one hour and half respectively. Ferric chloride (M.W. 279.3, Min. assay 97%) was added to the aerated wastewater in the rapid mixing tank with dose 60 mg/l. Ferric chloride was chosen from jar test experiments which have been carried out by taking samples from preaerated wastewater to fill up the six one-liter beakers of the installation. Different coagulant dosages were added to each beaker. The experiment was started up with flash stirring using rush diffused air for one minute for coagulation followed by slow stirring using calm diffused air for 20 to 30 minutes for flocculation, then stirring was stopped to allow flocs to settle for 30 minutes.

The clarity of the supernatant was used to determine the optimum coagulant dosage by measuring turbidity level. The coagulants, which were used in jar test, were alum for eight trials with different dosages, ferric chloride and slag for four trials each with different dosages. Measurement of the turbidity of supernatant was used to select the best dosage of the six samples.

The solution of the ferric chloride was prepared in the laboratory of the plant. The degree of concentration was 10% so the rates of the solution which were added through the two runs were 17.7, 12.4 ml/hr respectively. Mixing and flocculation processes were carried out by using pressurized diffused air, which consisted of porous stone sheets to induce fine air bubbles. Air was supplied by an air pump through a piping system constructed using plastic pipes, nozzles, elbows and tees.

Composite samples for the raw wastewater (at the inlet of the system), the aerated wastewater (from the preaeration tank) and the settled wastewater (at the outlet of the system) were taken six times per day at 7am, 10am, 1pm, 4pm, 7pm, 10pm. (each sample was 1 lit).

The physico-chemical parameters were measured for these composite samples to express the characteristics of the wastewater before and after the treatment. The excess sludge was removed daily by a valve in the bottom of the sedimentation tank. TSS and volume of sludge were determined also.

### 2.5 Parameters Measured

The raw wastewater and the treated wastewater were analyzed to determine the efficiency of treatment. The physico-chemical parameters measured included: turbidity, temperature, pH-value, dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD<sub>5</sub>), total solids (TS), fixed residual solids at 500°C and volatile solids.

### 3. RESULTS

Forty-eight raw, preaerated and treated sewage samples have been taken for the experimental work and analyzed for physico-chemical parameters. Turbidity (Btu) of the supernatant has been used as a control parameter for the determination of the optimum dosage of coagulant during the entire trail. The results are presented in fig.5 and fig.6 to show the relationships between unit loading rate of COD<sub>tot</sub> & TS and unit removal rate. The unit removal rate is determined at two incremental steps of the treatment process. The two incremental steps include the total removal due to preaeration & chemical precipitation processes (**Pch**-step) and chemical precipitation process only (**Ch**-step). The unit loading rate and the unit removal rate are calculated as follows

$$\text{Unit Loading Rate (mg/mg)} = \text{RS} / \text{CD}$$

$$\text{Unit Removal Rate Pch-Step (mg/mg)} = (\text{RS} - \text{SS}) / \text{CD}$$

$$\text{Unit Removal Rate Ch-Step (mg/mg)} = (\text{PS} - \text{SS}) / \text{CD}$$

In which,

RS = Raw Sewage

SS = Settled Sewage

PS = Preaerated Sewage

CD = Coagulant Dosage

Using the semi-technical scale field installation shown in Fig.3. Two runs have been investigated to evaluate the system performance for which each run has been continued for six days. The efficiency depends mainly on the aeration period of the preaeration process and the optimum dosage of the most effective coagulant. The preaeration period during the first run was one hour whereas it was taken up to one and half hour during the second one. According to the results of the laboratory pre-investigation, ferric chloride has been proven as the most effective coagulant at an optimum dosage 60 mg/l.

A daily sample was taken periodically from different locations of the system for physico-chemical analysis. These locations included sewage source, preaeration basin as well as settling basin effluent. The physico-chemical analysis included the determination of chemical oxygen demand (COD) fractions, total solids (TS), total suspended solids (TSS), volatile suspended solids (VSS) and total fixed solids (TFS).

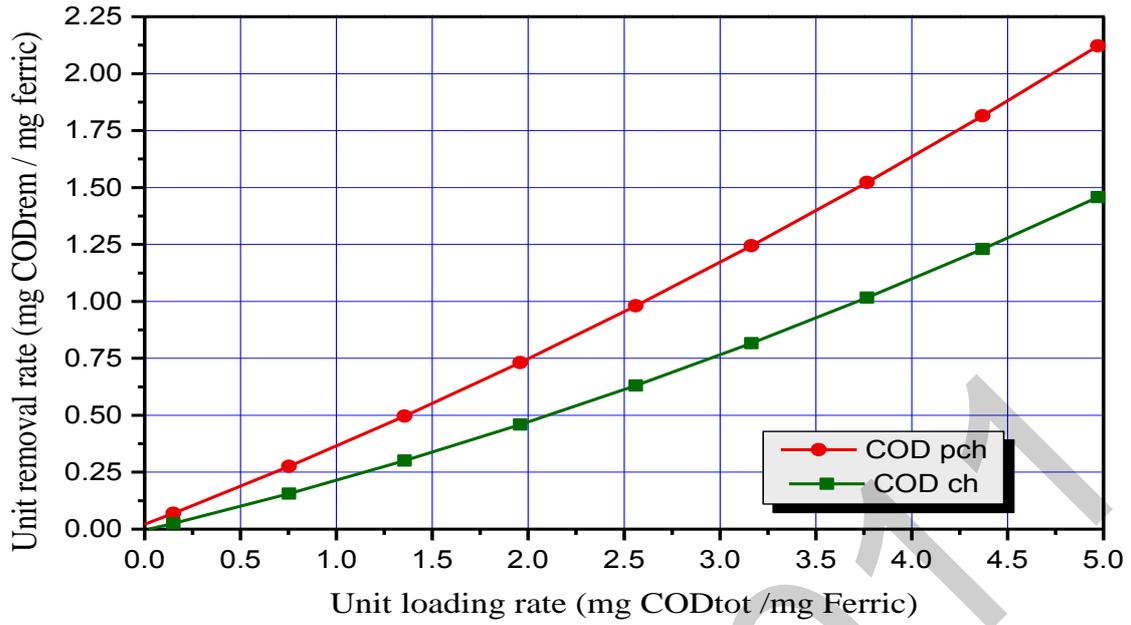


Figure 5: Relation between unit loading rate of  $COD_{tot}$  & unit removal rate of  $COD_{rem}$  for ferric experiments

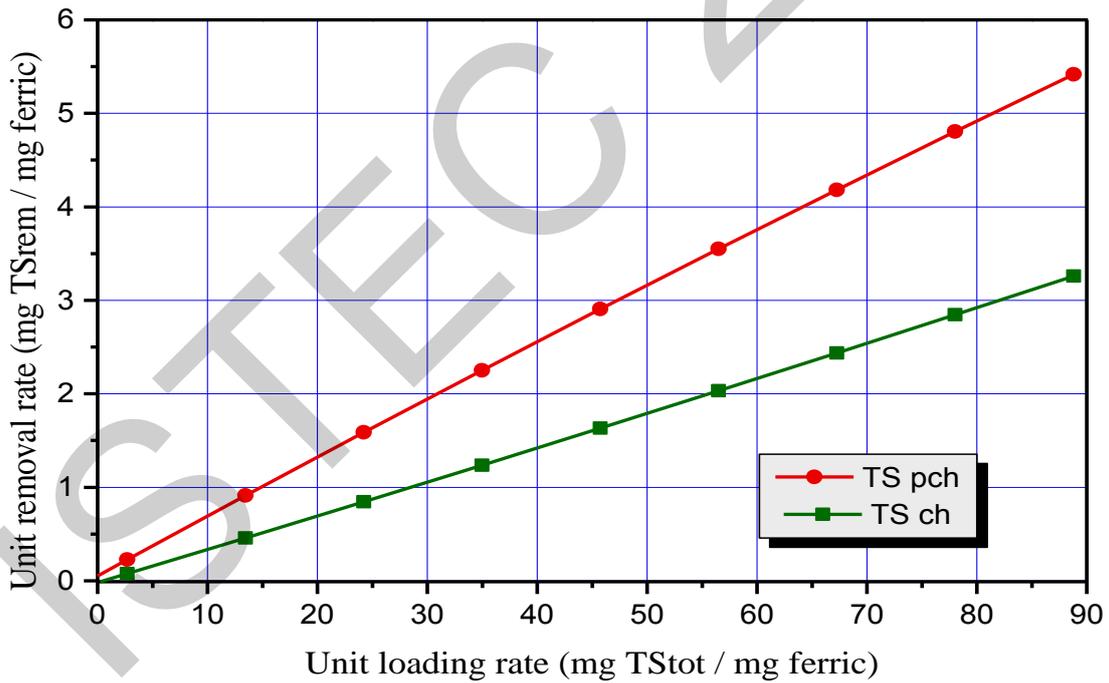


Figure 6: Relation between unit loading rate of  $TS_{tot}$  & unit removal rate of  $TS_{rem}$  for ferric experiments

The results are presented in Fig.7. to Fig.18. to show the relationships between total chemical oxygen demand (COD<sub>tot</sub>), total suspended solids (TSS), unit loading rate of chemical oxygen demand and time in hours according to preaeration and chemical precipitation processes.

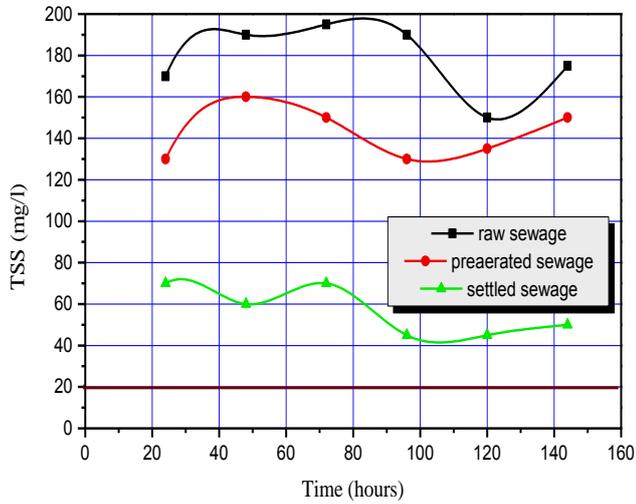


Figure 7: Relation between TSS & time for run 1

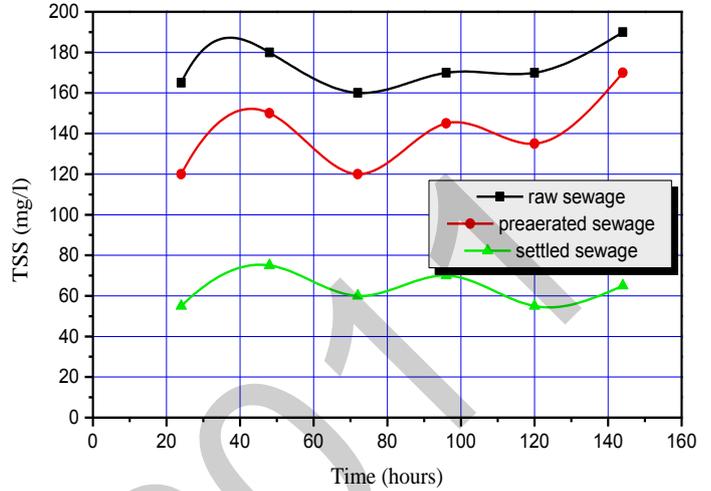


Figure 8: Relation between TSS & time for run 2

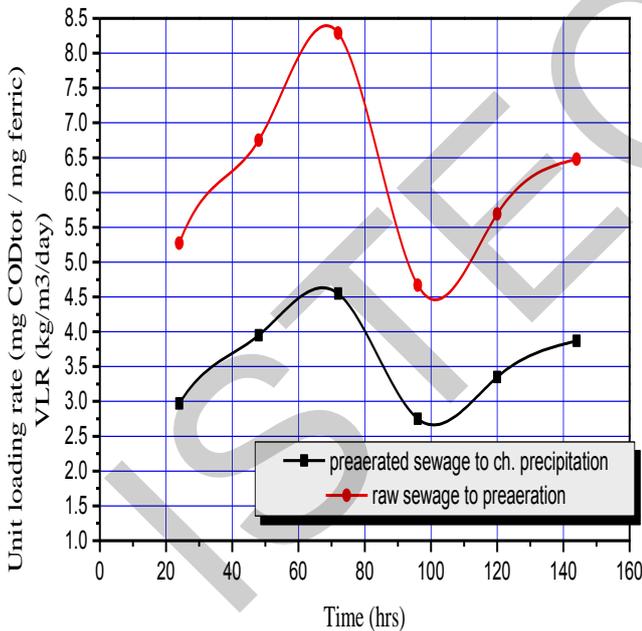


Figure 9: Relation between unit loading rate, VLR & time for run 1

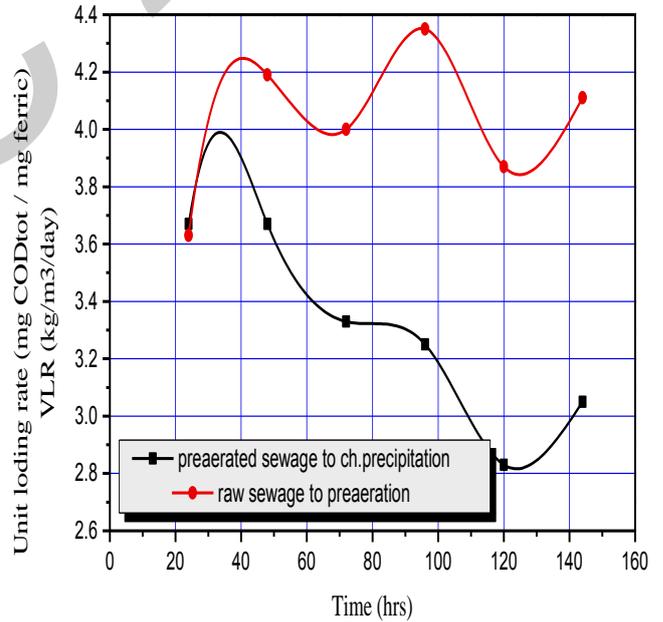


Figure 10: Relation between unit loading rate, VLR & time for run 2

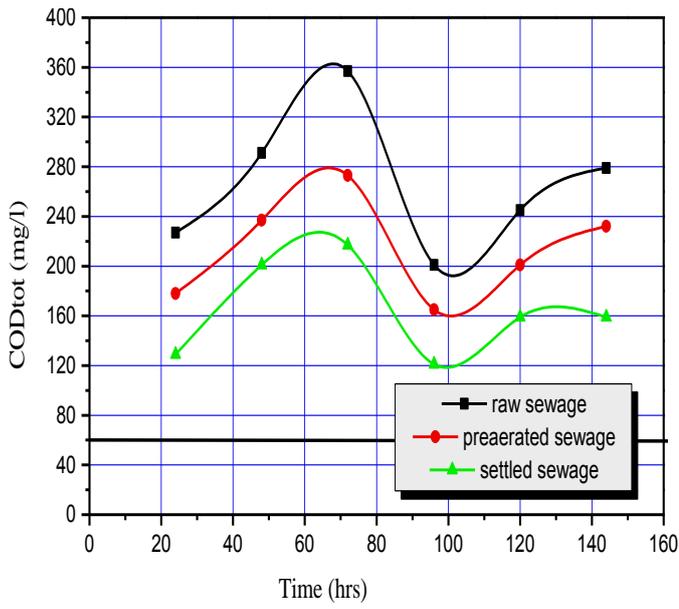


Figure 11: Relation between COD tot & time for run 1

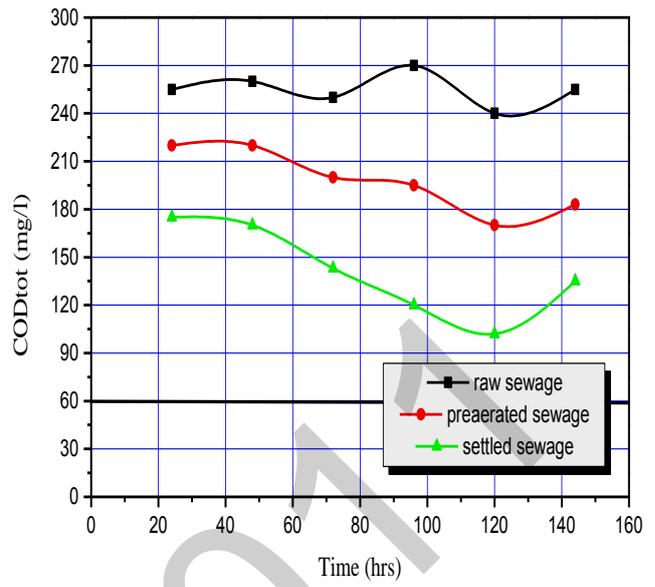


Figure 12: Relation between COD tot & time for run 2

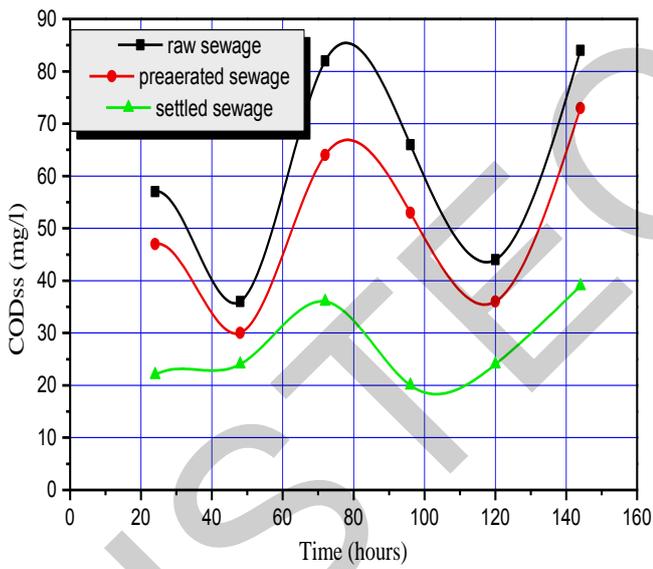


Figure 13: Relation between CODss & time for run 1

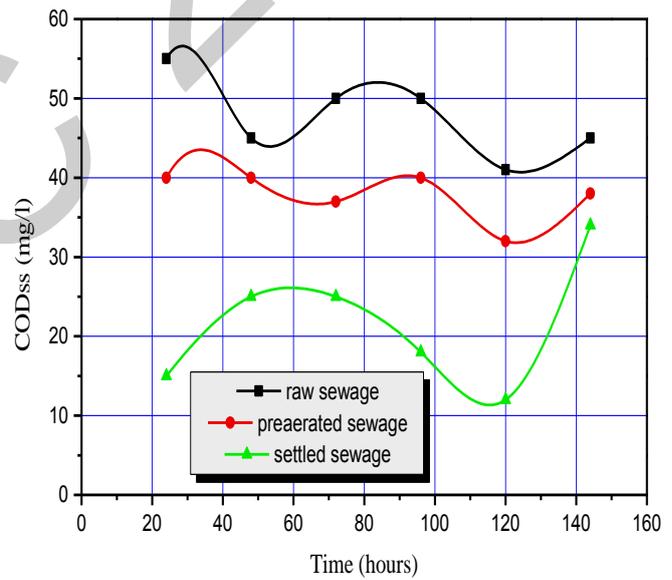


Figure 14: Relation between CODss & time for run 2

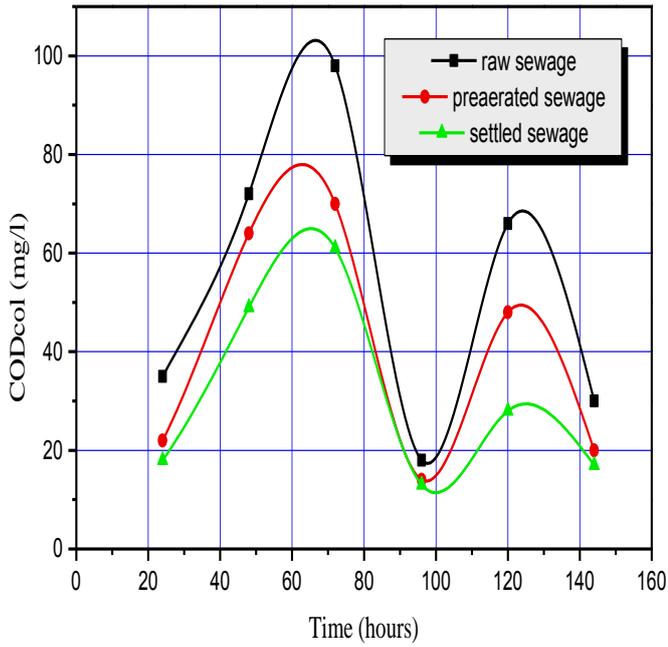


Figure 15: Relation between CODcol & time for run 1

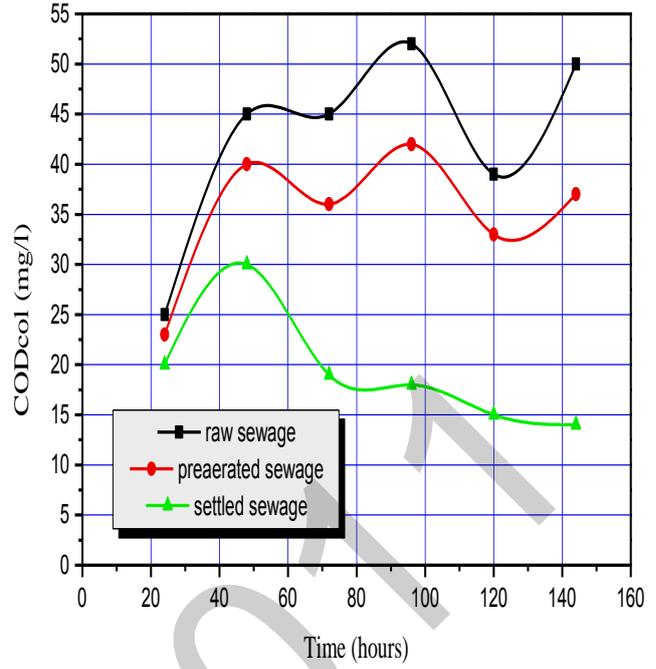


Figure 16: Relation between CODcol & time for run 2

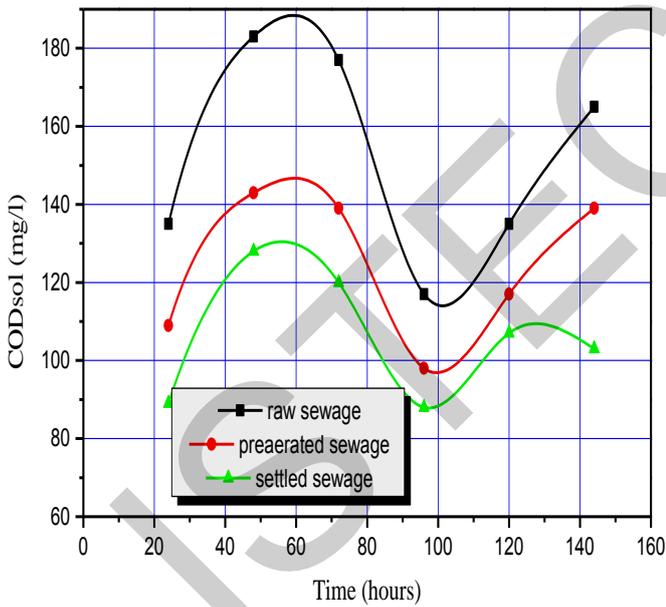


Figure 17: Relation between CODsol & time for run 1

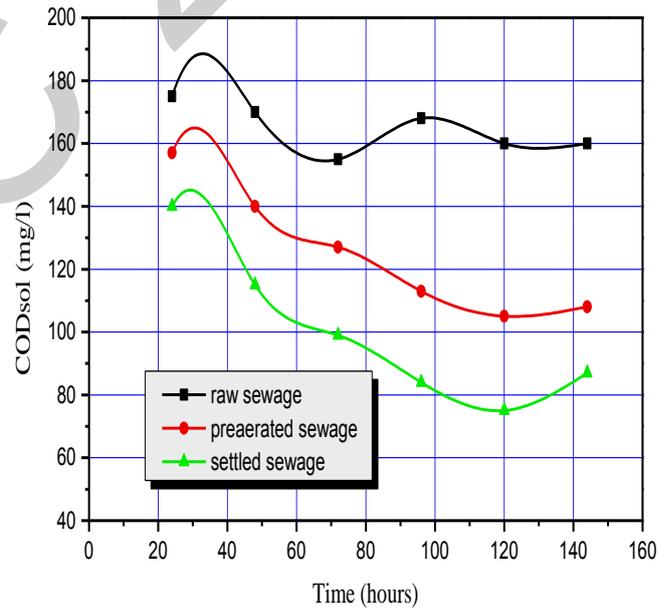


Figure 18: Relation between CODsol & time for run 2

#### 4. DISCUSSION

Chemical coagulation of wastewater proceeded by bioadsorption of soluble fraction is the main goal of this study. The experimental set-up of the semi-technical scale field installation investigation has been designed to cope with this goal. The field investigation included the methodology that consisted of all processes involved in the treatment scheme.

Raw sewage has been preaerated before running the chemical precipitation process to prevail the bioadsorption process of the soluble fraction. It was anticipated that the reduction of soluble fraction will advance the efficiency of (COD<sub>tot</sub>) removal as it is well-known that addition of metal coagulant to (waste) water will virtually increase the soluble portion of (COD) as reported by Metcalf and Eddy.

Pressurized air was used to induce mixing either during coagulation or during flocculation to enhance and continue the favor preaeration conditions of the sewage samples as well as reopening flocs built-up in a smoothly scheme as reported by Varley, J. More than one run has been prevailed with the same coagulant to cover as maximum range of sewage strength as possible.

As the preaeration process affects the whole treatability process, it was decided to consider the aeration time is the main parameter of running the field plant under condition that the retention of wastewater in the next basins (flocculation & sedimentation) are still with the design operating ranges.

The preaeration process has been processed using pressurized diffused air at concentration range of 2.0-3.0 mg O<sub>2</sub> /lit. Two runs depending on the aeration period of the preaeration process have been investigated to evaluate the system set-up for which each run has been continued for six days.

The flow rates of these runs were 0.5 & 0.35 l/min as a result of using aeration time one hour & one and half hour respectively. The analysis of the results show that the removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the first run ranges between 17 to 24% & 15 to 22% & 12 to 38% & 14 to 22% respectively whereas the removal efficiency of (TS) and (TDS) ranges between 2 to 4% & 1 to 3% respectively. The removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the second run ranges between 14 to 30% & 12 to 28% & 8 to 26% & 11 to 35% respectively whereas the removal efficiency of (TS) and (TDS) ranges between 2 to 4% & 1-3% respectively.

According to analysis of the results of the jar test treatability investigation, it can be assessed that cement slag is not effective for the removal of colloidal fraction COD<sub>col</sub> as alum and ferric chloride. Hence, it cannot be used as a coagulant at all. Also it can be noted that alum and ferric chloride can provide high efficiency for the removal of coarse suspended solids fraction COD<sub>ss</sub> and colloidal fraction COD<sub>col</sub>. The results of ferric chloride are satisfactory and so high than expected that it can be considered preferable than the use of alum for its economy and availability as well as avoiding the dewatering problems of aluminated sludge.

According to the previous results of the laboratory pre-investigation, ferric chloride has been proven as the most effective coagulant at an optimum dosage 60 mg/l. Ferric chloride (M.W. 279.3, Min. assay 97%) has been added to the aerated wastewater in the rapid mixing tank with dose 60 mg/l. The degree of concentration was 10% so the rates of the solution which have been added through the two runs were 17.7, 12.4 ml/hr respectively. Mixing and flocculation processes have been carried out by using pressurized diffused air.

Sedimentation process has been carried out to remove readily settleable solids and floating material of sewage coming from the flocculation basin and thus reduce the suspended solids content. The analysis of the results due to chemical precipitation show that the removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the first run ranges between 16 to 32% & 20 to 63% & 8 to 42% & 9 to 26% respectively whereas the removal efficiency of (TS), (TSS), (VSS) and (TDS) ranges between 5 to 7% & 47 to 67% & 63 to 77% & 1 to 6% respectively. The removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the second run ranges between 21 to 40% & 33 to 63% & 13 to 63% & 11 to 29% respectively whereas the removal efficiency of (TS), (TSS), (VSS) and (TDS) ranges between 4 to 7% & 50 to 62% & 62 to 80% & 1 to 4% respectively.

The overall results of the treatment process is represented by the overall removal efficiency of The results analyzed for the treatment scheme, which includes preaeration process followed by chemical precipitation show that the removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the first run ranges between 31 to 44% & 34 to 70% & 28 to 58% & 21 to 38% respectively whereas the removal efficiency of (TS), (TSS), (VSS) and (TDS) ranges between 6 to 10% & 59 to 77% & 73 to 83% & 1 to 7% respectively. The removal efficiency of (COD<sub>tot</sub>), (COD<sub>ss</sub>), (COD<sub>col</sub>) and (COD<sub>sol</sub>) for the second run ranges between 32 to 58% & 45 to 73% & 12 to 66% & 20 to 54% respectively whereas the removal efficiency of (TS), (TSS), (VSS) and (TDS) ranges between 6 to 10% & 59 to 80% & 70 to 85% & 2 to 6% respectively.

## 5. CONCLUSIONS & RECOMMENDATIONS

The main aim of the study is the investigation of the removal of different COD fractions of domestic sewage using Preaeration & Chemical Precipitation processes. According to the results of the prevailing study, It can be concluded that the treatment system using preaeration and chemical precipitation induces a good performance for removal of colloidal and coarse suspended solids fractions. The removal of soluble fraction is not high enough to permit for final effluent for disposal into waterways so post treatment using activated sludge is suggested to reduce the residual soluble fraction so as the final effluent characteristics can comply with the regular standards for disposal into waterways.

Also, it can be recommended that:

1. Cement slag is not effective for the removal of colloidal fraction COD<sub>col</sub> as alum and ferric chloride. The results of ferric chloride are satisfactory and so high than expected that it can be considered preferable than the use of alum for its economy and availability as well as avoiding the dewatering problems of aluminated sludge so ferric chloride is assessed as the most effective coagulant at optimum dosage 60 mg/l.
2. Preaeration process may cause pre-flocculation as sludge flocs can be formed in the preaeration tank enhancing the removal of some coarse suspended solids and colloidal particles.
3. The air mixing may be considered better than the mechanical paddles due to the enhancement of bacterial activity as well as avoiding paddles caused vortex action that leads to destroy of sludge flocs and increasing costs for operation & maintenance.

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# FINITE ELEMENT SIMULATION OF INTACT FEMUR FOR OUTER AND INNER SURFACES

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## Abstract

Finite element simulation has become increasingly important for analyzing femoral bone. Existing study only analyzed femoral at outer surface. The aim of the study was to validate simulation work with experimental work and to evaluate Von mises strains for inner surface of the femur. A standardized femur was taken from BEL bone repository, Italy. It was used as a basis for finite element modeling. The model is assumed to be isotropic and linear elastic. The load case comprise of head load and abductor load. For this study, ANSYS Workbench version 11.0 was used for the analysis. The values in anterior, posterior, medial and lateral positions of the femur have been recorded. The strains in different direction and surfaces of the femur for hip loading models were plotted and compared with experimental model and other researcher's finding. The finding of Von Mises strains for inner surface of the femur is important for the study of total hip replacement (THR).

**Key words:** Biomechanics; Hip; Finite element method; Simulation

## Introduction

The femur is one of the most highly loaded bones in the human body. Along with experimental work designed to verify the authenticity of the finite element (FE) model, the FE method has been employed to obtain comprehensive information about the states of stress and strain in the intact femur.<sup>1-4</sup> Most of the experimental and simulation studies performed, to date, have assumed that the intact femur was being subjected to simple forces, together with the reaction force and the abductor load.<sup>5,9</sup> The finite element method (FEM) is one of the tools used for the solution of complex problems, such as those in orthopedic biomechanics.<sup>4</sup> Since the past four decades, two- and three-dimensional FEM have been applied.<sup>3</sup> FEM demands meticulous attention during the modeling of the intact femur and while creating the FE mesh.<sup>6</sup> In general, there are two basic ways to generate an FE model from computed tomography (CT) scans: geometry-based and voxel-based.<sup>11</sup> One of the ways to create an FE mesh for the intact femur is by using the automated mesh generation (AMG) technique, which has been verified by carrying out experimental work.<sup>6</sup> However, experimental work on the intact femur gives data only for outer femoral surface strain.<sup>1</sup> To the best of the authors' knowledge,

there are no literature reports on simulation work on the inner surface of the intact femur. Therefore, this study has sought to verify the FE simulation work on the outer femoral surface with experimental work<sup>6</sup> by using von Mises strain, and then using the verified model to determine the strain on the inner surface of the intact femur.

**Material and methods**

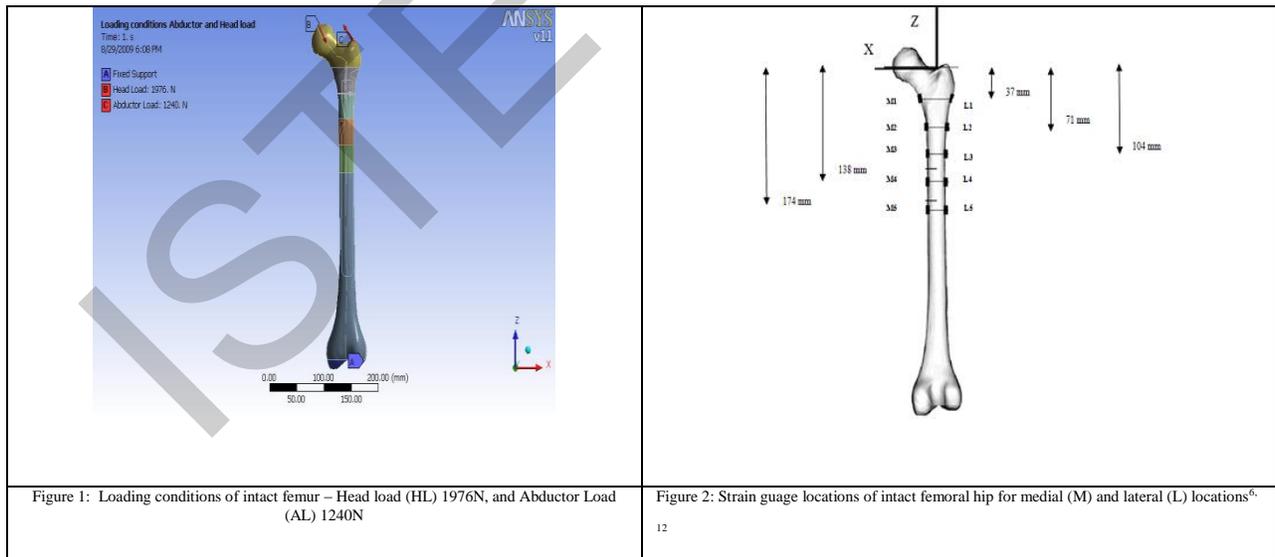
In the present study, the model of an adolescent -sized femur (length 420 mm, canal diameter of 13.0 mm) was selected for which the widely used standard Initial Graphics Exchange Specification (IGES) format file was used.<sup>6</sup> Finite element models were generated by using the ANSYS Workbench software (version 11.0). The material used for the femoral bone was a glass fiber with a Young’s Modulus of 14,200 MPa and a Poisson’s ratio of 0.3.<sup>6</sup> The model was assumed to be homogeneous, isotropic, and linearly elastic. The FE mesh of the model consisted of a total 16692 elements and 32024 nodes. The femoral bone was fixed at the distal end; the loading condition is illustrated in Figure 1. A head load (HL) and an abductor load (AL) were considered for the loading conditions. The components of the loads in x, y, and z directions acting on the femur are given as follows<sup>6</sup>:

For the head Load (HL) = 1976 N ( $F_x = 927.68N, F_y = 0; F_z = -1744.7 N$ ) and for the abductor load (AL)= 1240N ( $F_x = -797.06N, F_y = 0; F_z = 940.89N$ )

The methodology of the analysis involved two steps. Firstly, strain values were obtained at the medial (M), lateral (L), anterior (A), and posterior (P) positions on the outer surface of the intact femur. These locations were denoted as M1, M2, M3, M4, M5, L1, L2, L3, L4, L5, A1, A2, A3, A4, A5, P1, P2, P3, P4, and P5, as shown in Figures 2 based on their respective distance from the datum. Secondly, the strain values for the inner lateral (L), inner medial (M), inner anterior (A), and inner posterior (P) surfaces were included in the results. The results for the outer and inner strain values were then plotted and have been shown in Figures 3 and 4(a)–4(d). Finally, the results were analyzed and discussed.

**Results and Discussion**

The first part of the study was to benchmark the model by comparing the results of the simulation with that of the experimental work for the outer femoral surface. Figure 3 shows the comparison of the data obtained from ANSYS V11.0 simulation for experimental and AMG simulation results for the axial strain along the intact femur.<sup>6</sup> There was good agreement between the



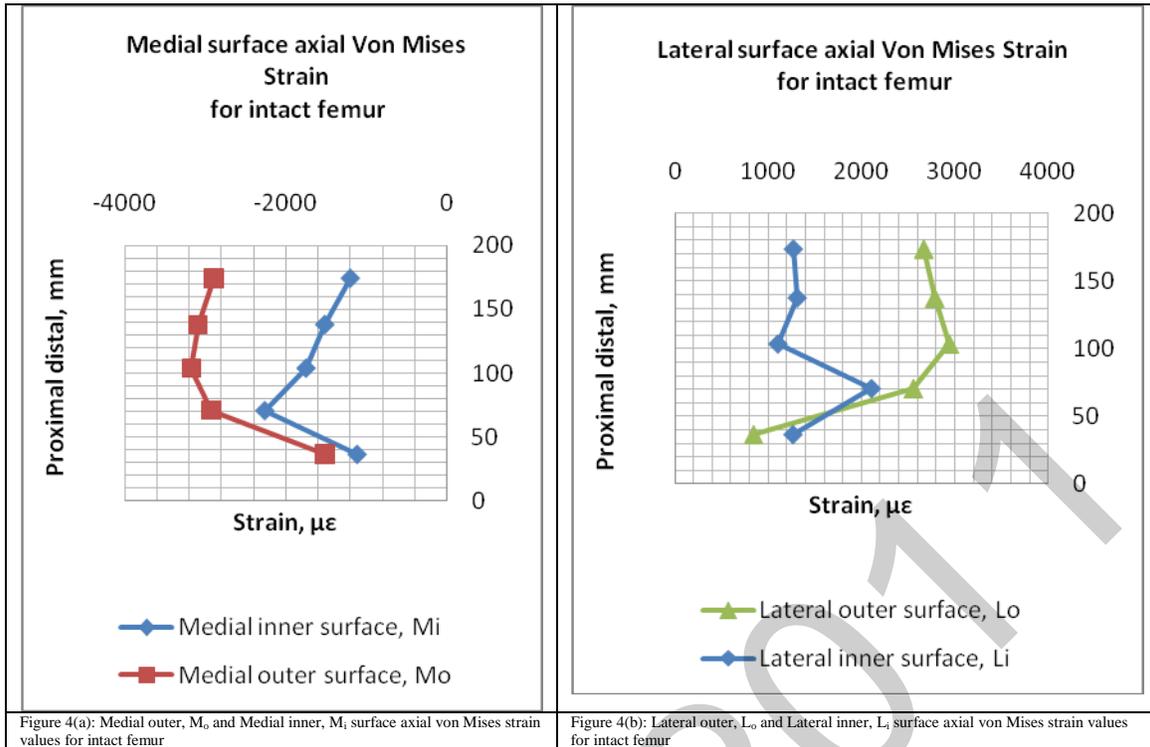


Figure 4(a): Medial outer,  $M_o$ , and Medial inner,  $M_i$  surface axial von Mises strain values for intact femur

Figure 4(b): Lateral outer,  $L_o$ , and Lateral inner,  $L_i$  surface axial von Mises strain values for intact femur

experimental and simulation results, which indicated that the model developed was acceptable in terms of geometry, boundary conditions, and loading. After benchmarking, the same model was used for simulation of the inner surface. Figures 4(a), (b), (c), and (d) show the von Mises strain results obtained for the medial (M), lateral (L), anterior (A), and posterior (P) locations in the outer and inner surfaces of the intact femur. It can be seen that for the medial (M) and lateral (L) positions in the outer surface of the femur, the highest peak occurs at the M3 and L3 locations, and the smallest peak occurs at the M1 and L1 locations. For the medial (M) and lateral (L) positions on the inner surface, the highest peak occurs at the M2 and L2 locations, and the smallest peak occurs at the M1 and L3 locations. For the anterior (A) and posterior (P) positions on the outer surface of the femur, the highest peak occurs at the A1 and P2 locations, and the smallest peak occurs at the A5 and P4 locations. For the anterior (A) and posterior (P) positions on the inner femoral surface, the highest peak occurs at the A2 and P1 locations, and the smallest peak occurs at the A5 and P4 locations. Figure 5(a) shows the minimal and the maximal von Mises strain values while Figure 5(b) shows the minimal and the maximal von Mises stress values for the intact femur. From these figures, it can be seen that the strain values at the outer and inner surfaces were not the same. This indicates that the stresses on the femur were not uniform, which gave rise to circumferential bending. This phenomenon was due to the fact that the load was applied on the femoral head, and because the line of action of the load did not coincide with the axis of symmetry of the femur. This offset caused bending of the femur. Therefore, strain measurement at the outer femoral surface alone is not sufficient to predict the inner femoral surface strain. Hence, the results of the present study are very important, especially because experimental measurement of inner femoral surface strain using strain gauges is not easy due to the limited space available. In the case of total hip replacements (THRs), inner surface strain is likely to be one of the factors to cause loosening of the THRs as the femoral implant makes contact with the inner surface of the femur. The effect of inner femoral surface strain on implant behavior will be the subject of a future paper. The aim of the present study was to validate simulation work, particularly, the FE model, the geometric model, constraints, and loading arrangement by comparing FE results with experimental results by using outer surface strain values. The models were later used to evaluate the von Mises strain for the inner surface of the femur. During the benchmarking stage, it was found that the present simulation results for strain at the outer femoral surface were very close to the experimental results (Figure 3).<sup>6</sup> Generally, the outer von Mises strain values were greater than the inner von Mises strain values for the medial (M) and lateral (L) surfaces of the femur. For medial (M) and lateral (L) positions on the outer femoral surface, the highest peak occurs at the M3 location and the smallest peak occurs at the M1 and L1 locations. For the anterior (A) and posterior (P) positions on the outer femoral surface, the highest peak occurs at the A1 and P2 locations while the smallest peak occurs at the A5 location. All these results are similar to those reported by McNamara et al. (1997).<sup>2</sup> However, the smallest peak which occurred at the P4 location was not in agreement with results reported by McNamara et al. (1997)<sup>2</sup> according to which the smallest peak occurred at the P1 location.<sup>2</sup> For the medial (M) and lateral (L) positions on the inner femoral surface, the highest peak occurred at the M2 and L2 locations while the smallest peak occurred at the M1 and L3 locations. For the anterior (A) and posterior (P) positions on the inner femoral surface, the highest peak occurred at the A2 and P1 locations while the smallest peak occurred at the A5 and P4 locations.

Thus, by knowing the location and values of the highest peak for the inner surface of an intact femur, better understanding can be gained about various problems related to THRs, such as i) the method to reduce fixation failure<sup>7</sup>, ii) the means to improve the longevity of THRs,<sup>8</sup> iii) the method to reduce the factors contributing to the probability of failure, such as uncertainty in joint loading, cement strength, and implant interface strength, and iv) ways to predict long-term events like loosening of the THRs.<sup>9</sup> As for the minimal and the maximal von Mises stress and strain values for the intact femur shown in Figures 5(a) and 5(b), the greatest amount of stress or strain would be expected to occur at the greater trochanter.<sup>10</sup> This location is in the region where femoral neck fractures could happen, and is also, in the vicinity of the implant rim.<sup>4</sup> The FEM used in this study was based on a number of assumptions and simplifications. These assumptions were that i) the bone has no muscle, ii) that there was only one load, and iii) that the material is linearly elastic, homogeneous, and isotropic. These parameters will be taken into account for future FE analysis.

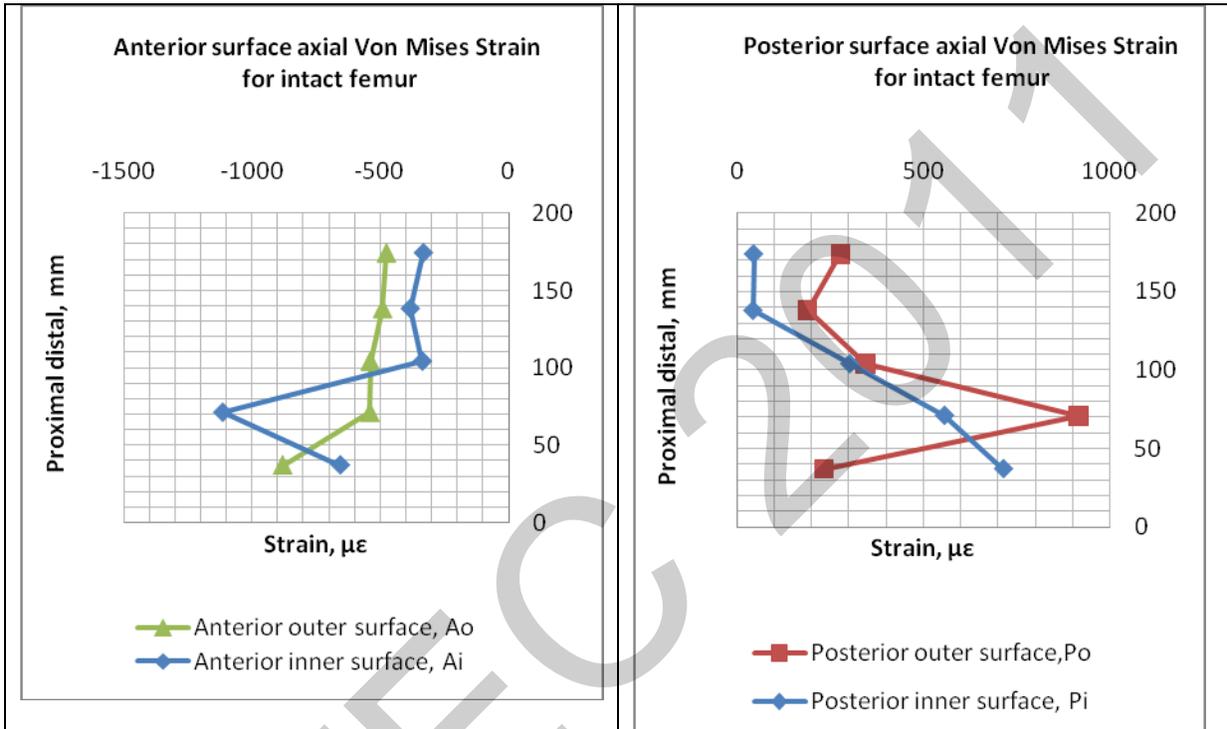


Figure 4(c): Anterior outer, A<sub>o</sub>, and Anterior inner, A<sub>i</sub> surface axial von Mises strain values for intact femur

Figure 4(d) : Posterior outer, P<sub>o</sub>, and Posterior inner, P<sub>i</sub> surface axial von Mises strain values for intact femur

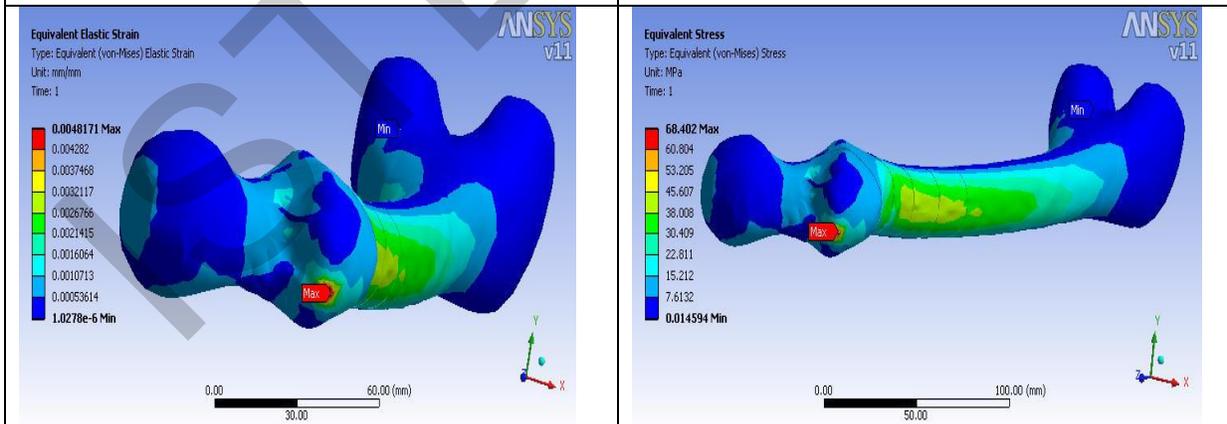


Figure 5(a): Maximal von Mises strain, 4917.1 µ, and the minimal von Mises strain, 1.0278 µ, for intact femur

Figure 5(b): The maximal von Mises stress 68.402 MPa, and the minimal von Mises strain, 0.014594 MPa, for intact femur

**Conclusions**

In summary, it can be concluded that a benchmarked FE model of a femoral bone was successfully developed and realized in this study. Our results show that when the glass fiber material of the femoral bone model is modeled based on the assumption that it is linearly elastic, homogeneous, and isotropic, a very good agreement was observed between experimental<sup>6</sup> and FE analysis results. Strain distribution in the femur indicated that the strain was not uniform on the outer and inner surfaces of the femur, resulting in

circumferential bending due to load offset. Thus, measurement of von Mises strain values for the inner surface of the femur is important for the study of total hip replacements (THRs).

### Acknowledgement

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# FORMULATION AND ELABORATION OF A ULTRA HIGH-PERFORMANCE CONCRETE (UHPC) BASED ON LOCAL CALCINED CLAY

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## Abstract

Although still, composed of cement, aggregates and water, the ultra high performance concretes (UHPC) are new materials that have high mechanical properties, combined with durability. This type of concrete used in large amounts of silica fume, ultra fine addition that gives very high performance but also relatively expensive. Replacing it with another additive such as clays, after thermal activation and conversion into metakaolin, have features that allow a glimpse of a recovery in the construction field.

This work is concerned with the valorization of a local calcined clay named Djebel Debagh quality 3 (DD3), for the formulation and elaboration of ultra high performance concretes.

To reach our purpose, the amount of additives used is 25%, whose role is to consume portlandite  $\text{Ca}(\text{OH})_2$  released during cement hydration. While the percentage of metal fibers varies from 1 to 3% to obtain ductility and high mechanical strength.

The results show that the addition of calcined clay DD3, in substitution of silica fume can be successfully used to develop an ultra high performance concrete because the new material obtained is sufficiently strong, more performance in terms of hydration and attractive in terms of cost. In addition, it allows considering the development of new recovery materials such as clay.

**Keyword:** Resistance, ductility, metakaolin, pozzolanic activity, UHPC

## 1. Introduction

In the mid-20th century, researchers have mainly reported on adherence steel-concrete and more specifically on the performance of the reinforcement that led to the idea of prestress providing the prestressed concrete. During this same period, scientists are individualized to improve the concrete components by obtaining strength between 80 and 100 MPa, but their technologies and methods were difficult to generalize

The first cementitious materials in ultra-high performance appeared in the 1970s (cement pastes "compact" to 640 MPa, W/C = 0.21 with heat curing at 250 °C and pressing at 345 MPa, by [Roy and Gouda, 1973].

The UHPC materials are cement matrix, with compressive strength greater than 150 MPa. These materials are added to metal fibers (UHPC) to obtain a ductile behavior in tension. They are also characterized by their strong binding assay and selection of which particular aggregates are the subject [AFGC, 2002]

The UHPC is used both by the concrete industry to build prefabricated products and directly on site. They are generally self-compacting and pumpable perfectly. Generally these concretes are made with addition of silica fume as an addition ultrafine however the latter has a high cost, for this reason the research is interested to find an alternative.

The objective of this study is the development of a fibrous concrete to ultra high performance (cement, sand, meta kaolin, metal fiber and adjuvant) with varying percentages

The study of the Physical and mechanical characteristics of components and the mechanical behavior of the material using conventional techniques based on the principles of resistance materials

The elaboration of compositions of fiber-reinforced concrete, which must have all the qualities required for rheological concrete structures, hence the need for a study to develop a method for optimal formulation of concrete fibers and compare the characteristics of this material to those of a traditional concrete formulated optimally

## 2. Experimental program

### 2.1. Used materials

#### 2.1.1. Cement:

The cement used is Portland cement CEM I-442 NA 42.5 N-ES

The composition of cement and its mechanical, chemical and physical characteristics are shown in the table below

**Table 1. Physico mechanical and chemical properties of cement used**

standard	NA443 :2005	
The standardized designation Na 442: 2006	Portland cement CEMI 442-NA-42, 5N-ES	
last dénomination	Sulphate-resistant cement (SRC)	
Class	ES (designed to work in highly aggressive environments especially for concrete work in the presence of water containing high percentage of sulfate)	
Composition of the cement	Clinker $\geq 95\%$ gypsum $\leq 05\%$ 0% secondary constitute	
Class of resistance	Resistance minimum guarantees to 02 days	Resistance minimum guarantees to 28 days
42,5n	08MPa	40,0MPa
Technical Characteristics	C3A C4AF + 2 (C3A) Ignition weight loss insoluble residue MgO SO3 chloride expansion Time to start making	$\leq 5,0\%$ $\leq 20,0\%$ $\leq 3,0\%$ $\leq 0,75\%$ $\leq 4,0\%$ $\leq 3,5\%$ $\leq 0,10\%$ $\leq 5\text{mm}$ $\geq 60\text{min}$

2.1.2. The sand

In this study, we are limited to one composition in aggregates; with only one type of sand The sand used was fine sand from the sandpit of Oued Souf

**Table 2. Physical properties of sand**

properties	value
The bulk density (g/cm3)	1.7
The absolute density (g/cm3)	2.72
Sand Equivalent Visual (%)	75
Fineness modulus	2.53

2.1.3. The adjuvant

The adjuvant used is named "MEDAFLOW 30" from the company Granitex it is a superplasticizer high range water reducer of the third generation. It is designed based on poly carboxylates that significantly improve the rheological properties of concrete. The MEDAFLOW 30 provides concrete and mortars of very high quality

**Characteristics**

form	color	PH	Density	Chloride content	dry extract
Liquid	yellow	6 -6.5	1,06 $\pm$ 0,01	< 1 g/l	30 %

**Dosage**

Recommended Dosage: 0.5 to 2.0% by weight of cement is 0.5 to 1.850 liters per 100 kg of cement. The optimum dosage should be determined on site depending on the type of concrete and the desired effects

2.1.4. The metallic fibers

The fibers selected for this study are metallic fibers steel (local wireless) from 1 to 15mm in length and 1.2 mm in diameter (Figure 1)



**Figure 1. Metallic fibers used**

### 2.1.5. Silica fume

Silica fume is an amorphous silica powder extremely fine particle size which is between 0.05 and 0.5 microns, recovered in the chimney during the condensation reaction gases from the manufacture of silicon or alloys of these.

### 2.1.6. metakaolin

The clay used is clay Jebel Debagh grade 3 (DD3). This clay was calcined in a laboratory furnace at a temperature of 750 ° C. At this temperature, the calcination of the clay is maintained for a period of 4 hours to undergo polymorphic transformations. After cooling, the calcined clay was ground to pass through a sieve full of mailles 75µm



Figure 2. The clay DD3 after calcination

Table 3. Chemical composition of additions

elements (%)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Mg O	Na <sub>2</sub> O	SO <sub>3</sub>	K <sub>2</sub> O	LOI
DD3	40,47	43,3	0,28	1,49	0,39	0,206	0,00	1.287	0,00
SF	94.30	0.69	0.14	1.17	0.29	0.238	0.00	1.430	4.74

In order to evaluate the pozzolanic character of the clay used, we determined the pozzolanic reaction in a solution of lime, the study of the reactivity of pozzolan samples was inspired by the Chappelle test [Chinje melo and Billong, 2004 , Benedict, 1967], which is to determine the difference between the initial and final concentration of lime solution and allowing the rates fixed by CaO calcined clay. The results of the pozzolanic reactivity of the samples: silica fume and calcined DD3 are shown in Table 4

Table 4. Pozzolanic reactivity of metakaolin and silica fume

Samples	Temperature (°C)	Lime as CaO in solution (g/l)	Amount set by 1 g of Cao sample compared to the initial amount of CaO (1.18 g / l)	
			Concentration (g/l)	Pourcentage (%)
DD3	750	1,81	0,259	85,70
SF	-	0.064	1.116	94.60

Pozzolanic reactivity is indicated by the amounts of CaO determined by the clay (DD3) and silica fume. All sample results show a decrease in the concentration of CaO in the lime solution of 85%. This decrease is further level of silica fume. The calcination at 750 ° C allows the clay from the water content (dehydroxylation) and the formation of metakaolinite [Chinje melo and Billong, 2004; Jouenne 2001; Venuat Michel, 1989 ; Brault, 2001] with an amorphous structure which makes it more reactive than the starting clay. This is an acid-base reaction. This explains the strong decrease in CaO concentration of the solution

## 2.2. Formulation of concrete

The formulation of UHPC is much more complex to identify because of the number of parameters that come into play (cement, sand, additions, admixtures, fibers, water) and their nature in relation to the formulation of concrete. Most formulas are designed UHPC currently experimentally. The method used to design the formulation of UHPC compositions tested in this experimental study is based on the method of Bonneau [Bonneau, 1997. ; Taфраoui, 2009]. Table 5 presents the thirteen (13) formulas used after optimization of the granular skeleton and superplasticizer dosage, from sand Oued Souf, enhanced or non-steel fibers, silica fume or metakaolin.

All concretes were mixed in a mortar mixer vertical axis 5 liters for the homogenization of the powders and the fluidity of the mixture. The following mixing sequence as follows:

- Introduction of cement, and the addition of dry sand into the mixer,
- Mixing of dry powders for 2 minutes,
- Introduction of water and mixing for 3 minutes,
- Introduction of superplasticizer and mixing up thinning (variable length) possible introduction of fibers, and the final mixing about 1 minute.

The mixing sequence is simple and effective action of adjuvants. A change in the sequence of mixing can significantly alter the effectiveness of super plasticizers. Using a different mixing sequence can lead to different performances. However, the sequence of mixing may vary depending on the W / C, the quantity of cement and ultrafine and effectiveness of the super plasticizer used.

**Table 5. The thirteen (13) formulations of UHPFRC**

	Composition	Percentage(%)and weight[Kg/m <sup>3</sup> ]							
		cement	sand	water	adj	FA	DD3	SF	w/C
Group I	BDFA01	800	897,6	160	53,33	(2%) 150	(20%) 160	/	0,2
	BDFA02	800	897,6	160	53,33	(3%) 225	(20%) 160	/	0,2
	BDFA03	800	897,6	160	53,33	(2%) 150	(30%) 240	/	0,2
	BDFA04	800	897,6	160	53,33	(3%) 225	(30%) 240	/	0,2
	BCSDFA	800	897,6	160	53,33	(2,5%) 187,5	(25%) 200	/	0,2
	BFFA	800	897,6	160	53,33	(3%) 225	/	(20%) 160	0,2
Group II	BDD3-01	800	897,6	160	53,33	0	(20%) 160	/	0,2
	BDD3-02	800	897,6	160	53,33	0	(30%) 240	/	0,2
	BCSD	800	897,6	160	53,33	(0%) 0	(25%) 200	/	0,2
Group III	BFA-01	800	897,6	160	53,33	(2%) 150	0	/	0,2
	BFA-02	800	897,6	160	53,33	(3%) 225	0	/	0,2
	BCSFA	800	897,6	160	53,33	(2,5%) 187,5	(0%) 0	/	0,2
controls	BCS	800	897,6	160	53,33	225	(0%) 0	/	0,2

The nomenclature and the optimal mixing time of the various compositions are shown in the following table

**Table 6. Nomenclature and optimal mixing time of the different compositions of UHPFRC**

Nomenclature	Composition	Mixing time	
Group I	BDFA01	Concrete with 20% DD3 and 2% of metallic Fiber	08:04
	BDFA02	Concrete with 20% DD3 and 3% of metallic Fiber	08:26
	BDFA03	Concrete with 30% DD3 and 2% of metallic Fiber	11:42
	BDFA04	Concrete with 30% DD3 and 3% of metallic Fiber	12:03
	BCSDFA	Concrete with 25% DD3 and 2.5% of metallic Fiber	08:21
	BFFA	Concrete with 20% SF and 3% of metallic Fiber	07:12
Group II	BDD3-01	Concrete with 20% of DD3	11:35
	BDD3-02	Concrete with 30% of DD3	08:34
	BCSD	Concrete with 25% of DD3	06:43
Group II	BFA-01	Concrete with 2% of metallic Fiber	06:35
	BFA-02	Concrete with 3% of metallic Fiber	06:01
	BCSFA	Concrete with 2.5% of metallic Fiber	05:35
controls	BCS	controls concrete (without DD3 and metallic Fiber)	07:43

We note that, in all cases, the time of manufacture of a UHPC does not exceed 15 minutes. We also note that the replacement of silica fume by metakaolin leads to a slight increase in mixing time, which may be related to the shape of the ultrafine grain less favorable workability. Finally, the addition of fiber requires a larger mixing time for a similar workability.

### 3. Test results

#### 3.1. Fresh concrete

During manufacture, the characterization of UHPC is required. This behavior is to know in the fresh state from the simple and reproducible tests. The main tests are designed to quickly verify the flow of material.

##### 3.1.1. Spreading test

The test most commonly used to characterize mobility in a confined environment, as the easiest to implement, is spreading test conducted using a cone with mortar ("small" Abrams cone) Indeed, the value of the spread given by the average of two measurements of the diameter of the pancake of concrete found to be more representative than the collapse in the case of concrete is put in place by gravity. This test can also visually supervise the segregation of the concrete.

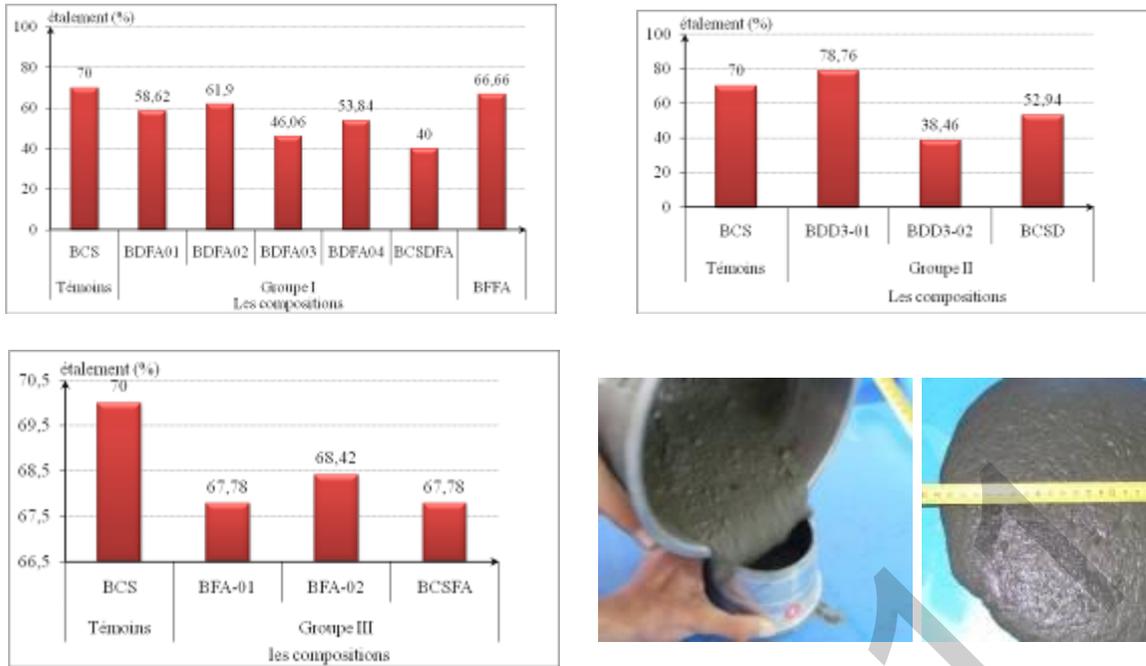


Figure 3. Spreading test

At the same water content and adjuvant, the UHPFRC with metakaolin have a spread of between 46% and 61%. These results show that the concrete is between a concrete farm a normal concrete. Note also that the workability of concrete fiber decreases relative to that of control concrete, this can be explained by the presence of fibers primarily large enough percentage that decreases the mobility of the matrix. For concrete and BDFA03 BDFA04 we note that the spread is lower compared to that of BDEA01 BDFA02 and indeed the incorporation of large amounts of DD3 results in an increase in the volume, by absorption of water tends to dry the mixture. The UHPFRC with metakaolin have a spread less than UHPFRC with silica fume. These differences seem to show a water demand and a higher viscosity in the presence of metakaolin

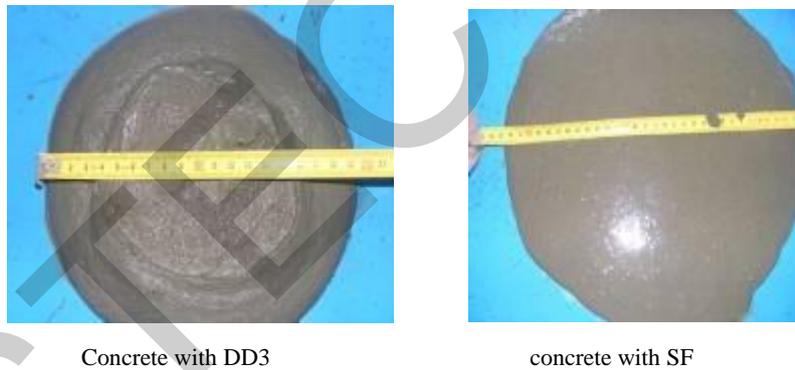
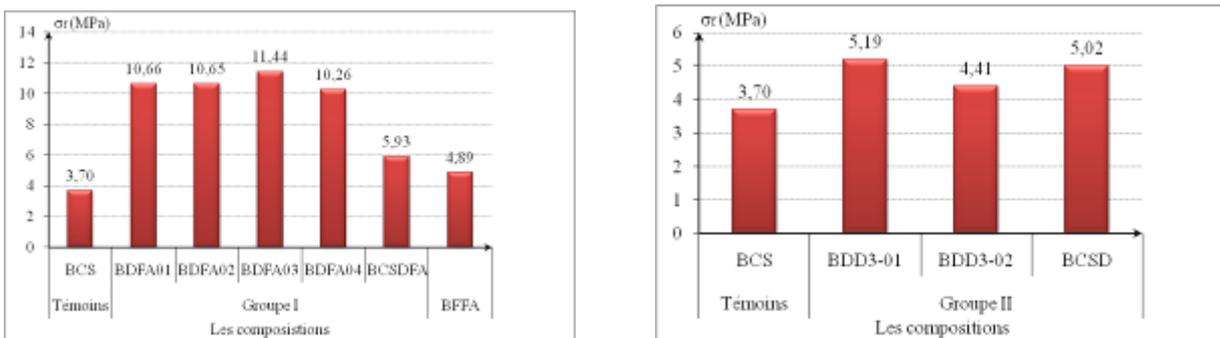


Figure 4. Comparison of the spread of fiber-reinforced concrete with DD3 and concrete with SF

### 3.2. Hardened concrete

#### 3.2.1. Flexure Test

The specimens of size 4 \* 4 \* 16 cm<sup>3</sup> are subject to the test 28 days after casting. They are based on two supports separated by 120mm and are subject to a vertical load. The load is applied gradually at a rate controlled load until the break



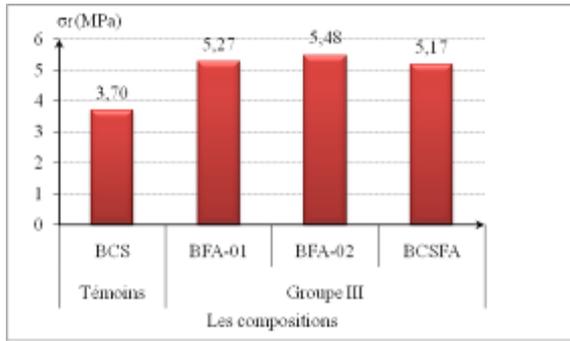


Figure 5. Flexure tests (4-point)

The results of flexural strength are obtained on an average of three samples for different compositions. For the four compositions UHPFRC we note that there is a slight trend in the flexural strength. This constraint is always greater than that of the control concrete, but it is less than that prescribed by the bibliography for UHPFRC to be greater than 30 MPa, this can be explained by a phenomenon of segregation of fibers which occurred after development samples because of a low density of fibers used. Then the fibers have not played their role perfectly in the flexural strength.

3.2.2. Compressive tests

The six pieces of specimens obtained after Flexural strength are then subjected to a uniaxial compression on the frame compression in the same press, using a constant loading speed. The conduct of the trial is to center each half prism laterally relative to the plates of the machine. For identical operating conditions, all specimens were placed between the plates of the press in the same position as those held in the mold. The test results of compressive strengths

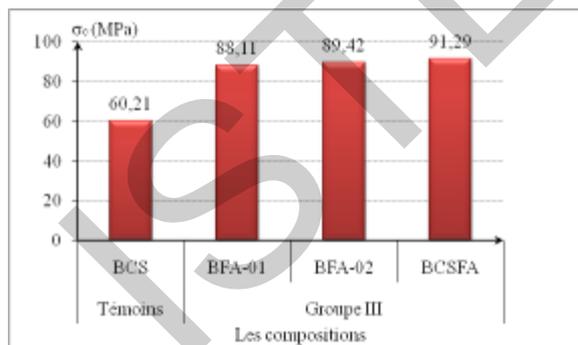
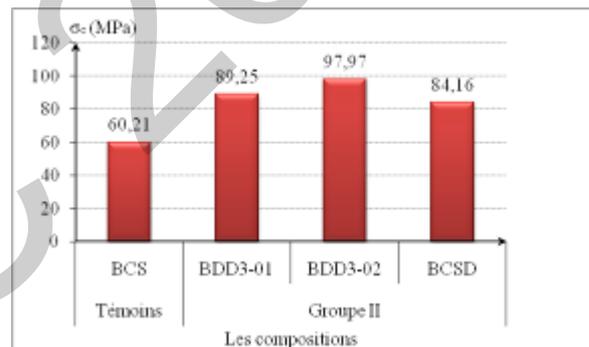
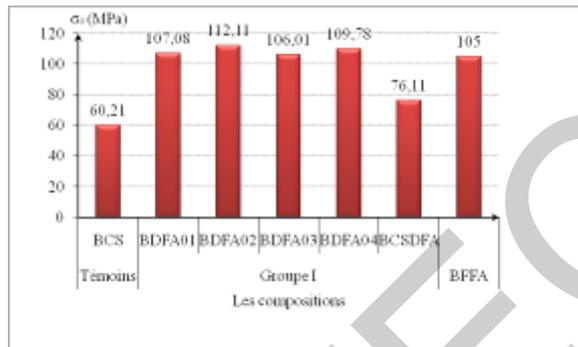


Figure 6. Compression tests of the different variants in 28 days

From these results we can note: A continuous increase in compressive strength at the age of 28 days for all the specimens of concrete, this is due to the strengthening of the structure by the addition of DD3 and metal fibers. For the four compositions UHPFRC the compressive strength at 28 days is always greater than 100 MPa. The compressive strengths of concretes containing metakaolin are broadly equivalent to those of the concretes containing silica fume.

For the variant BDFA02 adding fiber and DD3 with percentages (3% MF and 20% DD3), significantly increases the compressive strength, it can be explained by the adhesion mortar metallic fibers, as well as 'role to fill and densification has to play the metakaolin with a very high fineness, and pozzolanic reactivity which allowed the consumption of portlandite Ca (OH)<sub>2</sub> and the formation of new CSH which strengthening the structure, and W/C that minimize the porosity and consequently increases the mechanical strength.

For BDFA01, BDFA03 and BDFA04 there is a slight variation of the compressive stress from the concrete BDFA02. The replacement of metakaolin by silica fume in concrete BDFA02 results in a negligible variation of the strength.

### 3.2.3. Mode of failure

The observation of the rupture in the flexural test shows that for concrete without fiber rupture is brutal and without significant deformation. This is due to the rather fragile material.

For the fibered concrete rupture is more brutal but slow. Visually, there is a macro crack for a few millimeters in the lower part of the specimen. The length of the crack increases with increasing load. After break, we see that there is no separation between the two sides of the specimen. They remain bound by the fibers that form a bridge between them.

The opening of the crack is based on the dosage of fibers in concrete. Note that for a dosage of 3% of the two fiber portion of the specimen are assembled. That it is due to the large number of fibers which prevents their separation by inking.



Figure 7. Rupture for concrete without fiber



Figure 8. Rupture for concrete bound by the fiber

## 4. Conclusion

In this work we have demonstrated that was perfectly possible to elaborate an UHPFRC using the sand from Oued Souf, calcined clay of Jebel Debagh local metallic fibers. Such materials could be considered in the manufacture of building element such as beams or bridges. The result allows us to draw the following conclusions:

1. The method of Bonneau has led to a satisfactory composition of controls concrete (CCS), presenting strength of 60 MPa and 3.70 MPa in tension at 28-day.
  2. The use of calcined clay of Jebel Debagh gives good characteristics in terms of economic as well as mechanical. calcined clay has a low cost compared to the use of silica fume in formulation of UHPFRC
  3. The workability of concrete in the presence of DD3 is not very important compared to the control concrete; this problem can be solved in another part of the work.
- Finally we can say that further improving the quality of the fibers used are not likely to reach a fiber-reinforced concrete manufacture of high performance, compressive strength up to 200 MPa

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# FORMULATIONS CONTAINING BLUEBERRY EXTRACTS (VACCINIUM MYRTILLUS L.)

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## ABSTRACT

The blueberry is a fruit originally native to North America. Consumption has increased globally, mainly due to its reputation for boosting health and longevity. Currently, the cosmetic products market is focused on formulations containing substances with antioxidant activity. The biological properties of the blueberry have already been linked to their polyphenolic content. The aim of this study was to develop and evaluate cosmetic formulations containing Brazilian freeze-dried blueberry extract. Extracts of ripe blueberry fruits were optimized varying the parameters time of extraction and heat, and temperature. The extract with higher polyphenolic content was lyophilised and added to a non-ionic cream in concentrations of 4% and 8%. Rheological behaviour, pH, spreadability, sensorial characteristics and free antiradical activity were tested. Preliminary results suggest that the formulation developed has potential as an antioxidant cosmetic product, though more analysis will be required before the product can go to market.

Keywords: blueberry, cosmetic, antioxidant, formulations.

## INTRODUCTION

The blueberry was introduced into Brazil in the 1980's by the Brazilian Agricultural Research Corporation (Embrapa/CPACT, Pelotas/RS), with the main target cultivation area being in the south of the country due to the favorable climate conditions for its growth. The plant is described as a small bush bearing bittersweet berry fruits of a dark blue-purple coloration when ripe. Among those fruits studied having antioxidant potential, the blueberry shows a greater polyphenol concentration, both in the pulp and peel. High levels of anthocyanidins are found mostly in the water-soluble purple pigment of the peel. These molecules promote collagen synthesis, this being one of the main structural components of dermal connective tissue, providing benefits to the skin and also supporting the vascular system. Additionally, these antioxidant molecules are able to prevent the deleterious effects of oxidation, inhibiting the onset of lipid peroxidation, sequestering free radicals and protecting aerobic organisms from oxidative stress, which is defined as an increase in the formation of reactive oxygen species (ROS)(Colleti, 2009 ; Lüdke, 2007 ; H. Rodrigues & al., 2003 ; S. Rodrigues, Gularte, Pereira, Borges, & Vendruscolo, 2007; Silveira, Vargas, & Rosa, 2007).

Polyphenols are a secondary product of plant metabolism, constituting a complex phytochemical group of more than 8000 known structures. These substances are divided into: anthocyanins, flavans, flavanones, flavones, flavonols and isoflavonoids. The flavonoids are among the most important phenolic compounds found in the blueberry and present the greater therapeutic activity. From the age of 20 onwards, almost imperceptibly, the human skin begins to lose some properties of strength and self-regeneration. It is a slow and irreversible process, which varies according to skin type. This progression is dependent on several endogenous (chronological aging) and exogenous (photoaging) factors, with signs appearing from an age range as early as the thirties or more subtly being perceived by the sixties. The causes of skin aging are related to age, genetic tendencies, environmental factors and lifestyle (Buchli, 2002; Dalcin, Schaffazick, & Guterres, 2003 ; Krambeck, 2009 ). It is suggested by some researchers that imbalances in the body's antioxidant defense mechanism can be one of the main reasons for the aging process, with increases in ROS production leading to oxidative stress (Lima & ABDALLA, 2001). Thus, there is a constant preoccupation in cosmetology to prevent and mitigate skin aging by means of research and study of effective antioxidants agents. This study aimed to produce and evaluate potential antioxidant cosmetic formulations containing lyophilized (freeze-dried) Brazilian blueberry extract.

## MATERIALS AND METHODS

### Materials

Blueberry fruits were obtained from the city of Arvorezinha in Rio Grande do Sul, Brazil. Harvesting of the berries took place when they had reached the stage of maturity at which they would be sent to market, and only fruits showing no signs of damage, disease or pest attack were chosen. Subsequently, the fruits were refrigerated at  $-5\pm 2^{\circ}\text{C}$ , before being crushed to obtain the extract. Analysis of the collected extract was performed three times.

### Extraction optimization

Different parameters were investigated in order to achieve a blueberry extract rich in polyphenols for use in a cosmetic formulation. A hydroalcoholic solvent (10% v/v) was used, acidified to pH 3 with tartaric acid at a ratio of 1:2 (drug/solvent). The extraction parameters evaluated were: temperature, heating and maceration times (Table 1) (Magri & Heberlé, 2009).

**Table 1. Parameters for the blueberry extraction optimization.**

Extracts	Maceration time (days)	Temperature (°C)	Heating time (min)
E 1	3	40°C	240
E 2	3	70°C	240
E 3	7	70°C	180
E 4	7	70°C	240
E5	7	70°C	300
E6	14	70°C	180
E7	14	70°C	240
E8	14	70°C	300
E9	21	70°C	180
E 10	21	70°C	240
E 11	21	70°C	300

#### Determination of phenolic compounds using the Folin-Ciocalteu method.

The total phenolic compound of extracts was determined using the Folin-Ciocalteu reagent, following the method described by Singleton and Rossi (Singleton & Rossi, 1965). Sample readings were made using a spectrophotometer (Cary 100 Bio, Varian) at 765 nm. The total phenolic compound content was obtained through building a calibration curve, using gallic acid in concentrations of 50 to 500  $\mu\text{g.mL}^{-1}$ , as the standard substance with results being expressed in mg of EGA (equivalent to gallic acid) per L of extract.

#### Extract Lyophilization

The tested extract with the biggest total polyphenol content was freeze-dried (Lyophilized Liotop Model: L202) and frozen at -30°C.

#### Emulsion Preparation

A non-ionic base cream as described in the National Formulary was chosen as the base for the formulation. The aqueous phase was heated to 80°C in a glass beaker using a magnetic stirrer with heater (Model MA-085, Marconi), and the oil phase melted in a porcelain mortar using a hot water bath (Model MA-156, Marconi) at 75°C. The aqueous phase was then poured over the oil phase and manually stirred until cool (Brasil, 2005), with the lyophilized blueberry extract being subsequently incorporated. Two preparations were produced with each containing concentrations of 4% and 8% blueberry extract, respectively.

#### Organoleptic characteristics

Each preparation was evaluated for appearance and color. A visual assessment was made by adding a sample portion to a glass plate, placed over a white background, and comparing it to the original non-ionic base cream (Brasil, 2004).

#### pH Determination

The pH of each preparation was determined using a sample diluted by purified water (1:10 p/v) obtained by reverse osmosis (Marconi), and using a previously calibrated pH meter (DM-20, Digimed) (Amaral & Vilela, 2003; Brasil, 2010; Gil, Matias, & Serrano, 2005).

#### Assessment of Spreadability

The sample was applied to a glass support plate (20cm x 20cm) positioned over a sheet of graph paper and centralized using a circular plate with a central hole. This plate was subsequently removed and replaced at one minute intervals with plates of predetermined weights, with the diameter of the spread of the sample being measured. The spreadability ( $E_i$ ), at 25° C is calculated by the equation: (Isaac *et al.*, 2008; Spellmeier & Heberlé, 2007; Zanin, Miguel, Chimelli, & Dalmaz, 2001).

$$E_i = d^2 \times \pi / 4$$

Where:  $E_i$ : spreadability of sample to weight  $i$  ( $\text{mm}^2$ );  $d$ : mean diameter (mm).

#### Viscosity Determination

A study of the rheological behavior of the formulations was made with a rotational viscometer (DV-I+, RV series, Brookfield) using the spindle SC4-29, inserted on a sample without air bubbles and with a stable temperature (Brasil, 2004). This research evaluated viscosities from  $0.1\text{s}^{-1}$  to  $500\text{s}^{-1}$ , and from  $500\text{s}^{-1}$  to  $0.1\text{s}^{-1}$ , with a 1 minute delay between measurements.

#### Activity of free antiradicals

This analysis was made through use of the stable free radical DPPH (2,2-diphenyl-1-picryl-hydrazyl-hydrate) (Elmastas *et al.*, 2006). A DPPH methanolic solution of  $50.0\mu\text{g.mL}^{-1}$  was prepared, with 1.0mL then being added to a 3.0mL methanolic solution of the formulation samples, at concentrations of  $1.0\mu\text{g.mL}^{-1}$ ,  $5.0\mu\text{g.mL}^{-1}$ ,  $20.0\mu\text{g.mL}^{-1}$ ,  $40.0\mu\text{g.mL}^{-1}$ ,  $60.0\mu\text{g.mL}^{-1}$  and  $100.0\mu\text{g.mL}^{-1}$ . The mixtures were vigorously stirred and kept in the dark at room temperature for 30 minutes. After this time, the absorbance of the samples ( $n=3$ ) and of a control (1.0mL solution of DPPH  $50.0\mu\text{g.mL}^{-1}$  with 3.0mL of methanol) were read by a spectrophotometer (Cary 100-Bio, Varian) at a wavelength of 517 nm, which corresponds to the

maximum absorption for the free radical being used. Methanol was used as blank solution (Lange, Heberlé, & Milão, 2009). The ability of the extracts to reduce the free radicals is calculated according to the equation:

$$\% \text{ inhibition of DPPH} = [(A_0 - A_1) / A_0 \times 100]$$

Where:

A<sub>0</sub> = absorbance of the control reaction

A<sub>1</sub> = absorbance of the samples.

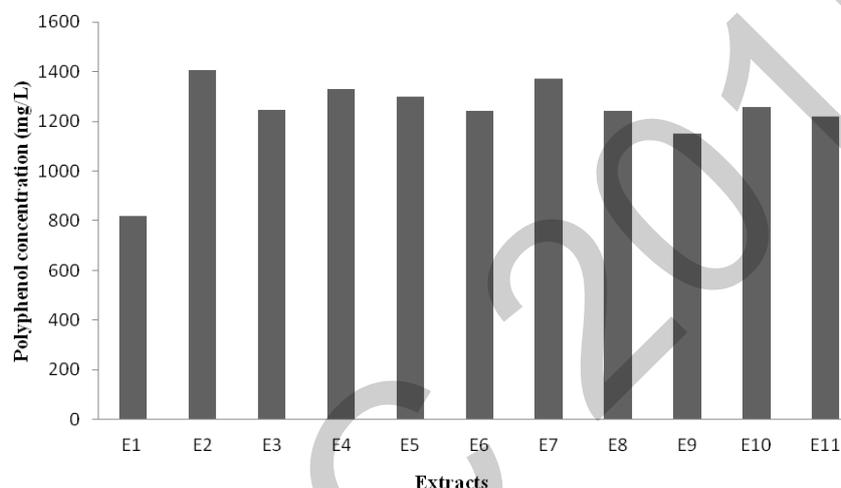
### Statistical Analysis

Anova and Tukey's test was used to analyze the obtained results with a degree of confidence of 95% ( $p=0.05$ ), through the Statistical Support System, SAE program (Ahlert, 2005).

## RESULTS AND DISCUSSION

### Extraction optimization

Overall, the extraction parameters affect the quality of the extraction solutions. According to Figure 1 the extract E2 showed the greatest polyphenol content ( $1420.45\text{mg/L} \pm 9.39$ ).



**Figure 1:** Total polyphenol content of extracts tested.

### Extract lyophilization

The lyophilized extract maintained the purple color of the liquid extract, presented a  $\text{pH } 3.72 \pm 0.02$  and had a yield of 3%.

### Organoleptic characteristics

The product containing 4% extract presented a pink color and glossy appearance, with this color becoming more intense in the product containing an 8% concentration of extract.

### pH determination

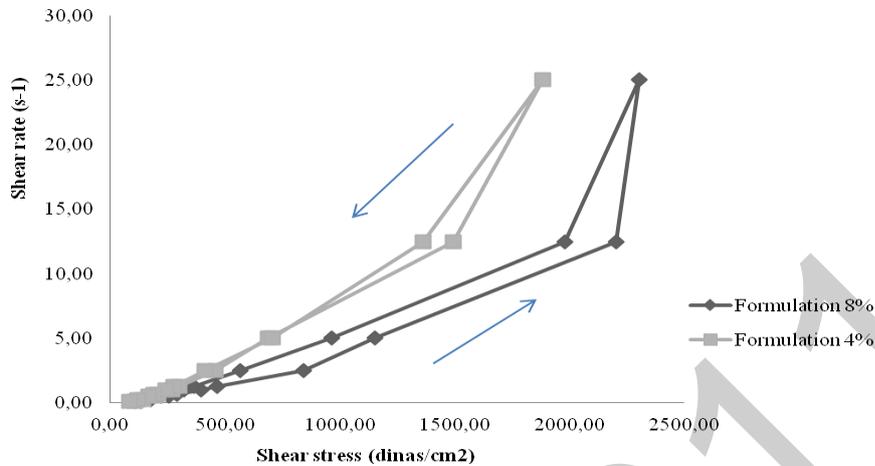
The formulation containing 4% extract of lyophilized blueberry had a  $\text{pH}$  of  $3.32 (\pm 0.006)$ , whilst that containing 8% extract had a  $\text{pH}$  of  $3.20 (\pm 0.01)$ . There was no statistically significant difference between the  $\text{pH}$  values of the formulations, however, these values are not suitable for dermatologic use as products remaining on the skin for prolonged periods must have a  $\text{pH}$  of between 5.5 and 6.5, compatible with the  $\text{pH}$  of the human skin (Isaac, *et al.*, 2008). Therefore, an adjustment was made to the  $\text{pH}$  of the formulations with the addition of  $10\mu\text{L}$  and  $20\mu\text{L}$  of AMP-95 to the products containing 4% and 8% extract, giving  $\text{pH}$  values of  $5.52 (\pm 0.08)$  and  $5.60 (\pm 0.07)$ , respectively.

### Determination of viscosity and spreadability

Rheology is the study of the flow or deformation of a material when subjected to a tension. It is important for quality control of the intermediate or final product as well as determining the shelf life and product acceptability to the consumer, and includes the analysis of viscosity and spreadability parameters. The viscosity of a fluid is given as its resistance to flow or movement. The higher the viscosity, the slower the speed at which the fluid moves, having a lower spreadability. The formulations showed non-Newtonian behavior (Figure 2) as the curve does not pass through the origin but intersects the shear stress axis, called the transfer value, and characteristic of plastic material where the flow does not begin until its transfer value is reached. The viscosity of a plastic decreases with increasing shear rate and this behavior makes the formulations suitable for topical use, making it easier to use and requiring the application of pressure to start the flow, thus preventing container leakage (Mariott, 2005, Sinko, 2008).

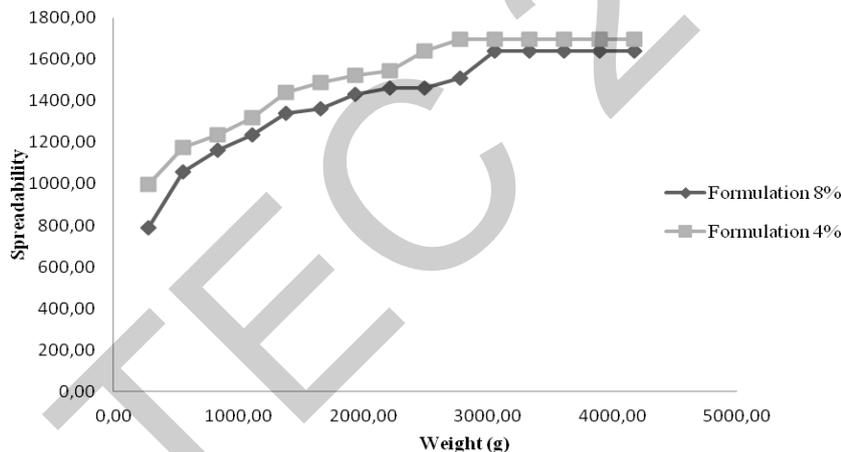
The thixotropy can be evaluated by the area of hysteresis on the rheogram (Figure 2), where the descending curve appears shifted to the left of the ascending curve. This parameter indicates the ability and time it takes for the formulation to return to its structure after the removal of applied tension. Achieving topical formulations with a thixotropic character is very

desirable as they become more fluid during application, making it easier to spread but recovering the initial viscosity as soon as application has ended, thus avoiding product leakage. However, it is important that the thixotropic value is not too high as the product will run off the skin after application due to very slow recovery of its structure (Gaspar & Maia Campos, 2003; Mariott, 2005; Sinko, 2008). The formulations analyzed presented similar rheological characteristics with no significant differences between the base values of maximum viscosity.



**Figure 2:** Rheogram of the produced formulations with 4% and 8% lyophilized blueberry extract.

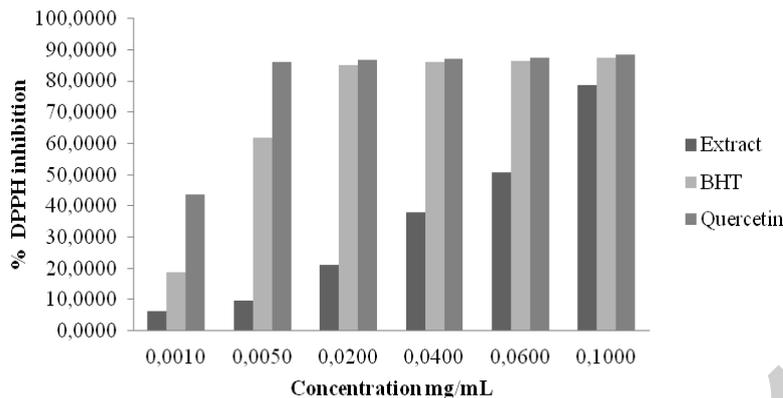
Figure 3 shows the spreadability of formulations with both showing similar behavior and no significant difference between the base values of maximum spreadability.



**Figure 3.** Spreadability of produced formulations with 4% and 8% lyophilized blueberry extract.

**Determination of antioxidant activity**

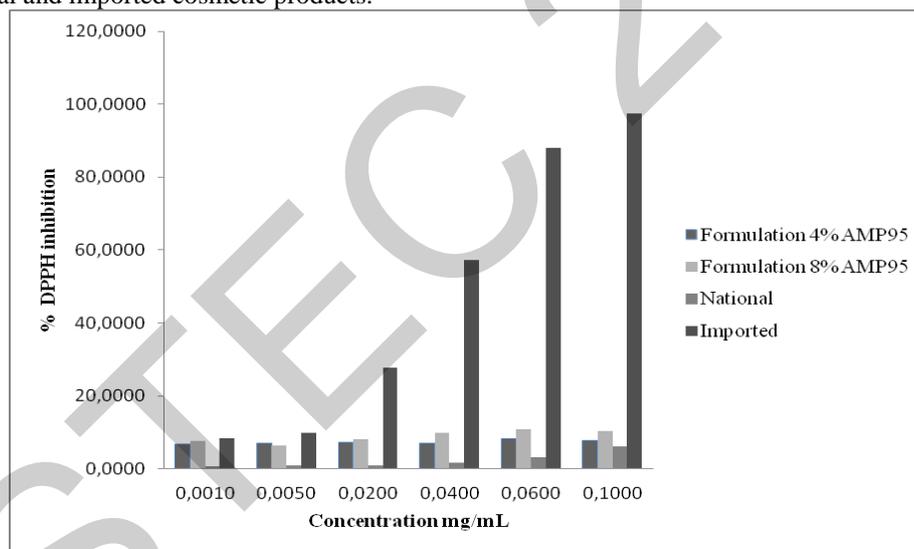
The evaluation model for antioxidant activity uses DPPH based on the ability of the stable free radical 2,2-diphenyl-1-picryl-hydrazyl-hydrate to react with substances that donate hydrogen, including compounds. (Mensor *et al.*, 2001). The antioxidant activity of lyophilized blueberry extract was compared with the standard natural and synthetic quercetin and BHT antioxidants (Figure 4). At the highest concentration, the extract demonstrated DPPH sequestering ability (radical scavenging activity) similar to the standard, however statistically significant differences were observed for all tested concentrations (Figure 4).



**Figure 4.** Antioxidant activity of blueberry extract, BHT and quercetina.

The results for the formulations with 4% extract, including the form alkalized with AMP-95, showed a significant difference only at a concentration of 0.0200 mg/mL (Figure 5). No significant difference for all concentrations was observed in the formulations containing 8% extract. These results demonstrate that adjusting the pH did not alter the antioxidant activity.

When comparing the antioxidant activity of the prepared formulations with two anti-aging skin products, one national and one imported, they produced the same inhibition of free radicals in comparison to the imported cosmetic product for the two lower concentrations, as shown in Figure 5. As regards the national cosmetic product, the formulations also showed no significant difference for the highest concentration, and for the other tested concentrations showed a higher antioxidant activity than both the national and imported cosmetic products.



**Figure 5.** Antioxidant activity for the alkalized formulations and the national and imported cosmetic product.

## FINAL CONSIDERATIONS

It can be concluded from the tests that the formulations containing 4% and 8% freeze-dried blueberry extract showed no significant difference in relation to spreadability and viscosity. In terms of antioxidant activity there was a difference only at the concentration of 0.06mg/mL. Adjusting the pH of the formulations did not alter their antioxidant activity, and they presented a superior antioxidant activity than the national cosmetic product analyzed. Based on these results it would appear that the formulations produced for this study show potential for development as antioxidant cosmetic products, though additional research is needed to continue the process of their development as an anti-aging product, such as those found on the market.

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# FROM MINIMUM TILLAGE TO NO TILLAGE, REACTION OF WAHA, VARIETY OF DURUM WHEAT, IN ALGERIAN SEMI ARID REGION

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**ABSTRACT-** The cereal grain producing regions in Algeria are semi-arid characterized by climatic constraints such as frost, the sirocco and especially irregular rainfall their deficit coincides with the demand for the cereal. To address this deficit, increased production must be achieved by improving efficiency, by correcting the climate constraint. Several studies have been conducted with the aim of diagnosing the behavior of grain and develop technical routes for different regions of the country. Our study is to compare three crop management practiced on durum wheat. The trial was conducted in the semi arid region of Setif. The techniques applied are conventional tillage (CT), the minimum tillage (TM) and direct drilling (SD).

The direct drilling gives good results with high leaf area and plant height which directly influenced the yield and its components. The length of the ear was very similar for both SD and CT techniques. For root development the SD has a tendency to expand horizontally in contrast to the TC and TM. The TM has a higher stomatal resistance than the TC and SD. From stage swelling the water content is high in SD. The technique of direct seeding promotes water retention especially at critical times. This shows the interest that can provide direct seeding in Algeria, where water shortages due to deficient rainfall is the main factor limiting cereal.

**Key words:** crop management, direct drilling, conventional tillage, minimum tillage, stomatal resistance, RWC, variety WAHA.

## INTRODUCTION

According Arabi and Roose (1989), limited production is generally attributed to several factors, some beyond the control of man like climate conditions as irregular rainfall, the climate accidents as frost and sirocco at the end of the cycle of plant. The other factors controlled by the man can improve this production are application of new crop management.

The general approach adopted in this study is to compare three different crop management: direct drilling, conventional tillage and minimum tillage to bring out the most efficient technique to saving water, adjusting and improving performance variety Waha.

## MATERIALS AND METHODS

The trial was conducted in the Experimental Station of the Agricultural Technical Institute average (ITMAS) located 3km south-west of Setif, at an altitude of 1081m. The latitude is 36 ° 9 North and 5 ° 21 longitude. The study area is characterized by a Mediterranean semi-arid climate with cold winters and hot dry summers. The cumulative rainfall from September 2008 to June 2009 was 369.7 mm. The rainfall peaked during the month of April with 77.5 mm and a minimum during the month of May with 3.4mm.

The soil of the experimental plot is clay to silty clay with a pH of 8.5. The plant material is a variety of durum wheat (*Eastivum durum*) the variety Waha. Our test was conducted on the same plot and on the same crop management of the previous year, on an area of 2340 m<sup>2</sup>. The field is divided into 3 units; each unit has a different crop management, direct drilling (DS) The conventional tillage (TC) and minimum tillage (MT). In each unit, the number of repetition of 4 has been adopted. Direct drilling was sown directly by a direct seed drill. The conventional tillage plot has been prepared by the moldboard followed by the Cover crop and the harrow. The minimum tillage has been using only the chisel and the harrow. Weeds were controlled using chemical herbicides. An addition of phosphate (TSP 46%) and nitrogen (ammonium nitrate 34.5%) were performed.

The notations and measurements were made during every cycle of the plant. For morphological traits we measured the following parameters: leaf area (LA, mm<sup>2</sup>) with a planimeter at boot, heading and flowering stages. Height (H, cm) of the plant is measured from the soil to the base of the spike at maturity. The length of the ear (LE, cm) was measured at maturity, the barbs not included. The root development was studied by the implementation of soil profiles on the three plots (SD, TC and TM). The depth of each profile is 45cm, the roots are carefully removed from the ground and then photographed.

For physiological traits we measured stomatal resistance (Rs; s.cm<sup>-1</sup>) determined using a diffusion porometer type AP4. For each treatment we considered the upper surface of the middle part of the leaf. Measurements were performed every stage of culture. The relative water content (RWC) on water content was measured using the method described by Barrs and Weatherley (1968). RWC was measured in each phenological stage of culture. The weight of fresh leaf (Pf) and saturated leaf with water (Psat) and dry leaf (Ps) were measured and repeated 4 times. The number of plant is measured at early stage. The number of spikes (NE) and the number of grains per ear (NGE), the 1000 grain weight (PMG), grain yield (RTD) are measured at maturity. The statistical analysis was performed using the software Stat Box Pro Version 7.1.0; it focused on an analysis of variance, a comparison of averages by the test of Newman and Keuls at 5%.

## RESULTS AND DISCUSSION

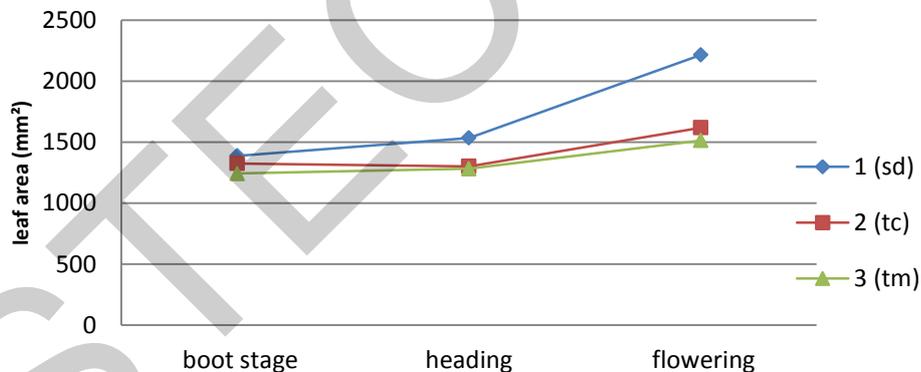
The effect of management and phenological stages on the leaf area present was very highly significant. Comparison of average crop management has two homogeneous groups is conducted in the plant till the leaf surface which is higher with the 1712.96 mm<sup>2</sup> compared to conventional work and work with minimum respectively 1414.83 and 1346.38 mm<sup>2</sup> mm<sup>2</sup>. A highly significant effect was noted for the interaction of two factors (Table 1).

**Table1.** Effect of crop management on the morphological traits of durum wheat inalgerian semi arid region.

Parameters	LE(mm <sup>2</sup> )	H (cm)	LE (cm)
Crop management (F1)			
SD	1712,96a	57,31a	5,50
TC	1414,83b	54,06ab	5,91
TM	1346,38b	52,31b	4,63
Phenologiaal stage (F2)			
Boot stage	1318,75b	-	-
Heading	1373,13b	-	-
Flowering	1782,29a	-	-
CV%	10,253	4,01	12,360
Proba F1	0,000***	0,029*	0,058 ns
Proba F2	0,000***	-	-
Proba F1xF2	0,005**	-	-
Average	1491,389	54,56	5,35

\*, \*\*, \*\*\* and ns =significant, highly significant, very highly significant and no significant  
a, b...= groups formed by the test of Newman and Keuls at 5%.

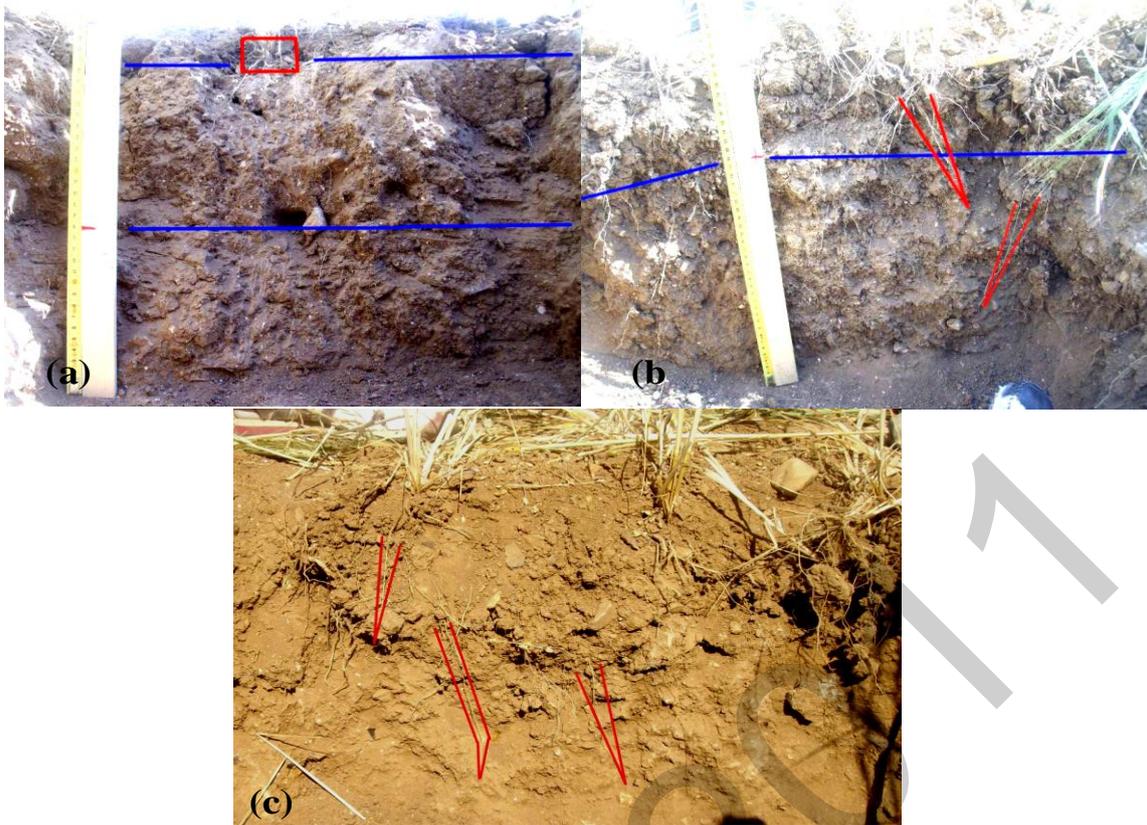
The evolution of leaf area, at boot stage, was the highest in direct drilling followed by conventional tillage then minimum tillage (Fig. 2). This is probably due to water retains in each crop management. Indeed, species arrive to reduce leaf area by water regime (Onyibe, 2004).



**Fig. 1.** Evolution of leaf area in different crop management

The height of stems shows a significant difference between the three crop management. Direct drilling presents the highest height with 57.31 cm above the minimum tillage with 52.31 cm and the conventional crop management with 54.06 cm. The height of Waha increases with the rate of rainfall and water supplies for irrigation (Ghouar, 2006). The length of the spike has not been greatly affected by the crop management.

On the ground (Fig.2), we see that roots tend to be developed horizontally in no-tillage because of the resistance of the soil which is quite important in not worked land. In conventional and minimum tillage, the roots tend to grow vertically or in depth in the soil which is till, that encourages deep rooting.



**Fig. 2.** Roots development in the three crop management conducted on durum wheat. *a* : direct drilling, *b* : conventional tillage and *c* : minimum tillage. The blue lines are the limits of the horizons, the red arrows are the extension of roots.

**Table 2.** Effect of crop management on the physiological traits of durum wheat in Algerian semi arid region.

Parameters	Rs (s/cm)	RWC (%)
Crop management (F1)		
SD	8,05 b	81,46
TC	9,12 b	79,19
TM	10,25 a	77,31
Phenological stage (F2)		
Boot stage	4,41 b	81,59
Heading	13,83 a	75,95
Flowering	14,85 a	71,31
CV%	13,643	9,947
Proba F1	0,000***	0,198 ns
Proba F2	0,000***	0,000***
Proba F1xF2	0,555 ns	0,677 ns
Average	9,140	79,320

\*, \*\*, \*\*\* and ns =significant, highly significant, very highly significant and no significant  
a, b...= groups formed by the test of Newman and Keuls at 5%.

The stomatal resistance is very highly affected by the crop management and phenological stages (Table 2). Minimum tillage presented stomatal resistance highest with 10.25 s.cm<sup>-1</sup> compared to conventional tillage and direct drilling (fig. 3). Flowering and grain milky stages noted highest stomatal resistance.

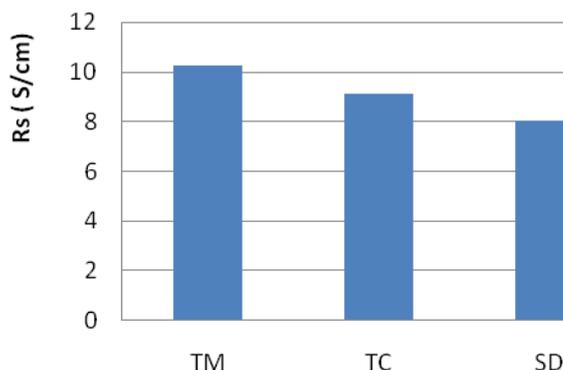


Fig. 3. Effect of crop management on the stomatal resistance.

This increase in stomatal resistance is caused by the closure of stomata which are opposed to the diffusion of water vapor and gases (Denden and Leumeur, 2000). The stomatal resistance was relatively low in from tillering to boot stage, this is due to large amounts of rain and low temperatures recorded in April, which coincided with those stages.

From the boot stage to flowering, stomatal resistance increases rapidly for three treatments. These stages were held in the month of May when rainfall was the lowest (3.4 mm). Chartzoulakis *et al.* (1999) consider that the stomatal resistance increases with the degree of water deficit.

The relative water content was affected by the phenological stages and not by the crop management (Table 2). The conventional tillage gives a better result at the 3 leaves stage followed respectively by the minimum tillage and direct drilling. From the boot stage, direct drilling gives the best results followed by conventional and minimum tillage, this is due principally to: i) the water economy in the last stages of culture, the RWC of plants is based on the level of soil moisture (Kasraoui *et al.*, 2004) and ii) the tillage allowed the conventional crop management a better use of depth water contrary with minimum tillage (no deep tillage).

Table 2. Average and statistical results yield and its components in relation to different cultural practices applied.

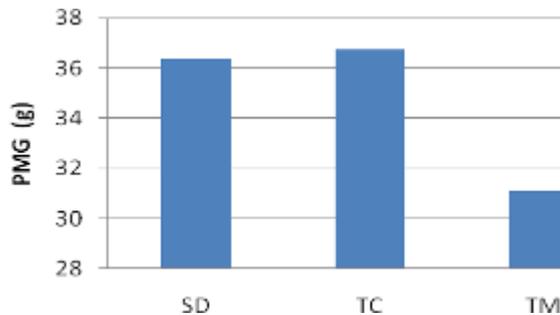
Parameters	NE	NGE	PMG	RDT
Crop management (F1)				
SD	462,00 a	23,67	36,37 a	40,33 a
TC	364,00 b	23,67	36,75 a	31,75 a
TM	336,00 b	20,83	31,10 b	21,72 b
CV%	13,778	13,517	3,364	23,761
Proba F1	0,003 **	0,215ns	0,000***	0,002**
Average	387,333	22,722	34,739	31,27

\*, \*\*, \*\*\* and ns =significant, highly significant, very highly significant and no significant  
a, b... = groups formed by the test of Newman and Keuls at 5%.

Direct seeding has presented a high number of spikes with 462 ears / m<sup>2</sup>. Conventional and minimum tillage have presented a lowest number of ears with 364 and 336 ears/m<sup>2</sup> respectively. This is related to the number of emerged plants in each technique. According to Kribaa (1992), a good water and nitrogen nutrition of wheat (Waha) leads to the achievement of good number of ears that can reach the thresholds of 423,2 ears/m<sup>2</sup>.

The average fertility of Waha is at around 22.72 kernels per ear. Cultivation techniques have exceeded this average, except for minimum work. The highest number of grains per spike is the presented by the direct drilling or no-tillage and conventional tillage with 23 kernels per ear. The minimum tillage presented the lowest value with 20 kernels per ear. Fertility is determined from early tillering to flowering, the period when the growth rate is most important. According Couvreur (1981), the number of kernels per ear is strongly influenced by the condition of the vegetative especially its volume.

A very highly significant effect of crop management was noted on the weight of thousand grains. Direct seeding and conventional tillage provided a high PMG compared to minimum tillage (fig. 3). This difference may be due to the conservation of soil moisture in dry periods during grain filling, which has enabled them to complete the growth cycle and also a better grain filling (Belguerri *et al.*, 2007). In wheat, the lifting stages, stem elongation and grain filling are considered key stages of development of major components of performance: the number of seeds/m<sup>2</sup> and weight of thousand gras.



**Fig. 4.** Effect of crop management on the weight of thousand grains in Waha, durum wheat variety.

The yield shows a very high significant difference between the three crop management tested. We notated two homogeneous groups: the first group is formed by direct drilling and conventional tillage, the second group is formed by the minimum tillage. The no-tillage and conventional crop management showed a high yield with 33.23 q/ha for direct drilling and 29.86q/ha for conventional tillage. The minimum work presented only 22.67q/ha with a difference of about 6 q/ha. The yield is based on water available in late stage (Belaid, 1987).

## CONCLUSION

The results of our experiments show that direct drilling or no-tillage gives good results compared to other crop management. The morphological parameters studied, show that the cultivation of wheat in direct drilling has presented the highest leaf area and stem height which has directly affect the yield and its components. The length of the ear was very close between the two techniques no tillage and conventional tillage. For root development is superficial in direct drilling. For the physiological parameters studied, direct drilling has exhibited low stomatal resistance and higher relative water content than the other techniques, what makes a good water supply plants.

The conventional crop management presented a highest weight of thousand grains. The yield wasn't different between prepared and no prepared soil.

If we look to the techno-economic aspect, we can say that direct drilling is widely economic than the other two techniques. With an economy of time spent in the field, which implies a gain of fuel, labor and machinery.

So, it remains to follow this technique for several years to confirm which is stable before the integration into the production system at the regional and national levels.

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# FUZZY CONTROLLER PARAMETER TUNING USING GENETIC ALGORITHM FOR A REAL TIME SYSTEM CONTROL

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## Abstract

In this paper, a methodology for combining genetic algorithm (GA) with fuzzy controller (FC) to create a genetic-fuzzy controller (GA-FC) is presented. Using GA, optimal or near optimal fuzzy rules and membership functions can be optimized simultaneously without a human operator's experience or a control engineer's knowledge. A water level control process is employed to test the performance of GA-FC controller. The process was first modeled using Non-linear Auto Regressive and eXogenous input (NARX) type Artificial Neural Network (ANN) approach. FC parameters were then tuned using genetic algorithm through the model. Finally, the performance of GA-FC structure was presented over the simulation and real time output signals. The main contribution of the study is that, the developed structure replaces the tedious process of trial and error for better combination of fuzzy parameters and can settle the problem of designing fuzzy controller without an expert's experience. The results proved that designed controller generate desired performance and it is quite effective for parameter optimization to be implemented in various real time applications.

**Keywords:** Water Level Control, Artificial Neural Network, Fuzzy Controller, Genetic Algorithm, Parameter Optimization

## I. INTRODUCTION

Process industries play a significant role in economical growth of a nation. Control of liquid level in tanks and fluid flow between tanks is a fundamental requirement in almost all process industries like water including waste water, chemical, petrochemical, pharmaceutical, food, beverages, etc. There exists a variety of methods for liquid level and flow control. [1] Stabilizing the water level of a plant around a predetermined level is an important problem since dynamics of those systems has nonlinear characteristics [2]. Several techniques have been proposed for nonlinear system identification. Most of them are based on parameterized nonlinear models such as Wiener-Hammerstein models, Volterra series, wavelet networks, neural networks, etc. [3] The artificial neural network model is an intellectual discipline that rose rapidly in the eighties. It is one non-linear system that simulates human brain structure and encourage behavior at the same time. It has been successfully applied to many fields [4]. In our study a water level control process, similar encountered adversities and nonlinear structure of the system let us use NARX type ANN for modeling approach. Modeling process is then followed by designing a controller. There have been many efforts to apply various control techniques to the water level control. Among such of advanced control techniques, fuzzy control technique receives many attention due to its resemblance to human-like characteristics. It was demonstrated that fuzzy control technique can be successfully applied to control water level process through several previous works. However, performance of fuzzy controllers are strongly depends on the initial assignment of membership parameters and rule structure and so on. To tune such parameters, cumbersome trial-and- error procedures by a designer are necessary. To get rid of this necessity, there has been an approach to apply genetic algorithm to tune the fuzzy controller. This paper is organized as follows: Water level control system and its modeling process using ANN is presented in section II. Section III describes the steps to optimize Fuzzy controller parameters simultaneously which are action values and membership function boundary values. Finally various real time and simulation experiments are performed in section IV while section V draws conclusion.

## II. WATER LEVEL CONTROL PROCESS

The purpose of water level control process is to keep the water level in the tube at a desired level and track the reference trajectory. Depending on the input current, pneumatic control valve allows water flow into the tube from the tank and causes level change in the tube. The operation is repeated throughout the control process till the water in the tube is set to the reference level. The control process runs as shown in figure 1. A reference trajectory or level is first set to be followed by the system. Fuzzy controller transfers the current water level in the tube (1) from pressure/current converter (2) and compares it with reference value. Depending on the error, the controller generates required control signal over current/pressure converter (3) to pneumatic control valve (4). Conic valve is opened in proportion to the control signal and water in the tank (5) is pumped (6) to the tube. The exhaust pipe (7) enabling continuous water flow out to the water tank is set open and also used as disturbance. Throughout the process control the aperture of pneumatic control valve changes flow and lets water flow into the tube while exhaust pipe flows out to the tank. Thus the system is able to follow the reference trajectory or level ensuring that flow disparity.

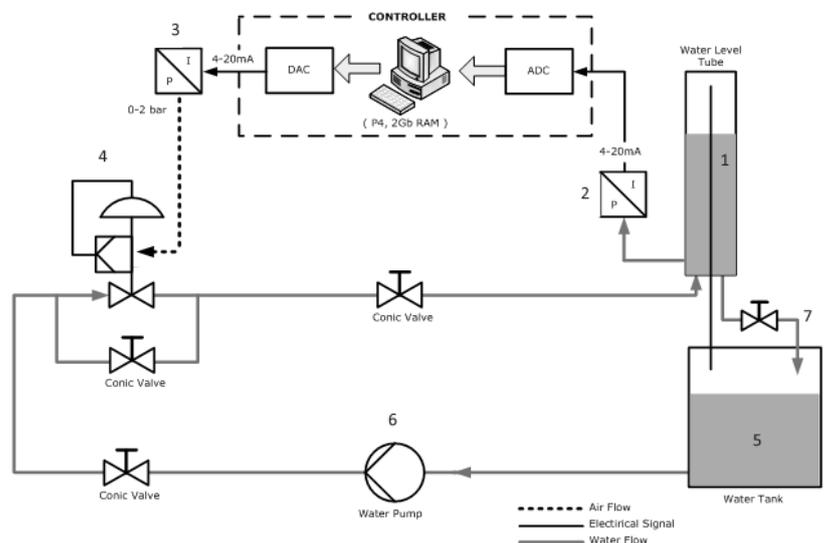


Figure 1. Process Block Diagram

**II.1 Structure Of Narx Type Ann**

ANNs have been applied to a large number of problems because of their non-linear system modeling capacity. Given a sample vector, ANNs are able to map the relationship between input and output; they “learn” this relationship, and store it into their parameters. As these two characteristics suggest, they should prove to be particularly useful when there is a little prior knowledge about the system. Many of ANN applications use simple multilayer perceptron (MLP) network training back propagation algorithm. A simple way to introduce dynamics into network consists of using an input vector composed of past values of the system inputs and outputs. This is the way by which the MLP can be interpreted as a NARX model of the system. This way of introducing dynamics into a static network has the advantage of being simple to implement [5]. The NARX model can be represented as given in equation 2;

$$o(k) = f(y(k-1), \dots, y(k-n); u(k-1), \dots, u(k-m)) + \varepsilon(k) \tag{2}$$

where  $o$  is predicted value,  $y(k)$  is process output,  $u(k)$  is process input,  $\varepsilon(k)$  is the approximation error at time instant  $k$ ,  $m$  is an input time delay,  $n$  is an output time delay,  $f$  is a non-linear function (activation function) describing the system behavior. Typical MLP network is arranged in layers of neurons, where every neuron in a layer computes the sum of its inputs  $\mathbf{x} = [v \text{ } f \text{ } r \text{ } d]^T$  and passes this sum through an activation function ( $f$ ). The output of the network ( $o$ ) is defined as a matrix form in equation 3;

$$\mathbf{o} = f^2(\mathbf{W}^1 f^1(\mathbf{W}^1 \mathbf{x} + \mathbf{b}^1) + \mathbf{b}^2) \tag{3}$$

Where  $\mathbf{W}_{(i,j)}$  is weight matrices ( $\mathbf{W}^1 = \begin{bmatrix} w_{1,1} & w_{1,2} & \dots & w_{1,50} \\ w_{2,1} & w_{2,2} & \dots & \cdot \\ \cdot & \cdot & \dots & w_{2,50} \\ w_{S1,1} & w_{S1,2} & \dots & w_{S1,50} \end{bmatrix}$ ,  $\mathbf{W}^2 = [w_{1,1} \ w_{1,2} \dots \ w_{1,S1}]$ ),  $\mathbf{b}_{(i)}$

is bias vector ( $\mathbf{b}^1 = [b_1 \ b_2 \ \dots \ b_{S1}]^T$ ,  $\mathbf{b}^2 = [b_1]$ ) and  $f$  is activation functions ( $f^1$  logistic,  $f^2$  linear).

Where  $\mathbf{W}_{(i,j)}$  is the weight between (i) the output and (j) the input and superscript defines layers number.

MLP networks can learn adjusting the weight using back propagation approach. The back propagation algorithm for the MLP is generalization of the least mean square (LMS) algorithm. This algorithm should adjust the network parameters in order to minimize the mean square error given in equation 4;

$$e = \frac{1}{2} \sum_{\mu=1}^p (t^\mu - o^\mu)^2 \tag{4}$$

where;  $t$  is target,  $o$  is MLP output,  $\mu$  is the sample instant in  $p$  size.

The steepest descent algorithm for the approximate mean square error at the  $k^{\text{th}}$  iteration is given in equation 5;

$$w_{i,j}^m(k+1) = w_{i,j}(k) - \eta \frac{\partial e}{\partial w_{i,j}} \quad b_i^m(k+1) = b_i(k) - \eta \frac{\partial e}{\partial b_i} \tag{5}$$

Where  $\eta$  is learning rate [6].

In order to design better ANN applications, the number of hidden layer and neurons in the hidden layer(s) play important roles while the choice of numbers depends on the application. Determining the optimal values of these numbers is another topic to work on. Although there is no theoretical basis for selecting these parameters, a few systematic approaches are reported one of which is heuristic [7]. Designed ANN architecture has two inputs for water level control process output ( $y$ ); input ( $u$ ) and the other output for predicted value ( $\hat{y}$ ). Hyperbolic tangent and linear activation function were used in hidden layer and output layer respectively. Time delay unit is described as ( $z^{-1}$ ) block and 3 time delay blocks were used both for input and output. As the ANN architecture of the system is built, the network can be used to get any output value for any input vector. This is called the “generalization property” of the network which is a term to test how successful the model is. Early stopping criteria are also used to improve the generalization property of designed network. During the modeling process, Levenberg-Marquardt (LM) and Bayesian Regularization (BR) training functions were employed for different number of hidden layers and different number of neurons for each hidden layer to get the best correlation coefficient. At the end of each training process, a different correlation coefficient value is produced. As shown in table 1 the options with low SSE (Sum of Squared Error) value and correlation coefficient converging to 1 are better ANN models while other options are poor in modeling ability.

**Table 1.** SSE and Correlation Coefficient (R) Values for Different ANN Models

Hidden Layers	Hidden Layer Neuron Number	Training Function	SSE Generalization	Correlation Coefficient (R)
2	10	Bayesian Regularization	4.27E-01	0.990
	20	Bayesian Regularization	4.11E-01	0.999
	30	Bayesian Regularization	3.48E-01	1.000
	30	Levenberg - Marquardt	3.82E-01	0.979
	50	Bayesian Regularization	3.93E-01	0.993
	10	Bayesian Regularization	4.02E-01	0.993
	20	Bayesian Regularization	3.84E-01	0.997
	22	Bayesian Regularization	3.55E-01	0.992

According to table 1, ANN model trained with Bayesian regularization with 1 hidden layer and 30 neurons in hidden layer has more satisfactory performance than the others for both learning and generalization phase. Thus ANN-30 network is preferred for modeling of water level control process. To test the model, both real time system output and model output were drawn for random generated input signals as given in figure 2. As it is seen from the open loop behaviour, ANN model and real system outputs are consistent and quite similar.

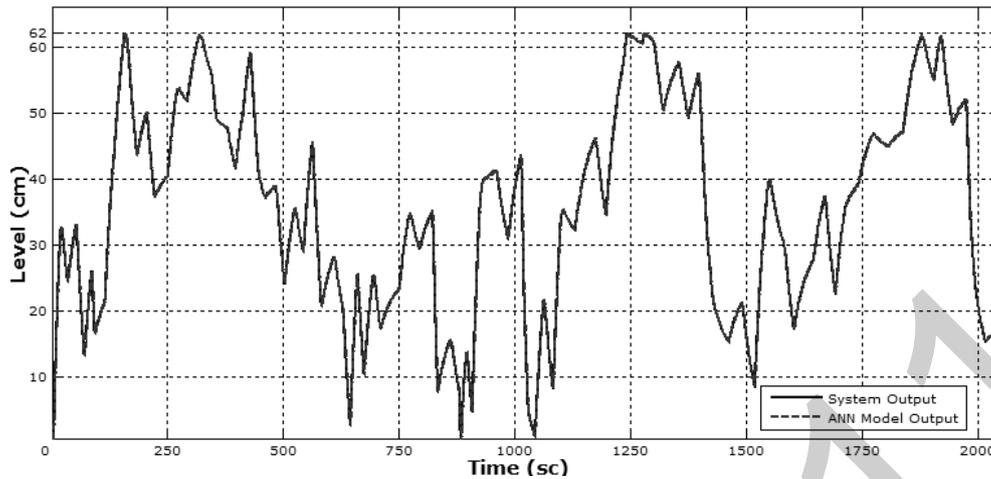


Figure 2. ANN Model and Real System Open-Loop Outputs for Various Inputs

### III. FUZZY CONTROLLER PARAMETER TUNING WITH GA

Several studies have shown FC to be an appropriate method for the control of complex or partially identified processes, many of which cannot easily be modeled in a mathematical way. Unlike a conventional controller, no rigorous mathematical model is required to design a FC and in many cases, they can be implemented easily. However, this simplicity also presents a bottleneck in their design. FC relies on heuristic knowledge that is subject to designer's interpretation and choice. The traditional approach to fuzzy design is laborious, time consuming and in most cases specific to each application. Optimal search algorithms such as GA and ACO could solve some of these problems [8]. Therefore, those techniques were proposed as alternative means for tuning Fuzzy controller parameters. Besides its widespread use, simultaneous optimization of both action values and membership function boundary values of fuzzy controller is important and new for water level control process [9]. Mamdani and Sugeno type controllers are used in design process of Fuzzy controlling. Sugeno type controller has two outstanding superiorities to Mamdani type controller. Because of the linear dependence of each rule on the input variables, the Sugeno method is ideal for acting as an interpolating supervisor of multiple linear controllers that are to be applied, respectively, to different operating conditions of a dynamic nonlinear system. Because it is a more compact and computationally efficient representation than a Mamdani system, the Sugeno system lends itself to the use of adaptive techniques for constructing fuzzy models. These adaptive techniques can be used to customize the membership functions so that the fuzzy system best models the data [10]. So, for our model and controlling process, Sugeno type Fuzzy controller is preferred consisting of 2 inputs which are error and change in error. Boundary values of the inputs and 15 action values are also optimized so that the real system can track the trajectory.

#### III.1. GA-Fuzzy Controller

Genetic algorithms (GAs) are optimization algorithms based on the mechanisms of natural selection and genetics. GAs are inspired by natural genetics and the Darwinian theory of evolution. A genetic algorithm involves simulated competition among a number of individuals representing solutions to a problem [11]. A set of genes corresponding to a "chromosome" in natural genetics is referred to as "string" in a GA. The mechanisms of GAs are surprisingly simple, involving nothing more complex than strings copying and partial strings swapping. GAs start with a population of strings and thereafter generate successive populations using the following three basic operations: reproduction, crossover, and mutation [12]. Reproduction is the process by which individual strings are copied according to an objective fitness value. Copying of strings according to their fitness value means that strings with a higher value have a higher probability of contributing one or more off-springs to pass to the next generation. This is an artificial version of natural selection. These strings are then extended into a mating pool for the crossover operation. Mutation is random alteration value of the string which is needed since, although reproduction and crossover search and recombine the existing representations effectively, they occasionally become overzealous and lose some potentially useful genetic material. The mutation operator prevents such an irrecoverable loss. The recombination mechanism allows mixing of parental information while passing it to their descendants, and mutation introduces innovation into the population. We must consider the mechanisms linking a genetic algorithm to the solved problem. There are two such mechanisms: (1) encoding solutions to the problems on chromosomes, and (2) evaluating function that returns a measurement of the worth of chromosome to the context of the problem. The evaluation function is the link between the genetic algorithm and the problem to be solved. Most of the computer time in GAs is spent by evaluating objective functions. The initial population for traditional GAs is usually chosen randomly. We used a byte encoding scheme instead of a traditional binary one. So GA is particularly presented as an alternative method to traditional optimal search approach for optimization problems enabling a substantial departure from the complexity and consequent difficulties involved in the design of Fuzzy controllers. GAs have been recognized as a powerful tool in many control applications such as parameter identification and control structure design. GAs have also found widespread use in controller optimization particularly in field of fuzzy logic and neural networks. In the early 1990s, GAs were first investigated as an alternative mean of tuning parameters of controllers. Then GAs have also been extensively applied to the off-line design of controllers, particularly as an alternative tuning technique for process which are otherwise difficult to tune. Action values,

membership function shapes and their boundary values are variables of Fuzzy controllers to be optimized. So both input and output parameters are variables and can be optimized concurrently [13]. In our study we implemented GA for tuning Fuzzy controller parameters offline and used depicted chart in figure 3.

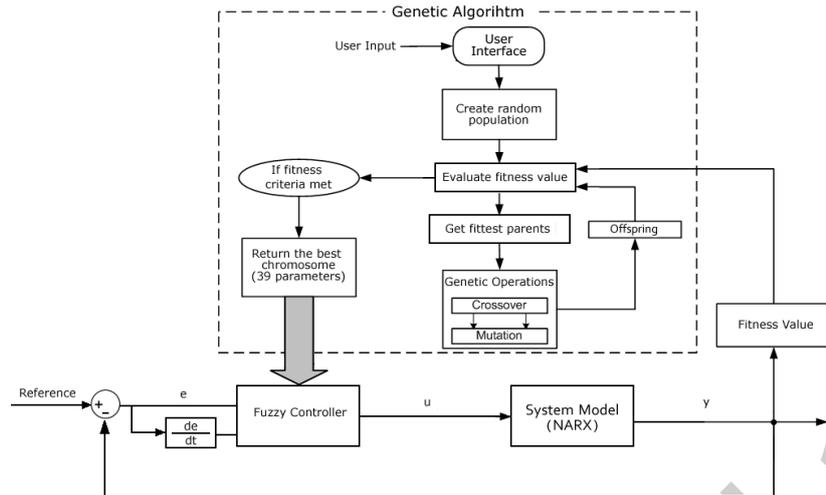


Figure 3. Implemented GA-FUZZY controller structure

The most important feature of GAs is the way to transform the system output to the cost functions ( $\phi$ ) is given in equation 6. Designed trajectory has different crossing points ( $t_1, t_2, t_3$ ), and therefore fitness function has different weight factors ( $\alpha = 0.1, \beta = 0.3, \delta = 0.6$ ) for each trajectory region and is able to minimize RMS error in all trajectory regions;

$$\phi = \frac{1}{T} \left[ \sum_{t_0}^{t_1} \alpha \sqrt{(p_{y(t)} - y_{(t)})^2} + \sum_{t_1}^{t_2} \beta \sqrt{(p_{y(t)} - y_{(t)})^2} + \sum_{t_2}^{t_3} \delta \sqrt{(p_{y(t)} - y_{(t)})^2} \right] \quad (6)$$

where  $\phi$  is fitness value, T is number of sampled data,  $y_{(t)}$  system output,  $P_{y(t)}$  desired trajectory output,  $\alpha, \beta$  and  $\delta$  are cost gain factors.

The performance of GA depends on the assigned parameter values. Using GA operators, 15 action values were optimized after 100 generations as listed in table 2. Remaining 24 boundary value parameters of input variables, error and change in error, were also optimized as listed in table 3 and table 4.

Table 2. Optimized Fuzzy Controller Action Values Using GA

e Δe	PB (Positive Big)	PS (Positive Small)	Z (Zero)	NS (Negative Small)	NB (Negative Big)
N	9.878	8.238	7.499	5.595	2.043
Z	9.951	9.951	8.434	5.342	2.014
P	9.902	8.061	8.517	5.987	2.107

Table 3. Optimized "Error" Membership Function Boundary Values Using GA

NB		NK			Z		PK		PB						
-25.296	-19.218	-42.306	-19.992	-0.7296	-0.1038	-0.6528	-0.306	0.4206	0.762	0.0684	0.6024	27.738	46.746	19.824	31.104

Table 4. Optimized "Change in Error" Membership Function Boundary Values

N		Z			P		
-2.57	-1.77	-2.79	-0.036	0.108	2.68	1,29	1,72

The optimized values for action values range from 2V to 10V. Controller output, action value, is used to change the aperture of pneumatic control valve. For the system 2V action value closes the valve completely to cut the flow while 10V opens to let water flow into the tube. Before starting the optimization process, type of membership functions to be used is also important. Because of its flexibility  $\Pi$  type membership functions were chosen for the inputs. So, for the first controller input which is error, NB (negative big), NS (negative small), Z (zero), PS (positive small) and PB (positive big), and for the second which is change in error, negative (N), zero (Z) and positive (P) membership functions were used.



### IV.3. Disturbance Rejection Experiments

Finally, to test the disturbance rejection capability of designed Fuzzy controller, the exhaust valve was closed %70 ( $t_1$ ) then opened to its initial position ( $t_2$ ). Closing the valve causes less water flow out to the water tank from the exhaust pipe and forcing fuzzy controller to update its control signal to compensate the momentary reference level. As it is seen from figure 6, 30 cm was set as reference level to the GA-FC system first and at  $t_1$  %70 disturbance is applied to the system for 35 seconds till  $t_2$ . Although %70 closure is a quite strong disturbance for the system it could set the system to desired level with quite few overshoots.

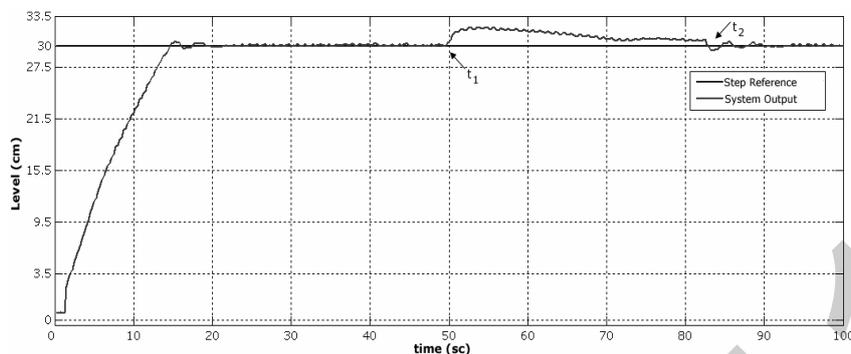


Figure 6. GA-Fuzzy system response to %70 disturbance

### V. CONCLUSION

In this paper we proposed two different optimization algorithms called ACO and GA to optimize fuzzy controller's consequent parts and membership function boundary values simultaneously. To test the controller therefore algorithm performances, a nonlinear behaviour water level control process was modeled using artificial neural network using NARX architecture. Optimization process followed modeling and both algorithms designed their own fuzzy controller optimizing its parameters. Performances of the controllers were then compared setting up various experiments. The results demonstrated that the application of ACO-FC and GA-FC for fuzzy rule induction are viable approaches and have quite good outcomes. The validity and versatility of the developed structures have also been demonstrated by applying to the real system. Designing fuzzy controller with GA and ACO does not require any prior knowledge and yields satisfactory results. Both algorithms enhance productivity of designing fuzzy controller, make the controller have comprehensive lookout and converge to optimum solution. For process control and parameter tuning applications the proposed optimization algorithms are promising. For future study it will be worthwhile to implement that structure ranging from modeling to optimization to various realtime system controlling applications.

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# FUZZY LOGIC AND LANGUAGE, THINKING, MEANING

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## Abstract

In this paper I associate the three concepts of language, thinking and meaning with Fuzzy sets and Systems and Fuzzy logic. I present some developments in 20<sup>th</sup> century history of science and humanities that show deep links between these concepts and we give a proposal for a fuzzy theoretical interpretation of what is meaning.

**Keywords:** Language, thinking, meaning, perception, fuzzy sets, family resemblance

## 1. Introduction

With this paper I give an introduction to the special session on “Language – Thinking - Meaning” of the ISTEC 2011 conference.

Reading an interview that was printed in the Azerbaijan International, in 1994 we can improve this view: when Zadeh was asked, “How did you think Fuzzy Logic would be used at first?” his retrospective answer was: “In many, many fields.” I expected people in the social sciences-economics, psychology, philosophy, linguistics, politics, sociology, religion and numerous other areas to pick up on it. It’s been somewhat of a mystery to me why even to this day, so few social scientists have discovered how useful it could be.

## 2. Language

In the 20<sup>th</sup> century Bertrand Russel who wrote an introduction to it where he tried to explain Wittgenstein’s thinking: “A picture”, he says, “is a model of the reality and to the objects in the reality correspond the elements of the picture: the picture itself is the fact. What the picture must have in common with reality in order to be able to represent it after its manner – rightly or falsely – is its form of representation”.

“In communication there seem to be problems at three levels: 1 technical, 2 semantic, 3 influential. The technical problems are concerned with the accuracy of transference of information from sender to receiver. They are inherent in all forms of communication, whether by sets of discrete symbols (written speech), or by a varying two-dimensional pattern (television). The semantic problems are concerned with the interpretation of meaning by the receiver, as compared with the intended meaning of the sender.

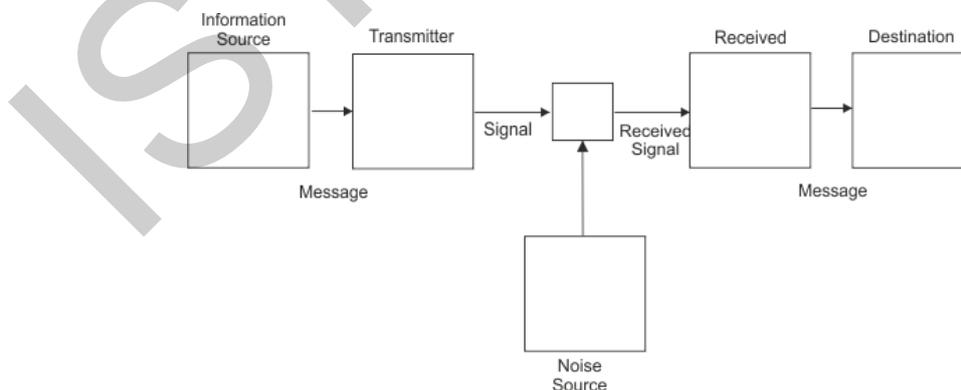


Figure 1: Shannon’s diagram of communication

Weaver’s midcentury expectations on the progress in science and technology to be anticipating important topics in the field of FSS and FL: vague, fuzzy or approximate reasoning, the meaning of concepts. However there is no direct relation between the work of Weaver and Zadeh but these aspects make it worth to study Weavers writings in this

context, to compare it with more recent scientific theories, to intensify discussions and to push interdisciplinary work between hard and soft and social scientist researchers in humanities and actors in arts, music and literature.

### 3. Thinking

Then unaware of Turing’s philosophical article, Zadeh wrote the paper “Thinking Machines – A new Field in Electrical Engineering”, which appeared in the student journal The Columbia Engineering Quarterly in New York City in 1950. Here, Zadeh put up for discussion the questions “how will ‘Electronic brains’ or ‘thinking machines’ affect our way of living?” and “what is the role played by electrical engineers in the design of these devices?” . He stated: “More generally, it can be said, that a thinking machine is a device which arrives at a certain decision or answer though the process of evaluation and selection.

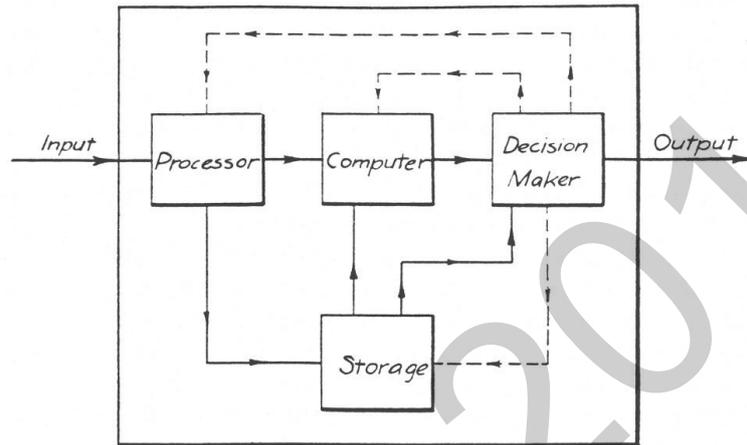


Figure2: Zadeh’s chart for the basic elements of a “Thinking Machine”

Zadeh illustrated his argumentation by peering forward into the year 1965, which was then 15 years in the future. Already in the 1990s he presented perception-based system modeling : “A system, S, is assumed to be associated with temporal sequences of input  $X_1, X_2, \dots$ ; output  $Y_1, Y_2, \dots$ ; and states  $S_1, S_2, \dots, S_2$  is defined by state-transition function  $f$  with  $S_{t+1} = f(S_t, X_t)$  and output function  $g$  with  $Y_t = g(S_t, X_t)$  for  $t=0,1,2, \dots$ . In perception-based system modeling, inputs, outputs and states are assumed to be perceptions, as state-transition function,  $f$  and output function,  $g$ .” FSS and FL enable computers and human beings to communicate in terms that enable them to express uncertainty regarding measurements, diagnostics, evaluations, etc. in theory; this should put methods of communication used by machines and human beings on levels that are much closer to each other.

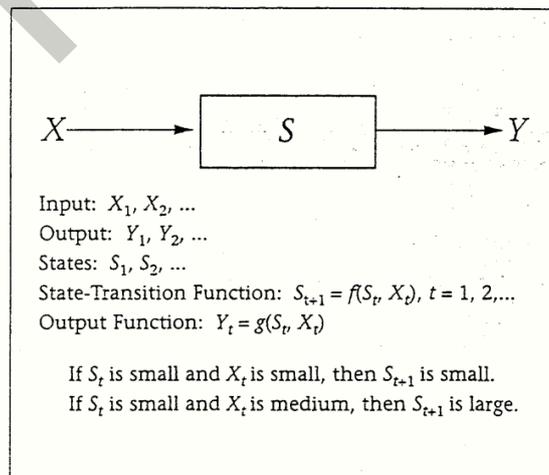


Figure 6. Perception-Based System Modeling.

### 4. Meaning

In his late philosophy Wittgenstein turned away from the epistemological system in the Tractatus with its ideal mapping between the things in reality and a logical precise language. If we are not able to find such an exact logical language

then we have to accept the fact that for all languages there is a vague lingual usage. Then, the images, models and theories that we build with words and propositions of our language to communicate on them are and will be vague (or Fuzzy).

## 5. Concluding Proposal

As we have seen in the previous sections, our perceptions and conceptions of external thing or objects are entities without sharp borders. They are fuzzy entities! They are fuzzy because they are hypotheses, i.e. we do not know whether they are true or false. Therefore, we will attach these hypotheses by a membership function. In our model we characterize a percept y as a result of interplays between

- Past experiences, including one`s culture,
- And the interpretation of the perceived.

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# GLOBAL STABILITY AND SETTLEMENT OF SEGMENTAL RETAINING WALLS REINFORCED WITH GEOGRID

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## ABSTRACT

Most of segmental retaining wall design procedures such as NCMA, BS8006, AASHTO and NCHRP do not take into account global stability and foundation settlement in their design calculation. A system to solve the problem and to predict the stability of the wall quickly and accurately by using simple input was planned to be developed. This study used a residual soil that was classified as SC-SM according to the Unified Soil Classification System (USCS). Geogrid used in this study had a characteristic strength of 40 kN/m while concrete blocks had a minimum strength of 35 MPa. Simulations were performed using two-dimensional FEM to calculate maximum deflection, maximum foundation settlement and maximum surface settlement. In addition, global stability was calculated by using phi/chi reduction method for each design. Prediction was done by using Response Surface Methodology. Mathematical models used for the RSM were MLR (Multiple Linear Regression), Pure Quadratic, Interactions and Full Quadratic. Among all the mathematical models in RSM, output of Full Quadratic was the closest to the target value.

**Keywords:** Prediction, Segmental retaining wall, Geogrid, FEM, RSM

## 1. INTRODUCTION

In Malaysia, the first reinforced retaining structure was built in 1982 and since then has expanded its use (Chiu 1987). Geogrid reinforced segmental retaining walls are used extensively throughout the world because of its low cost, simple construction and its ability to accommodate the deformation (Yoo and Kim 2008; Zhang et al. 2008). However, studies of this type of walls, especially on the mode of failure and the bonding mechanism of reinforcement are still at the level of exploration (Skinner and Rowe 2005; Al and Muhunthan 2006).

Reinforced retaining walls offer competitive solutions to the problems associated with lack of space caused by the phenomenal growth in the infrastructure at present. Research on the retaining wall is reported in many papers since its introduction e.g. Edgar et al. (1989), Faisal (1993), Wong et al. (1994), Ho and Rowe (1996), Kasa (1997), Bathurst et al. (2005) and Skinner and Rowe (2005). In the design of reinforced concrete, bond between the bar and the concrete provides sufficient tensile stress to the concrete. While the principles of reinforced soil, the tensile stress is caused by friction between the soil and buried layers of reinforcement (Ingold 1982).

Normally, backfill material used in the construction of the wall is granular soil such as river sand and mining sand. However, the price of sand is high at present. Another alternative is to use quarry dust or residual soil. Economically, residual soil has many advantages because it is easy to find in Malaysia at relatively low cost. By using residual soil, contractors can reduce construction costs and overall time since no transportation of backfill is needed (Kasa 1998).

Reinforced retaining walls can be constructed using various types of reinforcement and wall systems. Reinforcement may consist of metal strips or polymer products such as geotextiles, geogrid and geomembrane. Wall system may consist of a wall wrap (wrap facing), fully rigid wall, segmented block and modular block (Holtz 2001). Most widely used reinforcement in Malaysia is steel strip. Although it is well-received, there is still uncertainty about its durability, especially under wet soil conditions such as residual soil. A practical reinforcement for the work under the residual soil is geogrid which is durable and suitable for the environment. In addition, the geogrid is easier to handle, carry and install than steel strip (Kasa 1998).

The main objective of this study is (i) to predict the stability of geogrid reinforced segmental retaining wall in terms of global factor of safety, surface and foundation settlement and wall deflection, (ii) to compare the accuracy of statistical methods of MLR (Multiple Linear Regression), Pure Quadratic, Interactions and Full Quadratic to predict the stability of the wall, (iii) to observe the actual performance of segmental retaining walls by comparing results of field monitoring with the results of FEM calculations, and (iv) to produce a computer system that can predict the stability of walls quickly and accurately by using simple input such as slope angle, surcharge and height of wall.

Among the motivations for this study has to do with the problems faced by some local engineers who refused to recommend the construction of segmental retaining walls as an alternative to customers on the grounds that the design calculations received from the supplier do not take into account the global stability and foundation settlement. This is clearly stated in the design calculations. In other words, the supplier shall not be liable for if the occurrence of failure caused by the global stability or foundation settlement.

## 2. METHODOLOGY

Backfill material used in this study was classified as SC-SM (a mixture of sand and clay and inorganic clay) according to USCS (Unified Soil Classification System). Plasticity index value of this soil was between four and seven ( $4 \leq PI \leq 7$ ). According to the Design Manual Naval Facilities Engineering Command, 7.01 version published in September 1986, a typical value for the wet unit weight was  $20.4 \text{ kN/m}^3$  and internal friction angle 33 degrees. These values were used in all the segmental retaining wall designs. The geogrid had characteristic tensile strength of  $40 \text{ kN/m}$  and long-term design strength of  $21 \text{ kN/m}$ . The concrete block had a dimension of  $305 \text{ mm} \times 200 \text{ mm} \times 150 \text{ mm}$  with minimum strength about  $35 \text{ MPa}$ .

For predictions, RSM (Response Surface Methodology) was used. Four mathematical models of MLR, Pure Quadratic, Interactions and Full Quadratic were used to predict the stability of the wall. RSM was a technique used to model and analyze problems in which a response was influenced by several independent variables and the main objective was to optimize the response (Montgomery 2005). RSM was useful to develop, improve and optimize the response or responses. Most of the problems in the RSM, the response function,  $f$  was not known. The first order model was known as linear regression model. When there were more than two independent variables such as  $x_1$ ,  $x_2$  and  $x_3$ , the model was called MLR. In general, the equation was as follows

Multiple Linear Regression

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \varepsilon \quad (2.1)$$

The second order model was used when there was a curve in the first order model. The second order model was more flexible and had several functions such as Pure Quadratic, Interactions and Full Quadratic. The general equations were as follows

Pure Quadratic

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1^2 + \beta_5 x_2^2 + \beta_6 x_3^2 + \varepsilon \quad (2.2)$$

Interactions

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \varepsilon \quad (2.3)$$

Full Quadratic

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1^2 + \beta_8 x_2^2 + \beta_9 x_3^2 + \varepsilon \quad (2.4)$$

where  $y_i$  was the predicted value,  $x_1$  was slope angle (degree),  $x_2$  was surcharge (kN/m<sup>2</sup>),  $x_3$  was height of slope (m) and  $\epsilon$  was error.  $y_i$  and  $x_1, x_2, x_3$  were input values while  $\beta_0$  until  $\beta_9$  were output values obtained from analysis using the equations.

For the purpose of obtaining data, analysis of deflection, surface and foundation settlement and global FOS (factor of safety) were performed by using Plaxis ver. 8 while MATLAB ver. 2009 was used to make the statistical analysis. All software was working under Microsoft Windows XP system with Intel® Core™ 2 Duo, 2.80 GHz and 1.99 GB of RAM. FEM simulation of the retaining walls was carried out by using two dimensional analysis. A triangular-shaped element with 15 nodes was used since the weakness of using the element of six nodes was over prediction of bearing capacity and some calculations using phi/chi reduction method (Plaxis 2008).

Model of the retaining wall is shown in Figure 2.1. The height of wall was 5.5 m, the length of geogrid was 3.5 m and the depth of soil below foundation level was 6.0 m. Dimension of modular block was 30 cm long, 15 cm high and 20 cm wide. The width of drainage using granular materials was 30 cm. Interface elements were used to model the interaction between the geogrid and soil.

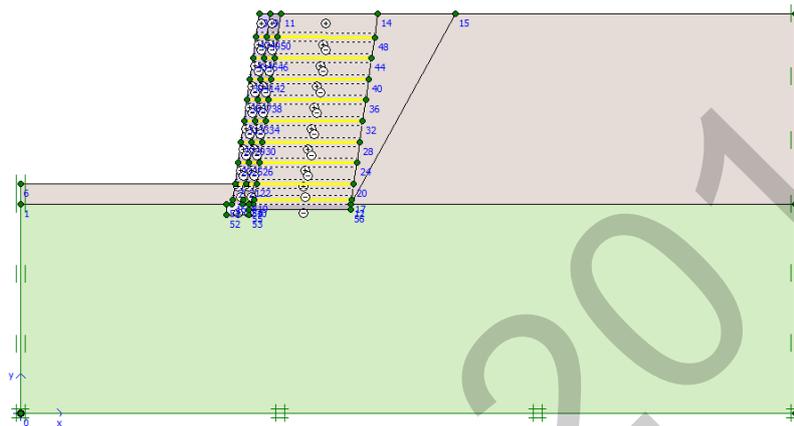


Figure 2.1 Geometry of retaining wall used in FE analysis

The input values for FEM simulation such as unit weight, cohesion and friction angle of the foundation, concrete blocks, drainage and residual soil were similar to the input values used in the NCMA design while other input values such as Young's modulus, Poisson's ratio and hydraulic conductivity which were not considered in the NCMA design were obtained from literature. To avoid any failure on the concrete blocks and drainage, a high value of strength ( $c = 200 \text{ kN/m}^2$ ) was used. High value of elasticity ( $EA = 1,200 \text{ kN/m}$ ) was also used for geogrid since the strength of geogrid did not affect the failure because soil would fail sooner in the event of excessive strain (Guler and Hamderi 2002). The output obtained from FEM analysis used for prediction using RSM was the value of (i) max. deflection, (ii) max. foundation settlement, (iii) max. surface settlement and (iv) global FOS.

To observe the actual performance of the wall and accuracy of FEM calculations, a full-scale wall was built. This five-meter high wall was installed with various instruments such as strain gauges, horizontal and vertical pressure cells, inclinometer, stand pipe and pneumatic piezometer and surface settlement markers at specified location as shown in Figure 2.2.

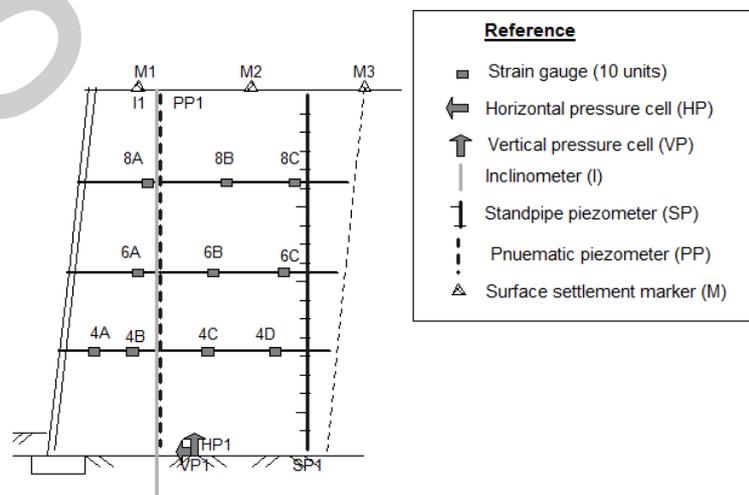


Figure 2.2 Location of various type of instrument

The purpose of strain gauges installed on the geogrid was to determine the tensile force distribution along the geogrid layers. Strain gauge type 5 YFLA applied in this study uses the principle of electrical resistance of a conductor. The conductivity changes when the material was strained. So, strain and tension can be calculated from the change in electrical resistance. Strain changes were measured by using a digital strain meter, TC-1K model.

Horizontal deflection of the whole wall was measured by using inclinometer. An inclinometer casing was installed behind the wall and readings were taken at every 0.5 m depth by means of inserting a sensor into the casing. Vertical and horizontal earth pressures including effective stress and pore water pressure were measured by using a pair of total pressure cell. Effectiveness of drainage system and water pressure in soil was measured by using a pneumatic piezometer installed at the base of the wall. In addition, a standpipe piezometer was used to measure water level by inserting a sensor up to the water level. To measure settlement, three surface settlement markers were installed after end of construction.

### 3. RESULTS AND DISCUSSION

Actual performance of the segmental retaining walls could be observed by comparing the results of field monitoring with the results of FEM calculation. According to the original design, this wall was with a surcharge of  $5.0 \text{ kN/m}^2$ , but during the monitoring, no load was applied in the field. FEM calculation results discussed here was based on the original design as the effect of the surcharge on the results of FEM calculations was too small. For example, the max. deflection of the wall without surcharge and with surcharge was 12.67 mm and 12.77 mm respectively, as well as the value of the max. foundation settlement, 15.86 mm and 15.87 mm respectively. Based on FEM calculations for the instrumented wall, it was found that the max. deformation was 27.82 mm. The max. effective stress was  $167.48 \text{ kN/m}^2$  and based on the analysis of phi/chi reduction method, the global FOS was 2.29.

Changes in the measurement of inclinometer over 203 days showed that the max. deflection of the wall was 13.0 mm at the height of 4.0 m from the base of the wall (See Figure 3.1). FEM results showed clear similarities with the value of 12.77 mm, a difference of only 0.33 mm. Location of the max. deflection was also similar, i.e. 4.0 m high. However, there were significant differences in shape of the distribution because the value of the measured deflection at the base of the wall was only 1.0 mm. This happened because the base of inclinometer casing was fixed to the concrete mix. In FEM simulation, there was no fixity considered. Based on the results, it could be concluded that the FEM simulation of the retaining wall could estimate the value of max. deflection accurately.

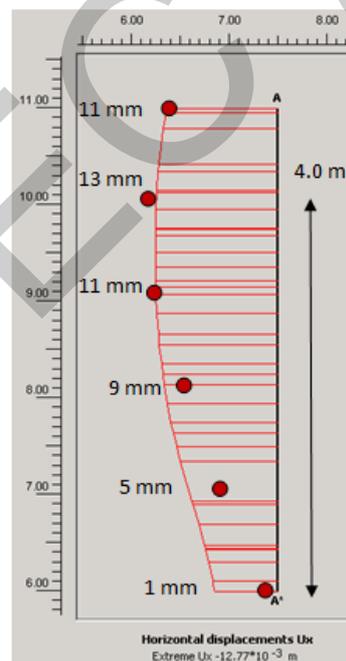


Figure 3.1 Horizontal deflection of the wall

The value of the max. surface settlement measured in the field was 17 mm. This value was different from the values obtained by FEM (24.55 mm) with a difference of 7.5 mm. In engineering practice, this difference could be considered small for a five meter high wall because the wall of this type could accommodate large deformation (BS8006 1995). Besides, if we looked at the distribution of the surface settlement, the location of the max. settlement for both cases was similar, i.e. at the center of the reinforced zone. No measurements were taken for foundation settlement in the field for comparison. The max. value calculated by FEM was 15.87 mm. The distribution of foundation settlement was shown in Figure 3.3.

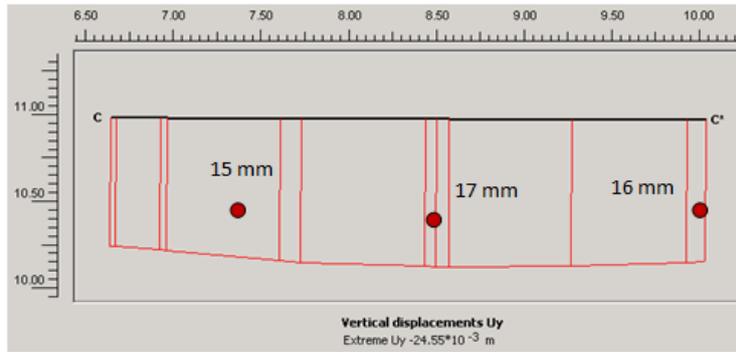


Figure 3.2 Surface settlement of the wall

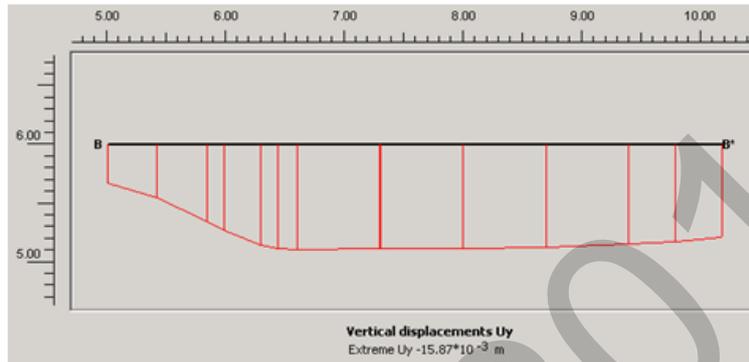


Figure 3.3 Foundation settlement of the wall

Value of RMSE (Root Mean Square Error) based on 232 data for each mathematical model was shown in Figure 3.4 while value of  $R^2$  was shown in Figure 3.5. From Figure 3.4, it was obvious that Full Quadratic was the best model for RSM since the value of RMSE for each output parameter, i.e. global FOS, surface settlement, foundation settlement, location of max. deflection and deflection was the lowest or closest to zero. Similarly, from Figure 3.5, it was obvious that Full Quadratic was the best model because the value of  $R^2$  for each output parameter was the highest or closest to one. Thus, equation of Full Quadratic was selected to be used in developing a computer system to predict the stability of the segmental retaining wall.

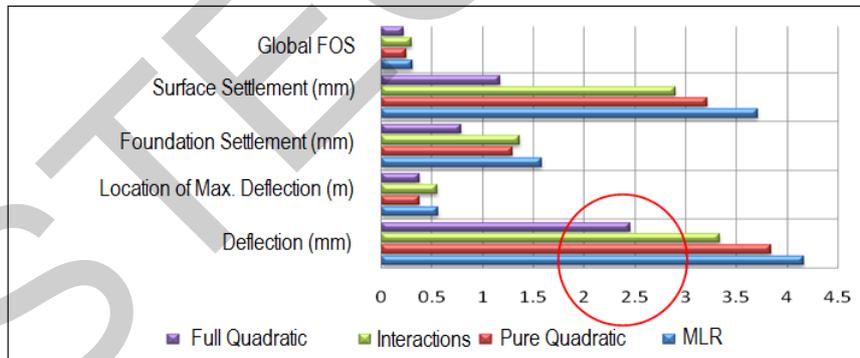


Figure 3.4 Value of RMSE for each mathematical model

#### 4. CONCLUSION

In conclusion, this study has successfully predicted the stability of geogrid reinforced segmental retaining wall in terms of global FOS, surface and foundation settlement and wall deflection, compared the accuracy of statistical methods of MLR, Quadratic Pure, Interaction and Quadratic Full, observed the actual performance of the retaining wall by comparing the results of field monitoring with the results of FEM calculations and produced a system that can predict the stability of walls quickly and accurately. Since Full Quadratic is the best mathematical model to predict global FOS, surface settlement, foundation settlement, location of max. deflection and deflection, it has been used to develop a computer system.

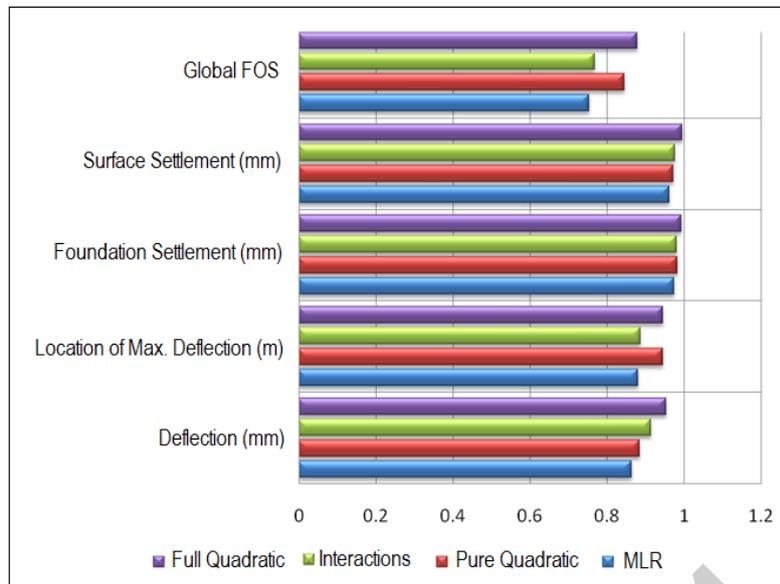


Figure 3.5 Value of  $R^2$  for each mathematical model

## 5. ACKNOWLEDGEMENT

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# GRANÜLE YÜKSEK FIRIN CÜRUFUNUN BETON ÖZELLİKLERİNE VE Klorür GEÇİRİMLİLİĞİNE ETKİSİNİN İNCELENMESİ

## THE EFFECT OF THE USE OF GRANULATED BLAST FURNACE SLAG ON THE CHLORIDE ION PERMEABILITY AND CONCRETE PROPERTIES

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### ÖZET

Bu çalışmada bir mineral katkı olarak granüle yüksek fırın cürufunun beton üretiminde kullanımının beton özelliklerine etkisi araştırılmıştır. Bu kapsamda çimento ile %15, %30, %45, %60 ve %75 oranlarında granüle yüksek fırın cürufu ikameli karışımlar üzerinde 7, 28, 56 ve 90 günlük basınç dayanımı ve elastisite modülü deneyleri yapılmıştır. Ayrıca 90 günlük numuneler üzerinde hızlı klorür geçirgenliği deneyi yapılarak granüle yüksek fırın cürufunun betonda boşluk doldurma etkisi incelenmiş ve şahit beton olarak isimlendirilen ve herhangi bir mineral katkı içermeyen betonla kıyaslanmıştır. Deney sonuçları göz önüne alındığında granüle yüksek fırın cürufunun betonla yüksek oranlarda bile ikame edildiğinde beton özellikleri üzerinde olumlu etkisinin bulunduğu görülmüş, böylelikle granüle yüksek fırın cürufu kullanılarak daha ekonomik beton üretiminin gerçekleşeceği ve bu mineral katkının hidrasyon ısısını azaltarak betonda erken rötre çatlaklarını önleyeceği anlaşılmıştır.

**Anahtar Kelimeler:** Beton, Granüle yüksek fırın cürufu, Basınç dayanımı, Hızlı klorür geçirgenliği.

### ABSTRACT

In this study, it was investigated that the use of granulated blast furnace slag in various replacement rates with cement as mineral additive on the compressive strength, elastic modulus and rapid chloride ion permeability properties of concrete. For this reason, binder content was determined as 400 kg/m<sup>3</sup> and cement was replaced at five proportions (15 %, 30 %, 45 %, 60 % and 75 %) granulated blast furnace slag. Totally 6 series of mix proportions, of which one of them was control mixture, six mixtures were containing granulated blast furnace slag as a mineral additive were tested in different combinations. Before rapid chloride ion permeability test, compressive strength and elastic modulus were performed at 7, 28, 56 and 90 days. Starting from the 90th day, the rapid chloride ion permeability experiment was conducted on cylinder specimens. The test results indicated that even the incorporating of granulated blast furnace slag at high replacement rates with cement performed better than control concrete mixture and the granulated blast furnace slag provided more economic concrete production than conventional concrete. Furthermore, the granulated blast furnace slag reduces heat of hydration and prevent early shrinkage cracks on the concrete surfaces.

**Keywords:** Concrete, Granulated blast furnace slag, Compressive strength, Rapid chloride ion permeability.

### 1. GİRİŞ

Beton yıllardır yapılarda başarılı bir biçimde kullanılan dayanıklı bir yapı malzemesidir. Betonun üretiminin kolaylığı, ekonomik olması ve istenen mimari şekli kolaylıkla alması yapılarda öncelikle seçilmesindeki en önemli nedenlerdendir. Servis ömrü boyunca yapılar çeşitli çevresel etkilere maruz kalmaktadır. Yapıya etki edecek çevresel hususlar iyi bilinmeli ve tasarımda dikkate alınmalıdır. Belirlenen çevresel etki altında yapı işlevini yerine getirmeye devam edebilmeli, yapıda kullanılan malzemelerin kalıcılık özellikleri yeterli olmalı ve böylece yapının performansı belirli bir düzeyin altında kalmamalıdır (Şengül 2003). Doğal kaynakların daha az tüketilmesi, çevre kirliliğinin daha aza indirgenmesi ve enerji maliyetlerinin azaltılması amacıyla endüstriyel atık kullanımı gün geçtikçe daha fazla ilgi çeken bir konu olmaktadır. Endüstriyel atıklardan yapay puzolan sınıfına giren ve termik santral baca külü olan uçucu küller kendisine inşaat sektöründe çok yaygın olmamakla birlikte kullanım alanı bulmuştur (Çelik 2004).

Demir elde edebilmek için, demir cevherlerinin, "yüksek fırın" olarak adlandırılan fırınlarda çok yüksek sıcaklıklara kadar (yaklaşık 1600 °C sıcaklığa kadar) ısıtılmaları, böylece oksijenden ve yabancı maddelerden arındırılmaları gerekmektedir. Kok kömürünün (karbon'un) yakıt olarak kullanıldığı bu fırınlarda, ayrıca, arıtma işlemine yardımcı olabilmesi için kalkertaşı da cevherle birlikte ısıtılmaktadır. Yüksek sıcaklığın etkisiyle, kok kömürünün karbonu ile demir oksitteki oksijen birleşerek karbon monoksit ve karbon dioksit gazları oluşturarak fırını terketmektedir. Geride, eriyik durumda demir ve eriyik durumda

olan CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, MnO, S gibi yabancı maddeler topluluğu kalmaktadır. Demirin yoğunluğu, yabancı maddeler topluluğunun yoğunluğundan daha yüksek olduğu için, eriyik durumdaki demir, fırının en alt bölümünde ve eriyik durumdaki diğer malzemeler ise demirin hemen üzerinde yer almaktadır. Demir ve diğer malzeme topluluğu ayrı ayrı çıkışlardan dışarı çıkartılmaktadır. Elde edilen yabancı maddeler topluluğu "yüksek fırın cürufu" olarak adlandırılmaktadır. Amorf yapıya sahip olan ve büyük miktarda SiO<sub>2</sub> ve Al<sub>2</sub>O<sub>3</sub> içeren granüle yüksek fırın cürufu, öğütülerek çok ince taneli duruma getirildiği takdirde, doğal puzolanların ve uçucu küllerin puzolanik özelliklerine benzer özellikler göstermektedir. Ayrıca, büyük miktarda CaO içermesi nedeniyle, öğütülmüş granüle yüksek fırın cürufunun kendiliğinden de bir miktar bağlayıcı özelliği bulunmaktadır. Granüle yüksek fırın cürufunun beton katkı maddesi olarak kullanılması Güney Afrika'da Stutterheim tarafından 1947-1953 yılları arasında yapılan araştırmalardan sonra başlamıştır.

Granüle yüksek fırın cürufu taze beton ya da harçların işlenebilirliğini artırırken terlemeyi azaltmaktadır. Dayanımı geliştirirken hidrasyon ısısını düşürmekte, permeabilite ve poroziteyi azaltarak alkali-agrega genişmesini düşürmektedir (Erdoğan 2003, Aldea 2000). Bu özelliklere sahip olması nedeniyle günümüzde birçok özel ve geleneksel beton uygulamalarında kullanılmaktadır.

Betonda kalıcılık bir yapının içinde bulunduğu ya da bulunacağı çevresel etkiler altında, servis ömrü boyunca, dayanım ve diğer işlevlerini koruyabilmesi özelliğidir (Öner 2005). Beton dayanıklılığı çevresel koşullar ve bünyesinde bulunan kimyasallar ile ilgili bir konudur. Bununla birlikte ortamda su ve nemin varlığı beton içine zararlı maddeleri taşıyacağından dayanıklılıkta önemli bir faktördür. Betonun içerisine sızan su, karbondioksit, oksijen, sülfat, asit ve klor gibi maddeler, betonda değişik türlerdeki kimyasal olayların oluşmasına neden olmaktadır. Betonda yer alan kimyasal ve fiziksel olaylar sonucunda, beton daha boşluklu bir malzeme durumuna gelebilmekte, içerisindeki demir donatılar paslanabilmekte, aşınabilmekte ve iç bünyede çok büyük gerilmeler oluşabilmektedir (Massazza 1997). Bütün bu kimyasal ve fiziksel olaylar betonun hasar görmesine ve beklenen hizmeti veremez duruma gelmesine yol açmaktadır (Karakurt 2008). Klorür geçirgenliği betonun en önemli kalıcılık kriterlerinden biridir. Betonarme yapılara klorür iyonları nüfuz ettiğinde özellikle deniz yapılarında donatı korozyonunu hızlandırır ve betonun bünyesinde de bir takım mekanizmalar oluşturarak betonda bozulmalar meydana getirir.

Bu çalışmada; beton üretiminde bir mineral katkı olarak granüle yüksek fırın cürufu kullanımının beton basınç dayanımı, elastisite modülü ve hızlı klorür geçirgenliği özellikleri üzerindeki etkisi deneysel olarak incelenmiştir. Bu amaçla, çimentoya %15, %30, %45, %60 ve %75 oranlarında granüle yüksek fırın cürufu ikame edilerek betonlar üretilmiş ve bu betonlar üzerinde 7, 28, 56 ve 90 günlük basınç dayanımı ve elastisite modülü deneyleri gerçekleştirilmiştir. Hızlı klorür geçirgenliği deneyleri 90 günlük numuneler üzerinde yapılmış, böylelikle; granüle yüksek fırın cürufunun betonda meydana getirdiği puzolanik etki ile boşluk doldurma etkisinin bu betonların bazı mekanik ve kalıcılık özelliklerine etkisi belirlenmiştir.

## 2. DENEYSEL ÇALIŞMALAR

Çalışmada agrega olarak Sakarya-Geyve yöresinden tedarik edilen ve maksimum tane çapı 16 mm olan kalker agregası, çimento olarak TS EN 197-1 standardına uygun olarak üretilen CEM I 42.5 çimentosu kullanılmıştır. Mineral katkı maddesi olarak kullanılan granüle yüksek fırın cürufu Bolu Çimento Sanayi A.Ş. tarafından temin edilmiştir tedarik edilmiştir. CEM I 42.5 çimentosu ve mineral katkı olarak kullanılan granüle yüksek fırın cürufuna ait kimyasal, ve fiziksel özellikler Tablo 1'de gösterilmiştir.

Tablo 1. Çimento ve mineral katkılara ait kimyasal ve fiziksel özellikler

Kimyasal Bileşim (%)		
Bileşen Adı	Çimento	Granüle Yüksek Fırın Cürufu
SiO <sub>2</sub> Çözünen	22.06	40.98
Çözünmez kalıntı	0.12	-
Al <sub>2</sub> O <sub>3</sub>	4.25	10.82
Fe <sub>2</sub> O <sub>3</sub>	0.20	1.95
CaO	65.39	34.85
MgO	1.13	8.24
SO <sub>3</sub>	2.98	0.80
Kızdırma Kaybı	2.53	-
Tayin Edilemeyen	1.90	-
Serbest CaO	1.56	-
Na <sub>2</sub> O	0.54	0.36
K <sub>2</sub> O	0.55	1.13
Fiziksel Özellikler		
Özgül ağırlık	3.11	2.92
Özgül Yüzey (cm <sup>2</sup> /g)	4400	2910
Priz Başlangıcı (dak.)	135	-
Priz Sonu (dak.)	160	-

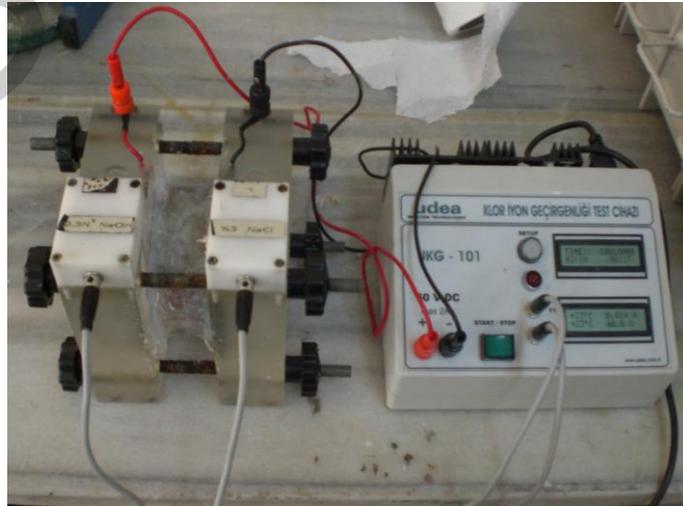
Numunelerin hazırlanmasında çimento miktarı  $400 \text{ kg/m}^3$  olarak belirlenmiş ve basınç dayanımı deneyi için kullanılan numuneler 10 cm ebatında küp olarak üretilmiştir. Deneylerde üretilen tüm numunelere katılan su miktarı, 150-160 mm arasında çökme değerini sağlayacak şekilde ayarlanmıştır. Üretilen numuneler kalıptan alındıktan sonra  $20 \pm 2 \text{ }^\circ\text{C}$ 'de kirece uygun su içerisinde deney zamanına kadar bekletilmiştir. Beton numuneleri üzerinde 7, 28, 56 ve 90 gün sonunda basınç dayanım deneyleri yapılarak, granüle yüksek fırın cürufu ikameli betonların basınç dayanımı değerleri şahit betonla karşılaştırılmıştır. Toplam 6 seri beton üretimi gerçekleştirilmiş, bu karışımlarda granüle yüksek fırın cürufu %15, %30, %45, %60 ve %75 oranlarında çimento ile ikame edilerek kullanılmıştır. Üretilen betonların karışım oranları Tablo 2'de verilmiştir.

Tablo 2. Her seri için beton karışımlarına dahil olan malzeme miktarları

Beton no	Beton kodu	Çimento ( $\text{kg/m}^3$ )	Granüle Yük. Fır. Cürufu ( $\text{kg/m}^3$ )	Su ( $\text{kg/m}^3$ )	s/ç oranı	su / toz mal.	Doğal kum ( $\text{kg/m}^3$ )	Kırmataş I ( $\text{kg/m}^3$ )	Kırmataş II ( $\text{kg/m}^3$ )	Çökme (mm)
1	ŞAHİT	400	-	205	0.51	0.51	877	513	341	156
2	GYFC15	340	60	208	0.55	0.52	875	511	342	157
3	GYFC30	280	120	218	0.60	0.54	872	512	340	154
4	GYFC45	220	180	216	0.64	0.54	879	511	345	159
5	GYFC60	160	240	211	0.55	0.52	875	513	344	156
6	GYFC75	100	300	214	0.59	0.53	876	515	343	158

Elastisite modülü deneyleri 15 cm çapında ve 30 cm yüksekliğindeki silindir numuneler üzerinde gerçekleştirilmiştir. Bu deney için hazırlanan silindir numuneler 7, 28, 56 ve 90 gün boyunca su içerisinde kür edilmiş ve her seri için 3 adet numune üzerinde bu deneyler yapılmış ve elde edilen sonuçların ortalamaları alınarak elastisite modülü değerleri belirlenmiştir. Statik elastisite modülü için deney numuneleri basınç dayanım deneyine tabi tutulmadan önce % 70 kükürt ve % 30 grafit tozundan oluşan karışım ile başlanmış. Daha sonra TS 3502 (1981) ve ASTM C 469 (1994)'a göre başlangıç ve sınır yükleri bulunarak numune sınır yüküne kadar yüklenip deformasyon çerçevesinin üzerindeki "birim kısalma ölçer" göstergesinin hareket edip etmediği gözlemlenmiştir. Başlangıç ve sınır yükleri 10 parçaya bölünerek başlangıç yükünden sınır yüküne kadar her parçadaki kısalma değerleri okunmuştur. Bu çalışmada başlangıç yükü 5000 kg, sınır yükü numunelerin basınç dayanımının % 40'ı olarak alınmıştır. Elde edilen sonuçlar ilgili standartlara göre değerlendirilerek numunelerin statik elastisite modülü değerleri belirlenmiştir.

Granüle yüksek fırın cürufu ikameli numunelerin dayanıklılık özelliklerinden birisi olarak klorür geçirgenlik özellikleri ASTM C 1202-97 (1997) standardı referans alınarak gerçekleştirilmiştir. Bu amaçla 10 cm çapında ve 20 cm yüksekliğinde üretilen silindirik numuneler 28 gün boyunca su içerisinde kür edildikten sonra 90. güne kadar açık havada bırakılmış ve 90. günde uçlarından kesilerek ortada kalan 5 cm kalınlığındaki dilim deney için kullanılmıştır. Bu dilim, hızlı klorür geçirgenliği deney aletine yerleştirilmeden önce bazı işlemlerden geçirilmiştir. Deneye başlanmadan önce deney numunelerinin yan yüzleri silikonla kaplanıp kurumaya bırakılmıştır. Daha sonra numuneler desikatöre yerleştirilerek 3 saat boyunca vakumlanmıştır. Ardından vakum haznesine su doldurularak numunelere vakum etkisinde 1 saat su emdirilmiştir. Deney numuneleri, ayrıca su içerisinde 18 saat bekletildikten sonra deneye hazır hale getirilmiştir.



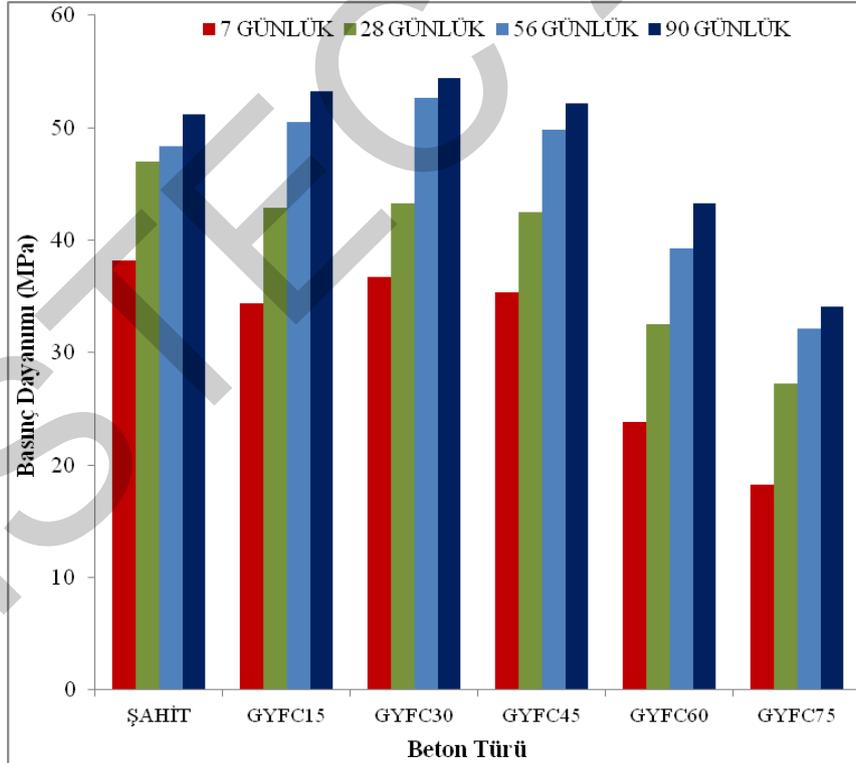
Şekil 1. Hızlı klor iyon geçirgenliği test cihazı

Hızlı klor iyon geçirgenliği test cihazı Şekil 1’de görüldüğü üzere elektronik ölçüm ve değerlendirme ünitesi ile pleksiglastan üretilmiş iki adet hücreden oluşmaktadır. 100 mm çapında ve 51 mm boyundaki deney numuneleri deney hücrelerine hücre ile arasında metal elek ve conta olmak üzere düzgün bir şekilde yerleştirilmiş ve test hücresi üzerindeki vidalar iyice sıkıştırılmıştır. Sızıntıları engellemek amacıyla beton ile test hücrelerinin birleştiği bölge silikonla kaplanmıştır. Mevcut iki test hücresinin birine % 3’lük kütleli olarak saf su ile hazırlanmış NaCl çözümü, diğerine ise 0,3 N (yine saf su ile) NaOH çözümü doldurularak deneye başlanmıştır. Hızlı klor geçirgenliği deneyi, betonun elektriksel iletkenliği esasına dayanmaktadır. Deney numunelerine 60 V sabit potansiyel farkı uygulanarak beton diskten geçen elektrik akım şiddeti miktarı belirli aralıklarla kaydedilmiştir. 6 saat boyunca her yarım saatte numunelerden geçen akım şiddeti ölçüldükten sonra akım şiddeti-zaman grafiği çizilerek grafik altındaki alan yardımıyla bu sürede iletilen elektrik akımı miktarı Coulomb cinsinden hesaplanmıştır.

### 3. DENEYSEL BULGULAR VE TARTIŞMA

#### 3.1. Basınç dayanımı

Granüle yüksek fırın çürufunun çimento ile farklı ikame oranlarında kullanılmasıyla üretilen betonlar üzerinde yapılan 7, 28, 56 ve 90 günlük basınç dayanımı sonuçları Şekil 2’de verilmiştir. Beton numuneleri içerisinde 7 ve 28 günlük en yüksek dayanım değerini şahit beton vermiştir. Granüle yüksek fırın çürufunun çimento ile %30 ikame oranında kullanılmasıyla üretilen karışımdan 56. günde en yüksek basınç dayanımı değeri elde edilmiş iken bu karışım şahit betona kıyasla % 8.21 daha yüksek basınç dayanımı değeri vermiştir. 90 günlük numuneler içerisinde en yüksek basınç dayanımı granüle yüksek fırın çürufunun çimento ile % 30 oranında ikame edilmesiyle üretilen karışımdan elde edilmiştir. Bu karışım şahit betona kıyasla %5.79 daha fazla dayanım değeri vermiştir. Şahit beton karışımının 7 günlük erken dayanım özelliklerinin granüle yüksek fırın çürufu içeren karışımlara göre daha iyi olması, erken yaşlarda puzolanik reaksiyonların yavaş olması nedeniyle puzolanik etkinin dayanıma olumlu bir katkı yapamamasına bağlanabilir. Granüle yüksek fırın çürufu içeren karışımların ileri yaş dayanımlarının şahit betona göre yüksek olmasının nedeni olarak ise granüle yüksek fırın çürufunun puzolanik özellik gösteren bir mineral katkı maddesi olmasından ötürü zaman içerisinde puzolanik reaksiyonlar sayesinde çimentonun bünyesinde bulunan serbest kireci bağlayarak yani kalsiyum hidroksit ile reaksiyona girerek yeni kalsiyum-silikat-hidrate bağlayıcı jellerini oluşturması, bu durumun da çimento-agrega ara yüzey bölgesini kuvvetlendirmesi gösterilebilir. Dolayısıyla, granüle yüksek fırın çürufu içeriği nedeniyle arayüzey bölgesi kuvvetlenen betonların basınç dayanımları şahit betona göre daha yüksek olmaktadır.

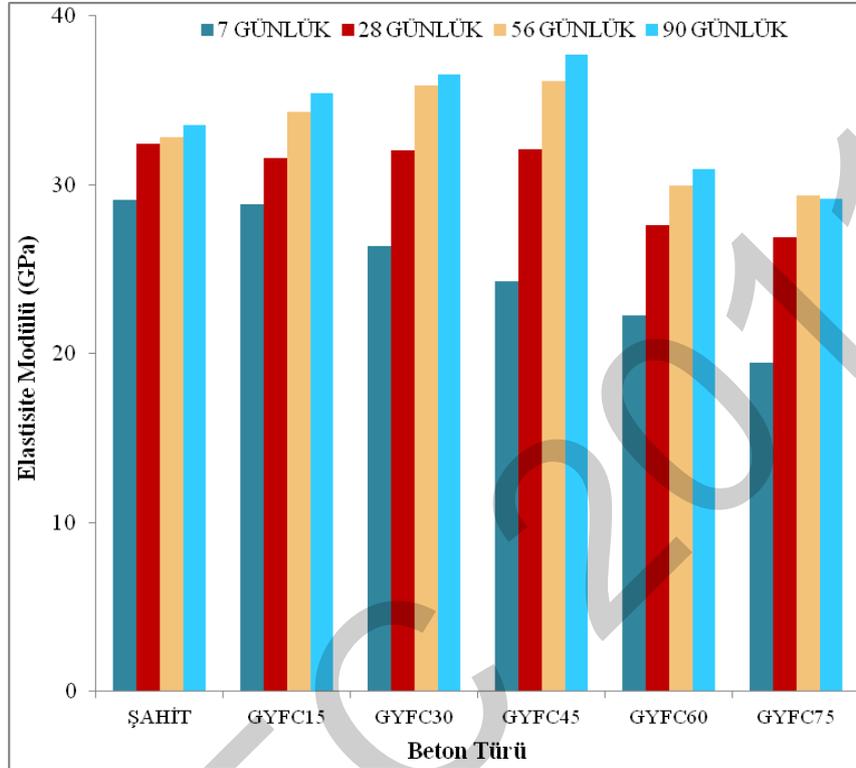


Şekil 2. Üretilen betonların 7, 28, 56 ve 90 günlük basınç dayanımı sonuçları

#### 3.2. Elastisite modülü

Granüle yüksek fırın çürufu ikameli numuneler üzerinde yapılan elastisite modülü deneyi sonucunda elde edilen değerler Şekil 3’te görülmektedir. Deney sonuçları değerlendirildiğinde 7 günlük numuneler içinde en yüksek elastisite modülü değerini şahit beton en düşük elastisite modülü değerini ise granüle yüksek fırın çürufunun çimento ile % 75 oranında ikame edilmesiyle üretilen karışım vermiştir. Şahit beton karışımından 28. günde en yüksek elastisite modülü değeri elde edilmiş iken granüle

yüksek fırın cürufunun çimento ile % 75 oranında ikame edilmesiyle üretilen karışımdan ise 28. günde en düşük elastisite modülü değeri elde edilmiştir. Granüle yüksek fırın cürufunun çimento ile % 30 oranında ikame edilmesiyle üretilen karışımdan 56. günde en yüksek elastisite modülü değeri elde edilmiş iken granüle yüksek fırın cürufunun çimento ile % 75 oranında ikame edilmesiyle üretilen karışımdan en düşük elastisite modülü değeri elde edilmiştir. 90 günlük numuneler içinde granüle yüksek fırın cürufunun çimento ile % 45 oranında ikame edilmesiyle üretilen karışım en yüksek elastisite modülü değerini vermiş iken, granüle yüksek fırın cürufunun çimento ile % 75 oranında ikame edilmesiyle üretilen karışım ise en düşük elastisite modülü değeri vermiştir. Bu sonuçlar ışığında granüle yüksek fırın cürufunun çimento ile ikame oranının artması elastisite modülü değerlerinde düşüşe neden olmuştur. Granüle yüksek fırın cürufu içeren karışımların özellikle 56 ve 90 günlük elastisite modülü değerlerinin şahit betona göre daha yüksek olmasının nedeni olarak granüle yüksek fırın cürufunun puzolanik etkisi nedeniyle artan basınç dayanımının elastisite modülünü de artırmasına bağlanabilir.

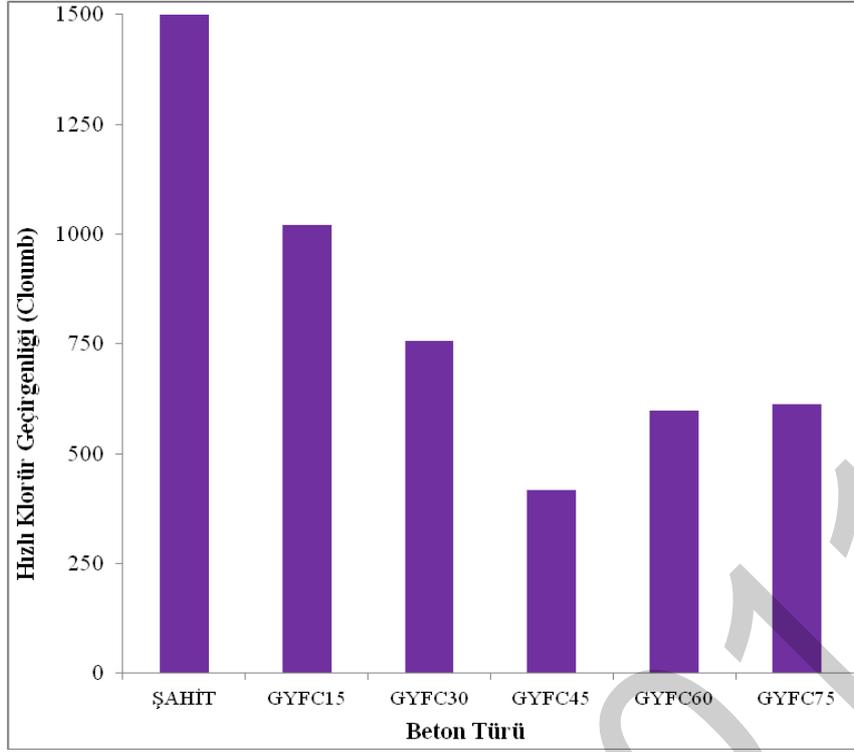


Şekil 3. Üretilen betonların 7, 28, 56 ve 90 günlük elastisite modülü deney sonuçları

### 3.3. Hızlı klorür geçirgenliği deneyi

Farklı karışımlarda hazırlanan ve granüle yüksek fırın cürufu içeren deney numuneleri üzerinde 90. günde ASTM C1202 standardı referans alınarak yapılan hızlı klorür geçirgenliği deneyleri sonucunda beton üretiminde mineral katkı kullanımının betonun klorür geçirgenliği değerlerini düşürdüğü görülmüştür. Tüm karışımlar içerisinde en düşük klorür geçirgenliği değerini granüle yüksek fırın cürufunun çimento ile % 45 oranında ikame edilmesiyle elde edilen karışım vermiştir ve bu değer ASTM C1202 (1997) standardına göre çok düşük boyutlardadır. Bu karışım aynı zamanda şahit betona göre % 75.33 daha az klorür geçirgenliği değeri vermiştir. Granüle yüksek fırın cürufu ikame edilerek üretilen karışımlar şahit betonla kıyaslandığında daha düşük klorür geçirgenlik değerleri vermiştir. Bununla birlikte, granüle yüksek fırın cürufunun çimento ile ikame oranı arttıkça Şekil 4'te görüleceği üzere klorür geçirgenliği değerlerinde %45 ikame oranına kadar azalma gözlenmiştir. Tüm karışımlar içerisinde en yüksek klorür geçirgenliği değerini ise şahit beton karışımı vermiştir.

Betonda klorür geçirgenliği öncelikle betonun bünyesinde bulunan boşluk sistemi ile ilgilidir. Daha az boşluk içeren, mikroyapısı daha sıkı olan ve boşlukları birbiriyle sürekli olmayan beton daha az iyon yükü ileterek daha düşük klorür geçirgenliği değeri vermektedir. Bu yaklaşımla granüle yüksek fırın cürufu ikameli betonların gerek mikro yapılarının oldukça sıkı olması ve gerekse bünyelerinde çok az boşluk içerip bu boşlukların sürekli olmaması nedeniyle klorür geçirgenliği değerlerinin düşük olduğu aşikardır. Özellikle granüle yüksek fırın cürufu betonda puzolanik etki meydana getirerek ve betonun bünyesindeki boşlukları doldurarak çok düşük klorür geçirgenliği değerlerinin elde edilmesine olanak tanımıştır. Karışımlar içerisinde şahit beton, diğer karışımlara göre daha fazla bağlayıcı içermesine rağmen, klorür geçirgenliği deneyinde filler ve puzolanik etkinin daha fazla önem taşıması nedeniyle, daha yüksek klorür geçirgenliği değeri verdiği görülmüştür.



Şekil 4. Üretilen betonların hızlı klorür geçirgenliği deney sonuçları

#### 4. SONUÇLAR

Yapılan deneysel çalışmadan elde edilen sonuçlar aşağıdaki gibi özetlenebilir;

- Basınç dayanımı sonuçları değerlendirildiğinde granüle yüksek fırın cürufunun çimento ile ikame oranı arttıkça her yaş grubunda basınç dayanımında düşüşler meydana gelmiştir. Tüm karışımlar içinde granüle yüksek fırın cürufunun çimento ile %30 oranında ikame edilmesiyle üretilen karışım genel olarak en yüksek basınç dayanımı değerlerini vermiştir.
- Granüle yüksek fırın cürufunun çimento ile ikame oranının artması elastisite modülü değerlerinde düşüşlere neden olmuştur. Karışımlar içinde granüle yüksek fırın cürufu içeren karışımların 56 ve 90 günlük elastisite modülü değerlerinin şahit betona göre daha yüksek olmasının nedeni olarak granüle yüksek fırın cürufunun puzolanik etkisi nedeniyle artan basınç dayanımının elastisite modülünü de artırmasına bağlanabilir.
- Granüle yüksek fırın cürufu ikameli deney numuneleri üzerinde 90. günde ASTM C1202 standardı referans alınarak yapılan hızlı klorür geçirgenliği deneyleri sonucunda beton üretiminde mineral katkı kullanımının betonun klorür geçirgenliği değerlerini düşürdüğü görülmüştür. Ayrıca, granüle yüksek fırın cürufunun çimento ile ikame oranı arttıkça klorür geçirgenliği değerlerinde belli bir noktaya kadar azalma görülmüştür.

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# HASTANE İÇ MEKÂNLARINDAKİ ELEKTROMAYETİK ALANIN İNSAN SAĞLIĞINA ETKİSİ VE DENETİMİ

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## Özet

Sağlık hizmeti sunulan hastaneler; içerisindeki çalışanların ve sağlıklarına kavuşmak için tedavi gören hastaların, önemli ve kritik anlarını paylaşan mekânlardan oluşmuş yapılardır. Söz konusu mekânların fiziksel koşulları; hastanın iyileşme sürecini uzatır ve sunulan tıbbi tedaviyi olumlu ya da olumsuz etkileyerek iyi ve kaliteli sağlık hizmet sunumuna kalite artırıcı ya da azaltıcı bir unsur olarak katkıda bulunur. İnsan sağlığına etki eden olumsuz çevre koşullarından olan elektromanyetik alanın denetlenerek yapılan çalışmalar mekânın şekillenmesinde belirleyici bir kriter oluşturmaktadır. Bu çalışmada; insan hayatının, sağlıklı bir şekilde devamlılığının sürdürülmesinde en önemli kurumlarından biri sayılabilecek hastane iç mekânlarında oluşan risklerden olan elektromanyetik alanın insan sağlığına etkisi incelenmiş ve bu hastalık yapıcı etkenleri mekânı şekillendiren tasarımcının göz ardı etmemesi gerektiğinin önemi vurgulanmıştır.

**Anahtar kelimeler:** Hastane, elektromanyetik etki, İnsan sağlığı

## HUMAN HEALTH EFFECTS AND CONTROL OF ELECTROMAGNETIC FIELD IN HOSPITAL INTERIORS

### Abstract

Hospitals, health service provided, shared important and critical moments of patients and employees, are buildings. The physical conditions of the mentioned places, the patient extends the healing process and provided medical treatment, positively or negatively affect the quality of health service delivery and good quality as a factor that contributes to the increasing or decreasing. Adverse environmental conditions that affect human health, the controlled studies of the electromagnetic field which is a criterion for determining the formation of the locality. In this study, human health effects of electromagnetic fields which risks consist of hospital interior spaces, considered one of the most important institutions in maintaining the continuity of human life, is examined and it is emphasized that the designer, shaping the space, should not ignore these disease-causing agents

**Keywords:** Hospital, Electromagnetic effect, Human health

### GİRİŞ

İnsanlık tarihi boyunca çalışan bireye, toplum içinde belirli bir rol, statü ve ekonomik olanaklar sağlayan çalışma hayatı, yaşamın önemli bir bölümünü oluşturmakta, fiziksel ve ruhsal olarak insan sağlığını etkilemektedir. Yapılan çalışmalar fiziksel çevresiyle uyum içinde bulunan insanların verimlerinin yüksek düzeyde olduğunu, fizik ve ruh sağlıklarının da yıpranmadığını kanıtlamaktadır.

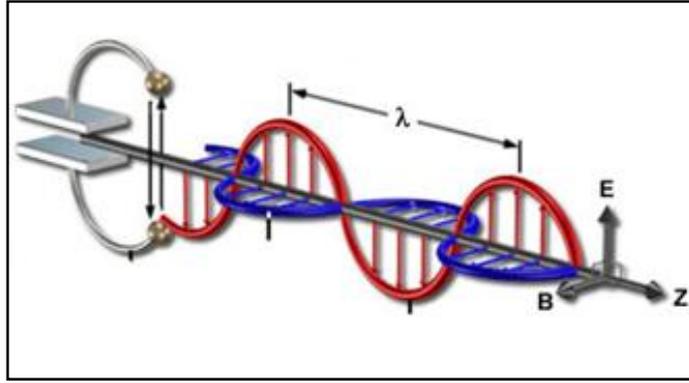
Hastaneler, sağlık hizmeti sunulan, içerisindeki çalışanların ve sağlıklarına kavuşmak için tedavi gören hastaların, önemli ve kritik anlarını paylaşan mekânlardan oluşmuş yapılardır. Söz konusu mekânların fiziksel koşulları; çalışanlarının iş verimini ve sunulan tıbbi tedaviyi olumlu ya da olumsuz etkileyerek iyi ve kaliteli sağlık hizmet sunumuna kalite artırıcı (ya da azaltıcı) bir unsur olarak katkıda bulunur. Elektromanyetik alan, belirli sınırlar içinde kaldığı sürece insan bünyesi ona uyum sağlar. İnsan sağlığına olumsuz etki edecek seviyede oluşan elektromanyetik alan, kişinin denge mekanizması olan “homeostazisi” bozarak strese yol açar ve bunun sonucunda hastalanmasına neden olur.

Bu çalışmada, insan hayatının ve yapılaşmanın en önemli kurumlarından biri sayılabilecek hastane iç mekânlarında olumsuz çevresel faktörlerden biri olan elektromanyetik alanın, insan sağlığına etkisi incelenmiş ve bu hastalık yapıcı etkisinin, mekânı şekillendiren tasarımcının göz ardı etmemesi gerektiğinin önemi anlaşılmıştır. [1]

### TANIM

Bir elektrik yükünün hareketi sonucunda uzayda oluşan değişikliklere elektromanyetik alan denir. Bileşenleri elektrik ve manyetik alandır.

Elektrik ve manyetik alanın kökenleri yüklere bağlıdır. Yüklü parçacıklar hareket etmiyorsa orada sadece elektrik alan oluşur. Eğer yüklü parçacıklar hareket ediyorsa elektrik alanla birlikte manyetik alanda oluşur ve etkileri gözlemci tarafından hissedilir. [2].



Şekil 1. Elektromanyetik (Z), Elektrik(E), Manyetik(B) alan dalgaları [5]

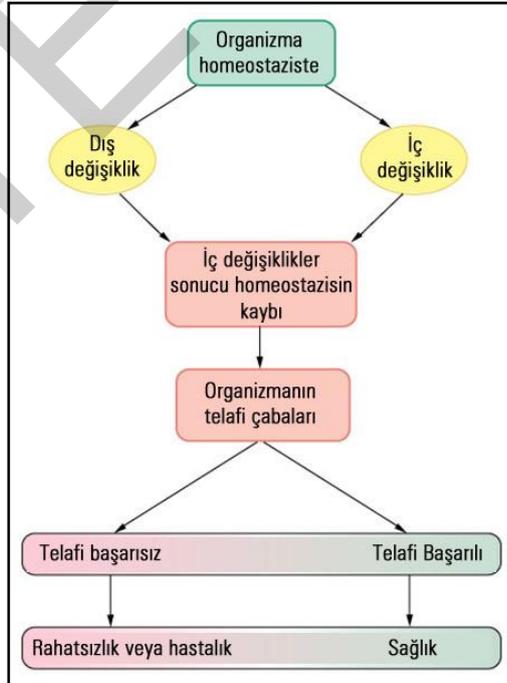
Elektromanyetik alan, elektrik alanı ile manyetik alanın karşılıklı etkileşimi sonucu oluşur. Bir elektromanyetik alan, belirli koşullar altında, elektromanyetik enerji taşıyan bir dalga hareketi olarak da tanımlanabilir. Elektromanyetik dalgalar biçiminde yayılan enerjiye elektromanyetik radyasyon (ışınım) denir.

EM dalgaların saniyede yaptığı salınım sayısı yani kendilerini tekrarlama sıklığına frekans ( $f$ ) denir ve birimi Hertz (Hz)'dir. Birim yüzeyden geçen ortalama güç ise EM dalga şiddeti olarak adlandırılır. Şiddet ( $I$ ) ile gösterilir. Dalganın bir salınımda aldığı yola dalga boyu denir. Birimi metredir (m). Dalganın ortalama hızı ise ( $v$ ) ile gösterilir [2].

## ELEKTROMANYETİK ALAN VE İNSAN SAĞLIĞI İLİŞKİSİ

Bilimsel araştırma ve geliştirme çalışmaları sonucu bir yandan modern ve daha refah içinde bir yaşam kalitesi üretilirken, diğer yandan yaşam kalitesini zorlayan kirliliğin de aynı oranda üretildiği görülmektedir. 19. yüzyılda elektriğin keşfi ile yeni bir yaşam boyutu açılmış ve bunu izleyen teknolojik yenilikler çoğalmıştır. Fakat bu bilgi ve teknolojik gelişim olumlu yönü ile yaşamı kolaylaştırırken olumsuz yönü ile yaşam kalitesini bozan unsurları da içermektedir [3].

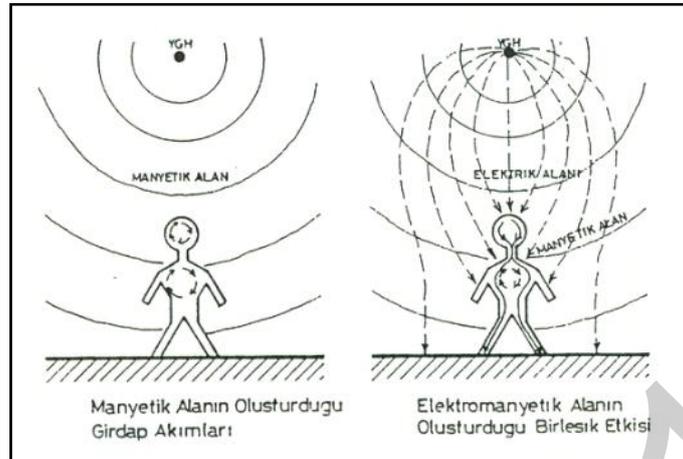
Elektromanyetik Alan, kişinin denge mekanizması olan "homeostazisi" bozarak strese yol açar ve bunun sonucunda hastalanmasına neden olur. Homeostazis; insanın biyolojik yapısının, yaşam koşullarına uyum sağlarken, dengelerin korunmasını sağlayan kendi kendini düzenleme süreci olarak tanımlanır. İnsan vücudu etkileşime hazır, açık bir sistemdir ve sürekli dinamik bir enerji ile insanın iç ve dış çevresinin etkileşimi sonucu, iç çevreyi dengede tutmaktadır. Homeostazi sonucunda kurulan dinamik denge, çevrenin sürekli denetim altında olmasını gerekli kılar [4].



Şekil 2. Homeostazis ve Kontrolü

Tüm canlı, cansız varlık ve maddelerin zayıf veya güçlü bir manyetik alanı vardır. İnsan vücudu her hücresi ile kendine özgü elektriksel devrelerden oluşan elektromanyetik bir makinedir. İnsan vücudunu oluşturan organlar belli bir manyetik alana sahiptir.

İnsan çevresinde oluşan yapay manyetik alanlar, insan vücudunun doğal dengelerini bozarak sağlığını etkiler ve rahatsızlıklara neden olur. Manyetik alanlar, elektrik alanlara göre insan sağlığı açısından daha etkilidir. Örneğin; elektrik alan duvarlardan geçemez, hatta insan derisinden bile geçerken şiddeti çok düşer. Öte yandan manyetik alanlar, özel olarak üretilmiş kimi maddeler dışında, hemen hiçbir engel tanımaz. Elektrik alanlar insan vücudunun yüzeyinde zayıf akımlar oluşturur; manyetik alan ise bedenine içine girerek bu tür zayıf akımların iç organlarda bile oluşmasına yol açarlar [5].



Şekil 3. Manyetik ve Elektrik Alanların İnsanda Oluşturduğu Akım Etkisi [6]

Elektromanyetik alan, 30 KHz den büyük, yüksek frekanslar insan vücudunda su moleküllerinin birbirine sürtünmesinden kaynaklanan termik bir etki oluşturur.

Temel sınır değeri olarak insan vücudu bir derecelik sıcaklık artışına neden olan elektromanyetik güç yutulmasından yola çıkılmaktadır. İnsan vücudu 37°C sabit sıcaklıkta beden dengesini korur ve sağlığını sürdürür. Eğer vücut sıcaklığı bir derece artar ve bu durum birkaç gün sürerse, insan vücudu bunu düzenlemekte zorlanır ve kısa dönemli olumsuz etkiler ortaya çıkar ve hastalık oluşur.

Tablo 1. Elektrik Manyetik Alan İle İlgili Oluşan Sağlık Sorunları [7]

Genel yakınmalar	Santral ve sempatik sinir sisteminde fonksiyonel bozukluklar, konsantrasyon bozukluğu, EEG değişiklikleri, terleme
Sinir sistemi etkileri	Santral ve sempatik sinir sisteminde fonksiyonel bozukluklar, konsantrasyon bozukluğu, EEG değişiklikleri, terleme eğilimi, parmaklarda titreme, hipotansiyon
Kalp Dolaşım Sistemine Etkileri	Hipotoni/hipertoni, taşikardi, EKG değişiklikleri
Kan sistemine etkileri	Periferik kanda niteliksel ve niceliksel değişiklikler
Reaksiyon zamanı	Reaksiyon zamanında değişiklikler, uyarıcı etki

## HASTANE İÇ MEKÂNLARINDA ELEKTROMANYETİK ALAN KAYNAKLARI

Hastanelerde elektromanyetik alan, elektrikli cihazların kullanılması veya elektrik iletimi olan cihazların etrafında bulunması ile oluşur. Teknolojideki hızlı gelişmeler ile sağlık sektöründe kullanılan; hasta izleme monitörleri, solunum cihazları, röntgen, tomografi vb. tıbbi elektronik cihazların yaygınlaşması ile hastane iç ortamlarında etrafa yayılan elektromanyetik dalgalarla elektromanyetik kirliliğe neden olmaktadır.

Hastane yapıları iç mekânlarında elektrikle çalışan tanı, tedavi ve cerrahi cihazlarının çok geniş kullanım alanı olduğundan elektromanyetik alan sık karşılaşılan bir etkidir. Hastane yapılarında yüksek elektromanyetik alan bölgelerinin tespiti için yapılan çalışmalarda elde edilen sonuçlar şöyledir; ABD’de yapılan bir çalışmada hastane ve gününbirlik cerrahi ünitelerinde yapılan ölçümlerde 0,8 mG ile 65 mG arasında değişen şiddette EMA ölçülmüştür. İtalya’da fizyoterapi bölümünde yapılan bir çalışmada yine yasal sınırlarda EMA ölçümü yapılmış ve tıbbi ekipmanlardan 4m uzaklaşma ile EMA şiddetinin iyice azaldığı belirlenmiştir [7].

Hastanelerde elektromanyetik alan etkisi;

### 1. Elektrik iletim ve dağıtım hatları

2. Hastanenin elektrik tesisatı (kablo sistemi)
3. Hastanede bulunan elektrikli cihazlar
4. Tanı ve tedavide kullanılan cihazlar (solunum cihazı, kalp-akciğer pompaları, hasta izleme monitörleri. MR)
5. Aydınlatma tesisatı gibi kaynaklarla meydana gelir [1].

**Tablo 2.** Yapı İçinde Elektromanyetik Alan Kaynakları

HASTANE İÇ MEKÂNLARINDA ELEKTROMANYETİK ALAN KAYNAKLARI		
Elektrik Tesisatı	Aydınlatma Ürünleri	Elektrikli Aygıtlar
-Kolon Hattı -Dağıtım ve Sigorta Tablosu -Elektrik Tesisatı Düzeni <ul style="list-style-type: none"> <li>• Sıva altı, sıva üstü</li> <li>• Gerilim ayar sistemi</li> <li>• Anahtar, priz v.b. tesisat düzeni</li> <li>• Kablolar ve uzatma kablolu</li> <li>• Buatlı ,tablolu ring tesisat tipleri</li> <li>• Pendantlar</li> </ul>	-Akkor Flamanlı Lambalar <ul style="list-style-type: none"> <li>• 220 V vakumlu lambalar</li> <li>• 220 V halojen lambalar</li> <li>• Düşük Gerilimli Lambalar</li> <li>• Halojen Lambalar</li> </ul> -Gaz Işınımlı Lambalar <ul style="list-style-type: none"> <li>• Floresan Lambalar</li> <li>• Kompakt Floresan Lambalar</li> <li>• Özel Amaçlı Gaz Dolgulu Yüksek Gerilimli Lambalar</li> </ul> -Armatür Tipleri ve Gereci <ul style="list-style-type: none"> <li>• Aplik, Abajur</li> <li>• Metal, Plastik, Bakalit v.b.</li> </ul>	-Tıbbi cihazlar <ul style="list-style-type: none"> <li>• Hasta başı monitörü</li> <li>• Defibrilatör</li> <li>• Pulse oksimetre</li> <li>• Fototerapi cihazı</li> <li>• Radyan Isıtıcı</li> <li>• Otoklav, Etüv</li> <li>• Ekg Cihazı</li> <li>• Küvoz</li> <li>• Cerrahi Aspiratör</li> <li>• Tıbbi Monitör</li> <li>• Efor Cihazı</li> <li>• Buzdolabı</li> <li>• Solunum cihazı</li> <li>• Kalp akciğer Pompası</li> <li>• Diyaliz Makinası</li> <li>• Klima v.b.</li> </ul>

## HASTANE İÇ MEKÂNLARINDA ELEKTROMANYETİK ALAN DENETİMİ

Dünya sağlık örgütünün (WHO) 1984'de yayınlanan raporuna göre, yerleşim birimleri ve çalışılan ortamlarda elektrik alan şiddetinin sınırı 10KV/m olarak belirlenmiştir. Başka bir raporda ise manyetik alan şiddeti için 0,1 mT üst düzey sınırı olarak önerilmiştir [6].

Yapının dışında ve içinde meydana gelen elektromanyetik alanların insan sağlığına olumsuz etkisini engellemek için elektrik ve manyetik iletkenliği çok yüksek gereçler kullanılmalıdır. Yapı dışından kaynaklı elektromanyetik alanın engellenmesinde, yapı etrafında ölçümler yapılmalı ve en düşük elektromanyetik alan düzeyi olan bölgelere kadar, elektriksel iletkenliği yüksek gereçler ile maskeleyilmelidir. Yapı kabuğunda elektriksel iletkenliği fazla olan yapı ürünleri kullanıldığında muhakkak topraklama yapılmalıdır. Ayrıca yapıları yıldırım gibi doğal elektrik olaylarından korumak için paratoner kullanılmalıdır.

Yüksek gerilim hatları çevresindeki hastanelerde, alternatif alan şiddeti 5 KV/m'yi geçmemelidir. Yüksek gerilim hattının bulunduğu yönde sağır cepheler getirilmeli veya uzun süre kullanılmayan WC, banyo depo gibi birimler burada tasarlanmalıdır. Hastane yapıları iç mekânlarında elektrostatik yüklenmelere neden olacak gereçler kullanılmamalı ve antistatik yapı malzemeleri kullanılmalıdır. Hasta yatak başında demirden herhangi bir eleman bulunmamalıdır. Bu mekânlarda ferromanyetik yapı malzemelerinden kaçınılmalıdır.

Hastanelerde "aşırı düşük frekanslı" manyetik alan kaynakları arasında en az dikkat çeken, duvarların içinden geçen elektrik kablolarıdır. Doğru tesisat ilkelerine bağlı kalınarak yapılan elektrik donanımı genelde çok düşük manyetik alanlar oluşturur. Ne yazık ki bir çok yapıda bu ilkelere uyulmamaktadır. Bununla birlikte elektromanyetik alan kaynakları etrafında sürekli ölçümler yapılarak denetim sürdürülmelidir.

Hastanelerde elektromanyetik alanlarla ilgili olarak risk bölgeleri konusunda çalışmalar bulunmaktadır, değişken iç çalışma koşulları nedeni ile (hastaların durumuna göre kullanılan elektrikli biyomedikal cihazlardan kaynaklı elektrik alan, manyetik alan, elektromanyetik alan) oluşan elektrik alan, manyetik alan ve elektromanyetik alan değerleri farklılık gösterir. Bu nedenle sürekli olarak elektrik alan, manyetik alan ve elektromanyetik alan ölçümü yapılabilir olmalıdır.

Kısaca; hastane iç mekânlarında, manyetik alanlara karşı üç türlü önlem alınmalıdır. Bunlar:

- 1- Manyetik alanlar ferromanyetik gereçler ile yönlendirilmeli
- 2-Yönlendirilemeyen manyetik alanlar tamamen maskelenmeli
- 3- Manyetik alanın, insan sağlığını olumsuz etkileyemeyeceği bir emniyet mesafesi belirlenmelidir. Bu üç yöntem yapı dışından ve içinden kaynaklanan manyetik alanlarda kullanılabilir.

## SONUÇLAR

Sağlık hizmeti sunulan hastaneler iç mekânlarında, elektrikle çalışan tanı, tedavi ve cerrahi cihazlarının çok geniş kullanımı, elektrik alan, manyetik alan ve elektromanyetik alan oluşumuna neden olmakta ve bu durum insan sağlığını olumsuz etkilemektedir. İnsan sağlığını olumsuz etkilerden koruyabilmek için;

Hastane yapıları iç mekânları için, elektrik alan, manyetik alan ve elektromanyetik alan ile ilgili olarak sınır değerler belirlenmeli, bu yapılarda düzenli ölçümler yapılarak, yapı kullanıcılarının korunmasına yönelik önlemler alınmalı ve kullanıcılar bilgilendirilmelidir.

Ülkemizde, hastane yapıları tasarlanırken elektriksel alanlar tesisatlar ve benzeri öğeler göz önüne alınarak düşünülmelidir. Yapının iç ve dış çevresinde meydana gelen elektrik alan, manyetik alan elektromanyetik alan denetimi ile ilgili olarak çalışmalar yapılmalıdır.

Yapının dışında ve içinde meydana gelen elektromanyetik alanların insan sağlığına olumsuz etkisini engellemek için; özellikle hastanelerde elektromanyetik alana maruz kalınan bölgelerde, elektromanyetik alan dalgaları etkisini engelleyen yapı malzemeleri seçilmelidir.

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# HIGH Q MICROCAVITIES IN 2D PHOTONIC CRYSTAL

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## ABSTRACT

In this paper, we present an numerical optical properties of a triangular periodic lattice of air holes patterned perpendicularly to a InP- based confining heterostructure with the effective RI  $n=3.32$  ( $\epsilon=11$ ) is selected. Perfectly matched layers conditions have been considered in the calculations to ensure no back reflection in the limit of the analyzed region. This crystal is lit by a Gaussian wave under normal incidence with a transverse magnetic (TM) polarized mode. A series of microcavities in 2D hexagonal lattice photonic crystal are studied in this paper. The microcavities are small sections of a photonic crystal waveguide. Finite difference time domain simulations show that these cavities preserve high Q modes with similar geometrical parameters and field profile. Effective modal volume is reduced gradually in this series of microcavity modes while maintaining high quality factor. The Q value larger than  $3 \cdot 10^6$  is obtained for one of these cavity modes.

## 1. INTRODUCTION

The discovery of photonic crystals has opened up many new methods to manipulate light [1- 2]. However, three dimensional photonic crystals usually involves complex connectivity and strict alignment, which make them rather challenging for fabrication [3, 4]. Alternatively, two dimensional photonic crystal slabs (2D PC's) have been proposed [5, 6], which promise easier fabrication using present techniques.

Over the past few years, much work has been devoted to the study of microcavities in these 2D PC. These microcavities exhibit attractive properties such as high quality factor (Q) and small modal volume (V), which make them potentially useful not only in miniaturized photonic devices but also in some quantum optical devices. The former applications include channel drop filter for the wavelength division multiplexer system, high efficiency light emission diodes and low threshold lasers [7-9]. Among the latter applications are controlled single photon source and entangled emitter-cavity systems [10, 11].

The applications mentioned above all require microcavities to confine light strongly and densely, that is, microcavities should have both high quality factor Q and small modal volume V. The ratio Q/V is a measure of the strength of various cavity interactions and should be as large as possible.

In this paper a series of microcavities in 2D hexagonal lattice photonic crystal are studied. The microcavities are small sections of a photonic crystal waveguide. Finite difference time domain simulations show that these cavities preserve high Q modes with similar geometrical parameters and field profile. Effective modal volume is reduced gradually in this series of microcavity modes while maintaining high quality factor.

## 2. THE PHOTONIC CRYSTAL DESIGN

In the designed structure shown in figure1a, a 2D triangular PC of air holes patterned perpendicularly to a InP- based confining heterostructure with the effective RI  $n=3.32$  ( $\epsilon=11$ ) is selected. The lattice constant is  $a=440\text{nm}$  while the hole radius is  $r=0.36a$ . High aspect ratio etching of the photonic crystal is achieved using Ar/Cl<sub>2</sub>-based chemically assisted ion beam etching. Details on the sample fabrication are given in [8, 12].

The computational method used is based on a 2D finite difference time domain (FDTD) method algorithm. Perfectly matched layers (PML) conditions have been considered in the calculations to ensure no back reflection in the limit of the analyzed region [13]. This crystal is lit by a Gaussian wave under normal incidence with a transverse magnetic (TM) polarized. The length of the photonic crystal is  $13a$  and the time step is chosen to 0.01. Note that it might be necessary to reduce the time step below the stability limit when simulating metals since the courant condition can change in this case.

Dispersion diagram showing normalized frequency versus the wave vector for TE and TM modes of the 2D photonic crystal is given in figure1b. It has been calculated along the  $\Gamma$ -K-M- $\Gamma$  edge for the Brillouin zone by employing a 2D plane wave expansion (PWE) method. The band diagrams show a two frequency band gap for TM polarized modes but no gap for TE modes with this refractive index contrast and relatively small  $r/a$ . In the TM band diagram of figure1b the fundamental band gap is centered near a normalized frequency of 0.3. It extends between the normalized frequencies  $\omega_1=0.2355$  ( $a/\lambda$ ) and  $\omega_2=0.3530$  ( $a/\lambda$ ), which corresponds to wavelength range  $1.24$ - $1.86\mu\text{m}$  for the waves with TM polarization.

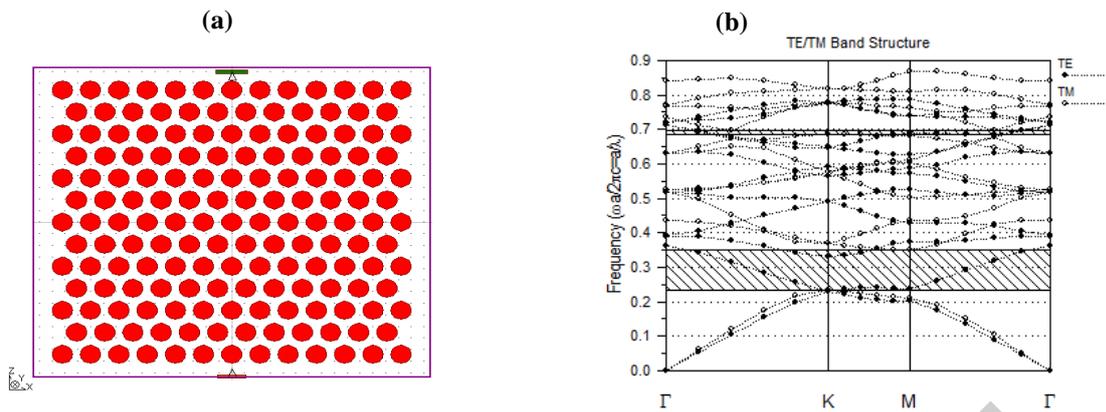


Figure1. (a) Sight of top of the photonic crystal with a triangular lattice of air holes, with hole radius  $r=0.36a$ . (b) Dispersions curves and band-gaps for TM and TE polarizations for the 2D lattice without defects.

### 3. THE MICROCAVITY DESIGN

The linear cavity is actually considered a waveguide photonic crystal missing-row closed at both ends by two photonic crystal mirrors. The mode of the cavity is mainly formed by the round-trip fundamental Bloch mode of the guide between the two mirrors, just like in a conventional Fabry-Perot cavity. 2D-FDTD method to calculate the spectral response of the structure, the quality factors of modes and the different components of the field at any point in space calculation. For the two structures presented later, the step size is 10 nm. The initial structure is the cavity  $L_2$  shown in Figure 2.

#### 3.1. MICROCAVITY $L_2$

The structure of our 2D PC cavity is shown in Fig. 2a, with two missing holes in the center. The computational method used is based on a 2D finite difference time domain (FDTD) method algorithm. This crystal is light by a Gaussian wave under normal incidence with a TM polarized. The length of the photonic crystal is  $17a$  and the time step is chosen to 0.01.

Figure 2(b) shows the spectral response of the microcavity formed by removing two adjacent air holes obtained with the FDTD method of the impulse response. A sharp peak appears inside the complete bandgap in TM polarization of the PC, at the resonance frequency of the microcavity.

We can note that for the cavity  $L_2$  it has 2 modes ( $1.324 \mu\text{m}$  and  $1.7767 \mu\text{m}$ ) which are propagated in the photonic band gap, the resonance wavelength  $\lambda_0 = 1.324 \mu\text{m}$  has the high quality factor (figure2b). The Q factor calculated at this resonance is  $Q=2.48 \cdot 10^5$ .

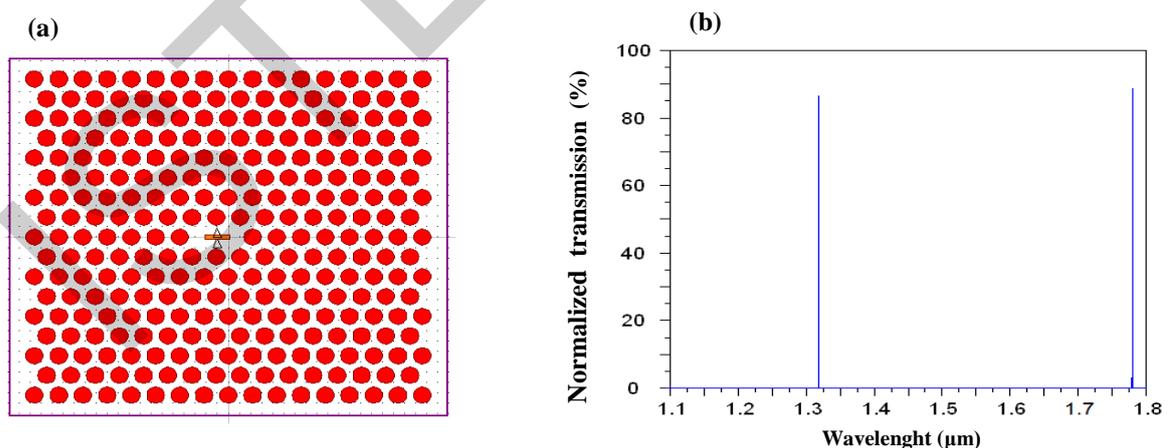


Figure2. (a) Sight of top of the  $L_2$  cavity made by removed two holes, (b) Transmission of the  $L_2$  cavity in a triangular lattice.

In order to improve the transmission efficiency and Q factor simultaneously of these structure, by reducing unwanted reflection due to mismatch and through minimization of propagation losses, we modified  $L_2$  geometry: two missing hole in a line where both lateral displacement of the first hole adjacent to the cavity. The holes that will be staggered to optimize the cavity are those located at two ends of the cavity as shown in Figure 3. They were moved to outside of the cavity a distance between 10 and 110 nm.

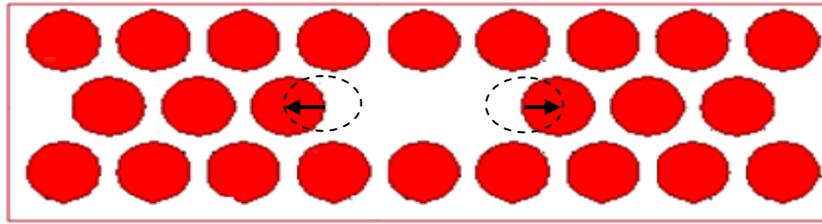


Figure3. Representation of the cavity  $L_2$ . The dotted lines indicate the original location holes on both ends and the arrow the direction of shift holes concerned.

The methods described above were used to calculate the Q factor and the fundamental mode of cavities with a range of displacements of the edge air holes (the nearest neighbors). The results are shown in Fig. 4 as a function of air hole shift. As the air holes are displaced, the Q factor increases drastically and then decreases. The maximum Q factor, as large as  $5.1411 \cdot 10^6$ , is obtained for an air hole displacement of 80nm.

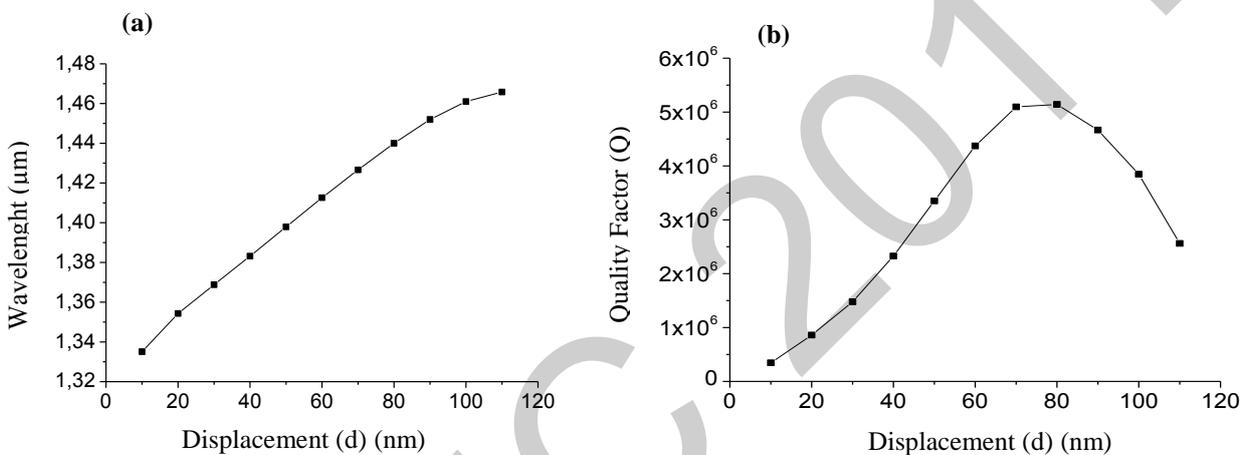


Figure 4: (a) Wavelength mode as a function of the symmetric lateral shift of the edge air holes of the  $L_2$  cavity, (b) Quality factor of the fundamental mode as a function of the symmetric lateral shift of the edge air holes of the  $L_2$  cavity

### 3.2. MICROCAVITY $L_3$

Figure 5 (a) shows a horizontal section in the space calculation of the  $L_3$  structure, that is to say, the horizontal distribution of the index. This cavity allows for very high quality factors (260 000 calculated and 45 000 measured) while maintaining a size of the order of optical wavelength. These cavities have been proposed by Noda et al. [14]. They are of great interest for the realization of low threshold laser nanosources and for a strong interaction between the cavity and sources.

Figure 5 (b) shows the results of a linear cavity. The spectrum calculated by TM polarization can be observed three cavity modes (1.2885  $\mu\text{m}$ , 1.342  $\mu\text{m}$  and 1.6743  $\mu\text{m}$ ). We will call the mode of the  $M_3$  mode resonance wavelength 1.342  $\mu\text{m}$ . This mode has a quality factor of  $3.804 \cdot 10^5$ .

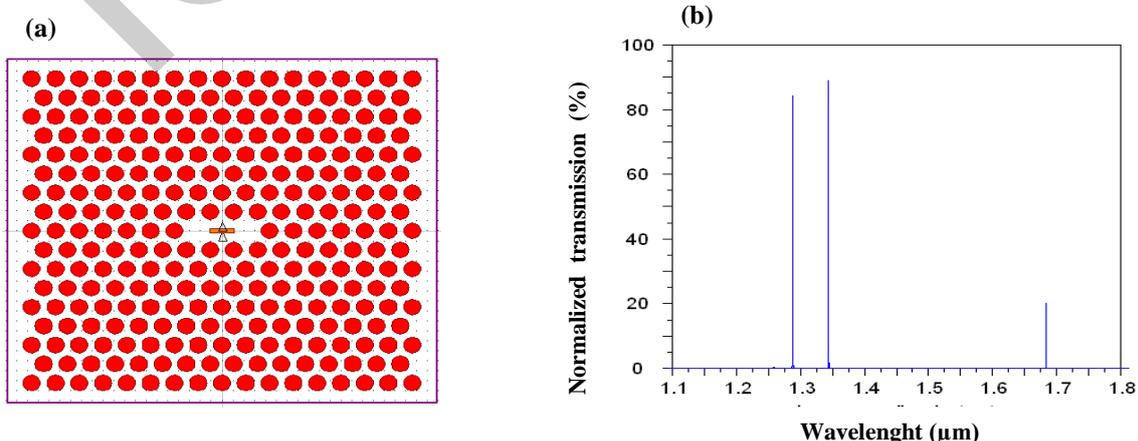


Figure5. (a) Sight of top of the  $L_3$  cavity made by removed two holes, (b) Transmission of the  $L_3$  cavity in a triangular lattice.

Figure 6 shows the dependence of the quality factor of the fundamental mode as a function of the symmetric displacement of the edge air holes. The quality factor increases as the edge air holes are symmetrically displaced. After careful scanning of  $d$ , we find the highest  $Q$  value  $Q=3.3251 \cdot 10^6$  with resonant frequency  $1.4254 \mu\text{m}$  can be achieved at  $d=80\text{nm}$ .

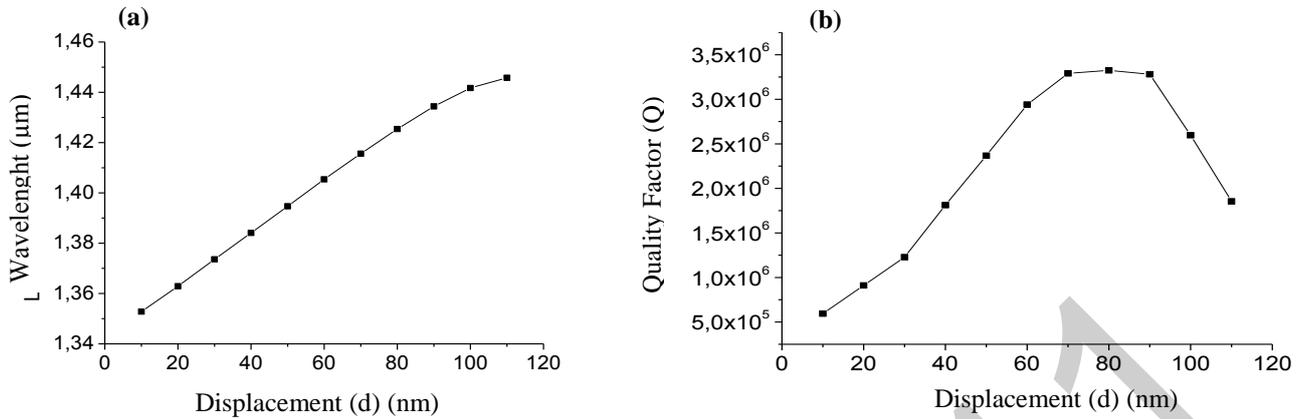


Figure 6: (a) Wavelength mode as a function of the symmetric lateral shift of the edge air holes of the  $L_3$  cavity, (b) Quality factor of the fundamental mode as a function of the symmetric lateral shift of the edge air holes of the  $L_3$  cavity

Figure 6 shows the electric field intensity profile for each of the two modes discussed above. From Fig. 7(a) to (b) we can easily see that as the number of missing holes decreases, the number of nodal points becomes smaller and the field gets more compressed in x directions, leading to reduced modal volumes.

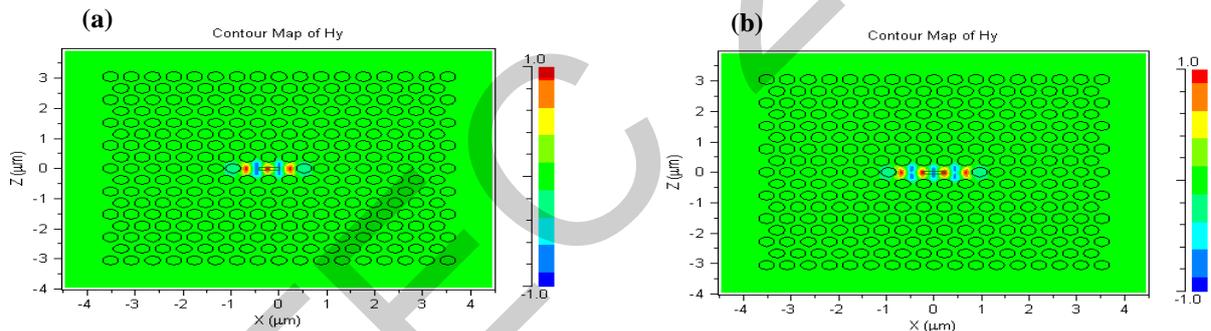


Figure 7: The intensity field distribution for the mode with the highest quality factor in : (a)  $L_2$  at  $\lambda_0 = 1.4399 \mu\text{m}$ , (b)  $L_3$  at  $\lambda_0 = 1.4252 \mu\text{m}$ .

The displacement of the holes results in a red shift of the resonance wavelength  $\lambda_0$ . The physical origin of this shift is an increase in the effective length of the cavity  $L+2d$ .

The reason why  $Q$  factor increases with displacing air holes is because the envelope function of the electric field profile of the cavity approaches a Gaussian function. On the other hand, when the holes are displaced too much, the electric field penetrates more outside the displaced holes. Then the optical confinement becomes more gradually around the holes, while the electric field distribution decays abruptly outside the holes. Therefore, the envelope function of the electric field profile of the cavity deviates from Gaussian function. Most likely due to this deviation  $Q$  factor of the cavity decreases with displacing air holes too much.

#### 4. CONCLUSION

In conclusion, we have studied theoretically the mode structure of  $L_2$  and  $L_3$  defects in photonic crystals. We fine-tuned the positions of air holes near the edge of the point-defect cavity in a 2D-PC according to a design rule which we discovered recently, that the envelope function of the mode profile in the cavity should gently vary but remain spatially localized. We have theoretically calculated that cavity  $Q$  factors can be increased significantly. The  $Q$  of the obtained microcavity is as large as  $5.1411 \cdot 10^6$ . This is larger than that of the cavity without any air hole displacement by a factor of 20.73. We show that end-hole displacement not only increases the  $Q$  factor of the fundamental mode but that it strongly redshifts those modes which have large end-hole-field overlaps, thus reordering the modes.

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# HYBRID ELECTROMAGNETISM ALGORITHM FOR PERIODIC VEHICLE ROUTING PROBLEM

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## Abstract

Electromagnetism algorithm is a meta-heuristic proposed to derive approximate solutions for computationally hard problems. In the literature, several successful applications have been reported for graph-based optimization problems, such as scheduling problems. In this paper, we propose an application of the electromagnetism algorithm to periodic vehicle routing problem (PVRP). Also we are going to minimize two main objectives; total traveling cost (or total traveling distance) imposed by entire vehicles and total waiting cost (or total waiting time) of all customers to take service. Distances are assumed Euclidean or straight line. These conditions are exactly consistent with the real world situation and based on our best knowledge completely are ignored in the literature. The proposed algorithm is compared with hybrid genetic algorithm on a set of test problems, demonstrate that the algorithm perform very competitively.

**Keywords:** Periodic vehicle routing problem, Electromagnetism algorithm, Insertion procedure

## 1. INTRODUCTION

The vehicle routing problem (VRP) is a generic name referring to a class of combinatorial optimization problems in which customers are to be served by a number of vehicles. The vehicles leave the depot, serve customers in the network and on completion of their routes return to the depot. Each customer is described by a certain demand. The VRP has extensive variants, including the PVRP: periodic VRP in which the customers are served in a period of time rather than one day, the VRPPD: VRP with pickup and delivery in which the customers may both receive and send products, the VRPTW: VRP with time windows in which the vehicles must arrive at the customers before the latest arrival time, while arriving before the earliest arrival time results in waiting and so on [Ho et al., 2008]. Besides, the VRP is NP-hard, which means that an efficient algorithm to solve the problem to optimality is unavailable. Therefore, solving the problem by an exact algorithm is time consuming and computationally intractable. To deal with the problem efficiently and effectively, one hybrid heuristic is developed in this paper.

Over the last 30 years or so, the classical VRP has attended strongly in the literature. Comparatively, the number of research projects on the MDVRP is fewer. Tabu search heuristics for the MDVRP have been proposed by Renaud et al. [Renaud et al., 1996] and Cordeau et al. [1997]. The recent paper deserves special attention as it describes a general heuristic that also solves periodic vehicle routing problems (PVRP) and periodic traveling salesman problems. Earlier, Chao et al. [2007] proposed a record to record improvement heuristic for the MDVRP.

Ho et al. [2008] developed two hybrid genetic algorithms (HGAs) for MDVRP. The major difference between the HGAs was the initial solutions. Pisinger and Ropke [2007] presented a unified heuristic which is able to solve different variants of the vehicle routing problem. Crevier et al. [2007] addressed an extension of the multi depot vehicle routing problem that vehicles may be replenished at intermediate depots along their routes. After all, by a general glance to the real world problems, we can find that a large number of problems can not exactly match to the classical VRP or MDVRP concepts. For more explanations, consider the following problems:

**Textile industry:** In the dyeing process of all kinds of fibers, there are several dyeing machines, one basket full of wet raw fiber and one or more parking sites (depots) for dyeing cranes. The crane carries the basket towards dyeing machine and puts it into the machine. By the time some setting is fixed, the crane moves towards another dyeing machine. Then the dyeing machine starts dyeing process on wet fibers. It needs the crane to put another full basket into it after finishing the process. To define the site of each machine for each crane, first zero point for crane must be set and based on that  $x$ ,  $y$  and  $z$  of machine position are specified. Therefore the movement is not in the least distance and the crane moves across  $x$ ,  $y$  and  $z$  axes. The crane does not come back to its parking during its trip, until there are one or some dyeing machines needing it. In this way, the vehicle starts its trip, serves some customers and then comes back to its parking. There are a fixed number of customers for the vehicle to meet. However, since customer demands are dynamic, after service completion of each customer, some other customers, previously engaged in dyeing process and not in need of the vehicle, might need the vehicle at this time. After each service, by addition of some new customers waiting, a new VRP might be faced. Hence, it would be desirable to minimize not only the total cost of trip, but also to minimize the total waiting cost of all customers.

**Cable industry:** A similar condition can be witnessed in cable industry. Three kinds of cable (air core, jelly and aerial) are produced in three stages called tandem, twiner and strander. One expert robot works between tandem stage and twiner and another between twiner stage and strander. The robots are located and fixed at the corners. They move toward each spool (pulley) through three axes ( $X$ ,  $Y$  and  $Z$ ), fixing some settings (like fixing the position of pulley, checking its thickness, its color, etc.). Then the pulley moves to the next stage, sometimes being replaced by a new pulley with the same demand. A robot does not return after starting its trip, unless some other pulleys need setting. Delays in the setting process leads to reduction in the quantity of production and also the longer the trip takes, the more costly it is. Therefore waiting cost and traveling cost are

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important factors to consider. It should be noted that robots take a large space in three dimensions and when more than one robot is needed, they must be located at two opposite sites (multi depot).

By observation of these cases mentioned above and also many other similar cases observed in the industrial world, there would be an incentive for us to think of a new definition for VRP. Such new definition must be adaptable to all these various cases.

## 2. PROBLEM DEFINITION

Mentioned examples of the real world problems consist of determining a set of  $m$  vehicle routes 1) of minimum total traveling cost of vehicles plus total waiting cost of customers; 2) starting and ending at the depot; and such that 3) customer demands arrive in a dynamic mode and there are more than one vehicle visit for each customer.

A slow and idle machine (customer) in the production process would apparently impose some extra cost to the company. Therefore, it is so important to minimize the waiting cost of customers to be serviced by the vehicle. Every customer may have a different waiting cost and considering this criterion is so important in determination of the vehicle route.

This paper aims at first providing a solution method for a condition in which there is only one vehicle. Then attempts are made to decompose multi vehicles to a single vehicle.

## 3. PROBLEM SOLVING

**3.1 One vehicle:** VRP can be regarded as a hard optimization problem. A simple EM may not perform well in this situation. Therefore, the EM developed in this paper benefits of a new approach for acceptance criteria and a local search. We use three different search neighborhoods as pairwise interchange neighborhood, forward insertion neighborhood and backward insertion neighborhood [2005]. One step in the local search is to decide whether the new route is accepted or not as the incumbent solution for the next iteration. A pure descent criterion would be to accept solutions with better objective function values. However, this acceptance criterion is prone to stagnation. As an alternative, we consider an acceptance criterion that is frequently used in simulated annealing (SA) algorithm. The hybrid system starts from determining whether a new solution obtained from one of initial solution using local search is accepted by SA or moved by EM.

This hybrid approach may encourage solutions converging toward better region quickly and to prevent from trapping into the local optimal and still maintaining the population diversity. The algorithm 2 is the pseudo code of the main procedure of the hybrid framework (objective function (1) is denoted as  $OF$ ).

Algorithm 2. HEM ()

1. Initialization ()
2. Priority assignment of initial solutions
3. While (has not met stop criterion) do
4. Initialize Max-iterations, Temp-start
5. Set Count = 1, T = Temp-start
6.  $B \leftarrow$  calculates the average  $OF$  of all solutions ()
7.  $x^c \leftarrow$  the worst  $OF$  among all solutions ()
8.  $x^{New} \leftarrow$  the best  $OF$  among all solutions ()
9. Randomly generate a neighboring solution of  $x^{New}$  using either the interchange neighborhood, forward insertion neighborhood or backward insertion neighborhood. Let the neighboring solution be called  $x^{Nei}$
10. Priority assignment of  $x^{Nei}$
11. Compute  $OF(x^{Nei})$
12. If  $OF(x^{Nei}) \leq B$
13.  $x^c \leftarrow x^{Nei}$
14. Else
15. Set  $D = OF(x^{Nei}) - OF(x^c)$ ;
16. Set  $T = \text{Temp-start} / \log(1 + \text{Count})$ ;
17. With probability  $e^{-D/T}$  set  $x^c \leftarrow x^{Nei}$
18. Else
19. Move  $x^{Nei}$  by EM () and let the new solution be called  $x^{New}$
20. Compute  $OF(x^{New})$
21. If  $OF(x^{New}) \leq B$
22.  $x^c \leftarrow x^{New}$
23. Else go to 9
24. End if
25. End if
26. Increment Count by 1
27. If  $\text{Count} < \text{Max-iterations}$ , go to step 6
28. End while

29. Output the best route or  $x^{best}$

According to the algorithm 2 (algorithm 2, line 1), we initiate the solutions in the population. Then, the neighborhood search procedure is implemented before the EM procedure (algorithm 2, line 9). To determine which solution is good or inferior one, an average objective value  $B$  is calculated. Then, if the solution is not worse than  $B$ , it is accepted and substituted with the worst solution in the population (algorithm 2, lines 12-13). Otherwise, this solution is accepted with probability of  $e^{-\Delta/T}$  and substituted with the worst solution (algorithm 2, line 17) or moved by modified EM algorithm with probability of  $1 - e^{-\Delta/T}$  (algorithm 2, line 19). After solutions are obtained, their  $OF$  can be calculated. The best  $OF$  is final solution. Finally, the initialization, priority assignment, solution charge, calculated total force, and move are modified. Following discusses these topics in details.

**3.1.1. Initialization**

In this stage,  $m$  initial routes are selected by random. We use path representation for each route. For example if the path representation is (3, 6, 4, 1), vehicle starts from the depot, travels to customers 3, 6, 4 and ends customer 1. finally, the vehicle returns back to the depot. Therefore one of neighborhood solution of cited path representation by pairwise interchange can be represented as (6, 3, 4, 1).

**3.1.2. Priority assignment**

In this step we assign one random variable  $x_k^i$  between 0 and 1 to each customer  $k$  in each solution  $i$ . For example consider one problem with 4 customers numbered 1 to 4 waiting for service. Assume the second initial solution is represented by (1, 4, 3, 2). We assign one random variable between 0.75 and 1 to customer 1, one between 0.5 and 0.75 to customer 4, one between 0.25 and 0.5 to customer 3 and finally one between 0 and 0.25 to customer 2. One of the results can be shown as follows:

$$x_1^2 = 0.89, \quad x_4^2 = 0.54, \quad x_3^2 = 0.48 \quad x_2^2 = 0.11$$

Therefore  $x^2 = (0.89, 0.54, 0.48, 0.11)$ . Also if there are  $n$  customers in each route, one random variable between  $(n-1)/n$  and  $n$  is assigned to the first customer, one between  $(n-2)/n$  and  $(n-1)/n$  to the second and so on. Finally random variable of the last customer is between 0 and  $1/n$ . Hence if there are  $m$  initial solutions, there are  $m$  random variables for each customer  $i$  ( $i=1, \dots, n$ ).

**3.1.3. Solution charges, electrostatic force and move**

In the previous section it was described that each solution  $i$  has one vector of random variable denoted as  $x^i$  including  $n$  random variables from  $x_1^i$  to  $x_n^i$ . Therefore  $OF(x^i)$  is equivalent to  $OF(solution(i))$ . Let the force exerted on neighborhood solution (denoted as  $x^{Nei}$  in algorithm 2, line 9) by current solution  $i$  use the fixed charge of  $q_i$ . We have:

$$q^i = \frac{B - OF(x^i)}{\sum_{k=1}^m (B - OF(x^k))}, \quad \forall i = 1, \dots, m \tag{1}$$

where  $B$  is the average  $OF$  of all solutions  $i$  ( $i=1, \dots, m$ ). It is clear that  $\sum_{i=1}^m q^i = 0$ . After the  $q_i$  is obtained, we calculate the force on  $x^{Nei}$  by other solutions  $i$ . To calculate the electrostatic forces imposed by all solution for  $x^{Nei}$ , we obtain electrostatic forces imposed to each particle of  $x^{Nei}$  (particle means  $x_1^{Nei}, x_2^{Nei}, \dots, x_n^{Nei}$ ) as follows:

$$F_k^{Nei} = \sum_{i=1}^n F_k^i = \sum_{i=1}^n (x_k^i \times q^i), \quad \forall k = 1, \dots, n \tag{2}$$

Therefore

$$x_k^{New} = x_k^{Nei} + F_k^{Nei}, \quad \forall k = 1, \dots, n \tag{3}$$

Hence we have one  $x^{New}$  with new particles. We sort all customers in  $x^{New}$  based on its  $x_k^{New}$  in decreasing order and obtain a new route of customers corresponding  $x^{New}$ . Thus solution  $x^{Nei}$  moves to  $x^{Nei} + F_k^{Nei}$ . For example if the solution related to  $x^{Nei}$  is represented by (2, 1, 4, 3) and new particles of  $x^{New}$  are (0.22, 0.52, 0.43, 0.85), the new solution will be (3, 1, 4, 2). Therefore to obtain  $x^{New}$  (algorithm 2, line 19), we follow algorithm 3.

Algorithm 3. Move neighborhood solution by EM ()

1. For  $i = 1$  to  $m$
2. 
$$q^i = \frac{B - OF(x^i)}{\sum_{k=1}^m (B - OF(x^k))}$$
3. End for
4. For  $k = 1$  to  $n$
5. 
$$F_k^{Nei} = \sum_{i=1}^n F_k^i = \sum_{i=1}^n (x_k^i \times q^i)$$

6.  $x_k^{New} = x_k^{Nei} + F_k^{Nei}$
7. End for
8. Output  $x^{New}$
9. Output new route based on  $x^{New}$

After each service, maybe we have some new customer waiting for service. The sequence of previous customers is kept fixed. To find the place of new customer(s), insertion procedure is used (if we face more than one new customer, we must prioritize them or select randomly one by one).

**3.2 Multi vehicles-Multi depots:** First it requires to cluster a set of customers to be served by the same vehicle, that is, the grouping problem. Each customer must be allocated to one of vehicles and major criterion is the total cost (allocation must lead to the minimum total cost). It is clear two major data are critical to determine the priority of allocation: service time and waiting cost. Each customer that has higher waiting cost and less service time has greater priority to allocate to the nearest vehicle. Grouping decision requires following steps:

1. For each customer  $i$ , calculate  $P_i = St_i / Wc_i$  ( $i=1, 2, \dots, n$ )
2. Sort  $P_i$  in ascending order
3. For  $j=1:n$   
Assign the  $j^{th}$  customer in the ascending list to the nearest vehicle
4. End

#### 4. COMPUTATIONAL RESULTS

This section describes the computational tests which are used to evaluate the effectiveness and efficiency of the proposed algorithm to find good quality results. For this purpose, we tested the following methods:

- HGA: hybrid genetic algorithm proposed by Ho et al. [2008]
- HEM: hybrid EM proposed in this paper.

It is noticeable that if during vehicle traveling, some new customers are added as waiting customers for service, we encounter a new VRP and HEM insertion procedure is used to find the route but we solve the problem again through HGA. Two different classes of problems were used in the computational experiments.

Class 1: single depot problem [SD]

Class 2: multi depots problem [MD]

Service time and independent work time for each customer are random integers from Uniform distributions [10, 15] and [30, 60] respectively. Computational testing was conducted on some of test problems. We randomly generated these problems because no suitable test exists for the VRP with considered features. Within the test, we varied two problem characteristics: number of vehicles and number of customers. Each problem is tested with 1, 3 and 5 vehicles and 10, 20 and 50 customers.

As an example of the notation, consider the MD510 set of problems: it consists of 10 instances generated with multi depots, 5 vehicles and 10 customers. Considering all configurations tested, we obtain a total of 150 problem instances.

One eight-hour work cycle takes into account. Each problem instance was solved using each method. The percentage relative error (PRE) for each method  $h$  is computed as follows:

$$PRE=(M_h-BS)/BS \tag{4}$$

where  $M_h$  is the solution for the method  $h$  and  $BS$  is the best solution among two methods. The average, minimum, and maximum PRE values for two methods are shown in Table 3. Both algorithms were coded by Matlab software and run on a PC that has a PENTIUM-III 850 MHz processor, with 256 Mb RAM.

Subscripts of numbers in min columns indicate the number of times that the method has reached the best solution. It is clear that the sum of these subscripts in each row must be greater than or equal to 10. Also to have equal condition between two methods both algorithms are run 10 independent times with a stopping criterion based on an elapsed CPU time given by  $a \times b / 2$  seconds ( $a$  is the number of customers and  $b$  is the number of vehicles). This allows to increase solution time as the number of customers  $a$  and the number of vehicles  $b$  grows.

Table 3. PRE values for computational test of two methods

Instances	HEM			HGA		
	Min PRE	Average PRE	Max PRE	Min PRE	Average PRE	Max PRE
SD110	0 <sub>9</sub>	0.035	0.345	0 <sub>1</sub>	2.045	3.574
SD120	0 <sub>8</sub>	0.234	2.277	0 <sub>2</sub>	1.383	2.962
SD150	0 <sub>10</sub>	0.000	0.000	0.022	0.169	0.285
SD310	0 <sub>8</sub>	0.409	3.990	0 <sub>2</sub>	2.955	5.392
SD320	0 <sub>8</sub>	0.339	1.841	0 <sub>2</sub>	1.224	2.326
SD350	0 <sub>9</sub>	0.157	1.569	0 <sub>1</sub>	0.926	1.800
SD510	0 <sub>9</sub>	0.244	2.443	0 <sub>1</sub>	4.148	7.010
SD520	0 <sub>8</sub>	0.609	3.155	0 <sub>2</sub>	1.390	2.633
SD550	0 <sub>10</sub>	0.000	0.000	0.028	1.138	1.727
MD310	0 <sub>10</sub>	0.000	0.000	0.018	2.251	6.614
MD320	0 <sub>7</sub>	0.314	2.080	0 <sub>3</sub>	1.169	3.167
MD350	0 <sub>10</sub>	0.000	0.000	0.409	1.360	2.425
MD510	0 <sub>7</sub>	1.296	6.037	0 <sub>3</sub>	3.207	6.855
MD520	0 <sub>8</sub>	0.486	2.513	0 <sub>2</sub>	1.327	3.377
MD550	0 <sub>9</sub>	0.048	0.485	0 <sub>1</sub>	0.740	1.650

Table 3 demonstrates that HEM outperforms HGA in average PRE for all cases.

## 5. CONCLUSIONS

This paper describes one definition of VRP to conform to the wide ranges of real world problems and one effective method was proposed to analyze the problem. We use two criteria that occur in the real world problem. Proposed method mainly generates good solution for the problem. In our problem, when any customer is waiting for service, no vehicle can be idle. This is so compatible with the real problems especially in production systems when machine is waiting for service or setting activities is made. Therefore the minimum number of required vehicles function does not involve in our problem. Computational experiments prove the compatibility of the proposed method compared to one of strongest algorithm in this area.

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# IMPROVED SENSING OF SQUARE LATTICE PHOTONIC CRYSTAL WAVEGUIDE

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## ABSTRACT

Photonic crystal (PC) waveguide is one class of PC devices that has been demonstrated for RI measurements. In this paper, we have reported a new design of infiltrated liquid sensors based on 2D photonic crystal slab with square lattice pattern of air holes. The properties of the sensor are simulated using the finite-difference time-domain (FDTD) method.

The transmission spectra has been measured by changing the refractive index of holes and it has been found that with increasing refractive index, wavelength position of transmission spectrum shifts. The radius of the air holes localized at each side of the line defect is optimized to realize high sensitivity, wide measurement range and improved transmission.

An improved photonic crystal waveguide sensor design is also described and a 160 nm wavelength position of upper band edge shift was observed corresponding to a sensitivity of more than 484 nm per refractive index unit (RIU).

**Key words** - refractive index measurements, PC waveguide, sensor, High sensitivity, FDTD method

## I. INTRODUCTION

Photonic crystals (PCs) are artificial optical materials with a periodic modulation of the refractive index. Depending on the exact periodic modulation PCs may possess a photonic bandgap (PBG). Thus, a given bandwidth of light cannot be transmitted through such a material. The basic property of a PCW is that a given bandwidth of light can be guided in the waveguide. As in a standard waveguide, the light is confined by the film thickness vertically and by the PC horizontally.

Optofluidics is an emerging field of research that integrates microfluidics with nanophotonics. Demonstrations of optofluidic devices exploit the characteristics of fluids to achieve dynamic manipulation of optical properties and reveal the promise for their widespread use [1].

There is, on the one hand, a potential to realize highly sensitive integrated sensors [2], while on the other, a flexible means to write, tune or reconfigure photonic devices for a swathe of applications [3]. Recently there have been advances in the development of fully integrated microfluidic and photonic platforms [4].

PCs are very much interesting for optofluidic sensors since they have natural photonic crystal voids, which enable fluid injection and it provides both localized control and

high refractive index modulation [5]. The latter is due to the potentially high light-liquid interaction that occurs when infiltrating the air holes that typically surround or form the PC waveguide.

Much attention has been drawn to photonic crystal sensors because of their high sensitivity and biocompatibility traits. Changes inside and around the photonic crystal provide the method of sensing by measuring power output and wavelength shifts.

PCs in which the light is guided along defects, such as missing rows of holes or rods can be designed to obtain a very high and spatially selective sensitivity to changes in RI superior to bulk devices.

Waveguides [6, 7], and interferometers [8] have successfully achieved label-free detection of molecules such as proteins and DNA. Most commonly, detection is achieved by functionalizing the surface of a resonant cavity or waveguide, which can then be used to selectively capture a specific target molecule.

Recently, silicon photonic crystals (PCs) have also been used in refractive index sensing applications. The photonic bandgap that arises from these periodically patterned dielectric lattices can be utilized for relatively low-loss waveguiding [9] and microcavities with quality factors (Q) as high as  $10^6$  [10], which are advantageous for optofluidic sensor platforms. PC-based biosensors detect molecules attached to the surface (surface-based sensing) or liquids filling the volume that surrounds the PC (bulk index sensing) via modulations of spectral features such as the waveguide cutoff [11,12] or microcavity resonance wavelength [11]. When analyte is exposed to a PC sensor, the effective index of the waveguide or cavity mode is modified, causing a shift in the cutoff or resonance wavelength.

Development of sensor designs that enhance sensitivity is especially important because it allows detection of lower concentrations of analytes and nondestructive analysis and detection of small molecules with a higher signal-to-noise ratio.

In this paper, we propose a new ultracompact RI (refractive index) sensor based on photonic crystal waveguide structure. We demonstrate the nanofluidic addressing of a single defect row of holes. Photonic crystal design consists of a square array of air holes in a silicon substrate (Si). Waveguides structures can then be created by introducing defects which support field localizations in the photonic bandgap. Photonic crystal waveguide sensors of the type discussed here are most sensitive to changes in the refractive index near their surface. The response to an effectively-infinite layer therefore sets an upper limit on the refractive index sensitivity. This limit of sensitivity was measured using a homogenous covering layer of homogenous de-ionized water ( $n_c=1.33$ ).

II- SIMULATION RESULTS AND DISCUSSION

A preliminary analysis of the unperturbed PC has been performed by using the RSoft (FullWave) FDTD software. The analysis performed in this work has been concentrated on the TE polarization (electric field component parallel to air hole axis). The PCW is realized in a silicon (Si) wafer. The PC structure consists of circular air holes in a square lattice structure with lattice pitch,  $a = 370$  nm, and hole diameter,  $d = 240$  nm (Fig.1). The waveguide (W1) is obtained by removing a single row of holes in the  $\Gamma$ -K direction of the PC. When the PC's air holes are full of homogenous de-ionized water, the wavelength position of upper band edge of this sensor will shift accordingly due to the variation of RI.

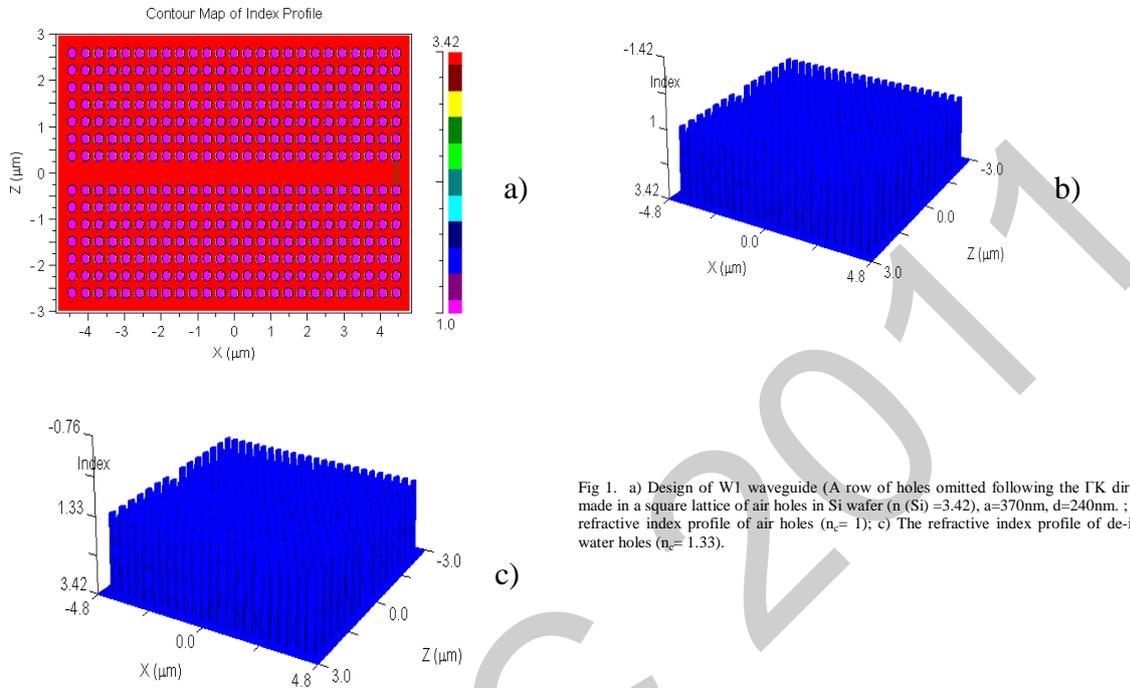


Fig 1. a) Design of W1 waveguide (A row of holes omitted following the  $\Gamma$ K direction) made in a square lattice of air holes in Si wafer ( $n(\text{Si})=3.42$ ,  $a=370\text{nm}$ ,  $d=240\text{nm}$ . ; b) The refractive index profile of air holes ( $n_c=1$ ); c) The refractive index profile of de-ionized water holes ( $n_c=1.33$ ).

Fig.2 shows TE-like mode transmission-spectra calculated using 2D Finite-Difference Time Domain (FDTD) method. Spectra are calculated for two homogeneous cover media, air ( $n_c = 1$ ) and homogenous de-ionized water ( $n_c = 1.33$ ). The curves show the change in wavelength position of upper band edge,  $\Delta\lambda$  versus change in cover RI,  $\Delta n_c$ , for the calculated spectra, where the reference wavelength is the wavelength position of upper band edge for air and the sensitivity is defined as  $\Delta\lambda / \Delta n_c$ . The wavelength of the upper band edge shifts by 20 nm as the refractive index increases from  $n_c=1$  to  $n_c=1.33$  corresponding to a sensitivity of 60.60 nm/RIU (RIU means the refractive index unit). The sensor is sensitive to the change of RI in the air hole and it can be optimized to realize high sensitivity, wide measurement range and improved transmission.

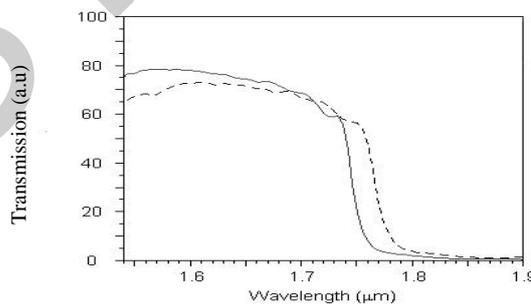


Fig 2 . Transmission spectra for TE-like polarization of a 2D silicon photonic crystal waveguide for air ( $n_c = 1$ ) (solid line) and homogenous de-ionized water (dashed line) ( $n_c = 1.33$ ) infiltrated holes, simulated by FDTD. The wavelength position of upper band edge shifts by 20 nm in the presence of a high refractive index material.

By varying the local refractive index, the effective refractive index of the slab and the refractive index contrast between the 'hole' and 'slab' regions change. The device can thereby be used as a sensor by monitoring the wavelength position of upper band edge shift resulting from the attachment of the target on the sensor surface.

Photonic crystal waveguide sensors are most sensitive near the silicon surfaces of the waveguide, where the electromagnetic field is the most intense. In the photonic crystal plane, this means that the region near the line defect is more sensitive than outlying regions.

In this section, only the two lines of air holes localized at a 16 nm shift was observed corresponding to a sensitivity of

Fig.3). As shown in Fig.4,

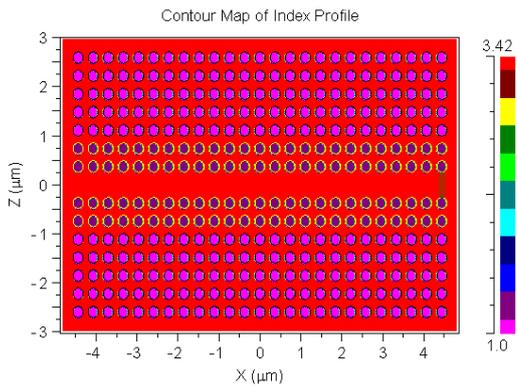


Fig 3. Modified photonic crystal waveguide sensor. In this case, only the two lines of holes next to the line defect are infiltrated.

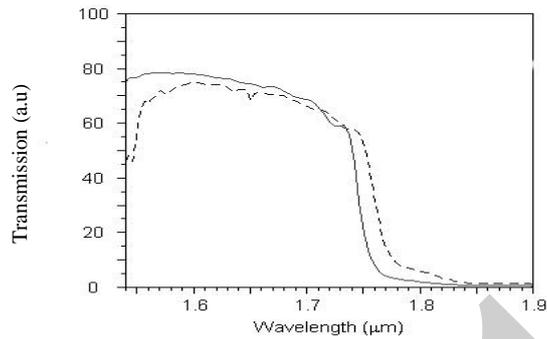


Fig 4 . Wavelength position of upper band edge of the reference waveguide (solid) and the modified photonic crystal waveguide as seen in Fig.3 (dashed). The wavelength of upper band edge -shifts by 16 nm.

Due to the dependence of the guided mode on the hole size of the PC waveguide [13], this parameter of the two lines of air holes localized at each side of the line defect should be selected carefully in order to realize the higher sensitivity, wide measurement range and high transmission. Therefore, with a proper operating frequency, the structure can work as an ultracompact RI sensor.

In this part only one line of holes bordering the guide are infiltrated as seen in fig.5.

A 15 nm wavelength position of upper band edge shift was observed corresponding to a sensitivity of 45.45nm/RIU (Fig.6).

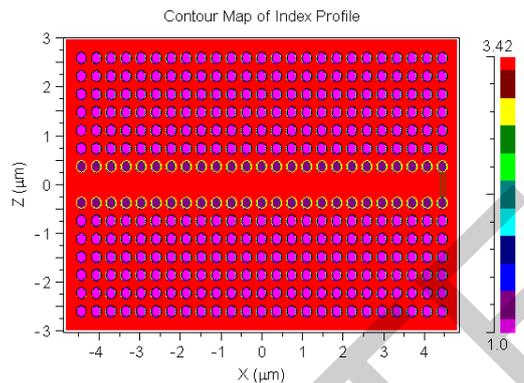


Fig 5. Only one line of holes next to the line defect is infiltrated with de-ionized water

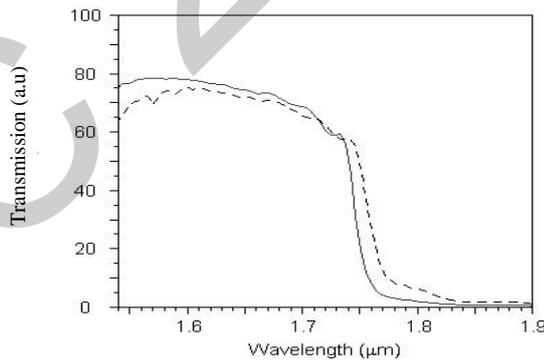


Fig 6. Wavelength position of upper band edge of the waveguide reference (solid) and the modified one as seen in Fig. 5 (dashed). A significantly shift (15 nm) was observed corresponding to a high sensitivity (45.45nm/RIU).

To improve the sensitivity, an optimized photonic crystal waveguide sensor design is described (Fig.7) where the air holes localized at each side of the line defect will be optimized and infiltrated with homogenous de-ionized water. This structure significantly increases transmission and the amount of surface area available for sensing in the central 'high-field' regions, thus significantly increasing its sensitivity. A 160 nm wavelength position of upper band edge shift was observed corresponding to a sensitivity of more than 484nm/RIU (Fig.8).

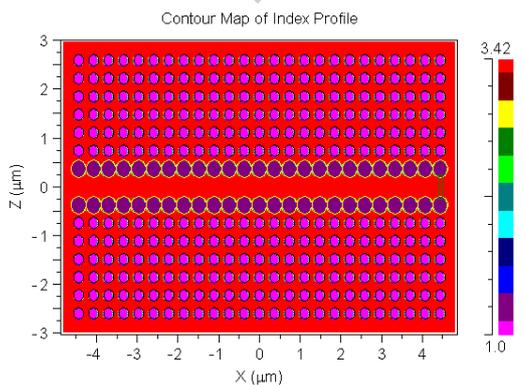


Fig 7. Improved photonic crystal waveguide sensor. The holes at each side of the line defect are optimized to realize high sensitivity; the larger holes are those which are to be infiltrated.

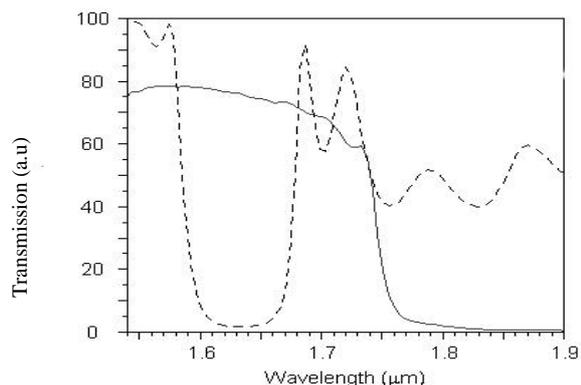


Fig 8 improved photonic crystal waveguide as seen in fig.7 (dashed). A large shift (100 nm) was observed corresponding to a very high sensitivity (more than 484 nm/RIU).

Therefore we can say that the modification and infiltration of air holes localized at each side of the line defect for water in the photonic crystal was found to have a significantly greater effect than the modification and infiltration of all holes. The sensitivity can be increased by improvements on the sensor setup such as temperature stabilization, coupling stabilization, continuous measurements of a reference waveguide, and topology optimization of the device geometry (the shape and size of the holes, width of the waveguide and thickness of the Si layer) [14], which all should improve the sensitivity to detect lower concentration.

### III-CONCLUSION

Development of sensor designs that enhance sensitivity is especially important because it allows detection of lower concentrations of analytes and nondestructive analysis. For instance, refractive index (RI) sensing techniques detect an analyte by a local refractive index shift.

This can be an advantage in biosensing as it typically involves an aqueous cover medium containing biological molecules and the detection of specific biological molecules is primarily done by immobilizing molecules at the surface (creating an adlayer of biological molecules), resulting in a RI change in the close vicinity of the silicon surface.

We have presented a photonic crystal waveguide used for RI measurements with square lattice of air holes. The radius of the air holes localized at each side of the line defect is optimized and infiltrated with homogenous de-ionized water to realize high sensitivity and improved transmission. A 160 nm wavelength position of upper band edge shift was observed corresponding to a sensitivity of more than 484nm/RIU.

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# INFLUENCE OF PROCESS CONDITIONS ON GLYCEROL ESTERIFICATION CATALYZED BY TETRA-N-BUTYLAMMONIUM-MODIFIED MONTMORILLONITE CATALYST

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**Abstract** - Selective synthesis of glycerol monolaurate from glycerol and lauric acid was investigated. Loading of tetra-n-butylammonium modified montmorillonite catalyst (1-5 wt. %), reaction temperature (110-140 °C) and glycerol to lauric acid ratio (4:1 to 8:1) were used as variables and the performance was based on lauric acid conversion and glycerol monolaurate yield. Geometrical constraint in the pores retarded the formation of higher glycerides. Increasing catalyst loading improved the monolaurate yield. Fast reaction occurred within the first 8 h and 3 wt. % was deemed the optimum catalyst loading. No further benefit was achieved above 130 °C and 6:1 for the reactant ratio. Impressive lauric acid conversion of about 80 % with corresponding glycerol monolaurate yield of 70 % were achieved in 8 h at 130 °C, using a reactant ratio 6:1 and 3 wt. % of catalyst. The modified montmorillonite was therefore active and highly selective for the production of monolaurate.

**Keywords:** Esterification ; Monolaurate, montmorillonite, tetra-n-butylammonium; selectivity.

## INTRODUCTION

The development and commercial use of biodiesel has been rapidly expanding over the last 10 years. In biodiesel production process, glycerol is produced at a rate of about 10 wt. % of total biodiesel produced and presently, its production creates a glut in the market (Bossaert et al., 1996). It plays a very important role as a major by-product toward the price trend of biodiesel (Abdullah et al., 2007). Several factors including its low price, availability and functionality make glycerol very attractive for many industrial processes. Glycerol is expected to become a major chemical platform for future biorefineries since it has emerged as an important organic building block (Hermida et al., 2011). As such, research attempts for the conversion of glycerol into value-added substances seem to worthwhile efforts.

Monoglycerides or more correctly known as monoacylglycerols, are glycerides consisting of one fatty acid chain covalently bonded to a glycerol molecule through an ester linkage. Monoglycerides consist of a hydrophilic head and a hydrophobic tail, which give them detergency characteristics. Therefore, monoglycerides and their derivatives have a wide application as emulsifiers in food, pharmaceutical and cosmetic industries (McClements, 2005 ; Bossaert et al., 1996). The global production of emulsifier is estimated at approximately 200,000-250,000 metric tons per year (Moonen and Bas, 2004) and expected to further increase in the future. These substances have various applications in different fields such as in cosmetics, pharmaceutical formulations, drug delivery systems, oil well drilling, textile, packaging, plastic processing and construction materials (Hermida et al., 2011). The conversion of glycerol to monoglycerides could provide interesting solution to improve the overall economy of biodiesel industry worldwide.

There are two major industrial routes to produce monoglycerides. They are usually manufactured through glycerolysis, a base-catalyzed transesterification of triglycerides with glycerol at elevated temperature. Secondly, monoglycerides may be produced through a direct, single esterification of glycerol with fatty acids catalyzed by acids (Wilson et al., 2000). As the three hydroxyl groups in glycerol do not strongly differ in reactivity, the current industrial processes for mono ester production both lead to mixtures of mono- (40-60 %), di- (35-45 %), and even triglycerides (Gupta, 1996). Techniques for purification of monoglycerides are expensive and involve the use of high temperature leading to the development of unwanted flavors and side products. Therefore, it is highly desirable to improve the monoester yield by choosing favorable reaction conditions and designing an appropriate selective solid catalyst.

Solid catalysts are reported to be sufficiently active catalysts for esterification of fatty acid with glycerol (Bossaert et al., 1999 ; Hermida et al., 2011). However, active catalysts could also promote the formation of di- and triglycerides to result in poor selectivity to monoglyceride. As such, solutions to selective monoglyceride production could stem from unique pore characteristics of the catalyst to consequently allow shape selective catalysis. Recently, there has been considerable interest to use clays to catalyze organic reactions (Bokade and Yadav, 2009). Montmorillonite, a natural smectite, has been found to be a useful catalyst in a variety of organic reactions due to its strong acidity, inexpensive compared to ion exchange resin, noncorrosive, reusability and non-polluting (Bahulayan et al., 2003 ; Abdullah et al., 2011). Reactions catalyzed by montmorillonite clays are usually carried out at relatively mild conditions with high yield and selectivity towards the desired products (Abdullah et al., 2011).

The use of montmorillonite in conjunction with phase transfer catalyst (PTC) provides potential synergical effects of their properties and catalytic activity. When mixed with organic molecules, this clay mineral presents a proton rich environment to theoretically affect the reaction. On the other hand, the catalytic abilities can also be improved by incorporating the organic cations in the interlamellar space which enables better accessibility of reactants. This study addresses the behavioral study of tetra-n-butyl ammonium montmorillonite in catalyzing selective synthesis of glycerol monolaurate from glycerol and lauric acid.

## MATERIALS AND METHODS

### Materials

Na-montmorillonite (Na-MMT) clay with a cation exchange capacity (CEC) of 119 meq/100 g was supplied by Kunimine Industry Co., Japan. The surfactant used in this study was tetra-n-butylammonium bromide (TBAB,  $C_{16}H_{36}BrN$ , FW: 322.368) from Sigma Aldrich. Lauric acid (Fisher) and glycerol (Fisher) with a purity of 99% were used without further purification.

### Catalyst Preparation and Characterization

A method as reported by He et al. (2009) and Wibowo et al. (2009) was used to prepare the modified clay catalyst. A stoichiometric amount of TBAB was first dispersed in 400 mL of distilled water at 80 °C under stirring at about 600 rpm. Then, 5.0 g of Na-MMT which was pre-dried at 105 °C for 1 h was added slowly and the stirring was continued for another 3 h. The organoclay product was then thoroughly washed until it was completely free of bromide anions as determined by the use of  $AgNO_3$ . It was then dried at room temperature, ground in an agate mortar, screened with a 200-mesh sieve and stored in a dry cabinet before use. The parent (NaMMT) and the modified montmorillonite catalyst (TBMMT) were characterized using XRD and surface analysis methods by means of a Siemens 2000X system and Micromeritics ASAP 2020 systems, respectively.

### Esterification of Glycerol with Fatty Acid

The esterification of glycerol with lauric acid was performed in a 250 mL stirred flask heated in an oil bath under atmospheric pressure. Variable amounts of catalyst between 1 wt. % to 5 wt. %, previously dried at 100 °C overnight were used in a reaction temperature range of between 110 °C and 140 °C for up to 12 h. The lauric acid to glycerol molar ratio was varied between 4:1 and 8:1. For product analysis, samples from the reaction vessel were withdrawn at various intervals to be analyzed for their composition. For the analysis of the product mixture, 100  $\mu$ L of the sample withdrawn from reaction vessel was first added into 100  $\mu$ L of water and 100  $\mu$ L of methyl acetate. The solution was then vortexed and the organic phase containing acylglycerols and fatty acid was separated by means of centrifugation. The composition was then analyzed using a Hewlett Packard HP 5800 gas chromatograph equipped with an FID.

## RESULTS AND DISCUSSION

### Characteristics of the Catalyst

The calculated basal spacing from the Bragg equation and the results of surface analysis on the catalysts are shown in Table 1. The basal spacing was found to increase from 1.1 to 1.7 nm when the TBAB was intercalated into the parent montmorillonite. The basal spacing of montmorillonite could reach about 2.0 nm was reported when a larger molecule octadecyltrimethylammonium bromide ( $C_{21}H_{46}NBr$ ) was exchanged into montmorillonite (Xi et al., 2004). As such, changes in the basal spacing could be influenced by the size of intercalated molecules in the clay inter layers.

Table 1. Basal spacing and surface characteristics of NaMMT and TBMMT.

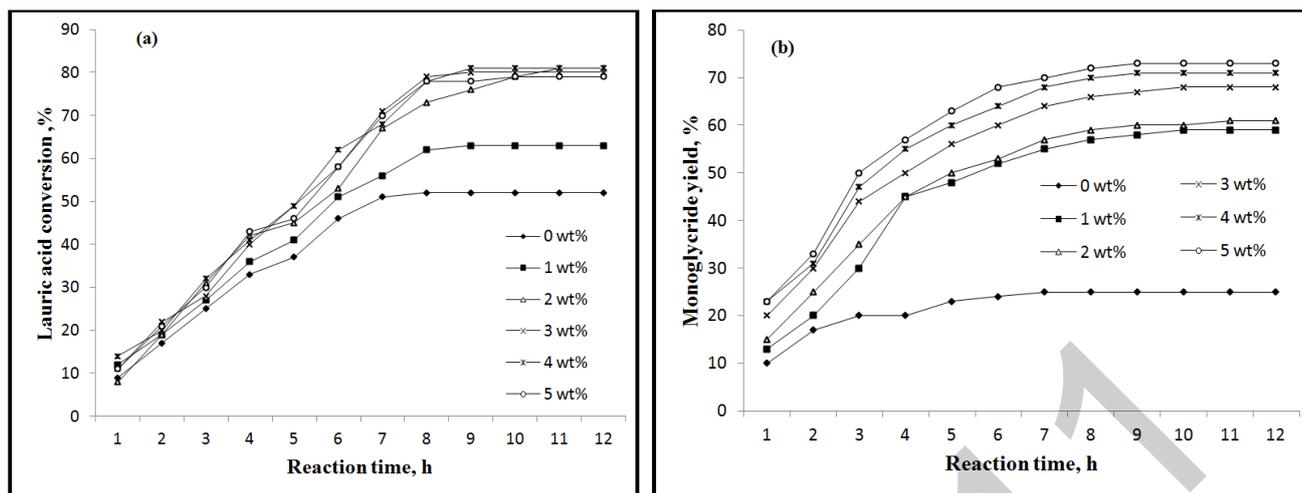
Sample	Basal spacing (nm)	$S_{BET}$ ( $m^2/g$ )	$d_{pore}$ (nm)	$V_{pore}$ ( $cm^3/g$ )
NaMMT	1.1	24	4.1	0.04
TBMMT	1.7	11	14.0	0.05

Significant enlargement of basal spacing could be of significant contribution when dealing with catalytic conversions involving large molecules such as fatty acid. Surface analysis showed that clay was a low surface area material with a surface area of 24  $m^2/g$  and the mean pore size was in mesoporous size range. As theoretically expected, the exchange of native sodium ions with the surfactants resulted in significant drops in the surface area and correspondingly, significant enlargement of the pores occurred. The effect on the pore diameter was indeed consistent with the basal spacing increase as noted in the XRD results.

### Effect of Catalyst Loading

The variations in lauric acid conversion and monoglyceride yield were demonstrated by keeping other variables constant in order to study the effects of catalyst loading on the esterification process. As noted in Figures 1(a), significant conversions took place without the use of any catalyst. This was attributed to autocatalysis by lauric acid which acted as a

catalyst besides being a reactant. However, the use of TBMMT clearly improved the glycerol monolaurate yield, suggesting some degree of shape-selective catalysis might have taken place. This was attributed to the higher number of active sites and pore characteristics to suppress the formation of by-products.



**Figure 1.** Effect of various catalyst loadings on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification with lauric acid (Glycerol:lauric acid molar ratio 6:1, 130 °C).

After relatively sharp increases in the first 8 h, the conversions leveled off for all catalyst loadings. Therefore, the reaction reached its equilibrium after about 8 h due to low reactant concentration and high concentration of products to shift the equilibrium towards the reactants side. The reaction time to reach equilibrium was not significantly influenced by the catalyst amount. However, increasing catalyst loading clearly resulted in higher conversion until about 3 wt. %. At higher loading, liquid phenomena between the glycerol and lauric acid which are mutually immiscible could play significant role in controlling the overall rate of reaction. Similar behavior was reported by Hermida et al. (2011) in a similar catalytic system using an acid functionalized SBA-15 catalyst.

Without the use of the catalyst, the monoglyceride yield reached in the esterification was only about 25 % and it was due to the co-formation of di- and triglyceride in the homogeneous reaction. This observation clearly showed the disadvantage of the homogeneous system. In the presence of a solid catalyst, the formation of di- and triglyceride with significantly larger molecule sizes was retarded due to geometric constraint in the catalyst pores. As such, the formation of monoglyceride was favored to give better yield. However, the formation of higher glycerides was still possible at larger pores, especially those at the interstices between catalyst particles. Unlike the trend in the lauric acid conversion, increasing catalyst loading to 5 wt. % led to a gradual increase in the yield.

Bossaert et al. (1999) comparatively studied the effect of variable loading of MCM-41-SO<sub>3</sub>H and SBA-15-SO<sub>3</sub>H catalysts between 0 and 5 % in the synthesis of monoglyceride performed under similar reaction conditions. Similar to this result, they observed a monotonous increase of the conversion and monoglyceride yield to imply that transfer of reactants from one liquid phase to another was not rate-limiting. This observation suggested the higher catalytic activity of TBMMT compared to those MCM-41-SO<sub>3</sub>H and SBA-15-SO<sub>3</sub>H. This conclusion was based on the effect that the overall reaction rate is governed by the rate-limiting step (Bokade and Yadav, 2009).

### Effect of Reaction Temperature

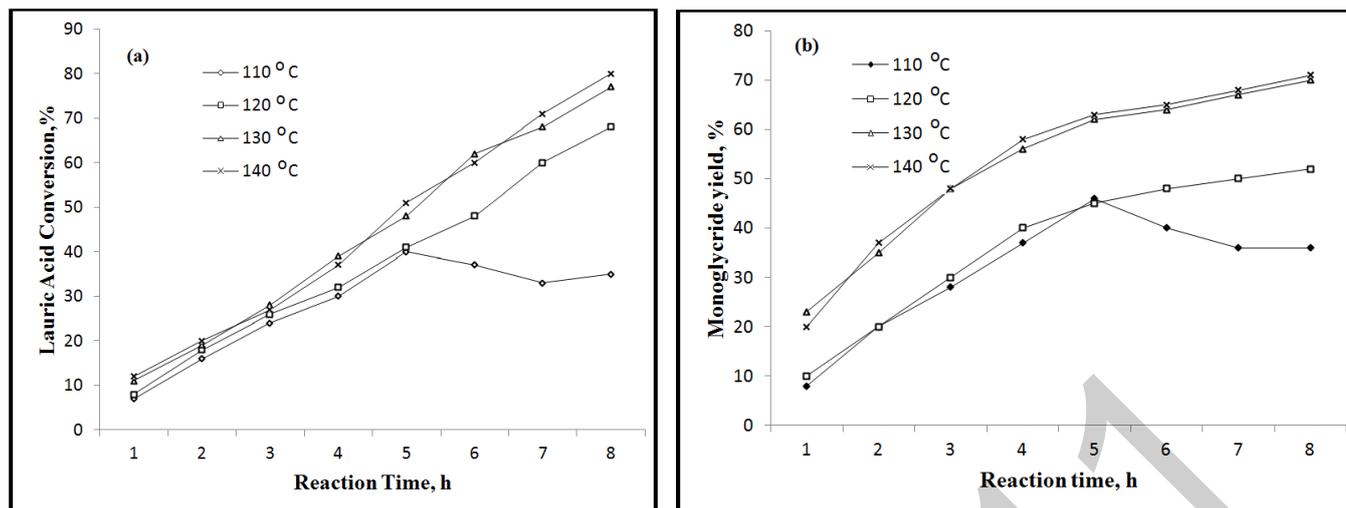
Figures 2(a) and 2(b) respectively illustrate the enhancement observed in lauric acid conversion and monoglyceride yield in the reaction carried out at 4 different temperature increase in the reaction temperature. At a temperature of 110 °C, the lauric acid reached a plateau after 5 h of reaction which could be attributed to a shift in the reaction direction. This observation led to a conclusion that the equilibrium in this reaction was influenced by the reaction temperature.

In order to carry out the esterification reaction to completion, appropriate temperature with efficient removal of water was required as water (by-product) could promote the reverse reaction. Monoglyceride yield of 70 % with corresponding lauric acid conversion of 80 % was achieved in 8 h at 130 °C. Higher temperature neither significantly improve the conversion nor the yield. It could be explained on the basis of increasing mass transfer of the fatty phase with the increase in temperature. As the reaction generally occurs in the fatty phase, glycerol molecules have to be transferred into this phase prior to the reaction. Then, glycerides (mono-, di- and triglyceride) were formed and an increase in the lauric acid conversion was observed (Wilson et al., 2000).

No significant improvement in the fatty acid conversion and glycerol monolaurate yield was observed by increasing the temperature beyond 130 °C. At lower temperatures, more reaction took place with increasing temperature as the system was kinetic-controlling. However, when the reaction was sufficiently fast at 140 °C, liquid phenomena such as diffusion rate of fatty acid in the excess glycerol could have compensated the beneficial effects of higher reaction temperature.

Sanchez et al. (1997), Bossaert (1999), Diaz et al. (2001) and Machado et al. (2000) investigated temperature effects in direct esterification of glycerol by fatty acid. The range of reaction temperature studied was 90–160 °C. At high fatty acid conversions, the selectivity to monoglycerides decreased due to the production of diglycerides and also triglyceride on the external surface of the catalyst. In this respect, TBMMT catalyst used in this study offered a particular advantage as

corresponding increase in the yield with increasing fatty acid conversion was obtained. The interlayer spacing within meso size range was deemed the responsible factor to the suppression of di- and triglyceride formations.

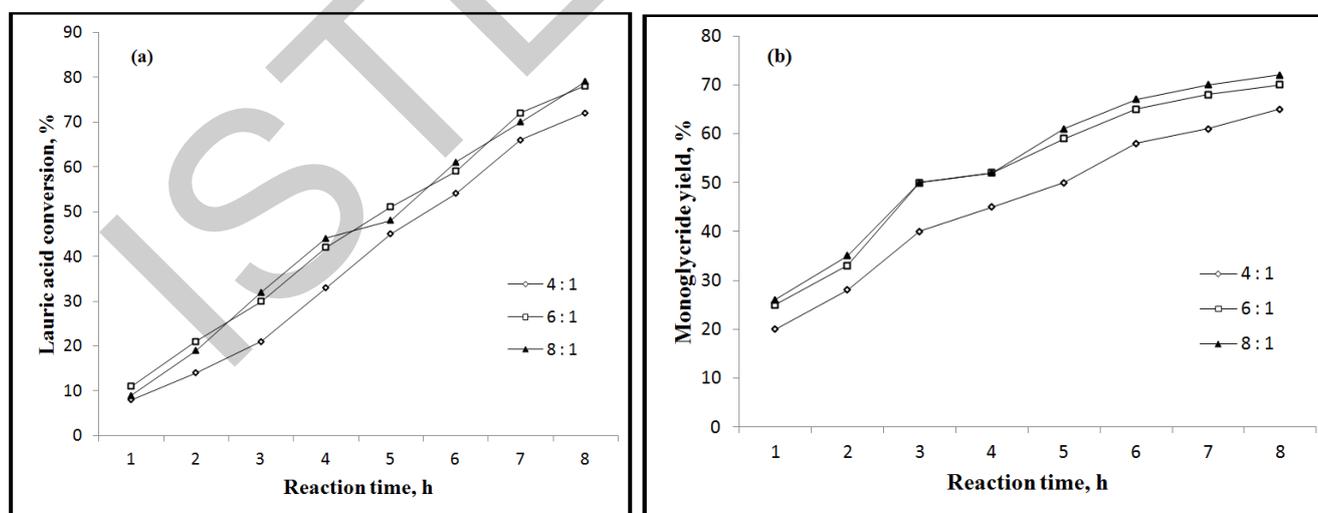


**Figure 2.** Effect of reaction temperature on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification reaction. (Glycerol:lauric acid molar ratio 6:1, catalyst loading 3 wt. %).

### Effect of Glycerol/lauric Acid Molar Ratio

Esterification of glycerol with fatty acid to produce monoglyceride is a reversible reaction. Based on stoichiometry, the esterification reaction requires glycerol/fatty acid molar ratio of 1:1 to produce monoglyceride. In reality, di- and triglyceride could also form in the reaction so that excess glycerol is needed. In order to investigate the effect of glycerol/lauric acid molar ratio on the esterification reaction, catalytic tests were performed with different glycerol/lauric acid molar ratios, i.e. 4:1, 6:1 and 8:1.

As can be seen in the Figures 3(a) and 3(b), the effect of glycerol/lauric acid molar ratio on the lauric acid conversion was insignificant beyond a ratio of 6:1. At lower ratio, significant improvement was achieved as more glycerol was available for effective contact with the relatively more viscous lauric acid. As a result, increases in the lauric acid and glycerol monolaurate yield were observed. Further increase to 8:1 meant significant dilution to the limiting reactant to bring about adverse effect to the reaction. However, it worth noting that the fatty acid conversion steadily increased with time with corresponding increase in glycerol monolaurate yield. In this respect, TBMMT catalyst offered an advantage over  $\text{HO}_3\text{S-SBA-15}$  mesoporous catalyst (Hermida et al., 2011).



**Figure 3.** Effect of glycerol/lauric acid molar ratio on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification reaction. (Catalyst loading 3 wt. %, 130 °C).

Selectively to monoglyceride has been reported to be significantly influenced by the increase in glycerol/lauric acid molar ratio. Bossaert et al. (1999) observed the effect of glycerol/fatty acid ratio in their study between 1:1 to 6:1. They reported that the increase in glycerol/fatty acid ratios would increase the monoglyceride selectivity. The effect of glycerol/fatty acid ratios was somehow similar to that reported by Sanchez et al. (1997) using glycerol/fatty acid ratios from 1:3 to 3:1. This was because there was a larger chance for a fatty acid to react with glycerol to consequently result in an increase in

monoglyceride selectivity. As the fatty acid conversion also increased, corresponding increase in the monoglyceride yield was observed.

## CONCLUSIONS

Geometrical constraint in the pores retarded the formation of higher glycerides. Fast reaction occurred within the first 8 h decreasing reactant concentration resulted in low rate of reaction after that. No further benefit was achieved above 3 wt. % of TBMMT catalyst loading due to liquid phenomena between the reactants and a reaction temperature of 130 °C and 6:1 for the reactant ratio were the optimum levels. Increasing catalyst loading improved glycerol monolaurate yield. Monoglyceride yield of about 70 % at corresponding lauric acid conversion of 80 % were achieved in 8 h at 130 °C using a glycerol/lauric acid molar ratio 6:1 and 3 wt.% of catalyst.. The modified montmorillonite catalyst show high catalytic activity and good selectivity to monolaurate. The behaviors were successfully correlated with the surface characteristic of the catalyst. Thus, TBMMT catalyst was an active catalyst to selectively produce glycerol monolaurate in the esterification reaction.

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# INHIBITION ACTION OF LAWSONE ON THE CORROSION OF MILD STEEL IN ACIDIC MEDIA

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## ABSTRACT

The use of inhibitors is one of the most practical methods for protection against corrosion. Lawsone, 2-hydroxy-1,4-naphthoquinone, the main active ingredient of Henna (*Lawsonia inermis*) plant was extracted, isolated and subjected to several studies. The corrosion inhibition of lawsone on the corrosion of mild steel in 1.0 M hydrochloric acid was studied using weight loss method. It was found that lawsone acts as a good corrosion inhibitor for mild steel in 1.0 M HCl medium. The inhibition efficiency increases with increasing of lawsone concentration. The inhibitive action was addressed in view of adsorption of lawsone molecules on the metal surface. It was found that this adsorption follows Langmuir adsorption isotherm in all tested systems and the adsorption is not activated.

**Key words:** Corrosion inhibition, Hydrochloric acid, Mild steel, 2-hydroxy-1,4-naphthoquinone

## INTRODUCTION

Corrosion problems have received a considerable attention because of the attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion. A corrosion inhibitor is a substance which is added in small amounts to a corrosive medium to reduce its ability for corrosion. Mild steel is an alloy of iron with carbon (carbon content 0.16-0.25%) which undergoes corrosion easily in acidic medium. The study of mild steel corrosion phenomenon has become important particularly in acidic media because of the increased industrial applications of acid solutions and also elevated levels of hydrogen ions in the atmosphere due to pollution. As an example, the refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attacking the equipment surface (Scattergood, 1992). The majority of well-known inhibitors are organic compounds containing heteroatoms, such as O, N or S, and multiple bonds, which allow an adsorption on the metal surface (Ali et al., 2003). These compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate. Four types of adsorption may take place by organic molecules at metal/solution interface: (a) electrostatic attraction between the charged molecules and the charged metal, (b) interaction of uncharged electron pairs in the molecule with the metal, (c) interaction of p-electrons with the metal and (d) combination of (a) and (c) (Shorky et al., 1998). However, the stability of the inhibitor film on the metal surface depends on some physicochemical characteristics of the molecule, related to its functional groups, aromaticity, possible steric effects, electronic density of donors, type of corrosive medium, structure, charge of metal surface and nature of interaction between the p orbital of inhibitors with the d-orbital of iron (Machnikova et al., 2008).

Although many synthetic compounds show good anticorrosive action, most of them are highly toxic to both human beings and the environment. These inhibitors may cause temporary or permanent damage to organ systems such as kidneys or liver, or to disturb a biochemical process or an enzyme system at some sites in the body (Raja et al., 2008). The toxicity may manifest either during the synthesis of the compound or during its applications. These drawbacks lead investigations to focus on the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors. Plant extracts have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention. Therefore, finding of naturally occurring substances as corrosion inhibitors is a subject of great practical significance (El-Etre, 1998, 2001, 2003)

Henna is the Persian name of a shrub known as *Lawsonia inermis* Linn. It is native to Asia and the Mediterranean coast of Africa, However, now it is spread to other parts of the world with warmer climate also. Henna leaves are harvested throughout the year, dried and ground to a fine powder for different applications including medicinal but largely as a cosmetics (Bhuvaeshwari et al., 2002). The extracted lawsone, 2-hydroxy-1,4-naphthoquinone, is the main active ingredient of Henna (Thomso, 1970). Two oxygen atoms are attached to the naphthalene carbons at positions 1 and 4 to form 1,4-naphthoquinone and a hydroxyl (-OH) group is present at position 2. In the present work, inhibition action of lawsone, 2-hydroxy-1,4-naphthoquinone, isolated from Henna extract as a cheap, eco friendly and naturally occurring substance on corrosion behavior of mild steel in 1 M HCl has been investigated using weight loss measurements.

## MATERIALS AND METHOD

**Isolation of Lawsone from Henna :** Powder of dried Henna leaves (40 g) was placed in a large beaker and distilled water (2 L) was added. The suspension was stirred with a magnetic stirrer with heating up to 70 °C. After 4 h, solid NaHCO<sub>3</sub> (8.4 g) was added. The suspension was filtered under gravity overnight using three large glass funnels with filter papers. The filtrate was acidified to pH 3 by adding of 0.12 M HCl. The resulting solution was extracted with diethyl ether (4 x 200 mL). The combined ethereal phases were washed with water (3 x 50 mL) and dried over anhydrous MgSO<sub>4</sub>. Ether was removed completely in a rotary evaporator to leave a reddish brown solid (760 mg) as the crude product.

The crude lawsone was purified by column chromatography, conditions: column 40 x 3 cm; stationary phase, silica gel 60; eluent ethanol-ethyl acetate (1:2 v/v). Initially fractions of 10 mL were taken and in the region of the lawsone zone the fraction size was reduced to 3 mL. The composition of all fractions was tested by TLC. The combined desired fractions contained a small amount of a less polar impurity and were recrystallized from glacial acetic acid to yield 78 mg of brown crystals. The recrystallized sample was identified as lawsone by melting point of 193-195 °C (lit. 195 °C) and its UV- visible spectrum.(Berger and Sicker, 2009)

**Specimen Preparation:** The mild steel sheets of 70 x 10 x 0.5 mm dimension were used for weight loss measurements. They were mechanically abraded with 200, 400, 800 and 1000 grades of emery papers. They were first washed with distilled water followed by acetone and dried using a stream of air and stored in moisture free desiccators before use.

**Solution Preparation:** 1 M HCl solution was prepared by diluting of 37 % HCl (Merck) using distilled water. The concentration of lawsone solution employed was varied from 10-500 mg L<sup>-1</sup> in 1.0 M hydrochloric acid.

**Weight Loss Measurements:** After weighing accurately, the specimens were immersed in test tubes which contained 50 mL 1 M HCl with and without addition of lawsone of different concentrations. After 4 h, the specimens were taken out, washed, dried and weighed accurately. Then the tests were repeated at the temperatures, 30, 35, 40 and 45 °C. The inhibition efficiency (E %) of lawsone for the corrosion of mild steel was calculated using the following equation (Singh, I., Singh, M., 1987)

$$E = (W_0 - W) / W_0 \times 100\%$$

where W<sub>0</sub> and W are the weight loss of mild steel in the presence and absence of the inhibitor, respectively.

## RESULTS AND DISCUSSION

The melting point of the isolated, pure 2-hydroxy-1,4-naphthoquinone was in the range of 193-195 °C which is same as the literature value, 195 °C (Krishnaswamy, 2003).

As it can be seen from the UV-vis spectrum of lawsone in 0.1 M HCl (Figure 1, a), absorption maximum appears at 334 nm. This spectrum of the isolated lawsone had a close resemblance with the spectrum reported in the literature (Berger and Sicker, 2009). The long tail of the band (Figure 1, a) at 334 nm that is reaching far into the visible region, is responsible for yellowish colour of lawsone. If one removes the acidic proton and measures the UV spectrum in 0.1 M NaOH, lawsone gives an orange colour solution with the spectrum band at about 453 nm (Figure 1, b),

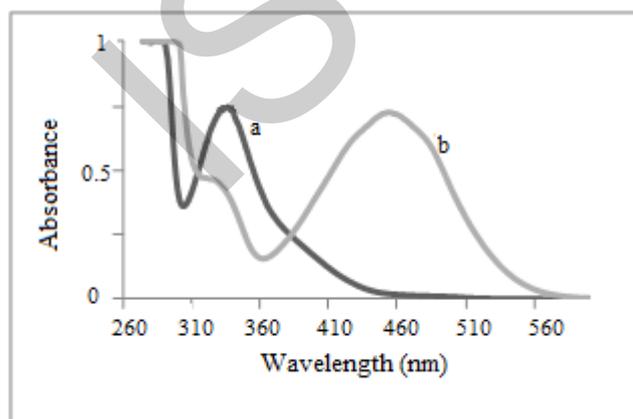


Figure 1. Absorption spectrum of lawsone (a) in 0.1 M HCl (b) in 0.1 M NaOH

The values of inhibition efficiencies (E) obtained from the weight loss for different concentration of lawsone in 1M HCl are given in Table 1. It is clear that inhibition efficiencies increases with increasing the inhibitor concentration.

Assuming that the corrosion inhibition was caused by the adsorption of lawsone, and the degree of surface coverage ( $\theta$ ) for different concentrations of lawsone in 1M HCl was evaluated from weight loss measurements using the Sekine and Hirakawa's method (Sekine,1987).

$$\theta = (W_0 - W) / (W_0 - W_m)$$

where  $W_m$  is the smallest weight loss.

For the value of  $\theta$  (Table 1), it can be seen that the values increased with increasing lawsone concentration as a result of adsorption of more lawsone molecules on the surface of steel at high concentrations.

Table 1: Corrosion parameters obtained from weight loss of mild steel in 1 M HCl containing various concentrations of lawsone at different temperatures.

Lawsone in 1M HCl (ppm)	Temperature, Inhibition efficiency (E %) and surface coverage ( $\theta$ )							
	30 °C		35 °C		40 °C		45 °C	
	E (%)	$\theta$	E (%)	$\theta$	E (%)	$\theta$	E (%)	$\theta$
10	64.66	0.693	55.66	0.617	47.50	0.493	19.96	0.402
25	79.55	0.853	68.48	0.806	58.40	0.716	26.66	0.635
50	86.17	0.924	74.18	0.898	63.30	0.843	33.79	0.786
100	89.91	0.964	77.40	0.952	66.00	0.925	41.25	0.892
150	91.23	0.978	78.54	0.972	67.00	0.956	41.91	0.934
250	92.31	0.99	79.47	0.988	67.80	0.982	42.75	0.970
500	93.14	0.999	80.18	1.000	68.40	1.000	44.20	1.000

Assuming that lawsone adsorbed on the surface of mild steel forming a monolayer and ignoring the lateral interactions between the adsorbed lawsone molecules, the Langmuir adsorption isotherm was used to investigate the adsorption mechanism by the following equation (Zhao and Mu,1999)

$$c/\theta = 1/K + c$$

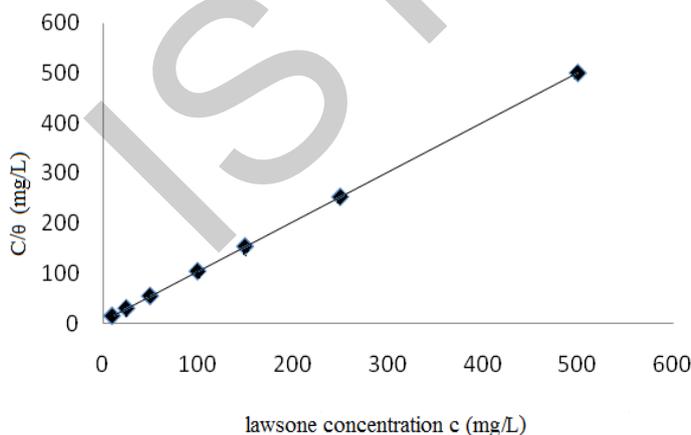


Figure. 3. The plot  $c/\theta$  ( $\text{mg L}^{-1}$ ) vs.  $c$  ( $\text{mg L}^{-1}$ ) at 35 °C ( $R^2 = 1.000$ )

Figure 3 is the relationship between  $c/\theta$  and  $c$  at 35 °C. The results given in the Table 2 show that linear correlation coefficient of 1.000 within the temperature range of 30 to 45 °C and the slopes were 0.992,0.987,0.976 and 0.970. The data indicate that the assumption and the deduction were correct and at all temperatures of the experiment lawsone formed a chemical bond on the adsorption sites of mild steel surface. It could be found that the adsorption coefficient (K) decreased with

increasing temperature. Lawsone gave higher values of  $K$  at lower temperatures, indicating that it was adsorbed strongly on the steel surface at lower temperatures and the adsorption process was not activated.

Table 2: Some parameters extracted from the linear regression between  $c/\theta$  and  $c$

Temperature ( $^{\circ}\text{C}$ )	$K$ ( $\text{mg}^{-1} \text{L}$ )	Slope	Linear correlation coefficient
30	0.222	0.992	1.00
35	0.158	0.987	1.00
40	0.095	0.976	1.00
45	0.066	0.970	1.00

**Mechanism of Inhibition** :Lawsone is a ligand that can chelate with various metal cations to form metal complexes. Therefore, the formation of insoluble complexes, by chelating of the metal cations with the lawsone molecules adsorbed on the metal surface, is a probable interpretation of the observed inhibition action of lawsone. The formation of metal complexes with stoichiometric ratio of 1:1 and 2:1 are shown in Figure. 2.

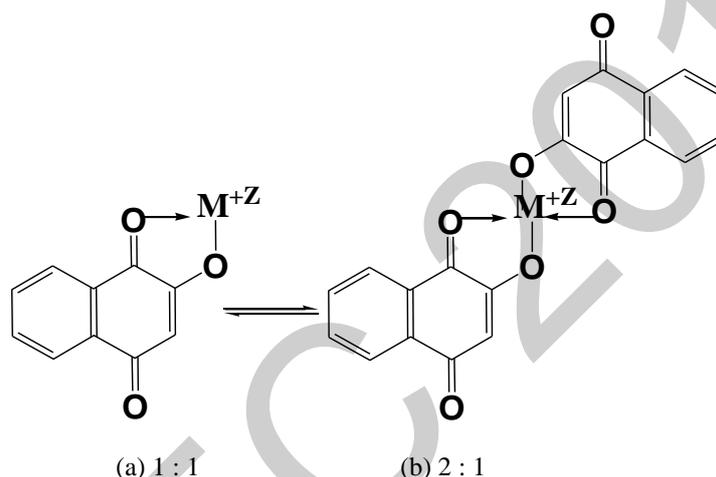


Figure 2. Forms of metal ion-lawsone complexes.

In the acidic medium, protonation of 2-hydroxy-1,4-naphthoquinone takes place resulting in the rearrangement (tautomerization) as shown in the Figure 2 to give 4-hydroxy-1,2-naphthoquinone. Such rearrangement, in the presence of metal cations, may enhance the complex formation ability. This could be the reason for the high inhibition efficiency in acidic media for mild steel.

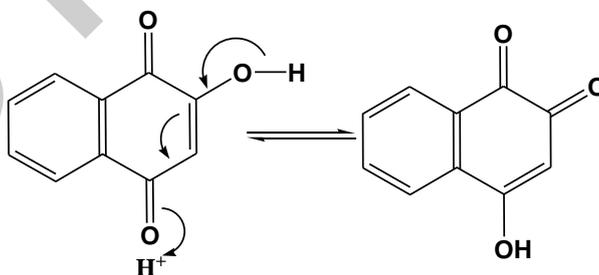


Figure.3. Forms of lawsone due to protonation.

## CONCLUSION

Lawsone was found to be an effective inhibitor for corrosion of mild steel in 1M HCl, and inhibition efficiency increased with decreasing temperature. The adsorption of lawsone on the mild steel surface from 1 M HCl obeys the Langmuir adsorption isotherm and the adsorption is not activated.

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# INVENTORY OF MEDICINAL PLANTS USED FOR TRADITIONAL TREATMENT OF ECZEMA IN THE HODNA (M'SILA - ALGERIA)

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**ABSTRACT:** The ethnobotany study in the region of Hodna helped to highlight the different traditional uses of plants by the villagers. The goal is to make an inventory of plants from traditional medicine that treat eczema. 1900 question cards were established in order to obtain information on medicinal plants in the area of study that deals with eczema, those targeted are herbalists, healers and villagers. The total number of people surveyed is 35 whose age is between 20 and 80. The result is the identification of 25 species distributed in 18 botanical families with a dominance especially *Lamiaceae*, *Liliaceae*, *Asteraceae* and *Oleaceae*.

**Keywords:** Medicinal plants, traditional treatment, Eczema, Hodna, Algeria

## 1. INTRODUCTION

Eczema is one of a group of skin, causing inflammation and dry skin and itching. The two types of eczema are the most common atopic dermatitis and contact dermatitis. The first is an inflammation that occurs due to family history related to the disease, the second is an inflammation that occurs due to exposure to allergens or irritants (Elwina, 2008). There is no known cure for eczema, thus treatments aim to control the symptoms: reduce inflammation and relieve itching.

Eczema is treated also in the field of herbal medicine, but before the selection of medicinal plants, an ethnobotanical survey was conducted in order to promote traditional medicine which is widely practiced in the region of Hodna to list all the plants that heal the disease of contact dermatitis is the case in our study (Fig. 1).

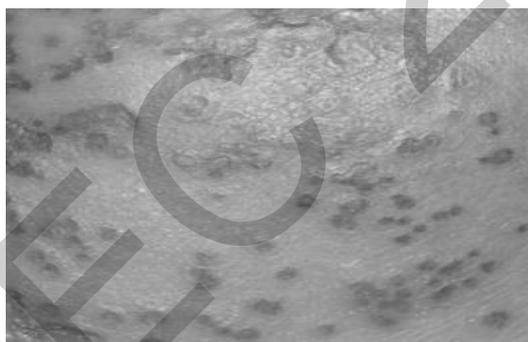


Fig. 1 : Contact Eczema (Elwina, 2008 )

## 2. MATERIALS AND METHODS

### 2.1 Study area

The region of M'sila, occupies a privileged position in the central part of northern Algeria. As a whole, it is part of the highlands of central and covers an area of 18,718 km<sup>2</sup> and it is located at an altitude of 500 m, is situated between 35° 42' 07" N 4° 32' 49"E (W.G.S., 84). The climate of the investigation area is continental, due in part to the Saharan influences. Summer is hot and dry while winter is very cold, with low and irregular rainfall, it is of the order of 100 to 250 mm /year (Seltzer, 1946 and Le Houerou, 1995). Morphology and its geographical position gives this region a unified ecological aspect represented by the predominance of the steppe, which covers 1.2 million ha (63% of the total area) of the state. The areas used for agriculture accounts for 20% of the total area devoted mainly to cereals, to arboriculture and market gardening.

### 2.2 Ethnobotanical surveys

The surveys were conducted during the period 2006-2010, information was collected on traditional uses of wild plants and also those cultivated. Using the 1900 questionnaire that have been developed, we conducted ethnobotanical surveys of the entire M'sila region (Fig. 1) in order to have as much information regarding the traditional use of medicinal plants by local people because of their knowledge entnomédicinales. All investigations described the information about (Babba Aissa, 1999):

- Date,
- Research area (district/village),
- Informants (name/age/sex/educational level),
- Scientific name of plant,
- Local name of plant, part of plant,
- Usage purpose of plant,

- Dosage,
- How to use it (decoction, infusion, maceration, etc.),
- Usage period of plant
- Side effect of plant.

### 3. RESULTS AND DISCUSSION

With the help of flora of Quezel and Santa (1962-1963), Ozenda (1983) and Maire (1952-1987) and the herbarium of the department of natural science and life of the University of M'sila, we determined the species collected in the field to compile a complete list of medicinal species identified in the study area and parallel to the results of surveys of villagers « 35 people: 6 women and 29 men of different ages, whose age is between 20 and 80 » (Table 1).

**Table 1:** Age group of people surveyed

Age group	Men	Women	Total
20-30	4	1	5
30-40	15	1	16
40-50	6	0	6
50-60	2	3	5
60-70	1	0	1
70-80	1	1	2
Total	29	6	35

The results showed that medicinal species identified are among 25 to 18 families and 24 genera (Table 2). It was noted that the Lamiaceae family is number one species identified (20%). The plant parts most commonly used are the aerial parts (42.30%), leafs (26.92%), flowers (11.74%). Instructions for use are varied, the decoction is the method of preparation the most common (28.89%), infusion (15.56%), lotion (13.34%), and maceration (11.11%).

**Table 2 :** Plants traditionally used to treat Eczema in the region of Hodna (M'sila-Algeria)

Botanical name / Family	Local name	Number of Informants	Parts used	Preparation
<i>Ajuga iva</i> (L.) Schreb. (Lamiaceae)	Chendgoura	2	Leaf	Decoction, maceration
<i>Allium cepa</i> L. (Liliaceae)	El Basla	1	Pulp	Uction
<i>Allium sativum</i> L. (Liliaceae)	Thoum	1	Fruit	Cataplastm
<i>Anthemis nobilis</i> L. (Asteraceae)	Babounej	4	Flower	Infusion, decoction, lotion, poultice
<i>Artemisia herba alba</i> Asso. (Asteraceae)	Chih	1	Aerial part	Decoction, lotion, maceration
<i>Atriplex halimus</i> L. (Chénopodiaceae)	G'taf	1	Leaf	Lotion
<i>Colocynthis vulgaris</i> (L.) Lud. (Cucurbitaceae)	Hadj	1	Flower	Decoction, massage.
<i>Fraxinus excelsior</i> L. (Oleaceae)	Dardar	1	Leaf	Infusion, powdered
<i>Globularia alypum</i> L. (Globulariaceae)	Tesselgha	1	Whole plant	Decoction
<i>Juniperus phoenicea</i> L. (Cupressaceae)	Ara-aar	2	Aerial part	Lotion, infusion, decoction
<i>Lavandula stoechas</i> L. (Lamiaceae)	Khodzama	1	Aerial part	Decoction, maceration
<i>Nerium oleander</i> L. (Apocynaceae)	Defla	2	Leaf	Cinder, decoction
<i>Olea europaea</i> L. (Oleaceae)	Zitoune	1	Fruit	Oil (unction)
<i>Pistacia lentiscus</i> L. (Anacardiaceae)	Dharou	1	Fruit	Oil (unction)
<i>Quercus ilex</i> L. (Fagaceae)	Balout	1	Leaf	Powdered, decoction
<i>Retama retam</i> Webb. (Fabaceae)	R'tem	1	Aerial part	Lotion
<i>Ricinus communis</i> L. (Euphorbiaceae)	Kharoua	1	Fruit	Decoction, Oil
<i>Rosmarinus officinalis</i> L. (Lamiaceae)	Iklil el djabal	1	Aerial part	Infusion
<i>Ruta chalepensis</i> L. (Rutaceae)	Fidjel	1	Aerial part	Decoction, infusion, powdered
<i>Salvia officinalis</i> L. (Lamiaceae)	Swak Nbi	1	Aerial part	Infusion
<i>Teucrium polium</i> L. (Lamiaceae)	Khayata	1	Aerial part	Decoction, maceration
<i>Thapsia garganica</i> L. (Umbellifereae)	Bounafaa	1	Aerial part	Cataplastm
<i>Thymelaea hirsuta</i> Endl. (Thymelaeaceae)	Methnane	2	Aerial part	Infusion, decoction, maceration
<i>Viola odorata</i> L. (Violaceae)	Banafsadj	1	Flower	Extract (compress)
<i>Ziziphus lotus</i> (L.) Desf. (Rhamnaceae)	Sedra	1	Leaf	Lotion, infusion

#### 4. CONCLUSION

This study has shed light on the different traditional uses of plants by villagers in the region of Hodna (M'sila) to treat Eczema. This work provides a list of classification of medicinal plants that treat eczema in the region of M'sila. We identified 25 medicinal species distributed in 18 botanical families with a dominance especially of *Lamiaceae*. At the end, this study provided important data as a basis for further studies of clinical, ethnopharmacological, etc ....

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# INVESTIGATION OF SCIENCE EDUCATION PRE-SERVICES' PHYSICS PROBLEM SOLVING STRATEGIES

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## Abstract:

Problem solving in physics is one of the most important step in the process of learning physics courses. The most important stages of the process in physics problem solving are knowledge about problem-solving strategies and using these strategies effectively. In this study, it was aimed to investigate students' physics problem solving strategies such as; writing data and requested lists, drawing a shape about the problem, using the symbols, to imagine the problem in mind, finding what the laws are all about the problem, writing about the formulas, tried to understand the problem, reading problem, associating, problem solving separated by sections, showing requested on the shape, re-reading the problem, etc...and to determine students' listing and arranging these strategies when solving a physics problem. This study conducted to 55 first-year science education pre-services from a public university in Turkey. Data collection tools are a "Physics Problems Solving Strategies Evaluation Form" which consist of 12 questions and 3 mechanic physics problem related to *Force and Motion* constructed by the researcher. As a result of the data evaluation, percentage distributions of the pre-services' preferred strategies to solve physics problems were given and the effects of problem solving strategies in a successful problem solving were determined.

**Keywords:** physics education, physics problem solving, problem solving strategies.

## 1.Introduction

Physics is a way that an understanding of the events occurring in the world and it explains them [1,2]. While physics is a basic part of our lives, it is called as "very difficult" and "very boring" by the students and students have failures at physics courses [3-7]. The reasons of their failures are physics is an abstract science and it consists of mathematical operations. Physics problems can be divided into two groups [9]. Some of them are calculations based problems which includes four arithmetic operations in mathematics and physics courses mostly. The other problems are based on some analysis, organizing data and classification [9]. Problem solving is an important element of the process of problem-solving strategies. According to Dhillon, problem solving strategies can be seen as general plan processes of problem solving behaviours. Problem-solving behavior includes students' problem solving activities. Each activity is a strategy or the implementation of a strategy [10]. For example, "planning" is a general problem-solving strategy [11]. This problem-solving behavior contains general strategy such as; description, classification, correlation of the quantities elicitation, symbols usage, the sub-units, A different problem-solving strategy is "creating and testing".

In this study, it was aimed to investigate students' problem solving strategies such as; writing data and requested lists, drawing a shape about the problem, using the symbols, to imagine the problem in mind, finding what the laws are all about the problem, writing about the formulas, tried to understand the problem, reading problem, associating, problem solving separated by sections, showing requested on the shape, re-reading the problem, etc...and to determine students' listing and arrangements these strategies when solving a physics problem.

## **2. Methods**

### *2.1. Purpose of the Research*

The purpose of this study is to investigate students' physics problem solving strategies and to determine students' listing and arranging these strategies. In the context of this study, the following research questions were investigated.

1. Which strategies are selected by students mostly when physics problem solving?
2. Do students have qualifications about arrangement of these strategies in a physics problem correctly?

### *2.2. Participant*

The participant of this study was 55 first-year undergraduate students (average age 19-20years). They are from science teaching department who were attending in a public university in Istanbul, Turkey. The socio-economic status of the undergraduates was similar and the majority of them are coming from middle-class families.

### *2.3. Instrument*

This study is conducted to 55 first-year science education pre-services from a public university in Turkey. Data collection tools are a 5 likert-type "Physics Problems Solving Strategies Evaluation Form (PPSSEF) " which consist of 12 questions about problem solving strategies and to apply these strategies3 mechanic physics problem related to *Force and Motion* constructed by the researcher. The questions which consists problem solving strategies were implemented randomly in PPSSEF. At the next step, students selected thier own strategies to solve 3 Force and Motion problems and the arrangement of these strategies were requested to students with reasons.

## **2. Findings and Conclusion.**

Students' responses to "Physics Problems Solving Strategies Evaluation Form" were evaluated, classified and percentage table was given in Table 1.

**Table1. Students' physics problems solving strategies and responses' percentages.**

Physics Problem Solving Strategies	Strongly Agree (%)	Agree (%)	Not Sure (%)	Disagree (%)	Strongly Disagree (%)
1-When solving a physics problem, first of all, i try to understand and interpret.	16	7.7	0	0	0
2-When solving physics problem, I think concepts and knowledge related to the subject.	4.4	9.9	4.4	1.1	0
3-I solve physics problems by taking into account the information which is reserved for solving and try to produce new information.	2.7	10.4	8.2	0	0
4-I can evaluate the results, which i found, according to scientific validity and frames, i make comments and i imagine new situations, examples when solving a physics problem.	1.6	3.8	13.7	3.3	0
5- I try to develop more than one hypothesis and I compare the results when solving a physics problem.	0	4.9	11.5	3.8	0
6-When solving a physics problem, if my solution is wrong, i try to find another solution.	4.9	12.1	1.6	0	0
7-I imagine the situation about physics problem and i draw appropriate shape.	3.3	10.4	3.8	0	0
8- I use all provided data in solving physics problems.	2.7	8.8	5.5	1.6	0
9-I try to predict the outcomes before problem solving.	0	0	5.5	12.1	0
10- I consider and use the physics laws according to thier priority.	10.3	4.2	0	0	0
11- I write data and requested information before solving a physics problem.	8.3	4.2	0	0	0
12-I re-read physics problem in the solution process.	3.4	2.7	8.3	0	0

As seen in Table 1, students' responses were given and students selected problem solving strategies which are randomly implemented presented in Table 1. According to the results; students are **strongly agree** with "when solving a physics problem, first of all, i try to understand and interpret" strategy at the 16 % rate, **agree** with "when solving physics problem, I think concepts and knowledge related to the subject" strategy at the 9.9 % rate, **agree** with "i solve physics problems by taking into account the information which is reserved for solving and try to produce new information" strategy at the 10.4 % rate, **not sure** "i can evaluate the results, which i found, according to scientific validity and frames, i make comments and i imagine new situations, examples when solving a physics problem" strategy at the 13.7 % rate, **not sure** "i try to develop more than one hypothesis and I compare the results when solving a physics problem" strategy at the 11.5 rate, **agree** with "when solving a physics problem, if my solution is wrong, i try to find another solution" strategy at the 12.1 % rate, **agree** with "i imagine the situation about physics problem and i draw appropriate shape" strategy at the 10.4 % rate, **agree**

with “i use all provided data in solving physics problems” strategy at the 8.8 % rate, **disagree** with “i try to predict the outcomes before problem solving” strategy at the 12.1 % rate, **strongly agree** with “i consider and use the physics laws according to thier priority” strategy at the 10.3 % rate, **strongly agree** with “i write data and requested information before solving a physics problem” strategy at the 8.3 % rate, **not sure** “i re-read physics problem in the solution process” strategy at the 8.3 % rate.

After this step, students were asked the arrangement of their own selected strategies and apply them to 3 physics problem solving. From the evaluation students’problems solving, it was seen that students managed to solve problem sucseessfully who are strongly agree with “when solving a physics problem, first of all, i try to understand and interpret, i write data and requested information before solving a physics problem, i consider and use the physics laws according to thier priority, when solving a physics problem, first of all, i try to understand and interpret” strategies at the high rates. In addition, students could reach to right answer who are agree with “i imagine the situation about physics problem and i draw appropriate shape, when solving a physics problem, if my solution is wrong, i try to find another solution ” strategies at the high rates.

According to findings from the research, students have behaviours or problem solving strategies such as; imagination the situation about physics problem and drawing appropriate shapes, try to understand and interpret, writing data and requested information before solving, etc,..at the highest rates. Besides, from the problems, it was seen that students are more sucseessful to reach right solution who can arrange strategies correctly.

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# ISOLATION, CHARACTERIZATION AND MICROENCAPSULATION OF PROBIOTIC *LACTOBACILLUS CURVATUS* G7 FROM CHICKEN CROP

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## ABSTRACT

The controlled release of bioactive substances to their site of action in the GIT is essential in modern drug and food industries. The major obstacles that probiotic bacteria should overcome are stomach acidity and bile salts. In this research a *Lactobacillus curvatus* strain was isolated from chicken crop; it was identified based on morphological and biochemical characteristics and tested for its probiotic properties. Furthermore; the survival of free and microencapsulated *Lb curvatus* in 1 % sodium alginate was evaluated in GIT-like conditions. The results showed that 27.87 % of the free cells were found to be resistant to acidic conditions (pH 2) after 1 hour of incubation, while only 2.09 % survived after 2 hours of incubation therefore the bacteria could not be capable of resisting in the stomach. Microencapsulation improved the viability particularly after 2 hours for the reason that 11.36 % of the cells survived after 2 hours. On the other hand, in bile salts, the percentage of survival of the free cells of *Lb curvatus* was 47 after 4 hours of incubation and decreased to 40 after 8 hours. However, the microencapsulated form resists more since 66 % of the cells survived after 4 hours and more than 52 % survived in bile salts after 8 hours. It appears evidently that cell entrapment in sodium alginate protects the bacteria from gastric and intestinal hostile conditions.

**Keywords:** *Lactobacillus curvatus*, probiotic, microencapsulation, chicken crop.

## INTRODUCTION:

Probiotics are defined by the FAO as “live microorganisms which, when administered in adequate amounts, confer a health benefit on the host” (FAO report).

Currently, probiotics are being used extensively in veterinary to replace the use of antibiotics. In poultry farming, probiotics are essentially used to provide beneficial microorganisms that were basically absent in chicken's digestive tract, thus, the least can profit by favorable effects offered by the introduced microorganisms (Lutful Kabirm, 2009; Gournier-Château et al., 1994). The two main commercial preparations are targeting the crop and the anterior small intestine as well as the caecum (Fuller et Turvey, 1997). The effects of some probiotic bacteria were reported; they include modification of the microbial composition and metabolic activity of the intestinal flora, inhibition of infective pathogens like *Escherichia coli*, *Salmonella typhimurium* and *Staphylococcus aureus* by competitive exclusion, and enhancing the growth and development indexes in chicken (Higgins et al., 2010, Awad et al. 2009, Reque et al. 2000). However, during GI passage, cultures are required to tolerate the low pH of the stomach, and the antimicrobial activity of bile salts, for that reason, it is important to find methods for enhancing the viability of microbial cells in the digestive tract, one of them is microencapsulation which consists of the technology for packaging active materials in miniature, sealed capsules that can release their contents at controlled rates under specific conditions according to Shahidi and Han (1993). Several studies have shown that microencapsulation of bacteria with alginate at different concentrations or other gels protects them against acid stress, allowing the cells to survive in the stomach and to be delivered in the intestine (Lee et al. 2004, Crittenden et al. 2006). Generally, most of the researchers are in agreement that alginate is the most suitable material for encapsulating food ingredients even though the recent studies are providing new improvements in capsule texture and rheology characteristics.

In the present study, a lactic acid bacterium from the crop content of chickens was isolated, identified and assessed for its ability to inhibit the growth of some pathogenic bacteria and to attach to intestinal epithelium. In addition, the tolerance of the bacterium to GIT-like conditions was evaluated before and after microencapsulation in 2 % sodium alginate.

## MATERIALS AND METHODS

### Isolation of lactic acid bacteria

A 10 g sample of the content of local chicken crop was serially diluted in normal saline, then; the appropriate dilutions were plated on MRS agar and incubated for 24 hours at 37°C. The obtained colonies were cultured in MRS broth and further purified.

### Test organisms

The following strains were used as test organisms for antimicrobial activity; *Escherichia coli*, *Klebsiella* spp. from a local rabbit GIT, *E. coli* ATCC 25929 and *Staphylococcus aureus*.

### Identification of LAB

The isolated strains were identified based on their morphological and biochemical properties according to **Bergey (1994)**. The tests included gram stain, catalase, arginine dihydrolase, acetoin production, citrate utilization, growth in hypersaline solution, fermentation type and sugars fermentation. The obtained results were analyzed by API-LAB program at the "Laboratoire de Biologie des Microorganismes et Biotechnologie" at Es-Senia University, Oran.

### Antibacterial activity

The antibacterial activity of *Lb. curvatus* culture, the cell-free supernatant and the NaOH neutralized supernatant (pH 6) against the cited bacteria was evaluated according to **Tagg et al. (1976)** based on disc diffusion method.

### Assay of the *in vitro* adherence of LAB to epithelial cells

The method described by Lin et al. 2007 was used for the assay of the *in vitro* adherence of LAB to epithelial cells. Segment of chicken crop were opened and washed with sterilized phosphate-buffer saline (PBS, pH 7.2). It was held in PBS at 4 °C for 30 min to remove the surface mucus and then washed three times with PBS. Epithelial cells were scrapped into sterilized PBS. The cell suspension was examined by microscopy to ensure that contaminated bacteria had been removed and the epithelial cell concentration was adjusted to approximately  $5 \times 10^4$  cells/ml. The adherence of LAB strain to the epithelial cells was assayed as follows: the overnight culture of LAB in MRS broth was centrifuged and the cell pellet was resuspended to approximately 1.108 CFU/ml in PBS (pH 7.2). One milliliter of the bacterial suspension was mixed with 1 ml of the suspension of epithelial cells from chicken. The mixture in a tube was rotated at 20 rev/min at 37 °C for 30 min. The adhesion was observed using light microscopy (magnification fold, 100x) after stained with 0.5% crystal violet for 5 min (**Lin et al. 2007**).

### Microencapsulation of LAB in 2% sodium alginate

Alginate (2 % w/v) capsules containing the *Lb. curvatus* cells were prepared by dissolving 2 g of sodium alginate in 80 mL distilled water under constant mechanical stirring, and heating at 80°C. The solution was autoclaved and cooled to 40°C to which 20 mL of a freshly prepared cell suspension was added and homogenized. The final solution contained approximately  $88.10^{11}$  UFC/mL. The mixture was injected through a needle into 100 mL of autoclaved and pre-cooled 0.05M CaCl<sub>2</sub> crosslinking bath. The resultant capsules were allowed to harden in the cross-linking solution for 30 min, and then washed three times with distilled water (**Boyaval et al., 1985**).

### Survival of LAB in acidic conditions

The viability of free and microencapsulated cells of *Lb. curvatus* in acidic conditions was tested by incubating MRS broth (pH 2) inoculated with approximately  $10^{10}$  UFC/ml (free or encapsulated cells) for 2 hours at 37° C. A viable count on MRS agar was carried out at 1h intervals over the assay period after appropriate serial dilution in normal saline. The plates were incubated at 37°C for 48 h. For microencapsulated cells, the count was determined after lysis of the capsules in 2M M phosphate buffer (pH7)

### Tolerance to bile

The viability of free and microencapsulated cells of *Lb. curvatus* in bile conditions was studied by incubating MRS broth supplemented with 0.3% bile salts with approximately  $10^{10}$  UFC/ml (free or encapsulated cells) for 8 hours at 37° C. A viable count on MRS agar was carried out at 1h intervals over the assay period after appropriate serial dilution in normal saline. The plates were incubated at 37°C for 48 h. For microencapsulated cells, the count was determined as described before.

## RESULTS AND DISCUSSION

Eighteen strains were isolated on MRS medium from chicken crop, after biochemical identification it appeared that most of them belonged to *Lactobacillus curvatus*. *Lactobacillus curvatus* J7 was chosen for further investigations.

### Antimicrobial activity test

The antimicrobial activity of the selected bacterium against some bacteria was evaluated in three ways in order to determine the nature of the inhibitory element. The crude culture, the crude cell-free supernatant as well as the neutralized supernatant were used to analyze the antagonistic effect; the results are shown in **table 1**.

**Table 1** Effect of different culture fractions on some test microorganisms.

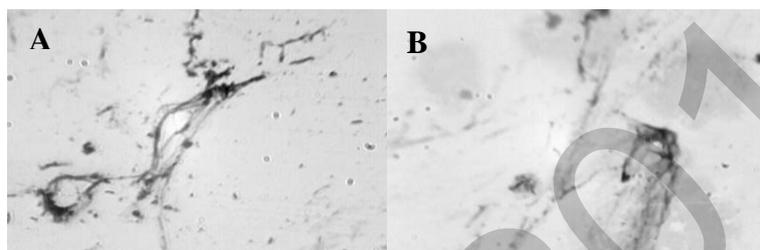
Tested fractions \ Test microorganisms	Inhibition zone diameter (mm)			
	<i>Klebsiella</i>	<i>E. coli</i>	<i>E. coli</i> ATCC 25929	<i>Staphylococcus aureus</i>
Crude culture	21	18	19	17
Cell-free supernatant	19	20	23	22
Neutralized supernatant	12	14	14	15

The culture of *Lb. curvatus* showed a good inhibitory effect against the four tested strains, the inhibition zone diameters are ranging from 17 mm for *S. aureus* to 21 mm for *Klebsiella*, in addition, the cell-free supernatant displayed also an inhibitory effect whereas the neutralized supernatant did not lose the whole inhibitory activity although the diameters of the zones are less important (from 12 for *Klebsiella* to 15 for *S. aureus*). Several mechanisms have been reported to describe antagonistic action of probiotic bacteria such as competitive exclusion, production of antimicrobial compounds, modulation of immune response, alteration of intestinal bacterial metabolic activity, alteration of microecology of the animal intestine, and inhibition of bacterial translocation. The production of antimicrobial agents could be easily demonstrated *in vitro* by the disc diffusion assay; they include fatty acids, organic acids, hydrogen peroxide, and diacetyl, acetoin and the small, heat-stable inhibitory peptides called 'bacteriocins' (Soomro et al., 2002; Simova et al., 2009).

In our experiment, the probiotic *Lb. curvatus* decreased the growth of the tested microorganisms not only by the production of lactic acid but other substances could be involved like bacteriocins or hydrogen peroxide this was confirmed by the residual activity found in the neutralized supernatants.

#### *In vitro* adhesion test

The adhesion test of *Lb. curvatus* to epithelial cells was conducted as described before as it is one of the most important criteria to select probiotic bacteria (Roy et al., 2006); the results shown in figure 1 indicated that the cells of the lactic acid bacterium are adherent to the selected epithelial tissue.



**Fig. 1** Adhesion of *Lb. curvatus* to epithelial cells (A: positive result, B: negative control).

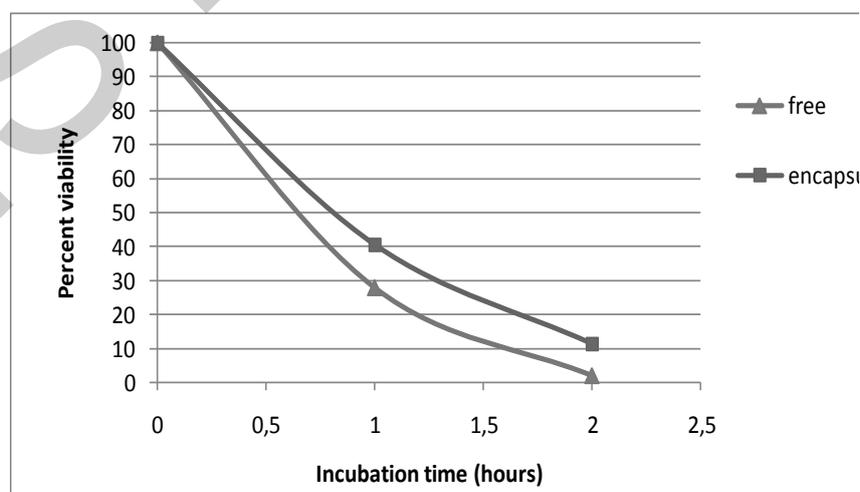
As described by Lin et al. 2007, *Lb. fermentum* cells; isolated from chicken crop highly attach the epithelial cells, which make them; in addition to the other properties; a good candidate to be selected as a probiotic.

The mechanism of adhesion of these cells is not completely understood, although it was suggested that some lactic acid bacteria like *Lb. plantarum* and *Lb. rhamnosus* are capable of colonizing the lower digestive tract for a long period resulting in the inhibition of pathogenic bacteria by competing to specific receptors required for adherence (Robin and Rouchy, 2001; Roy et al., 2006).

#### Survival test

Microencapsulation of *Lb. curvatus* was conducted by using 1% sodium alginate; the microcapsules prepared by extrusion technique were spherical and uniform in size (3 mm), each bead contains approximately  $9.10^{12}$ UFC. The survival of free and microencapsulated cells in acidic pH of the stomach was evaluated by a 2 h *in vitro* SGJ survival assay (Figure 2).

The viability of the free cells decreased intensively after the first hour of incubation in acidic conditions, it reached approximately 28 %; moreover, only 2 % of the cells remained viable after 2 hours, however, the cells in a microencapsulated state are slightly more resistant since after one hour, 40% of cells survived and after 2 hours, the viability attained 11%.



**Fig. 2** Effect of acidic pH (2) on the survival of free and microencapsulated *Lb. curvatus* cells.

The chicken GIT contained a complex microbial community distributed unequally in its different compartments; the normal flora consists mainly of lactic acid bacteria particularly lactobacilli, enterobacteria and other groups are also found

(Gabriel et al. 2005; Lin et al. 2007). Gizzard's microbial community is less abundant due to the high acidity; the hostile conditions of the duodenum reduced as well the incidence of microbes, although some lactobacilli, enterococci and coliforms were isolated (Fuller, 1984). Probiotics must then survive the transit through the gizzard to exert beneficial effects; therefore, resistance to a low pH (2) for at least 2 hours is required for a probiotic cell to be delivered effectively to the intestine. Several microencapsulation materials were used to protect probiotic cells including sodium alginate, carraghenane, pectin, whey proteins... (Voo et al. 2011; Kailasapathy, 2002). However; alginate matrix system is the most widely used and investigated biopolymer for cell bioencapsulation. It is biocompatible, and it can gel at mild condition with the presence of calcium cations. In a related study; *Lb. acidophilus* and *Lb. rhamnosus* were significantly protected from stomach conditions (Ding and Shah 2009), similarly; microencapsulated *Lb. acidophilus* and *Bifidobacterium sp.* showed 16 % and 16.7 % increase in viability after incubation at pH 2 for 2 hours when compared to free cells (Vidhyalakshmi, 2009). Lee and Heo (2000) showed that *Bifidobacterium longum* encapsulated in calcium alginate containing 2.0, 3.0, and 4.0% sodium alginate tolerated significantly incubation in a simulated gastric juice (pH 1.5) better than free cells. The death rate of the cells in the beads decreased proportionally with an increase in both the alginate gel concentration and bead size.

Figure 2 shows that *Lactobacillus curvatus* was most likely to survive the passage through the stomach, furthermore microencapsulation within alginate capsules resulted in an approximate 5.4-fold increase in the survival of cells in pH 2 after 2 hours of incubation.

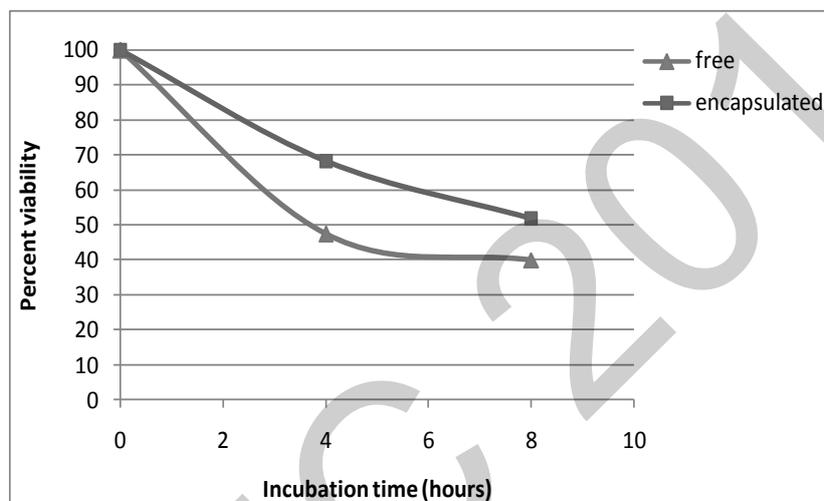


Fig. 3 Effect of bile salts (0.3%) on the survival of free and microencapsulated *Lb. curvatus* cells.

Viability of probiotic cells in the presence of bile salts was conducted as described by incubating the cells in MRS medium supplemented with 0.3 % bile salts. Results showed in figure 3 indicated that the viable count of free cells decreased by approximately 53 % after 4 hours of incubation, it decreased to reach 40 % after 8 hours with an average cell concentration of about  $(152.10^{12}$  UFC/mL), moreover; the gel-enclosed cells resisted more, more than 68 % of the cells were found to survive bile treatment for 4 hours; and more than 50 % tolerated the treatment after 8 hours.

Bile salts are the second barrier that probiotic cells should bypass to attain their site of action. In general, the required concentration of bile salts considered necessary to screen for resistant strains for human and animal use is 0.3% (Pacheko et al. 2010, Lin et al. 2007). Several studies reported the improvement of cell viability when exposed to bile salts by microencapsulation, Ding and Shah (2009) found that *Lb. plantarum* and *Bifidobacterium lactis type Bi-07* were slightly sensitive to bile toxicity (39 % of the cells survived the treatment); however, microencapsulation in 3% alginate enhanced the viability by 2-fold. In a different study; *L. bulgaricus* KFRI 673, an acid-sensitive strain was found to survive SGI exposure when protected in alginate microparticles coated with a high molecular weight chitosan (Lee et al. 2004). Conversely, *Bifidobacterium infantis*, *Lactobacillus casei* and *L. acidophilus* encapsulated in symbiotic beads composed of Hi-Maize starch (a prebiotic) and sodium alginate did not demonstrate a significant increase in survival when subjected to *in vitro* high acid and bile salt conditions (Sultana et al. 2000).

In this study; *Lb. curvatus* cells were found to be relatively resistant to bile toxicity, in addition; the use of alginate gel improved their tolerance, as approximately 1.3 –fold increase in viability was observed after 8 hours of treatment.

In conclusion, the isolated *Lb. curvatus* was found to present good probiotic properties, it displayed antimicrobial activity against some selected pathogenic bacteria, and a substantial adhesion capacity. Furthermore, the viability in GIT like conditions was increased by the alginate microencapsulation, which provides additional evidence that alginate-based microparticles are suitable for food ingredient delivery.

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# İSTANBUL'UN KENTSEL BİR PLANLAMA İLE YENİDEN YAPILANDIRILMASI

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## ÖZET

Türkiye'de, 1950 yılından itibaren büyük yerleşim merkezlerine, özellikle de İstanbul ve Ankara gibi kentlere doğru başlayan göç sonucu, sosyo-ekonomik sorunlara paralel olarak şehirlerde düzensiz büyüme ve genişleme gibi çok önemli ve etkisi günümüzde de artarak devam eden kentsel sorunları da beraberinde getirmiştir. Bununla birlikte ülkede uygulanan sosyal, ekonomik ve politik planlama yaklaşımında kolaycı ve kısa vadeli çözümlerin uzun vadeli, kamu çıkarını gözeten rasyonel planlama anlayışlarına tercih edilmesinin payı vardır. İstanbul şehrinin Türkiye ekonomisi, siyaseti ve kültür hayatındaki ağırlığı göz önüne alınırsa; ana vizyonunun İstanbul'un dünya kentine dönüştürülmesi olmalıdır. Dünya kenti ifadesiyle; yaşanabilir, sürdürülebilir, demokratik katılım ile yönetilebilir, doğal ve kültürel değerleri korunan bir kent kastedilmektedir. Bu amaçla, stratejik planı olan bir kent planına da ihtiyaç duyulmaktadır. İstanbul için ön görülen planlamanın hedefi; özgün ekolojik değerlerini, tarihsel-kültürel mirasını korumak ve geliştirmek olmalıdır. Ayrıca, bölge ve dünya ile birikimlerini ve değerlerini paylaşabilen, üçüncü boyutta siluet ve görünümünün de yeni değerler ürettiği, teknolojik ve sanat alanında öncü, sosyal sermayesi yükseltilmiş, her türlü kültürel etkinliklerin izlenebilmesinin sağlandığı, kültürel coğrafyalar temasında öne çıkan gizemli, rüya gibi bir dünya kentinin yaratılması gerekmektedir. Bu çalışmada, İstanbul'un yeniden ve planlı olarak yapılandırılmasının gerekliliği, mevcut durum vurgulanıp, öneriler ortaya konarak sunulmuştur.

**Anahtar Kelimeler:** Kentsel plan, sosyal sorunlar, sosyal göç

## RECONSTRUCTION OF ISTANBUL WITH AN URBAN PLANNING

### ABSTRACT

The immigration to the capital cities like Istanbul and Ankara which both are the biggest and most central places of Turkey has caused social and economical problems as well as non-estimated expansion and enlargement of the cities which has great influence in the recently grown urban problems. The importance of the long-term plans and legalization in the favour of the government's benefits has a great role in approaching the country in terms of politics, sociology and economy instead of the regular short-term and easy salvation issues. If the panorama of Istanbul may politically, socially, economically and culturally taken into consideration, one should easily realize that Istanbul should turn into the World-City. By the expression World-City we mean such a city which can be run democratically, lived easily with peace of mind, with its natural and cultural values preserved. There will also be demands to be strategic here. These plans should encompass the cultural, ecological, historical values at the same time. These plans should serve the concept of being able to share the cultural potentials and values in terms of being leader at technology and artistic activities, geographical potentials of being able to present its artistic features and being the land of dreams and utopia, should not be ignored. There are some advices in this study about serving the idea of re-making disciplinary plans and re-emphasising the values in the recent situation.

**Keywords:** Urban plan, social problems, social immigration

### KONU

Uluslararası metropoller yarışında İstanbul'un küresel cazibe merkezlerinden biri olmaya aday bir kent olduğu, kabul edilen bir durumdur. Anakent İstanbul'un, Türkiye ekonomisi, siyaseti ve kültür hayatındaki ağırlığı göz önüne alınırsa; İstanbul'un dünya kentine dönüştürülmesi ana vizyon olmalıdır. Dünya kenti ifadesiyle; yaşanabilir, sürdürülebilir, demokratik katılım ile yönetilebilir, doğal ve kültürel değerleri korunan bir kent amaçlanmaktadır. Bu kapsamda, stratejik planı olan bir kent planına ihtiyaç duyulmaktadır.

İstanbul için ön görülen planlamanın hedefi; özgün ekolojik değerlerini, tarihsel-kültürel mirasını koruyabilen ve geliştirebilen, bölge ve dünya ile birikimlerini ve değerlerini paylaşabilmektir. Ayrıca, üçüncü boyutta siluet ve görünümüyle yeni değerler üreten, teknolojik ve sanat alanında öncü, sosyal sermayesi yükseltilmiş, her türlü kültürel etkinliklerin sağlandığı, kültürel coğrafyalar temasında öne çıkan bir dünya kenti amaçlanmalıdır.

## Kentsel Yenileme ve Dönüşüm Politikaları

Türkiye'de çok partili döneme geçilen 1950 yılından itibaren büyük yerleşim merkezlerine özellikle de İstanbul ve Ankara gibi kentlere doğru başlayan göç olgusu, sosyo-ekonomik sorunlara paralel olarak hızlı kentleşme, şehirlerde düzensiz büyüme ve genişleme gibi çok önemli ve etkisi günümüzde de artarak devam eden kentsel sorunları da beraberinde getirmiştir. Bu duruma sebep olarak, ülkede uygulanan sosyal, ekonomik ve politik planlama yaklaşımında kolaycı ve kısa vadeli çözümlerin uzun vadeli, kamu çıkarını gözeten rasyonel planlama anlayışlarına tercih edilmesinin payı yadsınamaz bir gerçektir. 1980'li yıllarda ise dışı açık ekonomik politikaların etkisiyle kentler, global ekonominin ihtiyaçlarını karşılamak kaygısıyla hızlı bir dönüşüm geçirmiştir. Diğer taraftan hükümetlerin aynı düzlemde devam eden imar politikaları, gelecek perspektiflerinin belirlenmesinde bölge planlama biliminin yeterince değerlendirilmemesi, bir kentleşme politikasının ve bu konudaki yasal çerçevenin yetersizliği ile mevcut mevzuatın tam olarak uygulanmaması, düzensiz ve hızlı gelişmeye devam edilerek günümüzdeki sorunların ortaya çıkmasına neden olmuştur (Barlas, 2006).

İstanbul'un kentsel gelişimi, sözü edilen politikaların olumsuz bir sonucu olarak kentin yaşam kaynaklarının bulunduğu kuzey zonlarına yönelmiştir. Sürdürülebilir gelişim açısından İstanbul'un geleceği, kentin temel işlevlerinin bulunduğu alanların yeniden yapılandırılması, doğal kaynaklarının korunması, tarihi kent merkezlerinin ve dokularının rehabilite edilmesi/dönüştürülmesi ve uzun vadeli, yasal çerçevesi AB müktesebatı gereğince değerlendirilerek yeniden yapılandırılmış bir kent planlama politikasının oluşturulmasını gerekli kılmaktadır. Özellikle 17 Ağustos 1999 Marmara depreminden sonra mevcut konut stoku üzerine yapılan araştırmalar, sorunun konut miktarından çok konut niteliği üzerine olduğunu göstermiştir. Bu kapsamda, ülkenin mevcut kentsel sorunları dikkate alınarak, hızla eğilerek yasal ve kurumsal çerçevenin daha dengeli bölgelerin oluşturularak daha fazla yaşanabilirliğe sahip olan şehirler oluşturmak üzere iyileştirilmesi gerekmektedir. İstanbul özelinde, Türkiye'nin küresel pazarda yarışabilirliğini artırarak daha etkin bir konuma ulaştırma gerekliliği, planlama sisteminin yeniden yapılandırılması gereğini de zorunlu kılmaktadır (Şengül, 2006).

## KENTSEL DOKU VE BİNA ÖZELLİKLERİ

Kentsel doku incelemelerinde, fiziki elemanların (arsa, yapı, yol, otopark vb.) birbirine geçmiş biçimleri ile ilgili bir özellik oluşundan hareket edilmesi gerekmektedir. Bu kapsamda, yol genişliği ve yapı yüksekliği ilişkileri, yol ağının yapı ve nüfus yoğunluğuna uygun hiyerarşik ya da ızgara yapılanması ve boyutları, ada - parsel büyüklükleri ve bölümleri, yapı benzeri doku özellikleri gibi kent dokusu açısından sundukları farklı potansiyelleri açısından değerlendirilmelidir.

Kent nüfus artışının yanı sıra, ekonomik ve sosyal gelişmişliğin kentlerdeki yansıması öncelikle kent merkezi üzerinde yoğunlaşmaktadır. Kentin ekonomik, sosyal ve demografik değişimi kent mekanının değişiminde etkin rol oynamaktadır. Kentin sahip olduğu ulusal ve uluslar arası ekonomik etkinliklere bağlı olarak ekonomisinin büyümesi ve bunun kent merkezinde mekan talebi olarak yansıması kentin yeniden yapılanmasına yönelik form değiştirme talebini ortaya çıkarmasına neden olmaktadır. Ekonomik ve sosyal alandaki yeniden yapılanmalar, kent mekanlarını hızla değiştirirken, genel arazi kullanım modellerini de büyük ölçüde etkilemektedir (Catanese ve Synder 1988).

Kentsel doku ile ilgili çalışmalar, yerleşim alanlarında ortaya çıkabilecek değişik özellikteki dokuların incelenmesi ve değerlendirilmesini gerektirmektedir. Planlı gelişmiş eski ve yeni yerleşim alanları, toplu konut yerleşimleri, plansız gelişmiş eski ve yeni gecekondü bölgeleri, farklı doku karakteristiklerine sahip olmakta ve İstanbul'un kentsel dokusu, bu karakteristiklere bağlı olarak gruplanabilmektedir.

### *Planlı Gelişmiş Mevcut Alanlar*

Söz konusu kentsel doku grubu, planlı olarak, bitişik veya ayrıık düzende yerleşim alanları ile toplu konut yerleşimlerini kapsamaktadır:

- Planlı bitişik yapılaşmış kent dokusu (örn: Şişli, Beşiktaş, Bakırköy).
- Planlı ayrıık yapılaşmış kent dokusu (örn: Yeşilköy, Göztepe).
- Toplu konut alanları: Düşük yoğunluklu toplu konut alanları (örn: Levent ve Koşuyolu) ve yüksek yoğunluklu toplu konut alanları (örn: Ataköy'ün yeni mahalleleri ve Ataşehir).
- Tarihi doku (örn: Süleymaniye).

### *Plansız Gelişmiş Alanlar*

Bu kentsel doku grubu, plansız olarak gelişmiş eski ve yeni gecekondü bölgeleri ile dönüşüm süreci tamamlanmış alanları içermektedir.

- Düşük yoğunluklu (ilk dönem) gecekondü alanları (örn: Ümraniye'nin bazı bölgeleri).
- Yüksek yoğunluklu (apartmanlaşmış, 2981 no.lu yasaya göre Islah İmar planları ile yasallaştırılmış) gecekondü alanları (örn: Esenler, Bağcılar).

### Bina Özellikleri

2000 yılı bina sayımına göre, İstanbul'daki toplam bina sayısı 724,609'dur. Veriler kapsamında mevcut bina stokunun (i) Bina konstrüksiyon tipi, (ii) Bina yapım yılı, ve (iii) Bina kat adetleri açısından ele alınarak değerlendirilmesi gereklidir.

İstanbul'da kentsel konut dokusunun potansiyellerini değerlendirebilmek ve bu stokun gelecekte daha etkin kullanılabilmesi için, konut stokunun niteliksel durumu konusunda daha sağlıklı veri toplanması ve çalışmalar gerçekleştirilmelidir.

Yerleşim alanlarında değişik karakteristiklere sahip dokuların incelenmesi ve değerlendirilmesi, İstanbul'un gelecekteki farklı potansiyellerini ortaya koyması açısından önemlidir. Planlı ve plansız gelişmiş eski ve yeni farklı özellikteki kentsel doku örneklerinin İstanbul'un gelecekte göstereceği değişim ve gelişmeler açısından değişik fırsatlar taşıdığı açıktır. Örneğin tarihi özellikteki doku kültür ve turizm işlevleri ile gelişme açısından önem taşımaktadır. Plansız gelişen alanlar ise bütünüyle ele alınarak nitelikli bir çevre olarak geliştirilebilme imkanı taşımaktadır.

Bina özellikleri açısından, bina konstrüksiyon tipi, bina yapım yılı ve bina kat adetleri verileri büyük ölçüde mevcut konut stokunun özelliklerini de taşımaktadır ve kentsel doku gelişimi ile kalitesinin önemli boyutlarını oluşturmaktadır. Türkiye ve İstanbul için mevcut konut stoku verilerinin büyük bir bölümünün AB Konut İstatistikleri ile karşılaştırma olanağı bulunmaktadır. İstanbul'da kentsel konut dokusunu değerlendirebilmek ve bu stokun gelecekte daha etkin kullanılabilmesi için; konut sayısı, büyüklüğü, oda başına nüfus gibi mevcut bina ve konut stoku konusundaki göstergelerin yanı sıra, konut stokunun niceliksel durum konusunda daha sağlıklı veri değerlendirmesi gerekmektedir.

### İSTANBUL İÇİN BİR KENTSEL YENİLEME/DÖNÜŞÜM MODELİNİN OLUŞTURULMASI VE GELİŞTİRİLMESİ SÜRECİNDE DİKKAT EDİLECEK HUSUSLAR

İstanbul'da yenileme projelerinin gerçekleştirileceği iki önemli faaliyet alanı bulunmaktadır. Bu alanlardan birincisi küresel taleplerin baskısının yüksek olduğu ve aynı zamanda küresel ekonomideki yarışabilirliği karşılayacak potansiyellerin bulunduğu kent merkezi ile tarihi kent dokularıdır. İkincisi ise sağlıklı ve modern koşullara ulaştırılması hedeflenen niteliksiz konut bölgeleri ile gecekondular alanlarıdır. Bu bağlamda, İstanbul için yürütülen en kapsamlı kentsel yenileme ve dönüşüm projeleri İstanbul Büyükşehir Belediyesi ve ilçe belediyeleri tarafından yürütülmektedir (İ.K.A., 2006) İstanbul Büyükşehir Belediyesi bünyesindeki Yerleşmeler ve Kentsel Dönüşüm Müdürlüğü sorumluluğunda yürütülen kentsel dönüşüm projelerinden en önemlileri, proje aşaması tamamlanan ve uygulama aşamasına geçilecek olan Zeytinburnu Pilot Projesi ve yapılacak olan Küçükçekmece Olimpiyat Köyü ve çevresi Kentsel Dönüşüm Projesi ile Fatih İlçesi Kentsel dönüşüm Projeleridir. Fatih Belediyesi'nce yaptırılan İstanbul Tarihi Yarımada Balat ve Fener Semtlerinin Rehabilitasyonu Projesi de tarihi kent dokularının korunmasına yönelik olarak gerçekleştirilmiş bir projedir (TMMOB,2006).

Söz konusu kentsel dönüşüm projelerini yürüten İstanbul Büyükşehir Belediyesi (İBB) birimlerinden Yerleşmeler ve Kentsel Dönüşüm Müdürlüğü tarafından 3030 Sayılı yasa kapsamında; İBB'nin yetki sınırları içerisinde olmak üzere depreme hazırlık süreci kapsamında Deprem Master Planı hazırlanmıştır. 1/50000 ölçekli Metropolitan Alan Nazım Planının, vizyon 2023 perspektifinin gerektirdiği yeni yerleşmelerin ve kentsel yapılanmanın her ölçekte sağlanması hedeflenmektedir. İskan ve konut ile ilgili program, proje, yatırım ve uygulamaları, alan genelinde mekansal gelişme perspektifinin Avrupa Birliği ile ilgili gelişmeleri dikkate alarak, takibi, kentsel gelişimin sağlanması ile kentsel / bölgesel gelişme ve kapasite artırımına öncülük etmek üzere yapılandırılmıştır. Bu kapsamda yukarıda sözü edilen birim bünyesinde değişik disiplinlerden uzmanlarla oluşturulacak bir ekip çalışmasını yürütmek amacıyla İstanbul Şehircilik Atölyesi (İŞAT) kurulmuş ve İŞAT bünyesinde yapılacak çalışmaların Avrupa Birliği metropollerindeki şehircilik atölyelerinin formasyonunda icra edilmesi hedeflenmiştir. Yerleşmeler ve Kentsel Dönüşüm Müdürlüğü sorumluluğunda yürütülen ve yapılması planlanan kentsel yenileme ve dönüşüm projelerinden belli başlıları aşağıda belirtilmiştir:

- Zeytinburnu Pilot Projesi (İDMP-YEP-ZPP Uygulanabilir Pilot Proje Geliştirme Çalışmaları kapsamında)
- Küçükçekmece Olimpiyat Köyü ve Çevresi Kentsel Dönüşüm Projesi
- Fatih İlçesi Kentsel Dönüşüm Planlanması Projesi
- Geçici İskan Üniteleri Prototip Çalışması
- İstanbul Kalkınma Ajansı Çalışmaları
- İstanbul Ekonomik Gelişme Çalışmaları
- DPT-OECD-İBB İstanbul Gelişim Projesi
- DPT-İBB İstanbul NUTS Gelişim Projesi
- İstanbul için Proje Çevrimi kapsamında Kaynak Bulma Çalışmaları
- Sofia-Antipolis Konsept Araştırması ve İstanbul Silikon Vadisi Projesi (Cendere Vadisi)
- DPT ile Sürdürülebilir Mahalle Yenileşmesi için Eylem Planı
- DPT ile Beyoğlu Çöküntü Alanlarının Rehabilitasyonu Projesi
- DPT ile Gecekondular Alanlarının Yaşanabilir Mekânlara Dönüştürülmesi Projesi
- DPT ile Galata Kulesi ve Çevresi Hendek Caddesi Yeniden Geliştirme Projesi
- İstanbul Kaçak Yapılaşma Kronolojisi
- İstanbul için kentsel dönüşüm yasa çalışmaları

Projesi tamamlanan ve uygulama aşamasında olan Zeytinburnu Pilot Projesi İstanbul Deprem Mastır Planı (İstanbul Büyükşehir Belediyesi ile İTÜ, ODTÜ, YTÜ, BÜ arasında gerçekleştirilen protokol kapsamında, İstanbul için depremle ilgili hazırlıklar dahil, deprem öncesi ve sonrasında gerçekleştirilecek her türlü tespit ve işlemler için hazırlanan bir plandır) ve JICA (İstanbul Büyükşehir Belediyesi ile Japon Uluslararası İşbirliği Ajansının İstanbul ile ilgili hazırladığı deprem risk bölgeleri analizleri çalışmasıdır) raporları doğrultusunda Zeytinburnu ilçesinde AB uyum programları çerçevesinde yürütülecektir.

## İSTANBUL METROPOLİTEN ALAN NAZIM PLANI YAKLAŞIMLARI

### *Planlama Genel İlkeleri*

İstanbul anakentini oluşturan kentsel bütünlüğünün gelişmesinde; bölgesel, ülkesel denge ve uluslararası ilişkilerin rolü öncelikli olmalıdır. İstanbul kent bütününde fiziksel büyüme kontrol edilmeli, gelişme ve büyüme hızı yavaşlatılmalı, gelişme ve büyümenin metropoliten bölgeye dengeli dağılımı sağlanmalıdır. Yüksek yoğunluklu kentsel alanlarda, nüfus desantralizasyonunu sağlayacak yönde alt merkezlerin gelişimi desteklenmelidir. Düzensiz gelişen alanlarda kent bütünü ile ilişkili yeniden yapılanma ve sıhhileştirme yapılmalıdır. Kent makro formunun lineer ve kademelendirilmiş çok merkezli nitelikte gelişimi kabul edilmelidir.

### *Merkez Kademelenmesi*

Kentsel merkezlerde ve çöküntü bölgelerinde sıhhileştirme ve koruma programları planlanmalıdır. Ayrıca, sıhhileştirme plan ve uygulama programları geliştirilmelidir. Metropoliten alan alt bölge bütününde, çalışma imkânları ve alanları, nüfus ile dengeli geliştirilerek ihtisaslaşma sağlanmalıdır. İstanbul Metropoliten alan alt bölge bütününde lineer gelişmeyi destekleyen, ulaşım sistemi ve altyapı esası benimsenmelidir. İstanbul'un önemli kimlik belirleyicileri olan tarihi kültürel dokusu peyzajı, röperleri ve silueti dinamik koruma prensipleri ile korunmalıdır. İstanbul'un kimliği içinde çok önemli yer tutan, Boğaziçi, Haliç ve Tarihi Sur içinin mevcut değerleri ve birbirleriyle ilişkileri nedeni ile karma sit alanları olarak tespiti yapılmalı, özel rolleri ve statüleri belirlenmelidir (DPT, 2007).

Nüfus desantralizasyonu ile sosyal ve teknik altyapı standartlarının yükseltilmesi için yeni kanat çekim merkezleri önerilerek, 1.derece kademe merkezler olarak gelişimi sağlanmalıdır Metropoliten alan içinde yaşam standardını yükseltecek maksimum ve minimum yoğunluk değerleri belirlenmeli ve bu yönde iyileştirmeler yapılması programlanmalıdır.

### *İhtisas Şehirler ve Kanat Çekim Merkezleri*

Bir kentin fiziksel ve ekonomik yeniden yapılanması, nüfusunun ve ekonomik yapısının gelişimine ve değişimine bağlıdır. Kentin ekonomik yapısının incelenmesi, gelecekteki kentin büyüklük ölçüsünü verebileceği gibi; arazi kullanımı içerisinde, merkezi iş alanının (MİA) nasıl konumlanacağını da belirlemektedir (Berg ve Meer 1993). Bu kapsamda, Tarihi yarımada'nın tarihi ve doğal yapısı korunmalı ve bu alanda MİA'nın alansal gelişimi önlenerek, tarihi ticaret ve turizm merkezi olarak gelişimi sağlanmalıdır. Sur dışında ise, mevcut M.İ.A. alanının yükünü azaltabilecek ve uluslararası karar ve yönetim merkezi olabilecek yeni bir M.İ.A. alanı planlanmalıdır. Kent içi ulaşım sistemi olarak toplu taşıma sistemi öne çıkarılmalı, bu sistem karayolu, demiryolu, denizyolu ve havayolu sistemleri ile entegre olmalıdır. Kent içi ulaşım sisteminde önemli derecede olumsuz etkiye sahip Haydarpaşa limanının yük taşımacılığı işlevi desantralize edilmelidir. (Bu limanın kapasitesinden yeterince istifade edilmediği ve gelişme imkânına da sahip olmadığı açık bir gerçektir.) Metropoliten Alan Alt Bölgede 3. boğaz geçişi, daha güneyden bir tüp geçiş olarak planlanmalıdır. Metropoliten Alan Alt Bölge bütününde dağıntık yerleşmiş Üniversitelerin kampüs şeklinde gelişimi sağlanmalıdır. Plan dönemi içinde Lisansüstü eğitim ve araştırma-geliştirme ağırlıklı bir eğitim stratejisi benimsenmelidir (İMP, 2008).

Büyükşehir Belediye Sınırları dışında, diğer kamu kuruluşlarının sorumluluğunda bulunan karayolu şebekesi üzerinde, kent içi ulaşım için gerekli kapasitelerin oluşturulması sağlanmalıdır.

Metropoliten alan alt bölge bütününde nazım planın istikrarlı bir şekilde uygulanması için ilgili kamu kurum ve kuruluşların koordinasyonunun sağlanması gereklidir. Ayrıca planın uygulanabilirliğine aykırı yasa ve yönetmeliklerin yeniden elden geçirilerek, düzenlenmesi gereklidir.

## İSTANBUL'UN KENTSEL DÖNÜŞÜMÜ KAPSAMINDA ÖNERİLEN PROJELER

İstanbul Bölgesel Hizmet Merkezi'nin tema ve vizyon sonuçları temel alınarak, İstanbul'un kentsel dönüşümü kapsamında gerçekleştirilmesi önerilen hususlar aşağıda belirtilmiştir:

- Ulaşımın, finans, yönetim merkezleri, sağlık, turizm tesisleri arasında dengelenmesi İstanbul'un bir hizmet merkezi olmasında en önemli adım olacaktır. Yük taşımalarında Avrupa yönü çıkışı için Halkalı'da yük köyü oluşturulması (raylı sistem için) gerekmektedir.
- Deniz ulaşımına daha çok önem verilmeli,
- Raylı sistemlerinin kent içinde yeraltı metrosu olarak planlanmalı,
- Kent içi ulaşımının %70'i raylı sistemle sağlanmalı,

- Uluslararası düzeyde spor faaliyetleri düzenlenmeli,
- Turizm potansiyeline sağlık turizminin ilave edilmesi,
- İstanbul'un iki yakası arasındaki dengesiz üst düzey hizmet faaliyetleri düzenlenmeli,
- Metro sisteminin bütün kenti ağ şeklinde sarması ve ulaşımda entegrasyon sağlanmalı,
- Kara, deniz ve hava yolu ulaşım sistemleri entegre edilmeli,
- Ticarete yeni güçlü markalar oluşturulmalı ve İstanbul dünyanın ticaret merkezi olmalı,
- AB'nin ulaşım koridorlarının İstanbul'a kadar uzanması temin edilmeli, özellikle TER projelerine dahil edilmeli,
- Kaliteli bilim adamlarının fikirlerini ve projelerini değerlendirebileceği bir merkez haline getirilmesi,
- İstanbul dünyanın moda merkezi olmalı,
- Büyük alışveriş bölgesi oluşturulmalı,
- Ulaşım modları ile entegre alışveriş merkezleri oluşturulmalı,
- Dubai deneyimi göz önünde tutularak, İstanbul'un Avrupa ve Ortadoğu'nun yeni teknolojilere adapte olmuş haber ve yayın kuruluşları yapılmalı,
- Uluslararası düzeyde fuar etkinlikleri, planlı bir şekilde yıl boyunca her iki yakada düzenlenmeli,
- Üniversiteler; etkili araştırma yapan, bilgi üreten ve bilim adamlarını cezbeden bir merkez olmalı,
- Sağlık, medya, eğitim alanında mini kentlerin olduğu bir merkez planlanmalı,
- Mesleki eğitimin arttığı bir üniversite sistemi, araştırma, ihtisaslaşma enstitüleri oluşturulmalı,
- Golf-binicilik, su sporları, yelkencilik, motor sporları organizasyonlarının uluslararası alanda yapılması sağlanmalı,
- Kültürel ve tarihsel değerlerin iyi yönetildiği bir İstanbul hedeflenmeli,
- Gelişmiş sanayisi, ses getiren bilimsel aktivitelere ev sahipliği yapılabilen fuar ve kongreler düzenlenmeli,
- Büyük bir depremle tarihi kazanımların ağır biçimde tahribi göz önünde bulundurularak, gerekli çalışmalar başlatılmalı,
- İstanbul'un olimpiyat oyunlarına ev sahipliği yapabileceği seviyelere ulaşılmalı,
- Estetik bilinç gelişmeli ve yerleşmeli,
- İstanbul, rahat yaşanır, güvenli, temiz bir kent olmalı,
- Çok güzel, dünya kültürünün önemli birikimlerinden birini kapsayan boğaz ve Marmara şeridi dışında, kaotik, çirkin bir kentin yeniden kurulma adımları atılmalı,
- Daha yeşil bir kent yaratılmalı,
- Deniz kenarları ve ormanlar korunmalı,
- İstanbul, dinler ve kültür buluşma merkezi olmalı,
- Kültürel ve demografik çeşitliliğin iyi yönetildiği bir İstanbul olmalı,
- Tarihi yarımada Haliç ve Boğaziçi özgün kültürel yapısına dönüşmeli,
- Yarımada ve boğazda yer alan özgün doku alanlarının sosyal ve kültürel olarak sürekliliği sağlanmalı,
- Batı Asya ve Ortadoğu kültürlerinin ortak paydası olan metropolün, ruhuna uygun uluslararası organizasyonların yıl boyunca sürdüğü bir atmosfer oluşturulmalı,
- Güçlü üniversiteleri, kütüphaneleri, müzeleri ve bilim kuruluşlarıyla Balkanlar, Batı Asya ve Ortadoğu'ya yönelik sosyal, ekonomik ve coğrafik araştırmalara hız kazandırılmalı,
- İstanbul'da korunması gerekli kültür varlığı yapılarının harap hali ortadan kaldırılmalı,
- Teknolojik bilginin üretildiği ve ticaretleştirildiği İstanbul oluşturulmalı,
- Teknolojide önde gelen dünya şirketlerinin yönetim merkezlerinin İstanbul'da toplanması,
- Bilim ve teknoloji, sadece üniversitelerde veya teknoparklarda sınırlı kalmamalı,
- Kilosu 100 \$'ın altında ürünlerin üretilmediği bir İstanbul olmalı,
- Uluslararası eğitim merkezi olarak, üniversite çağı ve yaşam boyu eğitimde odaklanmalı, yaratıcılığın önde tutulması ve geleceğin bilim adamları yetiştirilmeli,
- Bilimin merkezinin yaygınlaştığı bir İstanbul,
- Katma değeri yüksek konularda üniversiteler ile sanayinin beraber çalıştığı İstanbul,
- Üniversitelerde makale sayısını arttırmak yerine fikri mülkiyetin (patent) esas alınması ve ileri ülkeler düzeyine yükseltilmesi,
- Düşünce ve davranış biçimleriyle bütünleşen, bilinçli kullanıcıların yaşadığı bir şehir haline getirilmeli,
- Kent yönetiminde katılımcı ve paylaşımcı bir sistemin oluşmasının sağlanması,
- Yerel yönetimlerle iç içe, kentli olma bilinci ve kentine sahip çıkan İstanbullular,
- Haberdar, katılımcı bir nüfus,
- İş, aş olanakları çözülmüş, yerleşme estetiğinin bilincinde kullanıcıya sahip olunması,
- Çağın tüm yaşamsal konumunu içeren doğayla barışık bir kent görünümü veren İstanbul olmalı,
- Tüm atıkların arıtılarak doğal ortama bırakılmasının görüleceği İstanbul,
- Yeşil alanları birbiriyle ilişkili sistem yaklaşımı ve çözümü ile yaşayan açık alanlar,
- Doğal yapısı, nitelikleri, ölçeği korunmuş kıyıları ve suyu temiz Boğaz ve Haliç,
- Irmakları/dereceleri iyileştirilmiş bir İstanbul,
- Kentsel rant problemleri çözülmeli,
- Zarar azaltma ve hazırlık çalışmalarının tamamlandığı, afet yönetiminin risk yönetimine dönüştürüldüğü, kontrol altında ve depreme hazır İstanbul oluşturulmalı,
- Tüm alt yapıların ve binaların deprem dayanıklı halde olması sağlanmalı. Merkezler ve yeni yerleşmelerde ve aynı ilkelerin uygulanması,

- Kentsel dönüşümün sağlandığı, gerekli güçlendirmelerin yapıldığı ve sağlam yapılardan oluşan planlı bir kent oluşturulmalı,
- Sosyal donatı alanlarının yeniden öngörülmesi,
- Sağlıklı, standartlı, renkli, canlı, 24 saat yaşayan kültürel ve tarihi merkezler olmalı,
- Açık alanlar ve mekânlar bütüne ve özüne uygun oluşturulmalı ve düzenlenmeli,
- Kamusal alanları yaya kullanımı adına arttırılmış, trafikten arındırılmış kentsel bir görüntü olmalıdır.

Yukarıda belirtilen hususların, gerçekleştirilmesi durumunda, İstanbul'un dünya kenti olması yolunda çok önemli parametreler olacağı düşünülmektedir.

## SONUÇLAR ve ÖNERİLER

İstanbul'da özel mülk sahipliği oranının ve kiracı sayısının yüksek oluşu geliştirilecek olan yenileşme projeleri için oldukça bağlayıcı bir unsur olarak görülmektedir.

Türkiye'deki klasik imar planlaması anlayışının kapsamı, sürdürülebilir kentsel gelişme ve sürdürülebilir kentsel yenileşmenin amaç ve hedeflerinden çok farklıdır. Bu noktada, yenileşme çalışmalarında üst ölçek plan kararları ile uyumsuzluk problemi olmaktadır. Bu itibarla, İstanbul için imar planlaması zihniyetini aşmış, dünya içindeki yerini geliştirebilecek ve potansiyellerini arttırabilecek bir stratejik planlama sisteminin geliştirilmesine ihtiyaç duyulmaktadır.

İstanbul'da son yıllarda yenileşme projelerine yönelik çabalar, yerel yönetimlerin bireysel çabaları ve uygulanan tekil projelerle gerçekleşmiştir. Ancak Türkiye'de kentsel yenileşmeye yönelik yasal çerçevenin tamamlanmamış olması, bu yönde gerçekleştirilen örnek çalışmalar için bir sınırlayıcı teşkil etmektedir. Bunun sonucunda kazanılan deneyimler daha geniş programlara dönüştürülememiştir. Buna yönelik programlar oluşturulması ancak yasal düzeyde gerekli çalışmaların yapılması ile gerçekleştirilebilecektir.

Yerel yönetimin çeşitli seviyelerinde katılıma izin veren yeni bir yönetim modeli ile planlama yaklaşımı oluşturulmalı ve bu yaklaşımın oturtulacağı yasal temelin ulusal düzeyde tanımlanması zorunlu olacaktır. Bu zorunluluk, merkezi yönetim ve yerel otoritelerin birbirinden kopuk politikalarının eşgüdümünü sağlayarak, daha dengeli bölgesel ve kentsel gelişmelerin oluşturulmasını sağlayacaktır.

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# KAMU İHALELERİNDE AŞIRI DÜŞÜK TEKLİF VEREN FİRMALARIN DEĞERLENDİRİLMESİ VE ÇÖZÜM ÖNERİLERİ

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## Özet

Kamu alımları için harcanan kaynak miktarı, gelişmekte olan ülkelerde Gayri Safi Milli Hâsılının yaklaşık %15'ini oluşturmaktadır. Sınırlı kamu kaynaklarının verimli bir şekilde kullanılması, kamu alım sistemi ile doğrudan ilişkilidir. Kamu ihale sisteminde temel amaç, istenen kaliteyi en uygun fiyata temin etmektir. Ülkemizde 2010 yılında yapılan kamu alımlarının yaklaşık % 35'i yapım işlerini kapsamaktadır. 2010 yılı içerisinde yapım işleri için harcanan rakam yaklaşık 19 Milyar TL'dir. Yapım işi projelerinde hedef; projenin kalite, süre ve maliyet üçgeni içerisinde optimum noktada tamamlanmasıdır. Bu durum, yapım işlerinde ihale süreci düşünüldüğünde Ekonomik Açından En Avantajlı Teklifin Belirlenmesi ve Aşırı Düşük Tekliflerin Değerlendirilmesi aşamasını ön plana çıkarmaktadır. Bu çalışma kapsamında, İstanbul Üniversitesi'nde son yıllarda yapılan ihaleler belirlenen kriterler çerçevesinde incelenerek, aşırı düşük tekliflerin önlenmesi ve değerlendirilmesine yönelik çözüm önerileri sunulmuştur.

**Anahtar sözcükler:** 4734, Aşırı düşük teklif

## THE EVALUATION OF FIRMS THAT OVER LOW BID IN PUBLIC PROCUREMENT BIDDERS AND SUGGESTIONS FOR SOLUTION

### Abstract

The amount of resources spent on public procurement constitute for developing countries approximately 15% of Gross National Product. Efficient use of limited public resources is directly related to public procurement system. The main objective of the public procurement system is to provide the desired quality at the best price. In our country, in 2010 approximately 35% of the construction works of public procurement. Spent for construction works in the year 2010 figure of about 19 billion TL. It is aimed to complete the optimum point within the triangle of quality, time and cost of Construction work projects. In this case, given the Most economically advantageous tender procedure for works contracts, the proposal brings to the fore stage of Determination and Assessment of abnormally low bids. Scope of this study, the criteria defined within the framework of the University of Istanbul in recent years by examining the requirements, and the prevention of abnormally low tenders submitted for the evaluation of proposals for solutions.

**Keywords :** 4734, Over low bid

### Giriş

Avrupa Birliği'ne üye ülkelerin kamu alımları, bu konuda düzenlenen AB Direktifleri'ne uygun olarak yapılmaktadır. Ülkemizde de 01/01/2003 tarihine kadar 2886 sayılı Devlet İhale Yasası çerçevesinde Kamu Alımları yapılırken, bu tarihten itibaren 22/01/2002 tarihinde 24648 Sayılı Resmî gazetede yayınlanan 4734 Sayılı Kamu İhale Kanunu doğrultusunda alımlar gerçekleştirilmektedir. 4734 Sayılı Kamu İhale Kanununa göre İhalesi yapılan işlerin sözleşmesi ise 4735 Sayılı Kamu İhale Sözleşmeleri Kanunu çerçevesinde yürütülmektedir.

Ülkemizde ise Kamu tarafından gerçekleştirilen Yapım, Mal ve Hizmet alımı gibi kamu harcamalarının GSMH'nın %12'lik kısmını kapsadığı görülmektedir (KİK., İstatistikleri). Bu oranın daha da yukarılara çıkması beklenmektedir. Yatırım programlarının öncelikli olduğu ülkemizde, bu yatırımlara harcanan kaynakların verimli kullanılması önemlidir.

2886 sayılı Devlet İhale Yasasının uygulamada karşılaşılan sorunlara çözüm getirememesi ve AB'ye üye ülke statüsünde olmamızdan dolayı uymak durumunda olduğumuz direktifler doğrultusunda düzenlenen 4734 Sayılı Kamu İhale Yasası ile ulaşılmaması istenen hedefler aşağıda sıralanmıştır (4734).

1. Saydamlık
2. Rekabetin sağlanması
3. Eşit muamele

4. Güvenilirlik
5. Kamuoyu denetiminin sağlanması
6. İhtiyaçların uygun zamanda ve uygun koşullarda karşılanması
7. Kaynakların verimli kullanılması

Yeni ihale yasasıyla ihtiyaçların zamanında ekonomik olarak en avantajlı şartlarda istenen kalitede karşılanması düşünülmektedir. Rekabet ortamının sağlanması ile kaliteli işin ucuza alınması rüşvet, hile ve adam kayırma gibi istismar unsurlarının ortadan kaldırılması amaçlanmaktadır.

İhale en basit tanımıyla bir tahsis yöntemidir (www.tcmb.gov.tr) . İhale ile kamu ihtiyaçlarının karşılanması söz konusu olduğunda Kamu İhalesi kavramı ortaya çıkmaktadır. 4734 Sayılı Kamu İhale kanunu ihale kavramını, Söz konusu kanunda “yazılı usul ve esaslara göre mal veya hizmet alımları ile yapım işlerinin istekliler arasında seçilecek birisi üzerine bırakıldığını gösteren ve ihale yetkilisinin onayını müteakip sözleşmenin imzalanması ile tamamlanan işlemler olarak tanımlamıştır”. Yine kanunda yer alan yapım kavramının tanımına bakacak olursak, “Bina, karayolu, demiryolu, otoyol, havalimanı, rıhtım, liman, tersane, köprü, tünel, metro, viyadük, spor tesisi, alt yapı, boru iletim hattı, haberleşme ve enerji nakil hattı, baraj, enerji santrali, rafineri tesisi, sulama tesisi, toprak ıslahı, taşkın koruma ve dekapaj gibi her türlü inşaat işleri ve bu işlerle ilgili tesisat, imalat, ihzarat, nakliye, tamamlama, büyük onarım, restorasyon, çevre düzenlemesi, sondaj, yıkma, güçlendirme ve montaj işleri ile benzeri yapım işleri” olarak ifade edilmiştir.

Yapım işlerini oluşturan inşaat projelerinin rantabl olabilmesi kalite, süre ve maliyet üçgeni içerisinde optimum çözüm noktasında projelerin gerçekleşmesi ile mümkündür. Diğer bir ifadeyle tanımlanan projenin süresi içerisinde istenen kalitenin altına düşmeden en düşük maliyetle gerçekleşmesine bağlıdır.

### Örnek İhalelerin İncelenmesi

Son yıllarda 4734 sayılı Kamu İhale Kanununa göre alım yapan özel bütçeli bir kamu kurumunun yaptığı (Yapı İşleri ve Teknik Daire Başkanlığı) KİK 19. Madde Açık İhale kapsamında yaklaşık maliyeti 4734 Sayılı Kamu İhale Kanununun 13. Maddesinin (b) bendinin 2. Ve 3. Alt bentlerinde belirtilen sınırlar içerisinde kalan yapım işleri ihaleleri (Elliye aşkın onarım, güçlendirme, yeni bina, restorasyon v.b. ihalesi), bu ihalelerin sonuçları, sözleşme sonrası uygulama aşaması ve geçici kabul süreçleri incelenmiştir. Bu doğrultuda aşağıdaki esaslar doğrultusunda incelenen çok sayıda ihaleden aşırı düşük tekliflerinde değerlendirildiği beş tanesi örnek olarak bu çalışma kapsamında verilecektir.

### İnceleme Kriterleri

1. İş Deneyim Belgesinin Niteliği
2. İş deneyim güncellenmiş tutarlarının teklif bedeline oranı
3. Kullanılmamış nakit kredi miktarının teklif bedeline oranı
4. Kullanılmamış teminat mektubu kredisinin teklif bedeline oranı
5. Tekliflerin ortalamasının yaklaşık maliyete oranı
6. Aşırı Düşük teklif sınırının yaklaşık maliyete oranı
7. İhale üzerinde kalan firma ve aşırı düşük teklif veren firmaların;
  - a. Teklifin yaklaşık maliyete oranı
  - b. Teklifin teliflerin ortalamasına oranı
8. Aşırı Düşük teklif veren firmalarda
  - a. Teklifin aşırı düşük sınır değerine oranı
9. Bilanço ve gelir tablosu istenen ihalede
  - a. Cari oran
  - b. Özkaynak oranı
  - c. Borç oranı
10. 3 senelik ortalama ciro değerinin teklif bedeline oranı

Ayrıca;

- A. Yapı Denetim görevlileri tarafından yapılan işin kalitesi aşağıdaki skalaya göre derecelendirilerek, yüklenicilerin iş kalitesi profili çıkarılmıştır.

#### İş Kalitesi

1. Çok Kötü
2. Kötü
3. Orta
4. İyi
5. Çok İyi
6. Mükemmel

- B. Yapı Denetim Görevlileri tarafından, İsteklilerin işi yaptıkları esnada idareye karşı tutum ve davranışları, teknik elemanlarının kapasiteleri ve işi yönetme kabiliyetleri, iş programına uymaları, geçici kabul işlemlerinin sorunsuz yapılması gibi başlıkları kapsayan Proje performanslarını aşağıdaki gibi değerlendirmişlerdir.

**Proje Performansı**

1. Çok Kötü
2. Kötü
3. Orta
4. İyi
5. Çok İyi
6. Mükemmel

- C. İhale Komisyonundaki teknik elemanlar tarafından Aşırı düşük Teklif veren firmaların savunmaları incelenerek 0-10 puan aralığında değerlendirilmiştir.

**Örnek 1.** 14 adet Geçerli Teklif, 4 Adet Aşırı Düşük Teklif (Tablo 1,2)

**Tablo 1.** Birinci İhale; Firmaların Değerlendirilmesi

FİRMA	İŞ DENEYİM TÜRÜ	İŞ DENEYİM TUTARI/TEKLİF	KULLANILMAMIŞ NAKİT KREDİ/TEKLİF	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ/TEKLİF
A	BİTİRME	2,00	5,61	5,55
B	BİTİRME	1,56	7,38	7,38
C	BİTİRME	24,19	20,28	20,28
D	DİPLOMA	10,87	12,35	12,43
E	DENETLEME	13,39	0,00	0,35
F	BİTİRME	7,48	29,58	51,63
G	BİTİRME	7,15	26,80	42,82
H	BİTİRME	2,08	3,00	2,58
I	BİTİRME	3,39	1,74	1,74
J	DENETLEME	3,48	1,71	2,04
K	DİPLOMA	11,37	1,54	1,54
L	BİTİRME	25,56	35,67	39,05
M	DENETLEME	10,73	5,12	5,12
N	BİTİRME	1,83	13,28	13,24

TEKLİFLERİN ORTALAMASI/YAKLAŞIK MALİYET %79.54  
AŞIRI DÜŞÜK TEKLİF SINIRI/YAKLAŞIK MALİYET : %70.40

İŞ KALİTESİ : İYİ  
PROJE PERFORMANSI : İYİ

**Tablo 2.** Birinci İhale; Aşırı Düşük Tekliflerin Değerlendirilmesi

	FİRMA	NETİCE Komisyon değer.	TEKLİF/YAKLAŞIK MALİYET (%)	TEKLİF/ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
<b>AŞIRI DÜŞÜK TEKLİF VEREN FİRMALAR</b>	C	KABUL EDİLMEDİ - 4	63,55	79,90	90,28%
	B	KABUL EDİLDİ - 10	69,87	87,84	99,25%
	E	SAV. VERMEDİ	58,62	73,70	83,27%
	A İşi Alan Firma	KABUL EDİLDİ - 9	68,97	86,71	97,97%

Yapı Denetim Görevlilerinin Değerlendirmesi (İşi alan firma : A)

**Örnek 2.** 7 adet Geçerli Teklif, 2 Adet Aşırı Düşük Teklif (Tablo 3-5)

**Tablo 3.** İkinci İhale, Firmaların Değerlendirilmesi

FİRMA	İŞ DENEYİM TÜRÜ	İŞ DENEYİM TUTARI/TEKLİF	KULLANILMAMIŞ NAKİT KREDİ/TEKLİF	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ/TEKLİF	3 SENELİK ORTALAMA CİRO/TEKLİF
A	BİTİRME	7,72	8,64	8,64	7,33
B	BİTİRME	6,30	1,13	2,09	1,95
C	BİTİRME	3,04	5,04	5,01	2,22
D	DİPLOMA	2,33	1,82	1,82	1,11
E	DENETLEME	3,17	0,95	0,95	1,51
F	BİTİRME	1,25	5,56	4,92	5,66
G	BİTİRME	1,83	6,76	10,91	0,87

**Tablo 4.** İkinci İhale; Firmaların Bilanço Kriterlerine Göre Değerlendirilmesi (son üç yıl)

FİRMA	CARİ ORAN	CARİ ORAN	CARİ ORAN	ÖZKAYNAK ORANI	ÖZKAYNAK ORANI	ÖZKAYNAK ORANI	BORÇ ORANI	BORÇ ORANI	BORÇ ORANI
A	1,43	1,28	2,77	0,14	0,42	0,69	0,00	0,01	0,00
B	1,33	0,93	0,53	0,26	0,31	0,27	0,00	0,09	0,37
C	-	1,08	1,09	-	0,32	0,36	0,00	0,04	0,03
D	0,85	0,99	1,00	0,31	0,20	0,29	0,50	0,00	0,30
E	1,10	0,96	1,03	0,40	0,18	0,37	0,00	0,00	0,73
F	-	0,98	1,10	-	0,35	0,34	0,00	0,01	0,09
G	1,23	1,66	1,40	0,11	0,11	0,12	0,00	0,00	0,00

Tabloda verilen bilanço kriterleri Cari Oran, Özkaynak Oranı ve Borç Oranı kavramları aşağıda açıklanmıştır.

**Cari Oran :** “Belli sürelerde nakit akışını sağlayabilmesi için gerekli likiditeye ve kısa dönem (bir yıl) içinde borç ödeme gücüne sahip olup olmadığını gösteren oran” Cari orandır. Dönen Varlıklar / Kısa vadeli borçlar formülü ile hesaplanır. Hesaplama yapılırken yıllara yaygın inşaat maliyetleri, dönen varlıklardan ve hak ediş gelirleri kısa vadeli borçlardan düşülür. Cari Oranın 0,50 ye eşit veya büyük olması gerekir (Bu oran 0,75 olarak bu sene içerisinde deęiştii).

**Özkaynak oranı :** “Aktif varlıkların ne kadarının öz kaynaklardan oluştuğunu gösteren oran” özkaynak oranı olarak isimlendirilir. Öz kaynak toplamı/ Toplam Aktif formülü ile hesaplanır. Hesaplama yapılırken yıllara yaygın inşaat maliyetleri toplam aktiften düşülür. Özkaynak oranının 0,10’a eşit veya büyük olması gerekir (Bu oran 0,15 olarak bu sene içerisinde deęiştii).

**Borç Oranı :** Kısa vadeli banka borçlarının öz kaynaklara oranını borç oranı olarak ifade ettik Kısa Vadeli yabancı kaynaklar içerisindeki banka borçları/Özkaynak toplamı formülü yardımıyla hesaplanır. Bu oranın 0,75’ den küçük olması gerekir (Bu oran 0,50 olarak bu sene içerisinde deęiştii).

TEKLİFLERİN ORTALAMASI/YAKLAŞIK MALİYET % 79.42  
AŞIRI DÜŞÜK TEKLİF SINIRI/YAKLAŞIK MALİYET : % 71.01

İŞ KALİTESİ : MÜKEMMEL  
PROJE PERFORMANSI : MÜKEMMEL

**Tablo 5.** İkinci İhale Aşırı düşük Tekliflerin Deęerlendirilmesi

Aşırı Düşük Teklif Veren Firmalar	Firma	Netice : Komisyon Deęerlendirmesi	Teklif/Yaklaşık Maliyet (%)	Teklif/Ortalama Maliyet (%)	Teklif/Aşırı Düşük Sınır Deęer (%)
	A	Kabul Edildi-9	67.71	85.25	95.35
	C	Kabul Edildi-6	69.84	87.93	98.34

Yapı Denetim Görevlilerinin Deęerlendirmesi (İşi alan firma : A)

**Örnek 3.** 7 adet Geçerli Teklif 1 Adet Aşırı Düşük Teklif (Tablo 6-8)

**Tablo 6.** Üçüncü İhale; Firmaların Deęerlendirilmesi

FİRMA	İŞ DENEYİM TÜRÜ	İŞ DENEYİM TUTARI/TEKLİF	KULLANILMAMIŞ NAKİT KREDİ/TEKLİF	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ/TEKLİF
A	DENETLEME	7,08	3,38	3,38
B	BİTİRME	12,67	12,14	11,03
C	BİTİRME	3,11	5,18	5,18
D	BİTİRME	5,03	18,83	30,08
E	BİTİRME	7,47	21,97	24,05
F	DİPLOMA	5,47	1,08	1,08
G	BİTİRME	4,86	7,48	7,43

TEKLİFLERİN ORTALAMASI/YAKLAŞIK MALİYET %78.01  
AŞIRI DÜŞÜK TEKLİF SINIRI/YAKLAŞIK MALİYET : %71.40

İŞ KALİTESİ : ORTA  
PROJE PERFORMANSI : ORTA

**Tablo 7.** Üçüncü İhale; Aşırı Düşük Tekliflerin Değerlendirilmesi

AŞIRI DÜŞÜK TEKLİF VEREN FİRMA	FİRMA	NETİCE	TEKLİF/YAKLAŞIK MALİYET (%)	TEKLİF/ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
	C	SAV. VERMEDİ	66,25	84,93	92,79

**Tablo 8.** Üçüncü İhale; Kazanan Firmanın Değerlendirilmesi

FİRMA	NETİCE	TEKLİF/YAKLAŞIK MALİYET (%)	TEKLİF/ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
A	İŞİ ALAN FİRMA	76,14	97,60	106,64

Yapı Denetim Görevlilerinin Değerlendirmesi (İşi alan firma : A)

**Örnek 4.** 7 Adet geçerli teklif 2 adet aşırı düşük teklif (Tablo 9-11)

**Tablo 9.** Dördüncü İhale; Firmaların Değerlendirilmesi

FİRMA	İŞ DENEYİM TÜRÜ	İŞ DENEYİM TUTARI/TEKLİF	KULLANILMAMIŞ NAKİT KREDİ/TEKLİF	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ/TEKLİF
A	BİTİRME	10,18	8,00	8,00
B	BİTİRME	8,38	32,85	57,74
C	BİTİRME	10,41	1,80	1,80
D	DİPLOMA	18,65	5,21	5,21
E	DENETLEME	11,73	37,17	41,67
F	BİTİRME	19,52	5,67	5,67
G	BİTİRME	4,35	1,31	1,31

TEKLİFLERİN ORTALAMASI/YAKLAŞIK MALİYET %74.44  
AŞIRI DÜŞÜK TEKLİF SINIRI/YAKLAŞIK MALİYET : %69.30

İŞ KALİTESİ : İYİ  
PROJE PERFORMANSI : ORTA

**Tablo 10.** Dördüncü İhale; Aşırı Düşük Tekliflerin Değerlendirilmesi

AŞIRI DÜŞÜK TEKLİF VEREN FİRMALAR	FİRMA	NETİCE	TEKLİF/YAKLAŞIK MALİYET (%)	TEKLİF/ORTALAMA MA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
	D	SAV. VERMEDİ		57,46	77,18
G	SAV. VERMEDİ		68,53	92,06	98,89

**Tablo 11.** Dördüncü İhale; Kazanan Firmanın Değerlendirilmesi

FİRMA	NETİCE	TEKLİF/YAKLAŞIK MALİYET (%)	TEKLİF/ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
A	İŞİ ALAN FİRMA	74.81	100.50	107.96

Yapı Denetim Görevlilerinin Değerlendirmesi (İşi alan firma : A)

**Örnek 5.** 6 Adet Geçerli Teklif 2 Adet Aşırı Düşük Teklif (Tablo 12-14)

**Tablo 12.** Beşinci İhale; Firmaların Değerlendirilmesi

FİRMA	İŞ DENEYİM TÜRÜ	İŞ DENEYİM TUTARI/TEKLİF	KULLANILMAMIŞ NAKİT KREDİ/TEKLİF	KULLANILMAMIŞ TEMİNAT MEKTUBU KREDİSİ/TEKLİF
A	BİTİRME	19,80	62,72	70,31
B	BİTİRME	15,91	12,50	12,50
C	DENETLEME	20,58	10,20	10,20
D	BİTİRME	19,00	3,28	3,28
E	DİPLOMA	15,37	4,29	0,43
F	BİTİRME	13,16	51,59	90,66

TEKLİFLERİN ORTALAMASI/YAKLAŞIK MALİYET % 80.85  
AŞIRI DÜŞÜK TEKLİF SINIRI/YAKLAŞIK MALİYET : % 72.80

İŞ KALİTESİ : ÇOK İYİ  
PROJE PERFORMANSI : MÜKEMMEL

**Tablo 13.** Beşinci İhale; Aşırı Düşük Tekliflerin Değerlendirilmesi

AŞIRI DÜŞÜK TEKLİF VEREN FİRMALAR	FİRMA	NETİCE Komisyon Değerleri.	TEKLİF/ YAKLAŞIK MALİYET (%)	TEKLİF/ ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
	C	KABUL EDİLMEDİ - 3	70,15	86,77	96,36
D	KABUL EDİLMEDİ - 6	72,78	90,01	99,97	

**Tablo 14.** Beşinci İhale; Kazanan Firmanın Değerlendirilmesi

FİRMA	NETİCE	TEKLİF/ YAKLAŞIK MALİYET (%)	TEKLİF/ ORTALAMA TEKLİF (%)	TEKLİF/AŞIRI DÜŞÜK SINIR DEĞER (%)
A	İŞİ ALAN FİRMA	76,36	94,44	104,89

Yapı Denetim Görevlilerinin Değerlendirmesi (İşi alan firma : A)

### İncelenen İhalelerin Değerlendirilmesi

1. İncelenen ihalelerde genel olarak tekliflerin aritmetik ortalamasının yaklaşık maliyete oranı %80 oranında gerçekleşmiştir.
2. İhaleye katılım az olduğu takdirde rekabetin sağlanamaması riski söz konusudur.
3. İstekli sayısı arttıkça Aşırı Düşük Teklif verilmesi olasılığı bu duruma paralel olarak artmaktadır.
4. İsteklilerin ihalelerde değerlendirme dışı kalmalarına sebebiyet veren eksiklikler incelendiğinde, İdari şartnamede yapılacak düzenlemelerle bu durumun önüne geçilebileceği görülmüştür.
5. Aşırı Düşük Tekliflerde, teklif rakamı Aşırı Düşük sınır değerinden uzaklaştıkça savunma verme oranı ve verilen savunmaların kabul edilme oranının düştüğü altı çizilmesi gereken bir realitedir.
6. Aşırı Düşük teklif sınırına çok yakın (binde mertebesinde) aşırı düşük tekliflerinde değerlendirme dışı bırakılabileceği tespit edilmiştir.
7. İş deneyim belgesi yerine İş denetleme sunan veya iş deneyim belgesi yerine ihalelere katılımda diplomalarını kullanan isteklilerin teklifleri aşırı düşük sınır değerinin altında kaldığında, sınır değerden uzakta oldukları, savunma vermedikleri savunma verdiklerinde de kabul edilme oranı düşük olduğu tespiti önemlidir.
8. İş deneyim belgesi yerine İş denetleme ve diploma kullanan firmaların firma deneyimine sahip olmadıkları düşünülmektedir.
9. Ekonomik olarak güçlü ve yeterli iş deneyimine sahip firmaların aşırı düşük teklif savunmaları iyi hazırlanmakta ve komisyonca kabule dilmektedir.
10. Yapı Denetim Görevlilerinin firmaların iş kalitesi ve iş performansı değerlendirme ekonomik olarak güçlü firmaların aşırı düşük teklif ile iş alsalar bile kaliteli iş yaptıklarını göstermiştir

### Sonuç ve Değerlendirme

İncelenen ihalelerle ilgili aşağıdaki hususların mevzuatta yer almasının yararlı olacağı değerlendirilmektedir.

1. Yapılan çalışma sonucu Aşırı Düşük Tekliflerin komisyonlarca incelenme aşamasında, isteklilerin teklif bileşenleri ile ilgili belgeye dayalı yazılı açıklamalarının yanı sıra aşağıdaki hususlarda dikkate alınmalıdır.
  - a. Teklifin aşırı düşük teklif sınırına uzaklığı yakınlığı
  - b. Firma deneyimi
  - c. İsteklinin Ekonomik gücü
  - d. İsteklilerin Daha önceki işlerde gösterdiği performans
  - e. Yıllık ortalama yapım işi gelirleri
2. Aşırı Düşük tekliflerin değerlendirilmesi amacıyla yukarıdaki bilgiler doğrultusunda bir karar destek modeli oluşturulması, Aşırı Düşük Tekliflerle ilgili komisyonların karar vermelerine yardımcı olacaktır.
3. İş deneyim belgesi olarak diploma sunan isteklilerin iş deneyim belgeleri tam olarak değerlendirilmemelidir. Bu tür iş deneyim belgeleri (1/5) veya KİK'ce uygun görülen bir katsayı ile çarpılarak dikkate alınmalıdır.
4. Rekabetin sağlanması amacıyla çok sayıda firmanın ihalelere katılımı sağlanmalıdır.

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# KAMU KESİMİ AÇIKLARININ EKONOMİK KONJONKTÜRE ETKİLERİNİN VAR MODELLERİ İLE ÇOK YÖNLÜ ANALİZİ: TÜRKİYE UYGULAMASI (1998-2009)

## MULTIFACETED ANALYSIS WITH VAR (VECTOR AUTOREGRESSİVE MODELS) MODELS ON IMPACTS OF PUBLIC DEFICITS ON ECONOMIC CONJUNCTURE: APPLICATION IN TURKEY (1998-2009)

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### Özet

Türkiye ekonomisi 1990'lı yıllardan bu yana, sürdürülemez iç borç ve kamu kesimi bütçe açıkları gibi ekonomideki yapısal sorunlarla mücadele etmektedir. Söz konusu yıllarda ülkeyi derinden etkileyen ilk kriz, Körfez Savaşı'nın ardından yaşanan 1994 krizidir. Arkasından Kasım 2000 ve Şubat 2001 krizleriyle birlikte ülke ekonomisi derin yaralar almıştır. Başta yüksek enflasyon olmak üzere aşırı oynak döviz kuru, yüksek faiz oranları gibi ekonomik istikrarsızların temel nedenleri arasında kamu kesimi açıkları gösterilmektedir.

Bu çerçevede hazırlanan çalışma ile Türkiye'de iç ve dış şokların, ekonomiye etkilerinin; kamu bütçe dengesine etkilerinin yönü ve boyutunun ekonometrik olarak modellenmesi ve iktisat politikası yapımalarına katkıda bulunmak hedeflenmiştir. Çalışma bu bağlamda; Türkiye'de cari açık/GSYH, bütçe açığı/GSYH, dış ticaret hadleri, reel döviz kuru, GSYH, devletin nihai tüketim harcamaları değişkenlerinin ekonomiye doğrudan ve dolaylı etkilerini VAR modelleri ile açıklamaya çalışmaktadır. Uygulama sonuçları; kamu kesimi dengesine yön verecek maliye ve para politikalarının, belirlenen hedeflere ulaşması için makroekonomik değişkenlerin doğru zamanda ve doğru biçimde uygulanmasına dair önemli ipuçları sunmaktadır.

**Anahtar Kelimeler:** Kamu Açıkları, VAR Modeller, Ekonomik Konjunktur, Etki-Tepki, Varyans Ayrıştırma

### Abstract

Since 1990s, Turkish economy has been fighting against structural problems in economy such as unsustainable internal debt and public deficits. First crisis having deep impact on the country during these years was crisis in 1994 following Gulf War. Subsequently, economy of the country was inflicted deep wounds with crisis on November 2000 and February 2001. Public deficits are shown as one of the main reasons of economic instabilities, particularly high inflation, too fluctuant exchange rate and high interest rates,

With the study designed within the aforesaid framework, the objective is to create economic model of impacts of internal and external shocks in Turkey on economics; direction and extent of such impacts and to provide contribution to makers of economic policy. In this context, this study tries to explain direct and indirect impacts of final consumption expenditures of the state, current deficit in Turkey/GNP, budget deficit/GNP, international terms of trade, real currency rates, GNP by using VAR models. Results of application provide substantial clues on application of macroeconomic variables in the right and timely manner in order to ensure that economic and monetary policies giving direction to public balance achieve the predetermined goals.

**Keywords:** Public deficit, VAR Models, Economic Conjuncture, Impulse-Response, Variance Decomposition

### 1.Giriş

Türkiye'de ard arda yaşanan ekonomik krizler ve uygulamaya konulan iktisadi politikaların önemli bir kısmını bütçe açıklarının kontrol altına alınması oluşturmaktadır. Bütçe açıkları; enflasyon, döviz kurları, cari açıklar, kamu harcamaları gibi birçok makro ekonomik değişken üzerinde negatif etkilere sahiptir. Ekonomideki negatif etkiler ise istikrarsızlıkların temelini oluşturmaktadır. Ekonomik istikrarsızlığın temel nedenlerinden biri olan bütçe açıkları, gelişmekte olan ülkelerde gelişmiş ülkelere nazaran, yapısal bazı sorunlar nedeniyle kronik hale gelebilmektedir. Bütçe açığı olgusu, finansman yöntemleri bakımından ülkeden ülkeye değişmektedir. Bu değişim ise makro ekonomik ilişkileri ve piyasalardaki koordinasyonu negatif yönde etkilemekte ve açıkların ekonomiye yayılmasında etkili olmaktadır (Egeli, 1999: 293),(Eun ve Resnick, 2004: 73),(Gartner, 2003: 15).

Bu çalışmada, makroekonomik değişkenlerin konjunktur üzerine etkileri ve bu etkilerin hangisinin ekonomiyi derinden etkilediğini araştırmak amaçlanmaktadır. Çalışmada ayrıca yapısal VAR modelleri aracılığıyla ekonomide gözlenemeyen yapısal şokların uzun dönem etkilerini ayrıntılı olarak değerlendirmek amaçlanmaktadır. Bu amaçla seçilen değişkenler; dış ticaret haddi (DTH), gayri safi yurt içi hasıla (GSYH), cari açık/GSYH oranı(CAGSYH), bütçe açığı/GSYH oranı (BAGSYH), reel döviz kuru(REDOV), devletin nihai tüketim harcamaları(DHAR)dır. Reel efektif döviz kuru 1995 yılı bazlı reel efektif döviz kuru endeksini temsil etmektedir. GSYH ve devletin nihai tüketim harcamaları değişkenleri ise 1998 bazlı olarak alınmıştır.

Bu konudaki ilk çalışma, S.Beveridge ve C.Nelson (1981) tarafından yapılmıştır. Yapılan çalışmada makroekonomik değişkenlerin konjunktur üzerine etkileri incelenmiştir. Daha sonraki dönemde yapısal VAR modellerini kullanarak; O.Blanchard ve D.Quah (1989), J.Gali (1999), A.Alexius ve M.Carlsson (2002), N.R.Francis , M.T. Owyang ve A.T.

Theodorou (2003) yapılan çalışmalar dikkati çekmektedir. Ayrıca, Domar (1944) ve Sargent ve Wallace(1981), Barsky, Mankiw ve Zeldes (1986), Bernheim (1987), Blanchard ve diğerleri (1990), Blejer, Cheasty (1991), Becker (1997), Romer (2001) çalışmaları ise kamu açıklarının olumsuz sonuçları ile ilgili olarak farklı görüşler ortaya atmışlardır.

## 2. Metodoloji

### 2.1. VAR Modellerinin Genel Özellikleri

VAR modellerinin temelleri; Sims'ın 1980 yılında yayınladığı çalışmasıyla, çok denklemlili modelleri ve yapısal ekonometrik modelleri eleştirisiyle başlamıştır. VAR modelleri, seçilen bütün değişkenleri birlikte ele alarak, sistemi bir bütün olarak ele alır. Değişkenler arası ilişkiler hakkında, önceden bir kısıt konulmaz. Böylelikle, araştırmacılar; model kurma aşamasında önceden yapmak zorunda oldukları varsayımların olumsuz etkilerini önemli ölçüde ortadan kaldırmış olur.

VAR modellerini avantajları şu şekilde sıralanabilir;

- Değişkenler arasında içsel ve dışsal ayırımının olmaması,
- Modellerde, belirli bir iktisat teorisine gerek olmaması,
- Modellerde belirlenen bir kısıtlayıcı yapının söz konusu olmaması,

şeklinde sıralanabilir.

VAR modellerinde; bir değişkenin cari değeriyle, modeldeki tüm değişkenlerin gecikmeli değerleri arasında regresyon denklemi tahmin edilir. Modelin matris formunda gösterimi şu şekildedir;

$$Y_t = \sum_{i=1}^k A_i Y_{t-i} + \varepsilon_t$$

Yukardaki  $Y_t$  matrisi; modelde yer alan değişkenlerin cari değerlerine ait sütun vektörüdür.  $A$  matrisi ise bütün elemanları

sıfırdan farklı olan katsayılar matrisidir.  $Y_{t-i}$  matrisi, modeldeki değişkenlerin gecikmeli değerlerinin yer aldığı  $z \times n$  boyutunda bir matrisi ifade etmektedir.  $\varepsilon_t$ , rassal hataları gösteren sütun vektörüdür. (Holden vd., 1992: 70-71, (Darnel, 1990: 113-114), (Kumar vd., 1995:365-366), (Killian, 1998:219), (Darnel, 1990: 121).

### 2.2. Etki-Tepki Analizi (Impulse- Response)

VAR modellerinde IRF analizi; makroekonomik araştırmalarda önemli rol oynaması nedeni ile ekonomik değişkenler arası ilişkileri inceleyen analiz yöntemlerinden biri haline gelmiştir. IRF analizi, VAR modelinde yer alan herhangi bir değişkende meydana gelen bir şok olduğunda, değişkenlerin bu şoka tepkilerini göstermektedir.

VAR modellerinden elde edilen etki-tepki fonksiyonları; sistem içindeki değişkenlerin herhangi birinde meydana gelen bir şokun, sistemdeki diğer değişkenleri nasıl etkilediklerini analiz etmek için kullanılır. Sistemdeki herhangi bir değişkene verilecek şok karşısında, hem ilgili değişkenin hem de diğer değişkenlerin verecekleri tepkiler ölçülmektedir. IRF katsayıları, VAR modelinin katsayılarından hareketle elde edilmektedir. (Lutkepohl, 1990).

### 2.3. Varyans Ayrıştırması (Variance Decomposition)

Varyans ayrıştırması VD; değişkenlerin kendilerinde ve diğer değişkenlerde meydana gelen şokların kaynaklarını yüzde olarak ifade eder. Diğer bir ifadeyle VD, bir değişkene ait tahmin edilen hata terimi varyansının diğer değişkenler tarafından açıklanma yüzdesini ifade eder. Ayrıca değişkenler arası nedensellik ilişkilerinin derecesi hakkında da bilgi verir. Sistemde yer alan değişkenlerin herhangi birinde meydana gelecek olan bir değişimin yüzde kaçının kendisinden, yüzde kaçının diğer değişkenlerden kaynaklandığını gösterir.

## 3. Bulgular

Tablo.1. Değişkenlerin Durağanlıklarının İncelenmesi

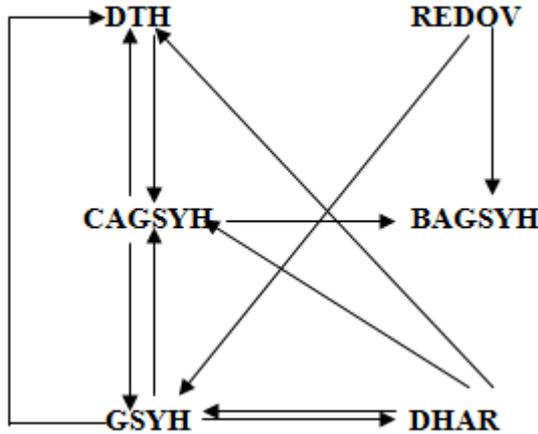
Değişken	Düzy/Birinci Fark	Augmented Dickey Fuller(ADF) Test İstatistiği		Philips Perron(PP) Test İstatistiği		Sonuç
		Sabit	Sabit+Trend	Sabit	Sabit+Trend	
BAGSYH	Düzy	-2.165496(1)**	-4.318237(0)	-3.199001(2)**	-4.318237(0)	I(1)
	Birinci Fark	-10.14430(0)	-10.03485(0)	-24.04263(4)	-25.47381(4)	
CAGSYH	Düzy	-2.624132(4)**	-2.849721(4)	-3.402881(4)**	-4.414059(4)	I(1)
	Birinci Fark	-7.749827(2)	-7.843725(2)	-13.23912(20)	-13.69858(19)	
REDOV	Düzy	-1.791067(0)**	-3.709965(1)**	-1.653600(1)**	-3.709026(1)**	I(1)
	Birinci Fark	-8.397049(0)	-8.300589(0)	-10.40957(8)	-10.25542(8)	
GSYH	Düzy	-1.393039(4)**	-2.250515(4)**	-2.337873(4)**	-4.681951(23)	I(1)
	Birinci Fark	-8.571562(2)	-8.461079(2)	-11.90159(11)	-11.97236(11)	

DTH	Düzyey	-1.783379(0)**	-2.743698(0)**	-1.653600(1)**	-3.709026(1)**	I(1)
	Birinci Fark	-5.265284(1)	-5.430833(1)	-5.019834(11)	-6.634214(19)	
DHAR	Düzyey	-0.730181(3)**	-1.170687(3)**	-5.625133(2)**	-10.98863(18)	I(1)
	Birinci Fark	-37.66358(2)	-37.73546(2)	-31.41569(10)	-30.66280(10)	

Not:ADF testinde parantez içindeki değerler, Schwarz Bilgi Kriterine göre seçilen gecikme uzunluklarıdır.PP tetstinde optimal gecikme uzunluğu, Bartlett kernel(default) spectral estimation yöntemi ve Newey-West Bandwidth(automatic selection) kriterlerinden yararlanılmıştır. \*\* işareti, %1 ve %5 düzeyinde  $H_0$  hipotezinin kabulünü ifade etmektedir.

Tablo.1, ADF ve PP birim kök test sonuçlarını göstermektedir. ADF ve PP testi sonuçlarına göre, BAGSYH, CAGSYH, DTH, DHAR REDOV ve GSYH değişkenleri, birinci farkları alındığında durağan hale geldikleri için bütünleşme derecesi I(1) bulunmuştur.

**Şekil 1.Dört Gecikme İçin Granger Nedensellik Testi Sonuçlarına Göre Değişkenler Arasındaki Nedenselliğin Yönleri**



Şekil 1'e bakıldığında, devletin nihai tüketim harcamalarının, cari açıkları etkilediği açıkça görülmektedir ( $DHAR \Rightarrow CAGSYH$ ). Kamu harcamalarındaki artış, enflasyonu yükselterek ticarete konu olan malların rekabet gücünü azaltmak yoluyla cari açıkları artırmaktadır. Bununla birlikte devletin nihai tüketim harcamaları; GSYH ve dış ticaret hadlerinin nedeni teşkil etmektedir ( $DHAR \Rightarrow GSYH, DTH$ ). Yani, kamu harcamalarında meydana gelen bir artış, milli gelirden yükselişe neden olmaktadır. Aynı şekilde; reel döviz kuru, bütçe açıkları ve GSYH değişkeninin nedenini oluşturmaktadır ( $REDOV \Rightarrow BAGSYH, GSYH$ ).

**3.2.Johansen Eşbütünleşme Testi Sonuçları**

**Tablo 2. Bütçe Açıkları/GSYH, Cari açık/GSYH, Devletin Nihai Tüketim Harcamaları, Dış Ticaret Haddi, Reel Döviz Kuru, GSYH Değişkenleri İçin İz (Trace) Testi Sonuçları**

$H_0$	$H_1$	Özdeğer (Eigenvalue)	İz Test İstatistiği (Trace Statistic)	%5 Kritik Değer
$r=0$	$r \geq 1$	0.548678	102.0568	83.93712
$r \leq 1$	$r \geq 2$	0.529182	67.05151	60.06141
$r \leq 2$	$r \geq 3$	0.301972	33.90700	40.17493
$r \leq 3$	$r \geq 4$	0.257853	18.08916	24.27596
$r \leq 4$	$r \geq 5$	0.070998	4.968029	12.32090
$r \leq 5$	$r \geq 6$	0.038505	1.727683	4.129906

\*Gecikme sayısı AIC'e göre 2 alınmıştır.

**Tablo 3. Bütçe Açıkları/GSYH, Cari açık/GSYH, Devletin Nihai Tüketim Harcamaları, Dış Ticaret Haddi, Reel Döviz Kuru, GSYH Değişkenleri İçin Maksimum Özdeğer (Maximum Eigenvalue) Testi Sonuçları**

$H_0$	$H_1$	Özdeğer (Eigenvalue)	Max. Özdeğer İstatistiği (Max. Eigenvalue)	%5 Kritik Değer
$r=0$	$r=1$	0.548678	35.00526	36.63019
$r \leq 1$	$r=2$	0.529182	33.14452	30.43961
$r \leq 2$	$r=3$	0.301972	15.81784	24.15921
$r \leq 3$	$r=4$	0.257853	13.12113	17.79730
$r \leq 4$	$r=5$	0.070998	3.240346	11.22480
$r \leq 5$	$r=6$	0.038505	1.727683	4.129906

\*Gecikme sayısı AIC'e göre 2 alınmıştır.

Tablo.2 ve Tablo.3'teki sonuçlardan görüldüğü gibi iz test istatistiği rakamları, %5 anlam düzeyinde kritik değerden büyük olduğu için en çok  $r=0$  ve ( $r \leq 1$ ) tane eşbütünleşme ilişkisi olduğunu ileri süren boş hipotezler reddedilmiştir. Buna karşılık  $r \leq 2$  bütünleşme ilişkisi olduğunu iddia eden boş hipotez reddedilememiştir. Yani değişkenler arasında 2 tane

eşbütünlük ilişkisi vardır. Maksimum özdeğer istatistiği rakamlarına göre ise değişkenler arasında hiç bir eşbütünlük ilişkisi bulunamamıştır. Bu sonuçlara göre; iz test istatistiği değerleri eşbütünlük vektörlerin önemli olduğunu gösterdiği için seriler arasında uzun dönemli ilişkinin olduğu varsayılabilir.

### 3.3.Varyans Ayrıştırma(Variance Decomposition) Analizi Sonuçlarının Değerlendirilmesi

Tablo.4.Varyans Ayrıştırma ve Etki-Tepki Analizi Sonuçları

DCAGSYH için Varyans Ayrıştırma:						
Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	100.0000	0.000000	0.000000	0.000000	0.000000	0.000000
2	90.76208	2.928812	0.093540	0.091276	0.439638	5.684656
3	85.98788	4.405488	0.764449	0.115659	0.464487	8.262038
4	84.37925	5.034003	0.748179	0.115818	0.924339	8.798408
5	83.80831	5.198760	0.743021	0.115151	1.202359	8.932396
6	83.53602	5.292937	0.741466	0.114199	1.265006	9.050368
7	83.36115	5.359715	0.738572	0.113939	1.275554	9.151066
8	83.25446	5.401627	0.737180	0.113737	1.284798	9.208200
9	83.19785	5.423326	0.736310	0.113602	1.293568	9.235346
10	83.16813	5.434449	0.735820	0.113524	1.298971	9.249101
DBAGSYH için Varyans Ayrıştırma:						
Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	1.626031	98.37397	0.000000	0.000000	0.000000	0.000000
2	8.493282	83.34452	0.015852	0.063335	6.553067	1.529950
3	8.374363	81.59934	0.187524	0.062418	8.268824	1.507533
4	8.353762	81.52178	0.204834	0.066528	8.337881	1.515218
5	8.361352	81.50117	0.205283	0.069194	8.334571	1.528433
6	8.377775	81.48224	0.207239	0.069511	8.332611	1.530627
7	8.381384	81.47846	0.207246	0.069509	8.332831	1.530574
8	8.381413	81.47777	0.207324	0.069514	8.333124	1.530855
9	8.381403	81.47768	0.207345	0.069514	8.333111	1.530946
10	8.381439	81.47760	0.207345	0.069515	8.333140	1.530962
DDTH için Varyans Ayrıştırma:						
Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	2.021616	1.306170	96.67221	0.000000	0.000000	0.000000
2	1.650046	1.183420	70.52740	0.851699	24.18890	1.598538
3	7.827145	1.177456	65.97746	0.805014	22.71123	1.501695
4	7.912513	1.288014	65.52607	0.810941	22.67839	1.784072
5	7.884564	1.361326	65.34518	0.812804	22.64199	1.954129
6	7.878906	1.393530	65.29068	0.812495	22.64765	1.976738
7	7.899575	1.398574	65.25404	0.812258	22.65602	1.979534
8	7.916898	1.401380	65.23409	0.812002	22.65246	1.983173
9	7.922065	1.403782	65.22520	0.811915	22.64951	1.987531
10	7.923260	1.405485	65.22105	0.811867	22.64823	1.990111
DDHAR için Varyans Ayrıştırma:						
Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	0.969852	0.001084	2.776292	96.25277	0.000000	0.000000
2	52.79647	0.340410	1.664426	9.362724	35.53049	0.305477
3	62.85997	0.343837	3.620004	6.033383	26.27752	0.865286
4	62.95798	1.150176	3.263359	5.436574	23.60516	3.586745
5	61.33974	2.139089	3.205989	5.231746	22.68404	5.399405
6	60.62561	2.640657	3.154216	5.129558	22.41033	6.039620
7	60.37232	2.856437	3.117218	5.065862	22.31662	6.271543
8	60.27688	2.967468	3.095572	5.028670	22.22129	6.410121
9	60.20691	3.037080	3.083537	5.009165	22.15748	6.505820
10	60.15897	3.078859	3.077225	4.998840	22.12413	6.561968
DGSYH için Varyans Ayrıştırma:						
Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	40.62572	1.446494	1.967013	1.040895	54.91987	0.000000
2	37.79438	1.494451	3.452781	1.413803	54.65437	1.190213

3	36.11358	1.645179	5.859884	1.457884	52.48966	2.433819
4	37.48638	1.690162	5.772025	1.425579	51.24777	2.378085
5	37.35192	1.702844	5.761681	1.428839	51.25414	2.500578
6	37.32190	1.723956	5.783687	1.427520	51.19717	2.545761
7	37.31347	1.729339	5.782379	1.427559	51.19923	2.548027
8	37.31679	1.729774	5.782139	1.427374	51.19610	2.547826
9	37.32003	1.730282	5.781802	1.427242	51.19187	2.548782
10	37.32005	1.730956	5.781617	1.427203	51.19004	2.550126

## DREDOV için Varyans Ayrıştırma:

Dönem	DCAGSYH	DBAGSYH	DDTH	DDHAR	DGSYH	DREDOV
1	9.142542	3.259122	6.541499	4.581673	6.510450	69.96471
2	8.806182	4.587858	6.140358	4.314792	6.332209	69.81860
3	8.958235	5.161198	6.213766	4.202410	6.235080	69.22931
4	9.436727	5.398243	6.126134	4.132053	6.566870	68.33997
5	9.975451	5.487805	6.059701	4.084682	6.620068	67.77229
6	10.19078	5.564893	6.024842	4.060991	6.609998	67.54850
7	10.26894	5.617884	6.007371	4.049017	6.602733	67.45406
8	10.30790	5.648062	5.997714	4.042485	6.604220	67.39962
9	10.33408	5.663354	5.992166	4.038743	6.606635	67.36502
10	10.35006	5.671551	5.989033	4.036625	6.607601	67.34513

Tablo.4'e göre; Bu sonuçlara göre; DBAGSYH değişkenindeki değişimin %98'i ilk dönemde kendi gecikmeleriyle açıklanabilirken, bu oran daha sonraki dönemlerde ise %81'e kadar gerilemiştir. Örneğin üçüncü dönemde, DBAGSYH değişkenindeki değişimin %81'i kendi iç dinamikleriyle açıklanırken, % 8.37'si DCAGSYH'deki değişimler tarafından; % 8.26'sı DGSYH değişkenince; %1.50'si DREDOV; %0.18'i DDTH değişkenince; %0.06'sı DDHAR değişkenince açıklanmaktadır. Bununla birlikte, bir değişken; kendi iç dinamikleri tarafından açıklanabiliyorsa, bu değişken en ekzogen(dışsal) değişkendir. Burada ise en dışsal değişken DBAGSYH değişkeni olmakla beraber, kendisinden sonra en çok etkilendiği değişkenler ise; DCAGSYH ve DGSYH'dir.

DCAGSYH değişkeninde herhangi bir şok olması durumunda; ilk dönem değişkenin kendi değişimiyle %100 oranında açıklanmakta; bu oran sonraki dönemlerde %83'e kadar düşmektedir. 10 çeyrek dönem sonunda ise; Cari açık değişkenindeki değişimin %83'ü kendi gecikmeleriyle açıklanabilirken; %9.24'ü DREDOV değişkeni tarafından; %5.43'ü DBAGSYH değişkeni ile; %1.29'u DGSYH ile; %0.73'ü DDTH ile; %0.11'i DDHAR ile açıklanmaktadır. Cari açık değişkenindeki değişimin büyük bir kısmı kendi iç dinamikleri ile açıklanabilirken, kendinden sonra en çok etkilendiği değişkenler ise DREDOV ve DBAGSYH değişkenleridir.

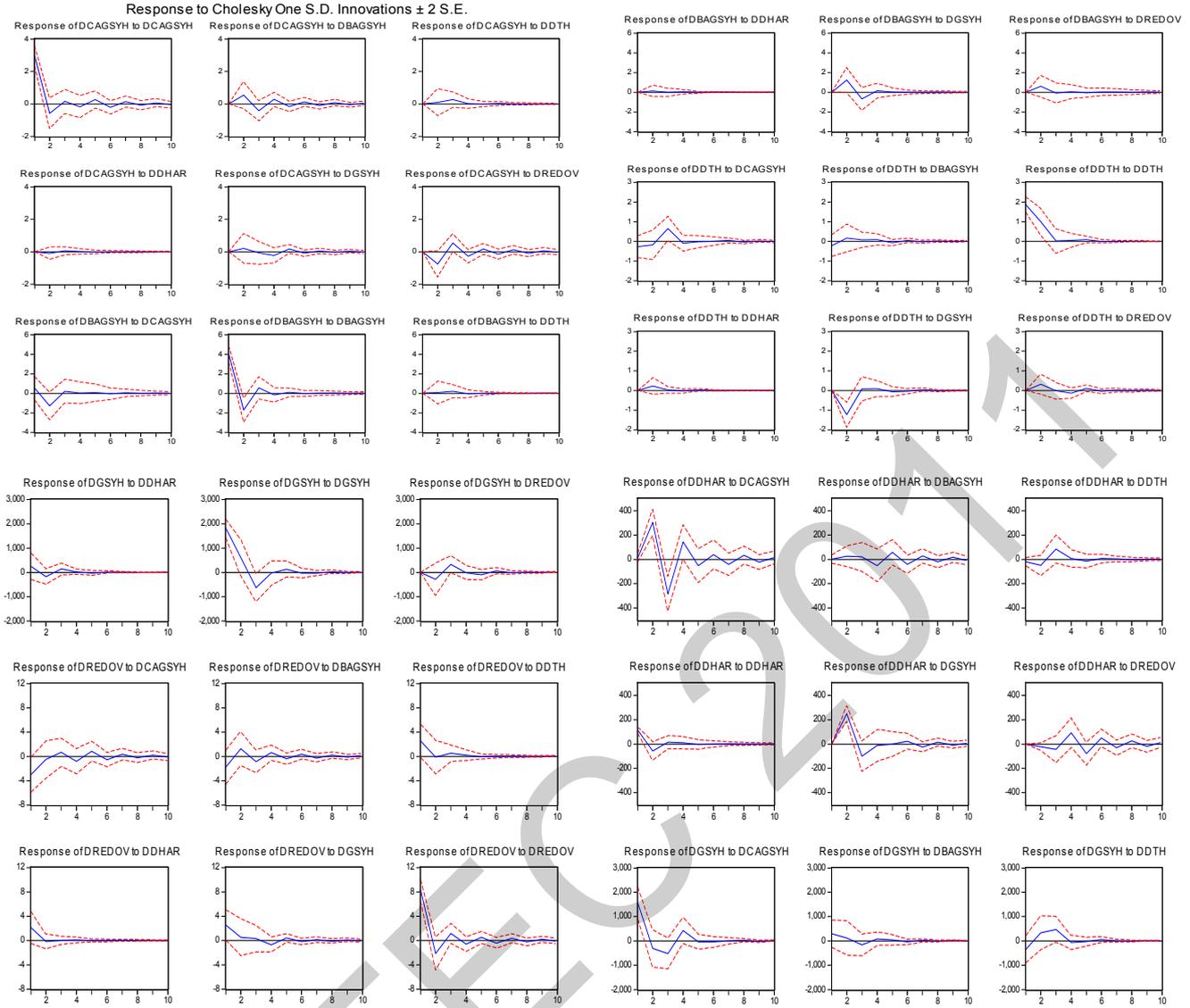
DGSYH değişkeninde herhangi bir şok olduğunda; ilk dönem %54'ü kendi gecikmeleriyle açıklanmakta daha sonraki dönemlerde ise bu oran %51'e kadar düşmektedir. 10 çeyrek dönem sonra ise; DGSYH değişkenindeki değişimin,%37'si DCAGSYH değişkenince, %1.73'ü DBAGSYH değişkeni ile, %5.78'i DDTH değişkeni tarafından, %1.42'si DDHAR ile, %51'i DGSYH'nin kendi iç dinamikleri ile %2.55'i ise DREDOV ile açıklanmaktadır. Kısaca; DGSYH değişkeninin kendinden sonra en fazla etkilendiği değişkenin, DCAGSYH değişkeni olduğu dikkati çekmektedir.

DREDOV değişkeninde bir şok söz konusu olduğunda; DREDOV değişkenindeki değişimi açıklayan en önemli değişkenin DCAGSYH değişkeni olduğu, DDHAR değişkeninin ise anlamlı bir etkisinin olmadığı görülmektedir. Reel döviz kurundaki dalgalanmaların %9'undan fazlasını DCAGSYH, ortalama %4'ünü ise DDHAR oluşturmaktadır. Diğer bir ifadeyle, DREDOV'unun kendi gecikmeleriyle açıklanma oranı dönemler boyunca azalmakta, DBAGSYH ve DCAGSYH, DGSYH değişkenlerinin etkisi ise artış göstermektedir. Bu sayısal sonuç ise bize bütçe açığının, bir ülkenin döviz açığının belirlenmesinde önemli rol oynadığının göstergesidir.

DDTH değişkeninde dalgalanmalar, 10 çeyrek dönem süresince, %96 oranından %65 oranına kadar azalan oranda, kendisinde gerçekleşen şoklar tarafından açıklanmaktadır. Kendisinden sonra en çok etkilendiği değişken; DGSYH ve DCAGSYH değişkenleridir. DGSYH'nın; dış ticaret haddi üzerinde, cari açıklara oranla daha büyük bir değişime neden olduğu anlaşılmaktadır. DDHAR değişkeninin zaman dilimi süresince yatay ve ortalama %0.80 oranında seyretmesi, dış ticaret haddi değişkeninin DDHAR değişkenindeki değişimi çok fazla etkilemediğini göstermektedir.

DDHAR değişkenindeki değişimin, ilk dönem %96, 10 çeyrek dönem sonunda ise %4'lük kısmı kendisindeki dalgalanmalar ile açıklanmaktadır. İkinci çeyrek dönemden itibaren ise açıklanma oranları DGSYH'nin %35'e ve DCAGSYH'nin %52'ye çıkarak açıklama oranları aniden artış göstermektedir. Yani DGSYH ve DCAGSYH'de meydana gelebilecek sapmalar DDHAR'daki sapmaların kendisinden sonraki en önemli nedenidir.

## Tablo.5.Etki-Tepki Analizi Sonuçları



Tablo.5'e göre, DBAGSYH değişkeninde bir standart sapma şok olduğunda; DCAGSYH ilk dönem tepki vermemiş, daha sonra artırıcı ve azaltıcı yönde tepkiler vermiştir. Genel olarak değerlendirildiğinde pozitif yönlü tepkiler vermiştir. Bu tepkilerin pozitif ve en yüksek seviyesi 2.çeyrek dönemde olmuştur. DGSYH değişkeninde bir dalgalanma olduğunda, DBAGSYH 2.çeyrek dönemde pozitif yönlü ve şiddetli tepkiler vermiştir. DCAGSYH değişkeninde bir standart sapma şok olduğunda; DBAGSYH değişkeninde ilk çeyrek dönem artış yönünde tepki vermiş, ikinci dönemde negatif, 3.dönemde tekrar pozitif yönde ve şiddetli tepki vermiştir. DDTH değişkeninde bir standart sapmalık şok olduğunda DCAGSYH değişkeninin 3.çeyrek dönem pozitif yönlü ve 0.266092 birim tepki vermiştir. DREDOV değişkenindeki bir standart sapma şoka; DCAGSYH değişkeni ise; 1.,3.,5.,7 ve 9.çeyrek dönemlerde anlamlı ve pozitif yönde tepki vermektedir. DDTH değişkeni ise bu söz konusu şoka, genel olarak negatif yönde tepki vermektedir. DDTH değişkeninde bir standart sapma şok olduğunda DGSYH değişkeni 3.çeyrek dönemde maksimum ve pozitif yönlü tepki vermiştir. DHAR değişkenine bir standart sapma şok uygulandığında; DBAGSYH ve DCAGSYH değişkenlerinin benzer sonuçlar verdikleri dikkati çekmektedir. DREDOV değişkenine DDHAR değişkeninin tepkisi ise; genel olarak negatif alanda ve istatistiki olarak anlamlıdır.

## 4.Sonuç ve Değerlendirme

Son derece hassas olan bütçe açıkları ekonomik değişkenindeki değişimler, şüphesiz diğer ekonomik değişkenleri de farklı biçimlerde etkileyecektir. Çünkü, ekonomideki bütün değişkenler, birbirleriyle etkileşim içerisinde. Burada sorgulanmak istenen, 1998-2009 yılları arasında Türkiye'de dış ödemeler dengesi üzerinde etkili olabilecek temel makroekonomi politikası aracı ne olmalıdır?, söz konusu değişkenler ekonomik konjonktürü ne yönde etkiler?, gelecekte ne gibi önlemler alınabilir? gibi sorulara cevap aranmıştır.

Etki-tepki analizi sonuçlarına göre; bütçe açıkları değişkeninde bir standart sapma şok olduğunda; cari açıklar pozitif yönde tepki vermiştir. GSYH değişkeninde bir şok olduğunda ise, bütçe açıkları pozitif ve anlamlı tepki vermiştir. Cari açıklarda bir dalgalanma olduğunda, bütçe açıkları dalgalı ve genel olarak pozitif yönde tepki vermiştir. Dış ticaret haddindeki şoka, cari açıklar pozitif yönde tepki vermiştir.Reel döviz kurunda bir değişim söz konusu olduğunda ise cari açıklar pozitif yönde, devlet harcamaları ise negatif yönde tepkiler vermiştir. Hiç şüphe yok ki; reel döviz kurunda meydana gelebilecek değişimler, Türkiye'nin uluslararası rekabet gücü bakımından önemli olduğu kadar; cari açık üzerinde de direkt etkiye sahiptir. Yani; TL'nin aşırı değerlendirilmesi, ihracatın görece fiyatlar bakımından rekabet gücünü azalttığından, dış ticaret dengesini; yani

diğer bir ifadeyle, cari açığı artırıcı yönde etkilemektedir. TL'nin değer kaybı ise, ithal malları üzerinden yurt içi fiyatlara yansiyacak enflasyon riskini içermektedir (Çalışkan Çavdar, 2010).

Varyans ayrıştırma analizi sonuçları değerlendirildiğinde ise; bütçe açıkları değişkeninin kendisinden sonra en çok etkilendiği değişkenler; GSYH ve cari açık değişkenleridir. Cari açık değişkeninin kendinden sonraki en çok etkilendiği değişkenler ise reel döviz kuru ve bütçe açıklarıdır. Reel döviz kuru değişkeninde bir şok söz konusu olduğunda; reel döviz kurundaki değişimi açıklayan en önemli değişkenin cari açık değişkeni olduğu dikkati çekmektedir. Bu sayısal sonuçtan ise; Türkiye'de cari açığın; döviz açığının belirlenmesinde kilit rol oynadığı ve karşılıklı bir etkileşimin söz konusu olduğu söylenebilir. Türkiye'de reel döviz kuru ve cari açık değişkenleri arasındaki bu söz konusu etkileşim; teknolojik verimliliğin dünya rekabet koşullarına uymaması; düşük karlar ile ihracatı sürdürme çabaları; ihracatın ithalata çok bağımlı oluşu gibi birçok yapısal faktöre bağlı olarak değişebilir. Ülkede ulusal paranın aşırı değerlenmesi; ithalatın ucuzlayıp, ihracatın pahalılaşmasına neden olduğundan, cari açığın artmasına neden olmaktadır. Cari açıklar nedeniyle, büyüme oranının düşmesi sonucunda ise bütçe açıkları artmaktadır. Dış ticaret haddi değişkeninde bir değişim olduğunda; kendisinden sonra en çok etkilendiği değişken GSYH ve cari açık değişkenleri olduğu görülmektedir. Türkiye'de dış ticaretin iyileşmesi ise; dış ticaret haddi değişkeninin eğilimine göre, ihracata yönelik sektörlerin hangi oranlarda kararlarında etkin olduğu ve ihracat stratejilerini ne ölçüde geliştirdiklerine sıkı sıkıya bağlıdır. Devletin nihai tüketim harcamalarındaki değişimin, büyük bir kısmı kendi iç dinamikleri tarafından açıklanmakla birlikte, kendinden sonra en fazla etkilendiği değişkenler ise GSYH ve cari açıklardır. Yani GSYH'da meydana gelebilecek sapmalar, devletin nihai tüketim harcamalarındaki sapmaların kendisinden sonraki en önemli nedenidir. Kısacası bu çalışmada kullanılan değişkenler, ekonomiye yön veren değişkenler olduğu için elde edilen sayısal bulguların değerlendirilmesi sonucunda, bulguların gelecek dönemlerde maliye ve iktisat politikalarına katkıda bulunacağı ve ekonomik konjonktüre yön veren bu değişkenlere farklı bir bakış açısı kazandıracığı düşünülmektedir.

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# KAPASİTELİ ARAÇ ROTALAMA PROBLEMİNDE GENEL DEĞİŞKEN KOMŞULUK ARAMA YAKLAŞIMININ UYGULAMASI

## GENERAL VARIABLE SEARCH METHOD FOR CAPACITATED VEHICLE ROUTING PROBLEM

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### ÖZET

Araç rotalama problemleri literatürde yoğun olarak incelenen bir konu olmuştur. NP-zor problem sınıfına dahil olan bu problemlerin klasik yöntemlerle çözülmesi çok uzun zaman almakta veya çözülememektedir. En iyiye yakın sonucu kısa sürede veren sezgisel yöntemler son yıllarda NP-zor problemlerin çözümünde geniş bir uygulama alanına sahip olmuştur. Bu çalışmada, 1997 yılında Mladenović ve Hansen tarafından geliştirilen, sistematik komşuluk değişimleri fikrini kullanan bir metasezgisel yöntem olan Değişken Komşuluk Arama, kapasiteli araç rotalama probleminde uygulanmıştır. Değişken Komşuluk Arama yaklaşımında kullanılan komşuluk yapıları büyük önem taşımaktadır. Bunun için alternatif komşuluk yapıları içerisinde en iyi sonuçları veren yapılar kullanılarak Genel Değişken Komşuluk Arama yöntemi hazırlanmıştır. Bulunan sonuçlar tablo halinde sunulmuştur.

### ABSTRACT

Vehicle routing problems have been studied extensively in the literature. These problems are included in the class of NP-hard problem, which takes a long time to solve or can not be solve by exact methods. Heuristic methods are frequently used to find a satisfactory solution which near best recent years. In this study, Variable Neighborhood Search metaheuristic method, developed in 1997 by Mladenovic and Hansen, that uses the idea of neighborhood changes systematically is applied to the capacitated vehicle routing problem. Neighborhood structures used in the variable neighborhood search approach are very important factor. So that, General Variable Neighbourhood Search method is prepared by using neighborhood structures which gives the best results of alternative. The results presented with the tables.

### 1. GİRİŞ

Bir algoritma bir problemi çözebilmek için iki önemli kaynağa ihtiyaç duymaktadır, bunlar zaman ve alandır. Bir algoritmanın zaman karmaşıklığı; n boyutlu bir problemi çözebilmek için ihtiyaç duyulan adım sayısıdır. Karmaşıklık genellikle “en kötü durum analizi” terimleri ile ifade edilmektedir. Eğer bir problemin çözülmesi için polinom zaman algoritması mevcut ise o problem “kolay” olarak adlandırılmaktadır. Aksi durumda (mevcut değilse) “zor” olarak adlandırılmaktadır (Talbi, 2009).

Bir problemin sonlu sayıda aşamada çözülüp çözülemeyeceği probleme yaklaşımda önemli bir konu olmuştur. Evrensel algoritmik modellerin 3 türü bulunmaktadır;

- Birinci türde; algoritma kavramı klasik olan hesaplama ve sayısal fonksiyonlar gibi matematiksel kavramlarla ilişkilendirilmektedir.
- İkinci türde; algoritmanın her ayrıık zamanda çok basit işlemleri yapan bir deterministik makine ile bağdaştırılmasıdır.
- Üçüncü türde; herhangi bir alfabede sözcüklerin değiştirilmesine dayalı kelime işlemcilerdir.

Bir problemin algoritmik çözümlerinin sınıflandırılmasında, yürütülmeleri için gerekli işlemlerin sayısı temel alınmaktadır. Bu ölçü “algoritmik karmaşıklık” olarak adlandırılmaktadır (Nabiyev, 2010).

Zor problemler, klasik yöntemlerle çözülmesi çok zor olan veya en iyi sonucun çok uzun sürede elde edilebildiği problemlerdir. Bu problemlerin çözümü için genellikle en iyi çözümü garanti etmeyen fakat en iyiye yakın çözümü bulmaya çalışan sezgisel yöntemler kullanılmaktadır.

Sezgiseller 2 başlık altında ele alınmaktadır; belirli (specific) sezgiseller ve metasezgiseller. Belirli sezgiseller belirli problem ve/veya olay için uygulanmaktadır. Metasezgiseller ise, hemen hemen her optimizasyon problemini çözmek için uygulanabilecek genel amaçlı algoritmalarıdır (Talbi, 2009).

Meta-sezgisel kelimesindeki sezgiselin İngilizcedeki karşılığı “heuristic”dir. “Heuristic”, bulmak, keşfetme anlamına gelen “heuriskein” kelimesinden türetilmiştir. “Meta” ise üst seviye anlamına gelmektedir. Temel sezgisel yöntemleri birleştirmeye çabalayan yeni yaklaşık yöntemler “metasezgiseller (metaheuristic)” olarak adlandırılmaktadır.<sup>1</sup>

### 2. ARAÇ ROTALAMA PROBLEMLERİ

Araç rotalama problemi; ilk olarak Dantzig ve Ramser tarafından 1959 yılında çalışılmasından itibaren 53 yıldır çalışılan bir konu olmuştur.

Araç rotalama üzerine yapılan çoğu literatür çalışması aşağıdaki özellikleri taşıyan problemlerle ilişkilidir (Caccetta ve Hill, 2001):

<sup>1</sup> [www.baskent.edu.tr/~ayyuce/END407%20Ders3a.pdf](http://www.baskent.edu.tr/~ayyuce/END407%20Ders3a.pdf), [Erişim tarihi:20 Nisan 2009]

Tek bir ürün, tek bir depodan, müşterilere bilinen taleplerle dağıtılmaktadır.

- i) Her müşterinin talebi bir araç tarafından sunulmaktadır.
- ii) Her araç aynı kapasiteye sahiptir ve tek bir tur yapmaktadır.
- iii) Her aracın katettiği toplam mesafede aracın belirli kapasitesi aşılamamaktadır.
- iv) Her müşteriye belirli bir zaman aralığında (penceresinde) hizmet sunulmalıdır.
- v) Amaç, tüm araçlar tarafından kat edilen toplam mesafeyi en küçükmektir.

Caccetta ve Hill'in belirttiği maddeler doğrultusunda, bir araç rotalama probleminin ele alınabilmesi için talep, uzaklık (maliyet), araç çeşit ve kapasitesi, zaman penceresi gibi bazı bilgilerin bilinmesi gerektiği ifade edilebilir.

Araç rotalama probleminin ana amacı malzeme dağıtım maliyetinin minimize edilmesidir. Araç rotalama problemi literatürde genellikle zaman pencereyi araç rotalama problemleri, kapasiteli araç rotalama problemleri, depo sayısına göre çok depolu veya tek depolu araç rotalama problemleri, talep yapısına göre stokastik veya deterministik talepli araç rotalama problemleri başlıkları altında ele alınmıştır (Pisinger ve Ropke, 2007). Araç rotalama problemi karmaşık yapıda ve çözümü uzun süren bir problem olduğundan çözümü için çoğunlukla sezgisel yöntemler kullanılmıştır.

Kapasiteli araç rotalama probleminde, aynı kapasiteye sahip araçlar bir depodan çıkmakta, n adet müşteriye uğramakta ve en kısa yolu katederek tekrar depoya dönüş yapmaktadır. Bu problemde her müşterinin belli bir talebi bulunmaktadır. Çalışmada kapasiteli araç rotalama problemi ele alınmıştır. Bu probleme ait matematiksel gösterim aşağıda yer almaktadır.

$$\text{Amaç fonksiyonu: } \min. \sum_{i=1}^n \sum_{j=1}^n d_{ij} \cdot X_{ij} \quad (1)$$

Kısıtlar:

$$\sum_{i,i \neq j} X_{ij} = 1 \quad (2)$$

$$\sum_{j,j \neq i} X_{ij} = 1 \quad (3)$$

$$\sum_i \sum_j D_i \cdot X_{ij} \leq Q \quad (4)$$

$$\sum_{j=1}^n X_{0j} = K \quad (5)$$

$$\sum_{i=1}^n X_{i0} = K \quad (6)$$

$$X_{ij} \in \{0,1\} \quad (7)$$

$d_{ij}$  : i ve j noktaları arası mesafe.

$X_{ij}$  : i den hemen sonra j noktasına gidilecekse 1; değilse 0'dır.

$Q$  : Araç kapasitesi.

$D_i$  : i. ilçenin toplam ürün talebidir.

$K$  : Araç sayısıdır.

$i$  : 0,1.....n

$j$  : 0,1.....n

Zor problemlerin çözümüne yönelik geliştirilen son meta-sezgisellerden birisi Değişken Komşuluk Arama yaklaşımıdır.

### 3. METODOLOJİ

Değişken Komşuluk Arama yaklaşımı çözülmesi zor olan karmaşık problemlerin çözümü için geliştirilmiş olan son metasezgisel yöntemlerden biridir. Bu yaklaşım ilk olarak N. Mladenović ve E. Hansen tarafından 1997 yılında geliştirilmiştir.

Değişken Komşuluk Arama yaklaşımı sistematik komşuluk değişimleri fikrini kullanmaktadır (Perez ve diğerleri, 2006).

Değişken Komşuluk Arama yaklaşımı, başlangıç noktasından yerel minimuma ulaşmada azalan (descent) metod olarak çalışmaktadır. Daha sonra bu çözümün önceden tanımlanmış farklı komşuluk serisi araştırılır. Her zaman, geçerli komşuluğa ait bir veya birkaç nokta yerel azalma metodunu çalıştırmak için başlangıç noktaları olarak kullanılır. Değişken Komşuluk Arama yaklaşımı diğer metasezgisellerden daha basit yollarla çok iyi çözümler sağlamaktadır (Perez ve diğerleri, 2006).

Diğer metasezgisellerden farklı olarak, temel Değişken Komşuluk Arama yaklaşımının planı ile yayılmalari basittir ve birkaç parametreye ihtiyaç duyar, hatta bazen hiçbiri gerekemeyebilir. Bu nedenle çok iyi çözümler sağlamasına ilave olarak, diğer metotlardan daha basit yollarla Değişken Komşuluk Arama yaklaşımının sebeplerinin daha yakından görülmesini sağlamaktadır. Basitliğine rağmen etkili olmayı sağlamaktadır. Değişken Komşuluk Arama yaklaşımı sistematik olarak aşağıdaki düşünceleri kullanmaktadır:

- Bir komşuluk yapısına göre lokal minimum olan, başka bir komşuluk yapısına göre de yerel minimum olmak zorunda değildir
- Bir global optimum tüm komşuluk yapılarına göre yerel optimumdur.

– Bir çok problem için yerel minimum, bir veya birkaç komşuluğa göre birbirlerine yakındır. Temel Değişken Komşuluk Arama algoritması Şekil 1’de gösterilmiştir.

**Başlangıçta** Komşuluk yapıları ( $N_k$ ) belirlenir,  $k=1, \dots, k_{maks}$   
Başlangıç çözümü  $x$  belirlenir  
Durdurma kriteri belirlenir

**Tekrarlanacak adımlar** durdurma kriteri gerçekleşene kadar;

1.  $k \leftarrow 1$  alınır
2.  $k = k_{maks}$  olana kadar şu adımlar **tekrarlanır**;  
  - (a) *Çalkalama (Silkeleme)*:  $x$  başlangıç çözümünün  $k$ 'ncinci komşuluğu içersinden rassal olarak  $x'$  noktası belirlenir ( $x' \in N_k(x)$ )
  - (b) *Yerel Arama*:  $x'$  başlangıç çözüm olarak alınır ve bazı yerel arama metodları uygulanır; elde edilen yerel optimum  $x''$  olarak atanır
  - (c) Eğer bulunan yerel optimum geçerli çözümden iyi ise  $x \leftarrow x''$

atayarak  $N_1$  yapısında ( $k \leftarrow 1$ ) aramaya devam edilir.  
Aksi halde  $k \leftarrow k+1$ ,  $k$ , 1 arttırılarak (a) ya dönülür.

Şekil 1. Temel Değişken Komşuluk Arama algoritması (Hansen ve Mladenoviç, 2001)

## 2.1. Değişken Komşuluk Arama Çeşitleri

Literatür taramasında karşılaşılan başlıca Değişken Komşuluk Arama çeşitleri şunlardır;

- ✓ Değişken Komşuluk Azalma
- ✓ İndirgenmiş Değişken Komşuluk Arama
- ✓ Genel Değişken Komşuluk Arama
- ✓ Değişken Komşuluk Ayırıştırma Arama
- ✓ Eğik Değişken Komşuluk Arama
- ✓ Paralel Değişken Komşuluk Arama

Bu başlık altında çalışmada ele alınan Genel Değişken Komşuluk Arama algoritması ile bu algoritmanın daha iyi anlaşılabilmesi için Değişken Komşuluk Azalma algoritması sunulmuştur.

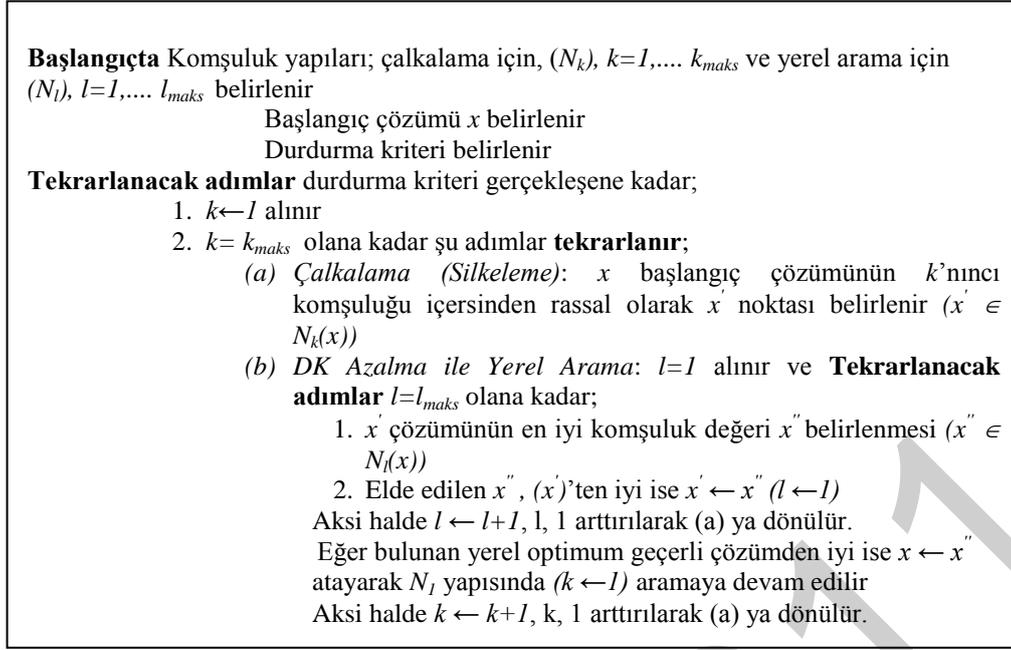
**Başlangıçta** Komşuluk yapıları ( $N_k$ ) belirlenir,  $k=1, \dots, k_{maks}$   
Başlangıç çözümü  $x$  belirlenir

**Tekrarlanacak adımlar** çözümde iyileşme elde edilmeyene kadar;

1.  $k \leftarrow 1$  alınır
2.  $k = k_{maks}$  olana kadar şu adımlar **tekrarlanır**;  
  - (a)  $x'$  olarak başlangıç çözümünün en iyi komşuluk değerini belirlenmesi ( $x' \in N_k(x)$ )
  - (b) Elde edilen  $x'$  çözümü başlangıç çözümü  $x$ 'ten iyi ise  $x \leftarrow x'$

atayarak  $N_1$  yapısında ( $k \leftarrow 1$ ) aramaya devam edilir.  
Aksi halde  $k \leftarrow k+1$ ,  $k$ , 1 arttırılarak (a) ya dönülür.

Şekil 2. Değişken Komşuluk Azalma algoritması (Hansen ve Mladenoviç, 2001)



Şekil 3. Genel Değişken Komşuluk Arama algoritması (Talbi, 2009)

### 3. UYGULAMA

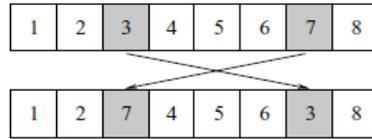
Değişken Komşuluk Arama yaklaşımında komşuluk yapıları ve başlangıç çözüm metodunun belirlenmesi önemli bir kriterdir. Bu çalışmada Süpürme Algoritması ile başlangıç çözümü elde edilmiştir.

İki aşamalı çözüm yöntemlerinden olan Süpürme Algoritması, 1974 yılında Gillet ve Miller tarafından geliştirilmiştir (Toth ve Vigo, 2002). Bu yöntemin ilk aşamasında yaklaşık rotalar belirlenmekte ve ikinci aşamasında rotaları geliştirmek için adaptasyon yapılmaktadır. Müşterilerin tümünden gelmiş olan taleplerin toplamının araç kapasitesine oranlanması ile minimum gereken araç sayısı bulunmaktadır (tam sayı olarak alınır) (Sule, 2001). Araç rotalama probleminin düzlemsel (planar) mesafesini uygulamaktadır. Uygun rotalar, deponun merkez alındığı bir doğrunun döndürülmesiyle oluşturulmaktadır. Bu döndürme esnasında, araç kapasite veya mesafe kısıtı aşılanaya kadar derece derece müşterilerin eklenmesiyle oluşturulmaktadır. Kısıt aşıldığı zaman yeni rotaya geçiş yapılmaktadır (Cordeu ve diğerleri, 2002). Uygulamada makrolar kullanılarak Microsoft Excell'de hazırlanmış olan programla hazırlanmıştır.

Genel Değişken Komşuluk Arama'da kullanılan komşuluk yapıları ise şu şekildedir;

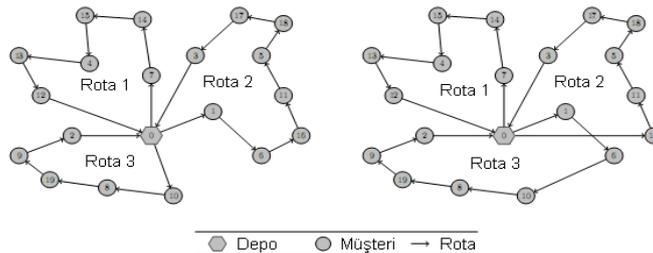
- Silkeleme aşaması için  $(N_k)$ ; Rotalar arası değişim 1-1, rotalar arası kaydırma 2-0, rota içi değişim 1-1, rota içi kaydırma 2-0.
- Yerel arama aşaması için  $(N_l)$ ; Rotalar arası değişim 1-1, rotalar arası değişim 2-1, rotalar arası kaydırma 2-0, rota içi değişim 1-1, rota içi kaydırma 2-0.

*Değişim* komşuluk yapısı hareketlerinde rota içi olduğunda, geçerli rotadaki bir elemanın aynı rotada bulunan başka bir elemanla yer değiştirilmiş, rotalar arası olduğunda farklı iki rota arasında bu işlem gerçekleştirilmiştir. Şekil 4'te rota içi değişim hareketine örnek gösterilmiştir. Rotalar arası olunca iki farklı rotanın elemanları arasında değişim gerçekleştirilmektedir.



Şekil 4. Rota içi değişim 1-1 operatörü. (Talbi, 2009)

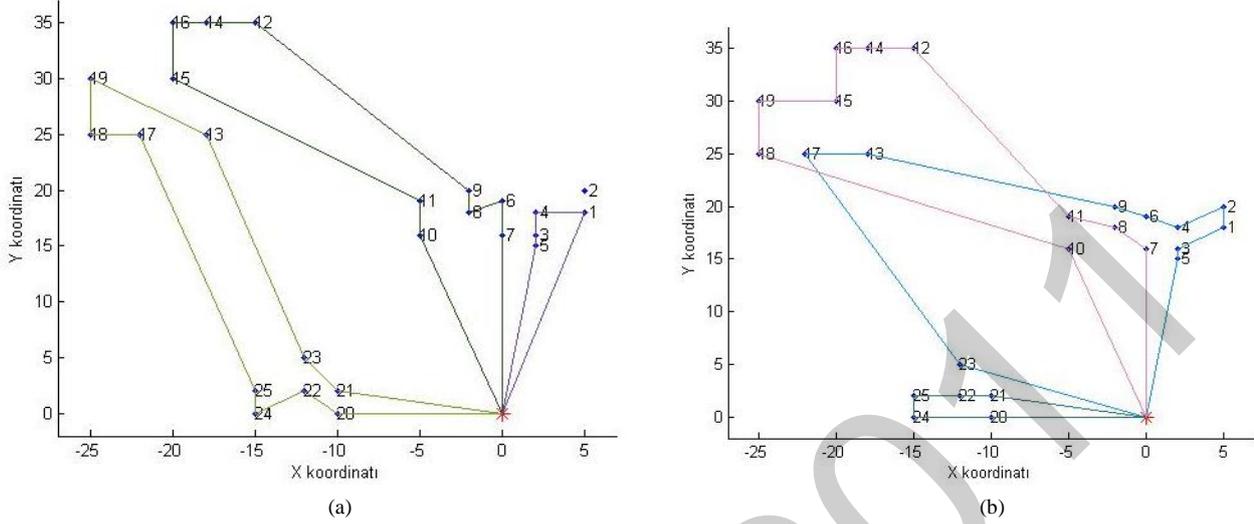
*Kaydırma* komşuluk yapısı hareketlerinde rota içi olduğunda, geçerli rotadaki bir elemanın aynı rotada bulunan başka bir noktaya yerinin kaydırılmış, rotalar arası olduğunda farklı iki rota arasında bu işlem gerçekleştirilmiştir.



Şekil 5. Kaydırma (2,0) komşuluk yapısında (1) ve (6) numaralı müşterilerin rota 2'den rota 3'e kaydırılması. (Ribas, 2011)

Şekil 5'te kaydırma (2-0) yapısı için bir örnek gösterilmiştir. Rota içi olunca aynı rotanın 2 ardışık elemanının rota içinde farklı noktalara kaydırılması ile gerçekleştirilmektedir.

Uygulamada Genel Değişken Komşuluk Arama aşaması için MATLAB'de hazırlanan kod çalıştırılmıştır. Program temel olarak matrislerin oluşturulmasına dayanmaktadır. Her komşuluk yapısı için ayrı fonksiyonlar tanımlanmış ve ana fonksiyon üzerinden atıflar yapılmıştır. Amaç fonksiyonu olarak en kısa yolun bulunması belirlenmiş ve programda katedilen mesafede azalma olması halinde, algorithmada bulunan "bulunan yerel optimum geçerli çözümden iyi" ifadesine uyarlanmıştır.



Şekil 6. Solomon C-101 problem kümesinden 50 müşteri için bulunan en yüksek (a:225,02) ve en düşük (b:217,69) değerli iki rotanın MATLAB'de gösterimi

#### 4. SONUÇ

Programın çalıştırılmasında kullanılan veriler literatürde sıklıkla kullanılan ve Solomon verileri olarak adlandırılan araç rotalama problemi verileridir. Bu veriler farklı müşteri noktaları ve farklı kapasiteler barındırmaktadır. Zaman penceresi verileri ele alınan problem kapasiteli araç rotalama problemi olduğu için dikkate alınmamıştır. Problem kümeleri 100'er müşteriden oluşmakta olup, farklı sayıda müşteri gruplarına bölünebilme imkanı sunmaktadır. Uygulamada kullanılan problem kümelerinden burada iki ana gruba ve altında farklı müşteri sayıları ile elde edilen sonuçlara yer verilmiş, Tablo 1'de sunulmuştur.

Tablo 1. Elde edilen sonuçlar

Problem kümesi	Müşteri sayısı	Araç kapasitesi	10 tekrar için en düşük ve en yüksek değerler			
			Araç (rota) sayısı I	Katedilen mesafe I	Araç (rota) sayısı II	Katedilen mesafe II
C101	25	200	3	217.69	3	225.02
C101	50	200	5	388.00	5	426.08
C101	100	200	10	881.61	12	1060.30
RC201	25	1000	4	532.17	6	823.29
C201	100	700	6	768.04	8	988.77

Tablo 2. Marius Solomon'un web sitesinde yer alan zaman pencereci değerler ile en iyi çözüm değerleri.  
(<http://w.cba.neu.edu/~msolomon/r1r2solu.htm>)

Problem	Müşteri sayısı	Araç kapasitesi	Araç sayısı	Katedilen mesafe	Yazarlar
C101	25	200	3	191.3	KDMSS
C101	50	200	5	362.4	KDMSS
C101	100	200	10	827.3	KDMSS
RC201	25	1000	3	360.2	CR+L
C201	100	700	3	589.10	CR+KLM

Tablo 1'de görüldüğü gibi Genel Değişken Komşuluk Arama (GDKA) yaklaşımı en iyiye yakın kabul edilebilir sonuçlar sunmuştur. Uygulama kolaylığı olarak ele alındığında MATLAB'de hazırlanan program ile kısa sürede sonuca ulaşılmıştır. Klasik yöntemlerin uygulanması ile en iyi sonuçlara çok daha uzun sürelerde ulaşılabileceği bilinmektedir. Daha önce yaptığımız başka rotalama çalışmalarında da 15 müşterili bir veri kümesinin dal-sınır kesin çözüm metodu ile çözülmesi için bir gün gibi bir süre boyunca paket program çalıştırılmıştır. Sonuç tablolarında süreler belirtilmemiş fakat 25 ve 50 müşterilik gruplar için

ortalama olarak 0,5 dakikalık bir süreden, 100 müşterilik gruplar için ise ortalama olarak 1 dakikalık bir süreden bahsetmek mümkündür. Kesin çözüm yöntemleri ile her ne kadar daha iyi sonuçlar elde edilse de, büyük boyutlu problemlerde ve probleme ait kısıt sayılarının artması durumunda sonuca ulaşma hızının düşmesi ile karşılaşılacaktır. Bu durumda metasezgisel yöntemler içinde basit bir yöntem olan Değişken Komşuluk Arama yaklaşımı ile iyi sonuçlar elde edilmektedir.

## EK

Tablo 2’de Solomon’un web sitesinden alınan en iyi sonuçları bulan çalışmalara ait kısaltmaların açıklamaları şu şekildedir;  
KDMSS - N. Kohl, J. Desrosiers, O. B. G. Madsen, M. M. Solomon, and F. Soumis, "2-Path Cuts for the Vehicle Routing Problem with Time Windows," *Transportation Science*, Vol. 33 (1), 101-116 (1999).  
CR - W. Cook and J. L. Rich, "A parallel cutting plane algorithm for the vehicle routing problem with time windows," Working Paper, Computational and Applied Mathematics, Rice University, Houston, TX, 1999  
L - J. Larsen. "Parallelization of the vehicle routing problem with time windows." Ph.D. Thesis IMM-PHD-1999-62, Department of Mathematical Modelling, Technical University of Denmark, Lyngby, Denmark, 1999  
KLM - B. Kallehauge, J. Larsen, and O.B.G. Madsen. "Lagrangean duality and non-differentiable optimization applied on routing with time windows - experimental results." Internal report IMM-REP-2000-8, Department of Mathematical Modelling, Technical University of Denmark, Lyngby, Denmark, 2000

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# KAYIP KİŞİLERİN MOBİL CİHAZLAR VE GPS İLE WEB TABANLI YER TESPİTİ SİSTEMİ

## A WEB-BASED SYSTEM FOR LOCATING MISSING PERSONS THROUGH MOBILE TOOLS AND GPS

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### ÖZET

Küresel konumlandırma sistemleri (Global Positioning System - GPS) dünya üzerinde yer tespitini mümkün kılan bir uydu ağıdır. Başlangıçta askeri amaçlar için kullanılan bu sistem, günümüz teknolojisindeki gelişmelerle bugün neredeyse her akıllı telefonda bulunmaktadır. Bu çalışmada yapılmak istenen, kaybolan kişilerin konumlarını GPS teknolojisi kullanılarak gerçek zamanlı olarak tespit etmektir. Bu tespit, web tabanlı bir mimari ile mobil GPS teknolojisi kullanılarak, kişinin uydu haritası üzerinde eş zamanlı olarak konumlandırılması ile sağlanmıştır. Bu çalışma yaşayan bir proje olup söz konusu taraflar kaybolan kişi ve çağrı merkezi çalışandır. Kaybolan kişi telefonundaki uygulama aracılığıyla o anki yer bilgisini hesaplar ve bu bilgiyi sabit çağrı merkezi hattına mail gönderir. Çağrı merkezi çalışanı gelen çağrıyı anında harita üzerinde görür ve kaybolan kişiye yer tespitiniz yapılmıştır mailini gönderir.

**Anahtar Sözcükler:** GPS, navigasyon, android mobil, yer bulma.

### ABSTRACT

Global Positioning System (GPS) is a network of satellites enabling locating objects on earth. In the earlier years, it was used for the military purposes but nowadays, with the advent of new technological improvements, it is used in almost every smart phone. This study aims at locating the missing persons in real time. It is achieved through integrating GPS technologies with web based systems, and locating the missing person on a satellite map. This study is components are missing person and emergency call center people. By using a program deployed in his cell-phone, a missing person calculates and sends his location to the emergency call-center through an email. Once the missing person's email gets to the center, his location is positioned on a satellite map instantly, and an acknowledgement is sent back to the missing person.

**Keywords:** GPS, Navigation, Android mobile, locating.

### 1.GİRİŞ

Amerika'da askeri amaçlı geliştirilmiş olup, daha sonra sivillerin de ilgisini çeken GPS (Government Positioning System) son yıllarda konum belirlemek amacıyla yapılan en önemli keşiftir(The International Trade Administration U.S., 1998). GPS modülleri internete gerek duymaksızın bulunulan konum hakkındaki bilgileri anlık olarak uydulardan alan yongalardır.

Sürekli gelişen ve değişen teknolojiye mobil uygulamaların insan hayatındaki değeri günden güne artmaktadır. Çünkü insanlar kullandıkları her makinenin taşınabilir(mobil) olmasını istemektedir. Mobil teknolojinin kullanımının kolay olmasının yanı sıra mobil cihazlara ulaşmak hiç de zor değildir.Günümüz teknolojisinde, neredeyse her akıllı telefonda GPS teknolojisi bulun-maktadır. Üzerinde çalışılan proje, küresel konumlandırma sistemini (GPS) konu almaktadır ve telefon şebekesinin varolduğu her yerde internetin de var olduğu prensibine dayanmaktadır.

Asırlar boyunca, kaybolmak, insanların başlıca korkularından biri olmuştur. Kaybolmanın basit bir tehlike olmadığını, çoğu zaman ölümle sonuçlandığını sürekli şahit olmaktayız. Kaybolan kişi adı üzerinde kayıp kişi yani elindeki cep telefonu kapsama alanı içinde olsa dahi, cep telefonuyla kendisinin nerede olduğunu karşı tarafa tarif edebilmesi mümkün olmayan kişidir. Kayakçıların ve dağcılarının kaybolması buna en güzel örneklerdir.

Eğer bir çalışmada insan hayatı söz konusuysa geliştirici, yayılabildiği kadar fazla kitleye yayılmayı hesap ederek işine başlamalıdır. Bu düşünce baz alınarak Andorid işletim sistemli mobil cihazlar kullanması tercih edilmiştir. Çünkü Android işletim sistemi, geleceğin mobil cihaz işletim sistemi olma yolunda emin ve hızlı adımlarla ilerlemektedir.Geliştirici için uygulama geliştirmesinin kolay oluşu, kullanıcı için ise ucuz ve kullanışlı oluşu kullanıcı ve geliştirici için her zaman tercih sebebi olmaktadır.

Android günümüzün en çok tercih edilen işletim sistemlerinden biridir. Bilinen bu veri baz alınarak proje asıl olarak bu işletim sistemi için geliştirilmiştir. Ancak istendiğinde başka işletim sistemleri için de dönüştürülebilir. Çalışmanın verimi açısından hangi dil hangi konuda iyi olduğu araştırılmış ve sonuç olarak çalışmada üç tane teknoloji birleştirilmiştir. Bu çalışmada asp.net ile python entegre bir şekilde çalışmaktadır. Python'ın mail okumadaki hızlığı, asp.net'in web kalitesi birleştirilmiş ortaya hızlı ve kaliteli bir proje çıkmıştır.

Bu çalışma, aslında çağrı merkezi işleyişinde çalışmaktadır. Mobil kullanıcı, kaybolan kişidir. Kaybolan kişinin yerini tespit eden ve ona mail ile dönen kişi ise çağrı merkezi çalışanıdır. Kaybolan kişi için karşı tarafın gerçek kişi olması güveni artıracığından çalışma tamamen mekanikleştirilmemiş olup, herhangi bir kaybolma durumunda kişilerin bu sistemi kullanmayı tercih etmesi amaçlanmıştır. Söz konusu çalışma şu şekilde çalışmaktadır; kaybolan kişi sabit çağrı merkezine kaybolduğunu bildiren bir mail atar, mailin içeriğinde ise kişinin o andaki koordinat bilgisi vardır. Mail anında çağrı merkezi çalışanın önünde açık olan web sayfasına yansır (Şekil 1). Web sitesi projenin asp.net kısmıyla Google ücretsiz olarak sağladığı Google Map'in kullanıldığı kısımdır. Burada kullanıcıdan gelen koordinat bilgisi gerçek zamanlı olarak haritada görünür ve kişinin yeri harita üzerinde tespit edilir. Makalenin ilerleyen kısımlarında sözkonusu çalışmanın nasıl çalıştığı ayrıntılı bir şekilde anlatılacaktır.

## 2. TEMEL BİLGİLER

Uydular ve GPS teknolojisi bu çalışmanın temel taşıdır. Çünkü makalede sunulan çalışma bu prensibi kullanarak çalışmaktadır. GPS (Global Positioning System) yani küresel konumlama sistemi 21'i kullanımda 3'ü yedekte olmak üzere toplam 24 uydudan oluşan sürekli kodlanmış bilgi ileten bir network, uydu bazlı radyo navigasyon sistemine verilen addr(Vikipedi,2011) Amerikan Savunma Bakanlığı'nın denetiminde ve idamesinde olan sistem 24 adet uydu takımından oluşur. Uyduların yörünge hareketi 12 saat sürmektedir. Ufuk çizgisi üzerinde erişilebilen maksimum uydu sayısı günün saati ve konuma bağlı olarak 8-12 arasında değişir. Üç boyutlu pozisyon elde edebilmek için en az 4 adet uydudan yayınlanan sinyalin işlenmesi gerekir. Normal şartlarda GPS sinyallerini engelleyecek fiziksel engel yok ise en az 6-8 arası sayıda uydu ile iletişim kurulur.

GPS alıcısı(Hofmann, Lichtenegger ve Collins,1997;Ayrıca bkz Colorado, 1999;Blewit,1997;Enge,2003) iki boyutlu konumlama (enlem, boylam) ve araç yer değiştirmesini hesabı için en az üç uyduya kilitlenmelidir. Dört ve daha fazla uydunun gözlenmesiyle alıcıyla üç boyutlu konumlama (enlem boylam yükseklik) elde edilebilir. GPS alıcısı pasif yapıda olduğundan yani havada bulunan sinyali işlediğinden (FM radyosu gibi) uydulara veya başka her hangi bir yere sinyal göndermez.

Üç boyutlu olarak uygun almanca donanımına sahip kullanıcılara sunmaktadır. GPS ayrıca bir çeşit UTC (Universal Time Coordinated) zaman bilgisini de sağlamaktadır. GPS iki farklı kalitede hizmet sunmaktadır: Standart Yer bulum Servisi (SPS) ve Hassas Yer bulum Servisi (PPS). Bunlardan SPS sivil kullanım için belirlenmişken, PPS askeri amaçlı olarak kullanılmaktadır (US Army Corps of Engineers, Department of Army, 1996).

Daha önceden de bahsedildiği gibi proje temelinde Android işletim sistemli cihazlar için tasarlanmıştır. Android, Google ve Open Handset Alliance tarafından kodlanmış Linux İşletim Sistemi tabanlı bir mobil cihaz (PDA ve cep telefonları) için geliştirilmiş açık kaynak kodlu bir işletim sistemidir. Açık kaynak kodlu olması ve Google'ın geliştiriyor olması onu çok esnek ve yeniliğe açık pozisyona getirmiştir

Google Android işletim sistemi üç ana temel üzerinde çalışmaktadır. Birinci ve en temel aşama Linux Kernel'i 2.6 üzerinden geliştirilmeye başlanılmıştır. Yani mobil cihazın içerisindeki entegre çiplerin wi-fi, kamera, bluetooth, GPS gibi telefonunuzda kullandığınız temel fonksiyonların çalışabilmesi için çiplerin tüm driverları içermektedir. Böylelikle mobil cihazda kullanılan çiplerin modellerine hızlarına göre sistemin alt yapısını düzenlemek mümkündür. İkinci kısımda ise "Libraries" diye adlandırılan Linux tabanında kurulan alt yapının uygulamalarla haberleşmesini sağlıyor ki C++ da geliştirilmiştir. Böylelikle ekranda görmek istediğiniz resimler ya da internete bağlanmak istediğinizde açılan tarayıcınız ilk olarak Libraries kısmında değerlendirilmektedir ve isteğinize göre işlem yapılması için sistemde gerekli olan yerlere komutlar gönderilmektedir. Android işletim sistemlerini diğerlerinden ayıran en önemli kısım Dalvik Java Virtual Machine'dir. Dalvik Java Virtual sisteminizin beyni olarak adlandırılabilir. Sistemin beynini oluşturan bu kısım bütün uygulamaları sıra ve belirlenen bir sistem içerisinde gerek bazı uygulamaları aynı anda gerekse bazılarını kapatıp bazılarını çalıştırarak sistemin ayakta kalmasını sağlayan bir Java platformudur.

## 3. İLGİLİ ÇALIŞMALAR

GPS teknolojisi var olduğundan itibaren çok geniş kitlelerin ilgisini çekmiş olup bu teknoloji baz alınarak türlü fikirler ortaya çıkmıştır. Bu fikirlerin hepsi henüz uygulanamamış olsa da hayata geçen insan hayatını kolaylaştıran çok sayıda uygulama vardır. Bunlardan bir tanesi görme engelliler için geliştirilmiş olan Blind Assist sistemidir (Sedimedia,2011). Blind Assist görme engelli kişiler için tasarlanmış özel bir asistan sistemidir. GPS ve GSM teknolojileri ile yapılandırılmış Blind Assist, görme engelli kişinin bulunduğu konumdan ulaşmak istediği noktaya kadar çağrı merkezinden canlı bağlantı ile yönlendirilmesini sağlayarak görme engellilere hayatı kolaylaştırır.

GPS teknolojisi ile yapılandırılan Blind Asist modülü, görme engelli kişinin bastonuna monte edilir. Modül kendisine uyumlu özel kulaklığı ile destek merkezi ile iletişimini sağlar. Görme engelli kişi Blind Asist modülü üzerinde bulunan düğmeye basarak; Destek merkezi ile canlı bağlantıya geçer ve çağrı merkezi görevlisine nereye gitmek istediğini belirtir. Bu uygulama görme engelli kişiler için çok önemli bir yardımcıdır.

Yine GPS teknolojisi kullanılarak geliştirilmiş bir başka uygulama ise GPS Tracker (Sedimedia,2011) adı verilen sistemdir. GPS Tracker; canlı veya hareket eden herhangi bir nesnenin harita üzerinden online takip edildiği sistemdir. GPS ve GPRS teknolojilerini kullanan GPS Tracker ile; çocuklar, yaşlılar, evcil hayvanlar, vahşi hayvanlar, kıymetli eşya taşıyan kuryeler gibi aklınıza gelebilecek hareket halindeki tüm canlılar anlık takip edilebilir GPS konum bilgisi teknolojisi ile çalışan GPS Tracker; takip edilecek hareketli canlı veya nesne üzerine yerleştirilir. Hareket eden kişinin nerede olduğu cep telefonuna yüklenen özel yazılım veya online internet bağlantısı ile anlık öğrenilebilir. Konum bilgisinin alınması için öncelikle GPS Tracker'a yer tespiti isteği yapılır. GPS Tracker yer tespit işlemini başlatır ortalama 60 sn içerisinde konum tespit edilir ve GPRS bağlantısı ile uzaktaki sunucuya (server) gönderir. Gelen konum bilgisi ile izlemeyi yapan kişi ve kişiler hareketli nesne veya kişinin konumunu anlık takip etmeye başlarlar. GPS Tracker'da sürekli konum bilgisi takip özelliği izleyen kullanıcı tarafından açılabilir veya kapatılabilir.

GPS ile geliştirilen uygulamalar aslında hep aynı mantık üzerine kuruludur, hepsinde amaç aynıdır : "takip etmek". Çünkü GPS zaten bir yer bulma aracıdır, yöntemidir. Yer bulmak da genelde hareketli varlıklar için önemlidir bu varsayımına dayanarak da en genel yer bulma yönteminin mobil cihazlar ile sağlanacağı gerçeği gözardı edilmemelidir. Verilen örneklerden de anlaşıldığı gibi bugüne kadar yapılan sistemler genelde mobildir. Mobil cihazların kullanımını ne kadar kolaylaştırdığını da var olan talebin de ne kadar fazla olduğunu daha önceden anlatmıştık.

#### 4.UYGULAMA VE MİMARİ

Makalede sunulan çalışma dört kısımda incelenebilir. Bunlar, uydu bölümü, kullanıcı (mobil) bölümü, web bölümü ve çalışan (sabit) hat bölümüdür. Aşağıda bölümler ayrıntılı bir şekilde anlatılmıştır.

Kaybolduğunu farkeden kişi öncelikle yanındaki akıllı cep telefonundan bulunduğu yerde şebeke var mı diye kontrol eder. Kullanıcının uygulamayı kullanabilmesi için kullandığı herhangi bir GSM operatörüne ait şebekenin var olması gerekmektedir, çünkü günümüz teknolojisinde mobil interneti kullanabilmek için telefon şebekesinin de olması gerekmektedir. Söz konusu çalışma telefon şebekesinin var olduğu her yerde mobil internetin de var olduğu prensibine dayanmaktadır. Şebeke ve mobil internet dışında kullanıcının uygulamayı kullanabilmesi için başka bazı istekler bulunmaktadır. Bunlardan birincisi kaybolan kullanıcının kullandığı cep telefonunun işletim sisteminin android olmasıdır. Söz konusu proje yalnızca Android işletim sistemli cep telefonları için geliştirilmiştir. İkincisi, cep telefonun donanımsal özelliklerinden biri olan, telefonda uydu alıcısının yani GPS alıcısının bulunmasıdır. Üçüncü durum ise kullanıcının uydu alıcısının çalışmasının engellenmemesi gereken açık bir ortamda bulunması gerektiğidir.

Söz konusu çalışmayı hem mobil hem de masaüstü uygulama olarak düşünebiliriz. Çalışmanın mobil kısmı kaybolan kişidir, masaüstü kısmı da çağrı merkezidir. Çalışmanın mobil kısmı şu şekilde çalışmaktadır. Kullanıcı uygulamayı açtığında telefondaki uydu alıcıları, dünya üzerini eşit aralıklarla sarmalamış 24 tane uydudan havaya yayılan yer bulma sinyallerini alırlar. Uygulama bu işlemi GeoPoint\_GPS.getLatitudeE6()/1000000 kod bloğuyla belli bir kesinlik ile yapar. Uydulardan alınan bu sinyalleri uygulama koordinat bilgileri olarak kullanıcıya geri döndürür. Her ne kadar kod ile kesinlik oranımızı ayarlayabilir olsak da sinyallerinin çok duyarlı olması, hava ve yer koşullarına göre çabucak değişebilmesi bu kesinlik oranını değiştirebilmektedir. Örneğin kapalı bir alanda sinyal alımı çok düşüktür ya da hiç yoktur. Alabilse de çok kısa sürer. Koordinat bilgileri kullanıcının ekranında görüldükten sonra projenin uydu tarafı görevini tamamlamıştır.

Kullanıcı koordinat bilgilerinin sabitlendiğini gördükten sonra elektronik posta gönder butonuna tıklar. Bu anda uygulamanın internet bölümü devreye girer. Çünkü elektronik postayı gönderebilmesi için internete ihtiyaç vardır. Posta gönder dediği anda kullanıcının isteği internet bulutuna girer ve kayıtlı posta adresi tespit edilir ardından kayıtlı posta adresine veriler paket halinde gönderilir. Elektronik posta gönderebilmesi Androidin mail intentleri sayesinde sağlanmıştır (Taç&Mermerkaya,2010,2011). Bu işlem de tamamlandıktan sonra çalışmanın kullanıcı bölümüyle işlemi sonlanmıştır.

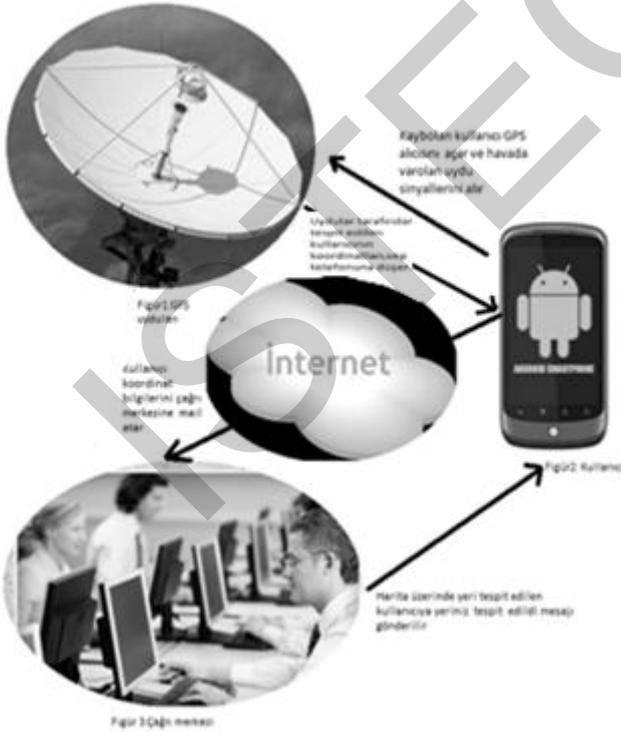
İnternet bulutunu aşarak çağrı merkezinin posta kutusuna düşen kaybolan kişinin koordinat bilgileri, artık çağrı merkezinde kurulu bulunan uygulama üzerinden işlenecektir ve kullanıcının yeri harita üzerinde tespit edilecektir. Bu işlemler ise şu şekilde gerçekleşmektedir. Çağrı merkezi çalışanı her zaman işinin başında olsa dahi sürekli posta kutusunu kontrol edemez. Bu durumu aşabilmek için gerçek zamanlı bir mail kontrollerına ihtiyaç vardır. Bu kısım python kodlarıyla (Özgül&Paraglyph,2011,2003) gerçekleştirilmiştir ve threadler kullanılmıştır. Threadler bilgisayarda olan diğer proseslerden etkilenmezler. Bu threadler çağrı merkezinin önündeki web sayfası açık olduğu müddetçe çalışırlar ve sürekli posta kutusunu kontrol ederler. Yeni bir posta geldiğinde bunu bir text dosyasına yazarlar. Posta iletişimi ise IMAP4 protokolü kullanılarak python tarafında sağlanmıştır. Dosyaya yazılan kısım mailin içeriği ve kullanıcının elektronik posta adresi bilgisidir. Yeni bir elektronik posta geldiğinde bir önceki elektronik posta bilgisi alt kısımda kalır. Yani harita sadece son gelen elektronik postadaki koordinatları harita üzerine yansıtabilir.

Bunu formatlayıp harita üzerinde görünür duruma getiren asp.net (Demirkol,2010) kodlarıdır. Burada python kodlarıyla asp.net kodlarının birlikte çalışabilmesi sağlanmıştır. Birlikte çalışabilmekten kasıt çağrı merkezi çalışanı uygulamayı (web sitesini) çalıştırdığında bir de threadlerin çalışmasını sağlayan uygulamayı çalıştırmak zorunda kalmamasını

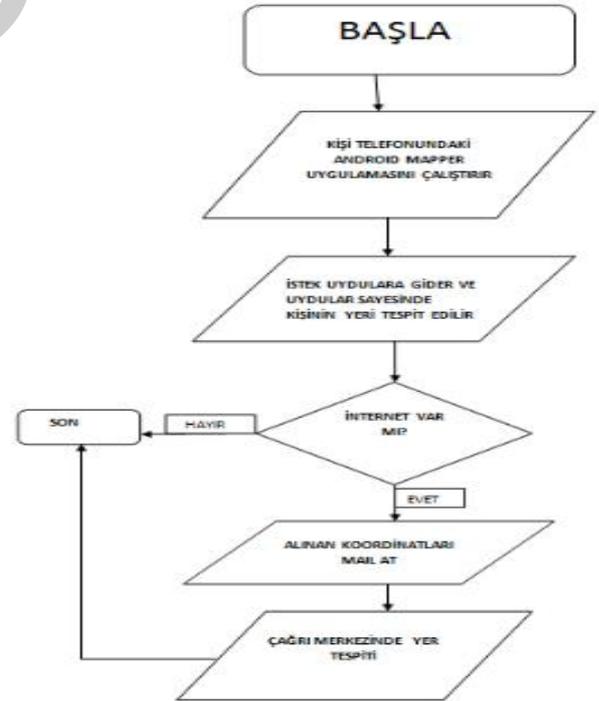
sağlamış olmaktadır. Bu kısımda harita olarak Google ın sağladığı Google Map kullanılmıştır. Web sayfası (Şekil 1) on saniyede bir yenilenir ve yeni bir elektronik posta gelmişse haritaya bir işaret düşer. Çağrı merkezi çalışanı bu durumu farkeder işarete tıklayarak koordinat bilgisini öğrenir ve kaybolan kişiye yerini tespit edildi postasını gönderir. Sistemin işleyişi ve sistemin akış diyagramı (Şekil 2 ve Şekil 3) de gösterilmiştir.



Şekil 1: Çağrı Merkezi Web Sitesi Ekranı



Şekil 2: Sistemin İşleyişi



Şekil 3: Sistem Akış Diyagramı

## 5. SONUÇ VE YORUMLAR

Makalede sunulan çalışma hedeflenen isterleri tam olarak yerine getirmektedir. Bu çalışmanın burada sona erdiği anlamını taşımamaktadır. Söz konusu çalışma geliştirmeye çok açık olduğundan gelecekte istenilen özellikler kolaylıkla eklenebilir. Daha önce bu çalışmaya benzer projeler yapılmıştır ancak bu çalışmayı özel kılan Android işletim sistemli mobil cihazlara göre tasarlanmış olmasıdır. Bu çalışma aslında hayati önem taşımaktadır. Sebebi ise kaybolmanın ölümle bile sonuçlanabileceği gerçeğidir. Düşünüldüğünde insan kendini relative olarak adresler ve tarif eder fakat bir dağda ise ve heryer karlarla kaplı ise tarif edebileceği yani bir yeri baz alarak yerini anlatabileceği bir durum söz konusu olamaz. Bu dağcılarının ve kayakçıların başına sık sık gelmektedir. İşte bu durumda gerçek adreslemeye yani kesin bir adrese ihtiyacı vardır. Bu da ancak koordinat bilgileriyle sağlanabilir ve söz konusu çalışma tam da bunu yapmaktadır.

Çalışmada üç ayrı dil entegre olarak çalışmaktadır. Geliştirme aşamasında hangi programlama dili hangi konuda iyidir şeklinde araştırılıp ona göre karar verilmiştir. Sonuç olarak Asp.net (C#), Python ve Eclipse (java) kullanılmıştır. Bu tercihler de projenin performansını olumlu yönde etkilemiş olup çalışmaya hız kazandırmakta yardımcı olmuştur.

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# KUZAY KIBRIS TÜRK CUMHURİYETİ ORTAÖĞRETİM İKİNCİ BASAMAK DERS KİTAPLARININ ÇEVRE İÇERİKLERİ

## CONTENTS OF THE SECOND STEP SCHOOL BOOKS IN SECONDARY EDUCATION IN TURKISH REPUBLIC OF NORTHERN CYPRUS

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### ÖZET

Bu araştırmada, Kuzey Kıbrıs Türk Cumhuriyeti ortaöğretim ikinci basamakta okutulan ders kitaplarının çevre içerikleri incelenmiş ve bu içeriklerin ezbere dayalı pasif bilgi niteliğinde ya da beceri, tutum, değer ve anlayış geliştirmeye yönelik davranış kazandırma niteliğinde olup olmadığının araştırılması hedeflenmiştir. Araştırma nitel araştırma yöntemi ve içerik analizi esasına göre yapılmıştır. Araştırma evrenini KKTC Milli Eğitim Gençlik ve Spor Bakanlığı ortaöğretim ikinci basamağı kapsamında bulunan 9, 10, 11 ve 12. sınıflarında okutulan ders kitapları oluşturmaktadır.

Buna bağlı olarak, KKTC ortaöğretim ikinci basamakta 2010-2011 eğitim öğretim yılında okutulan ders kitaplarının tümü incelenmiştir. Haftalık ders saatleri paralelinde, çevre konularından bahseden kitaplar (coğrafya, biyoloji, kimya ve seçmeli çevre ve sağlık bilgisi kitapları) ayrıca belirlenmiştir. Belirlenen bu kitapların çevre içerik analizleri yapılmış ve bu kitapların ezbere dayalı pasif bilgi niteliğinde mi, yoksa beceri, tutum, değer ve anlayış geliştirmeye yönelik davranış kazandırma amaçlı mı geliştirildiği saptanmıştır.

**Anahtar Kelimeler:** çevre bilinci, ders kitapları, çevre içerikleri.

### ABSTRACT

In this research, it has been aimed to investigate the textbooks which are currently being used in the second step of TRNC secondary education to find out whether their environmental contents are studied and these contents are based on memorized passive knowledge or aimed to develop a mentality based on skills, attitudes, values and understanding.

In addition, all the textbooks which have been used in the second step (9<sup>th</sup>, 10<sup>th</sup>, 11<sup>th</sup> and 12<sup>th</sup> forms) of TRNC secondary education in 2010-2011 academic year have been analysed and as the weekly lesson sessions determined, the books which have environmental contents (geography, biology, chemistry, optional environment and health studies books) were separately determined. The environmental content analysis of these books have been done and aimed to find out whether their environmental contents are based on memorized passive knowledge or aimed to develop a mentality based on skills, attitudes, values and understanding.

**Keywords:** enviromental conscious, course books, enviromental contents.

### GİRİŞ

Çevre eğitimi bireyin doğal ortamı algılamasını sağlamak, değer ve davranışlarını olumlu yönde etkilemek için hazırlanır. Temel amaç; çevre bilinci, doğal çevreyi koruma ve kullanma ile ilgili duyarlılığı geliştirmektir (Başal, 2005).

Avrupa Konseyinin Avrupa Birliği ülkeleri için yenilenmiş ve geliştirilmiş “Sürdürülebilir Kalkınma Çözümleri”nin yer aldığı raporunda sürdürülebilir bir kalkınmanın tek ve bütüncül bir çözüm ile mümkün olabileceği belirtilmiştir. Bu raporda 2006’dan 2010’a kadar tümü çevresel merkezli 7 temel öncelik yer almaktadır. Bunlar:

1. İklim değişikliği ve temiz enerji
2. Sürdürülebilir ulaşım
3. Sürdürülebilir üretim ve tüketim
4. Halk sağlığı tehdidi
5. Doğal kaynakların korunması ve yönetimi
6. Sosyal bütünleşme
7. Küresel açlığa karşı mücadele olarak belirlenmiştir.

Raporda sürdürülebilir kalkınmanın sadece alınan kararlarla gerçekleştirilemeyeceği, insanların bu kararları nasıl algıladıklarının ve davranışa nasıl yansıtıklarının da önemli olduğu belirtilmiştir. Dolayısıyla sürdürülebilir kalkınma ancak sürdürülebilir bir çevre eğitimi ile mümkündür.

Bu çalışmanın problem cümlesi “Ortaöğretim ikinci aşama kapsamında okutulan ders kitaplarının çevre içerikleri nasıldır?” olarak belirlenmiştir. Çalışmada KKTC Milli Eğitim Gençlik ve Spor Bakanlığı Ortaöğretim İkinci Basamak (9., 10., 11., 12. sınıflar) sınıflarında okutulan ders kitaplarının çevre içerikleri incelenerek; öğrencide bilgi, beceri ve anlayış geliştirmeye ne kadar yönelik olduğunun tespiti, ayrıca Avrupa Birliği Konseyinin hazırladığı rapora uyum sağlayıp sağlamadığının ortaya konulması hedeflenmiştir.

Çalışmada aşağıdaki sorulara cevap aranmıştır:

1. Çevre eğitimi ortaöğretim ikinci basamakta ayrı bir ders ya da ders kitabı olarak mı yoksa farklı derslerin bünyelerinde ünite ya da konu veya alt başlık olarak mı verilmektedir? Çevre eğitimi, programların genel hedeflerinde yer almakta mıdır?

2. Programlarda yer alan öğrenci kazanımları Avrupa Birliği Komisyonunun yedi öncelikli hedefleri ile hangi oranla uyumludur?

3. Programlardaki kazanımlar sadece bilgi edinme ve konu anlamaya yönelik mi hazırlanmıştır? Tutum, beceri, değer ve anlayış geliştirme hedeflenmiş midir?

İlgili alanyazın tarandığında KKTC Ortaöğretim İkinci Basamak sınıflarında okutulan ders kitaplarının çevre ile ilgili içerik analizleri ve çevre duyarlılıkları hakkında daha önceden bir araştırma yapılmadığı gözlenmiştir. KKTC Milli Eğitim Yasasının ve ders kitaplarının çevre eğitimine verdiği önemi saptamak ve sonuçlara ilişkin önerilerde bulunmak açısından, yapılan bu araştırmanın, ilgili alanyazına katkıda bulunacağı düşünülmüştür.

## YÖNTEM

Araştırma nitel araştırma yöntemi ile betimsel araştırma türünde yürütülmüştür. Betimsel araştırmalar olayı olduğu gibi araştırmaya ve var olan durumu belirlemeye çalışan araştırmalardır (Tanrıoğen, 2009). Araştırmada 9, 10, 11 ve 12. sınıflarda öngörülen coğrafya, biyoloji ve kimya kitapları nitel olarak taranarak içerik analizi yapılmış ve bulgular grafikleştirilip amaca uygunluğu tespit edilmiştir. Araştırmanın evren ve örneklemini Milli Eğitim Gençlik ve Spor Bakanlığı ortaöğretim ikinci basamak kapsamında okutulan 9, 10, 11 ve 12. sınıf ders kitapları ve KKTC Milli Eğitim Yasası oluşturmaktadır. Veri toplama aracı olarak doküman analizi kullanılan çalışmada veriler nitel olarak analiz edilmiş, tablo halinde sunulmuş yorumlanmıştır.

## BULGULAR VE YORUM

### KKTC Milli Eğitim Yasası

Kıbrıs Türk Milli Eğitimimin genel amaçları KKTC Milli Eğitim Yasası'nda aşağıdaki şekilde verilmiştir:

*5. Madde: Kıbrıs Türk toplumunun tüm bireylerinin aşağıdaki fıkralarda öngörülen esaslar çerçevesinde yetiştirmektir.*

*(1) Atatürk İlke Devrimleri ile yurttaşlar arasında bir fikir ve duygu ortaklığını amaçlayan çağdaşlaşmayı hedefleyen ve Türk milletini milli bilince vardırıran Atatürk milliyetçiliğine, demokrasi, sosyal adalet ve hukukun üstünlüğü ilkelerine bağlı, bunları koruyan ve geliştiren yurttaşlar olarak yetiştirmek,*

*(2) Kıbrıs Türk Toplumunun var olma mücadelesinin özünde yatan gerçekleri bilen, mücadele tarihinin bilincine varan ve bu mücadeleye inançla bağlanan, manevi ve kültürel değerlerini koruyan ve geliştiren, yurdunu ve toplumunu seven, Anayurdu Türkiye'ye, Türk ulusuna, öz yurduna, toplumuna ve ailesine güçlü bağlarla bağlı, yurduna toplumuna laik devletine karşı görev ve sorumluluklarını bilen ve bu bilinç ve nitelikleri sürekli davranışa dönüştürebilen barışçı ancak haklarını korumasını bilen yurttaşlar olarak yetiştirmek,*

*(3) Beden, zihin, ahlak ve duygu bakımından dengeli ve sağlıklı biçimde gelişmiş sağlam bir kişiliğe karaktere bilimsel düşünme gücüne geniş bir dünya görüşüne sahip insanı seven, insana ve insan haklarına saygılı girişime değer veren, toplumuna karşı sorumluluk duyan, her yönde gelişmiş, toplum ekonomisine katkıda bulunan toplum çıkarlarını kendi çıkarlarının üstünde tutan ve kendi mutluluğunu toplumun refah ve mutluluğunda gören, toplumun varlığını ve devletini özenle koruyan, gelişmesine çalışan ve onu her türlü tehlikeye karşı savunan ve sonuna kadar direnen, cesur, kişilikli, yapıcı, yaratıcı ve verimli yurttaşlar olarak yetiştirmek,*

*(4) İlgi ve yeteneklerini değerlendirmek ve ortaya çıkarıp geliştirmek suretiyle gerekli bilgi ve becerilerle onatmak; onlara birlikte ve dayanışma ile iş görüşme alışkanlıklarını kazandırmak; onların, kendilerini ve ailelerini mutlu kılacak ve toplumun mutluluğu ile kalkınmasına katkıda bulunacak bir mesleğe sahip olmalarını sağlamak; böylece bir yandan yurduna refah ve mutluluğu artırmak diğer yandan toplumsal birlik ve bütünlük içerisinde ekonomik, sosyal ve kültürel kalkınmayı destekleyip hızlandıran, toplumunu, ulusunu, çağdaş uygarlığın yapıcı, yaratıcı ve seçkin bir ortağı yapmak isteyen ve bu istek doğrultusunda sürekli çaba gösteren yurttaşlar olarak yetiştirmek.*

KKTC Milli Eğitim Yasası'nda belirtilen Kıbrıs Türk Milli Eğitimimin genel amaçları incelendiğinde çevre ya da çevre eğitimi ile ilgili doğrudan veya dolaylı herhangi bir konunun geçmediği görülmektedir.

Kıbrıs Türk Milli Eğitimimin genel ilkeleri KKTC Milli Eğitim Yasası'nda aşağıdaki başlıklarda verilmiştir:

1. Gençlik ve Eşitlik
2. Zorunlu Eğitim ve Öğretim Hakkı
3. Fırsat ve Olanak Eşitliği
4. Süreklilik
5. Her Yerde Eğitim
6. Karma Eğitim
7. Bilimsellik ve Çevresellik
8. Planlılık
9. Atatürk İlke ve Devrimleri ile Atatürk Milliyetçiliği
10. Ulusal Ahlak ve Kültürün Geliştirilmesi
11. Türk Dili ve Yabancı Dil Öğretimi
12. Laiklik ve Din Kültürü Eğitimi
13. Demokrasi Bilincinin Geliştirilmesi
14. Okul ve Ailenin İşbirliği
15. Uyumluluk
16. Eğitim Etkinliklerinin Yürütülmesi

KKTC Milli Eğitim Yasası'nda belirtilen Kıbrıs Türk Milli Eğitimimin genel ilkeleri incelendiğinde çevre ya da çevre eğitimi ile ilgili doğrudan veya dolaylı herhangi bir konunun geçmediği görülmektedir.

Kıbrıs Türk Milli Eğitimimin genel yasası içinde Ortaöğretime bakıldığında, Ortaöğretimin amaç ve görevleri Kıbrıs Türk Milli Eğitimin genel amaçlarına ve temel ilkelerine uygun olarak aşağıdaki şekilde yer almaktadır:

*(1) Atatürk milliyetçiliği doğrultusunda sosyal ve kültürel bütünleşmeyi sağlamak ve korumak;*

(2) Tüm öğrencilere ortaöğretim düzeyinde asgari ortak bir genel kültür vermek suretiyle onlara kişi ve toplum sorunlarını tanıma, bunlara çözüm yolları arama ve toplumun ekonomik, sosyal ve kültürel kalkınmasına katkıda bulunma bilincini ve gücünü kazandırmak;

(3) Öğrencileri toplum ekonomisinin gereklerini de gözetken çeşitli programlar çerçevesinde ilgi ve yeteneklerine göre geliştirerek yükseköğretime veya hem mesleğe hem yükseköğretime veya toplumsal yaşama ve iş alanına hazırlamak.

Yukarıdaki amaç ve ilkeler incelendiğinde çevre ile ilgili herhangi bir hedefe yer verilmediği anlaşılmaktadır.

Bu bulgulara ek olarak KKTC Anayasası da incelenmiştir. Elde edilen bulgular aşağıda sunulmuştur:

**Madde 37 (Toprağın Korunması);**

Devlet toprağın verimli olarak işletilmesini gerçekleştirmek ve topraksız olan veya yeter toprağı bulunmayan çiftçiye toprak sağlamak amaçlarıyla gereken önlemleri alır. Yasa bu amaçlarla, değişik tarım bölgelerine ve çeşitlerine göre toprağın genişliğini gösterebilir.

**Madde 38 (Kıyıların Korunması);**

1. Kıyılar Devletin hüküm ve tasarrufu altındadır ve yalnız kamu yararına kullanılabilir.

2. Belediye sınırları dışındaki kıyıların yüz metrelik şeridi içinde kalan bölge de yalnız Devlete ait, çok gerekli ve kamu yararına olan tesisler kurulabilir. Ancak, bu gibi tesisler, kıyıların doğal güzelliğini bozacak nitelikte olmaz. Mevcut bina veya tesislerin gelecekteki durumu yasa ile düzenlenir.

3. Belediye sınırları içindeki kıyıların korunması ve yüz metrelik kıyı şeridi içinde kalan bölgede inşa edilebilecek yapı ve tesisler ile mevcutların durumu kamu yararının ve kent planlamasının gereklerine uygun olarak yasa ile düzenlenir.

4. Ulusal güvenlik, kamu düzeni, kamu yararı, genel sağlık ve çevre korunması amacıyla yasa ile sınırlama konmadıkça, yurttaşların yüz metrelik kıyı şeridi içerisine girmesi kimse tarafından engellenemez ve giriş ücrete bağlı tutulamaz. Ancak, bu kural, mülkiyet haklarına tecavüz edilmesine olanak tanır biçimde yorumlanamaz.

**Madde 39 (Tarih, Kültür ve Doğa Varlıklarının Korunması);**

Devlet, tarih ve kültür değeri olan eser ve anıtlar ile doğa varlıklarının korunmasını sağlar; bu amaçla düzenleyici, destekleyici ve özendirici önlemleri alır. Bunlardan özel mülkiyete konu olanlara getirilecek sınırlamalar ve bu nedenle hak sahiplerine yapılacak yardımlar ve sağlanacak bağışıklıklar yasa ile düzenlenir. Yıkılan veya herhangi bir şekilde yok olan veya tahribata uğrayan tarihi yapıların yerine başka bir yapı inşa edilemez. İnşa edilme zorunluluğu doğarsa, yıkılan veya herhangi bir şekilde hasar gören tarihi yapı aslına uygun bir şekilde yeniden inşa veya tamir edilir. Devlet, bu amaçla gerekli önlemleri alır ve yasal düzenlemeleri yapar.

**Madde 40 (Çevrenin Korunması);**

1. Herkes, sağlıklı ve dengeli bir çevrede yaşama hakkına sahiptir.

2. Gerçek veya tüzel kişiler, hiçbir amaçla, insan sağlığını bozacak veya deniz varlıklarını tehlikeye düşürecek nitelikteki sıvı, gaz ve katı maddeleri denizlere, barajlara, göllere veya derelere akıtamaz veya dökemez.

3. Çevreyi geliştirmek, çevre sağlığını korumak ve çevre kirlenmesini önlemek Devletin, gerçek ve tüzel kişilerin ödevidir.

4. Devlet milli parklar oluşturulması amacıyla gerekli önlemleri alır.

Bulgular incelendiğinde KKTC Anayasası kapsamında çevre ile ilgili sadece 4 maddenin bulunduğu, bu maddelerin ise toprağın, kıyıların, tarih, kültür ve doğa varlıklarının ve çevrenin korunmasına yönelik kısa açıklamalardan oluştuğu görülmektedir.

### Ders Kitapları

KKTC Milli Eğitim Gençlik ve Spor Bakanlığının 2010-2011 eğitim öğretim yılında genel liseler, kolejler, anadolu liseleri, meslek liseleri, fen liseleri ve güzel sanatlar liselerinin 9, 10, 11 ve 12. sınıfları için uygun gördüğü bütün ders kitapları incelenmiştir. Okutulan tüm kitaplar arasından çevre konusundan bahseden kitaplar belirlenmiş, kitaplardaki çevre ile ilgili üniteler, alt başlıkları ve öğrencilerdeki çevre kazanımları Tablo 1’de sunulmuştur.

Tablo 1. Ders kitaplarında çevre ile ilgili üniteler ve kazanımlar.

Dersin Adı/ Yayın	Sınıf	Ünite/ Alt Başlıklar	Çevre Kazanımları
KIBRIS COĞRAFYASI KT Eğitim Vakfı Yayınları	9	ÜNİTE 5: KIBRIS’TA YER ALTI VE YER ÜSTÜ SULARI Atık Sular	KKTC’de atık suların değerlendirilmesine ve su kaynaklarının korunmasına yönelik önlemler.
KIBRIS COĞRAFYASI KT Eğitim Vakfı Yayınları	10	ÜNİTE 11: KIBRIS’TA TURİZM Ekoloji Turizmi	Kıbrıs’ın flora ve fauna zenginlikleri.
ORTAÖĞRETİM COĞRAFYA MEB Devlet Kitapları TC Milli Eğitim Bakanlığı Yayınları	9	ÜNİTE 9: İNSAN VE ÇEVRE Doğadan Nasıl Yararlanıyoruz, Doğanın Emrinde miyiz, Suçlu Kim?	Doğa, insan ilişkisi. Konuyla ilgili proje çalışmaları ile öğrenciler öğrendiklerini uygulamaya yönlendirilmektedir.
ORTAÖĞRETİM COĞRAFYA MEB Devlet Kitapları TC Milli Eğitim Bakanlığı Yayınları	10	ÜNİTE 11: ÇEVRE VE TOPLUM Doğal Afetler ve Toplum	Doğal afetlerden korunma, afetlerin artış gösterme nedenleri, insanın doğa dengesini bozması. Proje çalışmaları ile öğrenciler uygulamaya yöneltilmektedir.

ORTAÖĞRETİM COĞRAFYA MEB Devlet Kitapları TC Milli Eğitim Bakanlığı Yayımları	11	<p>ÜNİTE 1: EKO SİSTEM VE MADDE DÖNGÜSÜ Biyo Çeşitlilik Eko Sistemlerin İşleyişi Enerji Akışı ve Madde Döngüsü Hidro Elektrik Potansiyel</p> <p>ÜNİTE 7: ÇEVRE VE TOPLUM Doğal Kaynaklar ve Çevre Doğal Kaynakların Değeri ve Kullanımının Değişimi Doğal Kaynaklar Sınırsız mı? Enerji Kaynakları Doğal Kaynak Kullanımının Farklı Olmasının Çevresel Sonuçları Doğal Kaynak Kullanımının Farklı Olmasının Çevresel Etkileri Kaynakların Kullanımı ile Ortaya Çıkan Sorunlar Kaynakların Çevreye Etkisi Doğal Kaynakların Kullanımı Doğal Kaynakların Kullanımında Etkili Olan Faktörler Nelerdir? Doğal Kaynak Kullanımına Örnekler Doğal Kaynak Kullanımında Çevre Duyarlılığı Doğal Kaynaklar ve İnsan Faaliyetleri Arazi Kullanımının Çevresel Etkileri Arazi Planlamasında Dikkat Edilmesi Gereken Hususlar Arazi Kullanımının Çevresel Etkileri</p> <p>ÜNİTE 8: DOĞAL KAYNAKLARIN KÜRESEL ETKİLERİ Teknolojinin Çevresel Etkileri Atıklar Ekolojik Döngülere İnsan Müdahaleleri Küresel Çevre Sorunları</p>	Dünyadaki bitki ve hayvan çeşitliliği, canlıların yeryüzündeki dağılımları, ekosistemlerin işleyişi, döngüler ve besin zinciri, dünyadaki hidro elektrik potansiyel. Doğal kaynakların kullanımının tarihçesi, doğal kaynak kullanımına dünyadan örnekler, kaynakların farklı kullanımından doğan çevresel sonuçlar, enerji kaynakları ve kullanılmaları sonucu çevreye verdikleri zararlar. Teknolojik gelişmelere bağlı ortaya çıkan kirlenmeler, atıkların sınıflandırılması, çevreye etkileri, ekolojik döngüler, insan müdahaleleri.
ORTAÖĞRETİM COĞRAFYA MEB Devlet Kitapları TC Milli Eğitim Bakanlığı Yayımları	12	<p>ÜNİTE 1: DOĞADAKİ EKSTERM OLAYLAR Doğanın Ekstermleri İnsan ve Doğa Etkileşimi</p> <p>ÜNİTE 12: ÇEVRE VE TOPLUM Doğanın İşleyişi Çevre Koruma Uygulamaları Teknoloji ve Doğal Afetler Doğayla Uyumlu Yaşamak Sınırlı Kaynaklar Doğadaki Tehlikeler Doğal Kaynakların Kullanımı Günümüz Çevre Sorunlarının Olası Etkileri Çevre Koruma Uygulamaları Doğal Mirasın Korunması</p>	Dünyada süregelen ve yeni oluşan sıradışı olaylar, insan doğa ilişkileri, çevre, toplum ve doğa ilişkisi, çevre koruma, çevre teknoloji ilişkileri, sınırlı olan kaynaklar, bu kaynakların kullanımı, çevre sorunlarının etkileri ve çevre koruma uygulamaları.
SAĞLIK VE ÇEVRE BİLGİSİ KILAVUZ KİTABI KT Eğitim Vakfı Yayınları	9	<p>ÜNİTE 11: ÇEVRE VE İNSAN Ekosistemler Ekosistem Çeşitliliği Doğa Koruma Çevre Kirlenmesi Kirlenmenin Sınıflandırılması Ülkemizdeki Kirlilik Etmenleri Dünyada Sürdürülebilirlik</p>	Çevre ve insan ilişkileri, ekosistemler, doğanın korunması, çevre kirlenmesinin sınıflandırılması, ülkemizdeki kirlilik etmenleri, sürdürülebilirliğin önemi, hastalıklar, korunma yolları.

KKTC Milli Eğitim Bakanlığı tarafından öngörülen ders kitapları sınıflar bazında incelendiğinde çevre ile ilgili konuların ağırlıklı olarak 9, 10, 11 ve 12. sınıfların Coğrafya kitaplarında yer aldığı görülmektedir. Dağılım, 9 ve 10. sınıflarda birer ünite, 11. sınıfta üç ünite ve 12. sınıfta iki ünite şeklindedir. Coğrafya kitapları göz önüne alınırsa çevre ile ilgili ünite ve konuların daha çok 11. sınıfta işlendiği görülmektedir. Kitaplarda ünite, alt başlıklar ve çevre kazanımlarına göre bilgiler ve öğrencilerin uygulama yapmasına yönelik projeler yer almaktadır.

Coğrafya kitapları haricinde 9. sınıf Sağlık ve Çevre Bilgisi kitabında da genel olarak çevre hakkında bilgiler verildiği gözlemlenmektedir. Yine İngilizce müfredat veren kolej ve anadolu liselerinin İngilizce coğrafya kitaplarında çevre konularına yer verildiği gözlemlenmektedir. 10. sınıf Kimya ders kitabının 5. ünitesinde yer alan Hayatımızda Kimya ana başlığı adı altında çevre kimyası, sanayi ve çevre kirliliği, hava kirliliği, su kirliliği, toprak kirliliği, çevre, endüstri ve enerji ilişkisi gibi konular hakkında bilgi verilmekte, fakat öğrenci kazanımları ile ilgili hiçbir bulguya rastlanmamaktadır. 10. sınıf Biyoloji ders kitabının 3. ünitesinde Ekosistem Ekolojisi başlığı adı altında ekosistemin yapısı, enerji akışı ve madde döngüleri, ekosistemlerin öneminden bahsedilmekte, ünite sonunda öğrencileri uygulamaya yöneltecek etkinlikler bulunmaktadır. 11. sınıfların Biyoloji kitaplarında 3. ünite Komünite ve Popülasyon Ekolojisi başlığı altında komite ekolojisi, popülasyon ekolojisi ve biyomlardan bahsedilmekte, fakat uygulamaya dönük herhangi bir etkinliğe yer verilmemektedir.

2006 Avrupa Birliği raporundaki yedi öncelikli başlıkla, KKTC Milli Eğitim Yasası ve Ortaöğretim ikinci basamak ders kitapları karşılaştırılmıştır. Karşılaştırmaya göre kitapların çevre içerikli konularında iklim değişikliği ve temiz enerji ile ilgili alanlar olduğu saptanmış fakat bu alanların bilgi ve etkinlik açısından yetersiz kaldığı gözlemlenmiştir.

Sürdürülebilir ulaşım ile ilgili öğrenci kazanımlarına ya da konulara yer verilmediği görülmüştür. Ancak 9. sınıfların Sağlık ve Çevre Bilgisi kitabında sürdürülebilir kalkınmadan bahsedilmekte ve öğrenciler verilen bilgilerin yanında aktivitelerle uygulamaya yönlendirilmektedir.

Sürdürülebilir tüketim ve üretimle ilgili olarak ortaöğretim ikinci basamak ders kitaplarında herhangi bir konuya yer verilmemiştir.

Halk sağlığını tehdit eden konulara bakıldığında özellikle 9. sınıfların Sağlık ve Çevre Bilgisi kitabında bilgilerin ve uygulamaya yönelik projelerin olduğu gözlemlenmiştir.

Doğal kaynakları yönetme ve korumaya ilgili olarak Coğrafya 11 kitabında bilgi ve etkinliklerin genişçe yer aldığı gözlemlenmiştir.

Sosyal bütünleşme, nüfus ve göçle ilgili sadece 10 ve 12. sınıfların Coğrafya ders kitaplarında bilgilere rastlanmıştır. Fakat bilgiler kısa olarak verilmiş olup, çevre ile ilişkilendirilmemiştir.

Küresel açlıkla mücadele konusuna kitaplarda doğrudan değinilmediği gözlenmiştir. Konu, dolaylı olarak çevre felaketlerinin sonuçları içerisinde ele alınmaktadır.

## SONUÇ VE ÖNERİLER

Bu çalışmada 9, 10, 11 ve 12. sınıflarda okutulan ders kitaplarının içerikleri çevre boyutunda analiz edilmiştir. Öncelikle çevre konularını içeren ders kitapları tespit edilmiş, arkasından ünite ve konu içerikleri belirlenmiştir. Sonuç olarak çevre konularını doğrudan 9'uncu sınıfta okutulan Sağlık ve Çevre Kitabının içerdiği, ancak kitap içerisinde sağlık bilgisi konularına da genişçe yer verildiği görülmüştür. Bunun yanında Biyoloji ve Kimya ders kitaplarında çevre konularının sadece alanla ilişkili belli kısımlarına yer verildiği görülmüştür. Tüm kitaplar arasında çevre konularına en geniş oranda yer veren ders kitaplarının 9, 10, 11 ve 12. sınıflarda okutulan Coğrafya ders kitapları olduğu belirlenmiştir. Adı geçen sınıflarla ilgili ders kitaplarındaki çevre konularının daha çok bilgi vermek amaçlı ve dar kapsamlı oldukları ve çoğunlukla öğrencileri uygulamaya yönlendirecek, sürdürülebilir bir çevre amacı gütmedikleri tespit edilmiştir.

Ders kitaplarının içerik analizi Avrupa Konseyinin Avrupa Birliği ülkeleri için yenilenmiş ve geliştirilmiş "Sürdürülebilir Kalkınma Çözümleri"nin yer aldığı 2006 raporunun çevresel merkezli 7 temel önceliği ile kıyaslanmıştır. İncelemeye göre Sürdürülebilir Üretim ve Tüketimle ilgili olarak ortaöğretim ikinci basamak ders kitaplarında herhangi bir konuya yer verilmediği, İklim Değişikliği ve Temiz Enerji, Sürdürülebilir Ulaşım, Sosyal Bütünleşme ve Küresel Açlığa Karşı Mücadele ile ilgili konularda dolaylı ve dar kapsamlı bilgilerin yer aldığı, Halk Sağlığının Tehdidi ve Doğal Kaynakların Korunması ve Yönetimi ile ilgili bilgi ve etkinliklerin ise genişçe yer aldığı gözlemlenmiştir.

Çalışma sonuçlarına göre, araştırma boyutunda çalışmanın ilköğretim ya da ortaöğretim birinci basamak ders kitaplarına yönelik olarak yapılması önerilmektedir. Uygulama boyutunda ilgili bakanlık tarafından ders kitaplarının çevre ünitelerini, konularını ve kazanımlarını genişçe anlatacak şekilde geliştirilmeleri önerilmektedir. Ayrıca çevre içeriğinin sadece belli kitaplarda değil, tüm kitaplarda yer alması ve disiplinlerarası çalışmalara yönelmesi çalışılmalıdır. Üniteler ve konular öğrenciyi merkeze alan yeni eğitim yaklaşımları doğrultusunda hazırlanan etkinliklerle desteklenmeli, öğrencinin ilgi ve hassaslığı konuya çekilmelidir. Uygulamaya geçme öncesinde tüm öğretmenler çevre ile ilgili hizmet içi eğitime ya da seminerlere tabi tutulmalı, öncelikle öğretmenlerin bilinçlenmesi ve duyarlıklarının artması sağlanmalıdır.

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# LABIATES USED IN TRADITIONAL MEDICINE IN M'SILA (ALGERIA), A SURVEY.

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The objective of this study is the identification of labiates among the medicinal plants used in traditional medicine by the community of M'sila, South East of Algeria. Ethnobotanical data from local population were collected by direct interviews and a semi-structured questionnaire carried out by interviewers belonging to the population.

82 plant species belonging to 33 families were listed during the study. Their botanical and vernacular names, medicinal part used and uses are given. Various informations related to informants are noted. Labiatae species represent 22% of the total plants listed and 48.6% of the frequency of use. Among the diseases and ailments treated by labiates are stomach troubles and coli, diabetes, rheumatism, hypertension, anemia and cancer.

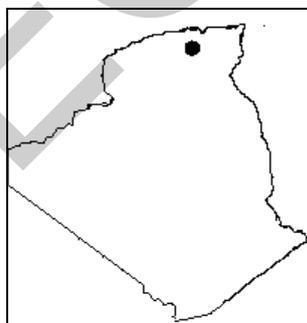
Medicinal plants are frequently employed for the treatment in the community of M'sila in spite of the availability of the prescribed drugs. The documentation of this ethnomédicinal knowledge is important. The evaluation of the pharmacological activity for the promising medicinal plants is suggested.

**Keywords:** labiates, medicinal plants, ethnobotany, traditional medicine, Hodna, Algeria.

## BACKGROUND

M'sila state (fig.1) is characterized by a little diversified flora. Nevertheless, the field reality proves the opposite. Traditional medicine is largely applied in this area and particularly to the south; what confirms its interest.

The area occupies a privileged position in the central part of northern Algeria. It covers an area of 18,718 km<sup>2</sup> and it is located at an altitude of 500 m, is situated between 35° 42' 07" N 4° 32' 49"E (W.G.S., 84). It has a continental climate with hot dry summer and very cold winter with irregular rainfall of the order 100 to 250 mm /year (Le Houerou, 1995). Its ecological aspect is characterized by predominance of the steppe (63% of the total area). Agriculture areas account for 20% of the total area devoted mainly to cereals, arboriculture and market gardening.



**Fig.1** A map of Algeria showing the location of M'sila in North center-East

## METHOD

To carry out this work, ethnobotanical information on the plants used by the population were obtained by visiting Traditional Medical Practitioners (TMP's), herb sellers and connoisseur in selected localities. The use of semi-structured questionnaire and oral interviews were adopted to obtain the relevant ethnobotanical data. The questionnaires are divided into 03 sections: (1) was about botanical and vernacular names, plant parts used and medicinal uses. (2). concern personal information on informer as age, sex educational level and duration of practice. In section (3) contains the code or/and the specimen collected.

The questionnaires were administered by trained interviewers from the population (from areas where the study is conducted) and in some cases, samples were bought in order to have the information. It was divided into three sections.

Plant samples collected were identified using flora of Quezel and Santa (1962-1963), Ozenda (1983) and Maire (1952-1987), and characterized by taxonomists of the department and deposited in Herbarium.

## RESULTS AND DISCUSSION

### Personal information on informers

Respondents interviewed in the survey include 18% of traditional medical practitioners (TMP's), 34% of herb sellers and 48% of connoisseurs. The age of 56% of them exceeds 30 years, 38% have no educational level and 70% are women. These results indicate the widespread use of plants because of

### Medicinal plants

A total of eighty-two plant species and seventy-one genera distributed over thirty-three families with a total frequency 663 are listed. The dominant families are *Lamiaceae*, *Apiaceae*, *Leguminosae* and *Liliaceae*. *Lamiaceae* was the most dominant (fig 2).

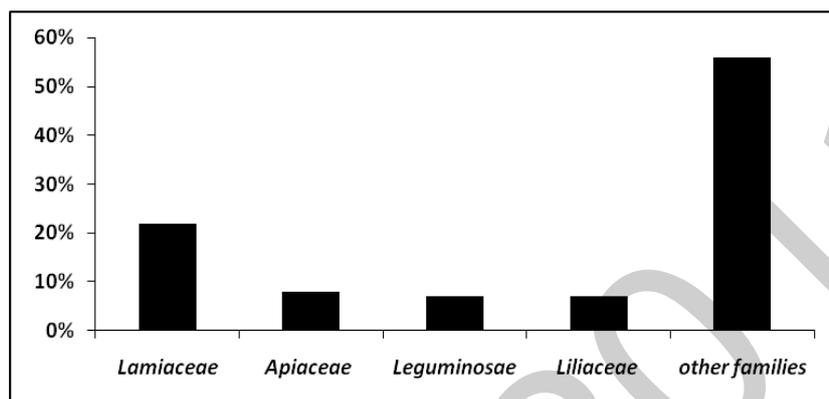


Fig.2 Predominant plant families of trado-medicinal use in M'sila.

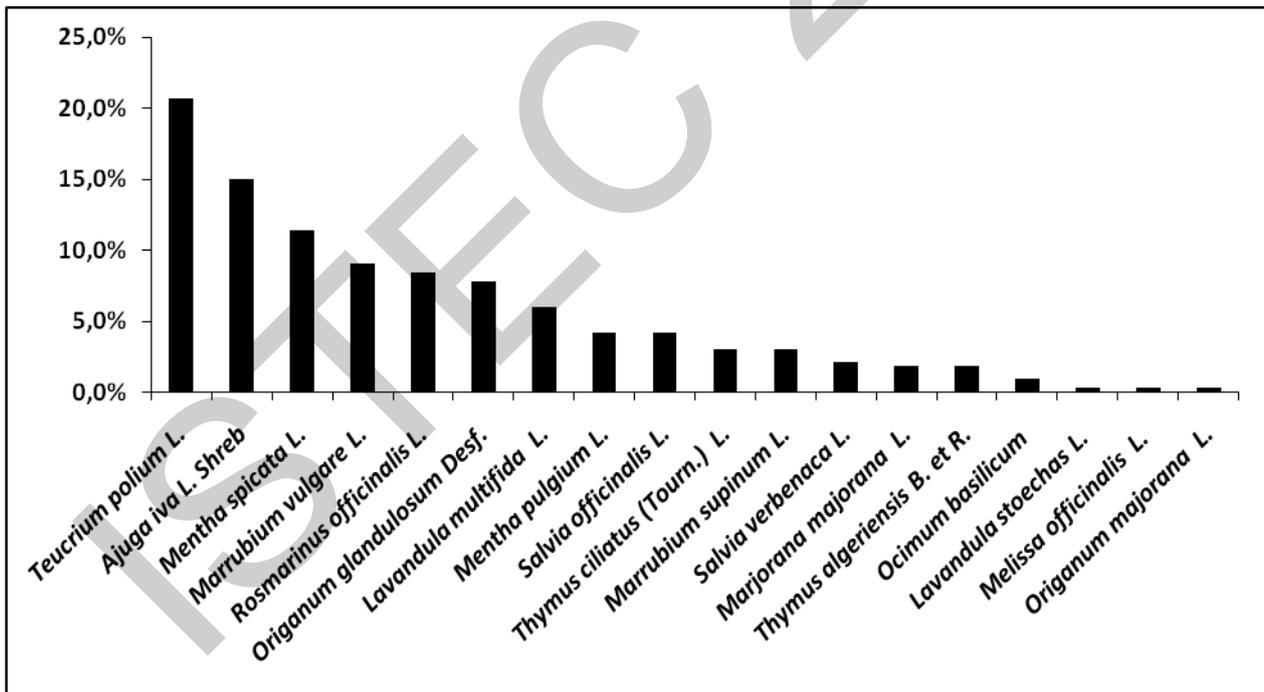
Labiatae species (listed in table 1) represent 22% of the total plants listed and 48.6% of the frequency of use. People of the study area use frequently plants as remedies for treatment of widespread diseases and ailments (Beloued, 2005) because of the important number of herb sellers without counting those who refuse interview. In addition high level contribution of women and educational level largely confirm the socioeconomic situation of the region.

Tab. 1 Medicinal plants, plant parts used, preparation and medicinal uses by local people of M'sila, Algeria

Plant name (local name)	part used	Preparation	medicinal uses
<i>Ajuga iva</i> L. Shreb (Chendgoura)	Whole plant	Infusion, Powder + honey	Stomachique; diabetes; hypertension; tonic; cephalgia; diarrhea; fever.
<i>Lavandula multifida</i> L. (Khzama)	Aerial part, leaf	Infusion, Ocular Drip, Cataplasm for head	Sedative; antispasmodic; cancer; astringent; stomachic.
<i>Lavandula stoechas</i> L. (Halhal)	Aerial part, leaf	Infusion, Decoction	Asthma, influenza, wounds,
<i>Marjorana majorana</i> L. (Madqouch)	Flowered tops, leaf	Infusion, Decoction	Regulation; sedative; cramp
<i>Marrubium vulgare</i> L. (Mariouet)	Aerial part, leaf	Cataplasm for the head	Diabetes; febrifuge; vermifuge; diarrhea.
<i>Marrubium supinum</i> L. (Mariouet)	Aerial part, leaf	Infusion, Ocular Drips	fever, otitis, slimming, hypertension, eczema
<i>Melissa officinalis</i> L. (Teronjene)	Aerial parts	Infusion, Powders, Shower	Sedative; hypotension; rheumatism.
<i>Mentha spicata</i> L. (Naânaâ)	Aerial parts	Infusion	Hypotension; sedative; disinfectant; astringent

**Tab. 1** Medicinal plants, plant parts used, preparation and medicinal uses by local people of M’sila, Algeria (*continued*)

<i>Mentha pulgium</i> L. (Fliou)	Aerial parts	Infusion	Antispasmodic, hypotension, stomach pains and stomatic
<i>Ocimum basilicum</i> (Hbaq)	Flower, leaf	Infusion	Tension; stomachic; sedative; aerophagia.
<i>Origanum glandulosum</i> Desf. (Zaâter)	leaf, flower, Flowered tops, aerial Parts, Roots	Infusion, Powder + olive oil	Hypotension, antispasmodic; astringent.
<i>Origanum majorana</i> L. (Zaâter el moulk)	aerial Parts	Evaporation of Powder + olive oil	Tension; stomachic; sedative; respiratory tract
<i>Rosmarinus officinalis</i> L. (Klil)	Aerial part, leaf	Infusion, compress	Pain abdominal; tonic; rheumatism; circular disorder.
<i>Salvia officinalis</i> L. (Miramia)	Aerial part, leaf	Infusion, Powder + honey, powder	Diabetes; stomachic; stomach pain, choleraic
<i>Salvia verbenaca</i> L. (Khayata)	Aerial part, leaf	Infusion, decoction	Aromatic, stomachic, tonic, vulnerary, disinfectant, antispasmodic, antisudorale, astringent (diarrhea), carminative,
<i>Teucrium polium</i> L. (Djaïda)	Aerial part, leaf	Infusion, powder	Disinfectant; stomachic; hemorrhoids; weakens
<i>Thymus algeriensis</i> B. et R. (Zâaitra)	Aerial part, leaf	Infusion, decoction	hypertension, carminative, diabetes, vermifuge, cholesterol, anginas, aromatic
<i>Thymus ciliatus</i> (Tourn.) L. (Djertil)	Aerial part, leaf	Infusion, decoction	Antibiotic vermifuge; carminative; tonic



**Fig.3** labiates used in traditional medicine in M’sila

Predominance of 04 families as cited in Fig.2 particularly Labiatae (Fig.3) is probably due to their availability in the region. Labiatae are more used for treatment of some important diseases or ailments especially: diabetes, rheumatism, hypertension, eczema, asthma, influenza and even cancer (Baba Aissa,1991; 1999; Bnouham *et al.*, 2002; Adebayo, 2009)

**CONCLUSION**

Traditional medicine is usually exerted by people because the use of the medicinal plants decreases the disadvantages of the chemical drugs.

This study aimed in part labiatae plants used by local people of M'sila, center-east of Algeria. These plants are used routinely for treatment gastrointestinal problems, hypertension and particularly for some diseases like diabetes, Asthma and eczema on the other hand. The main plants are *Teucrium polium*; *Ajuga iva*, *Marrubium vulgare*, *Mentha spicata* and *Rosmarinus officinalis*. The preservation of the traditional knowledge is an essential requirement for maintaining continuity and transmission of traditional medicine.

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# LABORATORY STAND FOR WIDEBAND ANALYSIS RADIOCOMMUNICATION SIGNALS

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## ABSTRACT

A laboratory stand for wideband analysis radiocommunication signals is presented in the paper. The stand is designed for signals acquisition in wide spectrum and research a field of digital signal processing. Procedures used for simultaneous acquiring many frequency channels in selected wide band are described. The method of detection of direct sequence spread spectrum signals (DS SS) which power spectral density is lower than noise is also discussed. Executed research were performed with signals locally generated and with signals from real radio communication systems.

**Keywords:** signal processing, wideband signals, data acquisition

## INTRODUCTION

Currently produced electronic parts and circuits allow to increase the speed of signal processing. A frequency sampling of A/D converters is still growing up and it enables registering signals of wider bands or higher carrier frequencies.

A method of simultaneous acquisition of many narrowband frequency channels with one receiving set is presented in the paper. The following procedures of signal processing are described: managing of filtering, down conversion and decimation; frequency synchronization; symbol synchronization and phase synchronization. This work shows that it is possible to receive narrowband signals acquired in wideband by a receiving set. Such simultaneous registration has some advantages over the traditional separate acquisition of every frequency channel: it needs less space on a hard drive, one receiving set is needed instead of a few, information about other transmissions are not lost during the acquisition, it is much easier to examine time relations between transmissions.

Moreover such acquired signal might be used to detect the DS SS transmissions. These transmissions are usually used in military systems to hide the signal below the noise. It makes such transmissions impossible to detect by traditional methods such as using signal analyzer. The method of detection DS SS transmission with laboratory stand for wideband analysis radiocommunication signals employment is also presented.

## DESCRIPTION OF LABORATORY STAND

A main aim of the laboratory stand for wideband analysis radiocommunication signals it to acquire signals in wide spectrum and then analyze them in post processing on the personal computer. It is the typical realization of software defined radio (Pereira, 2001; Faxin et al., 2006) where the main part in signal analysis and transmission receiving plays software.

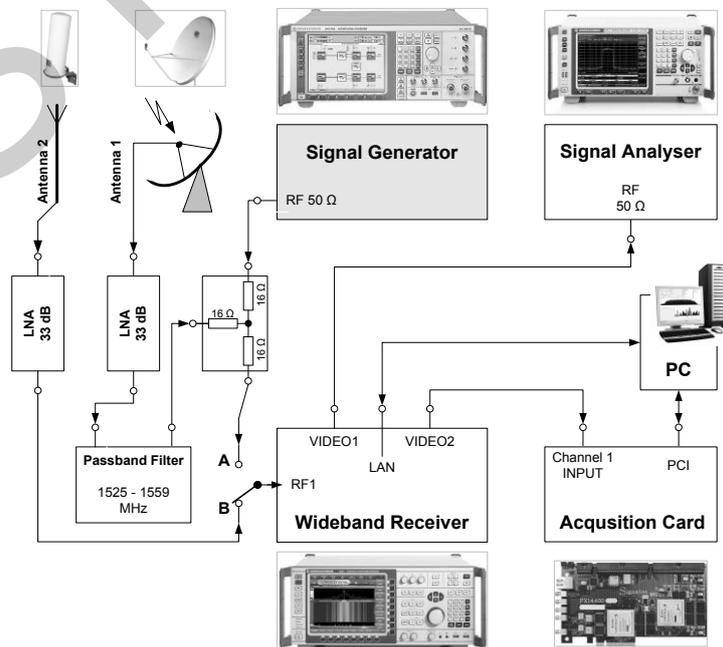


Fig. 1. The scheme of laboratory stand for wideband analysis radiocommunication signals

The laboratory stand shown in Fig. 1 consists of three parts:

- a kit of different antennas - an omnidirectional and directional antennas operating in the 0.3 - 18 GHz
- wideband receiver,
- computer with analog to digital converter (an acquisition card).

On the stand are also used following devices:

- a vector signal generator for simulation research,
- a signal combiner,
- a spectrum analyzer to control the work of receiver and acquisition card.

The omnidirectional antenna is used when acquiring signals from transmitters placed on the Earth surface, especially while the DS SS signals detection is proceeded. The satellite antenna allows to acquire signals from one of the communication satellite system. Presented stand allows to receive information transmitted in that satellite system from many frequency channels simultaneously.

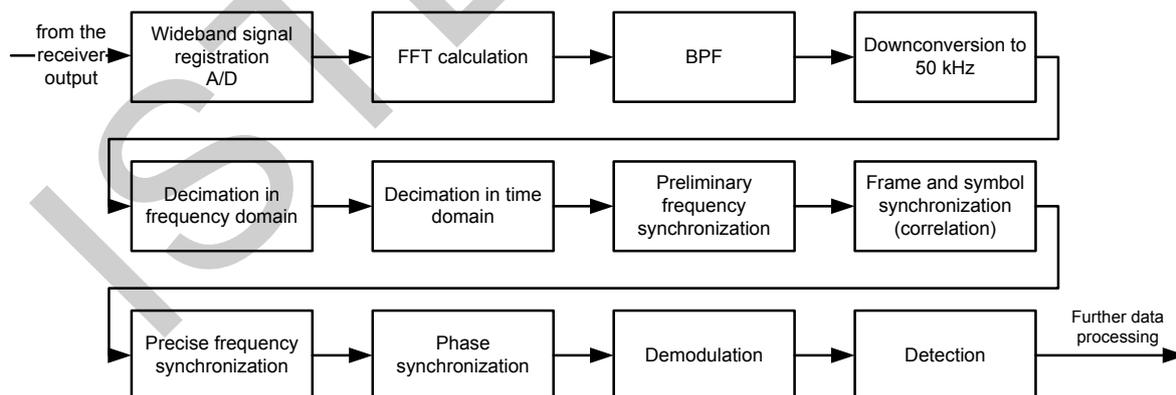
The detection of DS SS signals method is vulnerable to the influence of narrowband signals. That makes essential to perform a research which helps to work out the methods of decreasing the narrowband signals influence on the reliability of detection of direct sequence spread spectrum transmissions. In this research the vector signal generator was needed as a source of the spread spectrum signal. Signals from antenna were treated as narrowband disturbances.

The vector signal generator might be used in tests and researches of procedures which enables the simultaneous information receiving from mentioned satellite system. The generator helps in providing the predictable circumstances.

The receiver allows to acquire signals in band from 100 Hz to 20 MHz. In discussed laboratory stand this receiver transforms signals from radio frequency to intermediate frequency on which the receiving or detection procedures are performed. The acquisition is usually made in 20 MHz band on intermediate frequency equal to 11 MHz. Signals from wideband receiver are delivered to the acquisition board where they are converted to digital form most often with 50 MHz sampling frequency. The role of computer is to supervise the work of wideband receiver and acquisition card. The computer also does all of the signal computing: filtering respective frequency channels, another frequency down conversion, performing receiving procedures, filtering the narrowband distortions and realizing the detection of DS SS transmission. Most of this procedures are described in the following two paragraphs.

## WIDEBAND RECEIVING OF SATELLITE COMMUNICATION SIGNALS

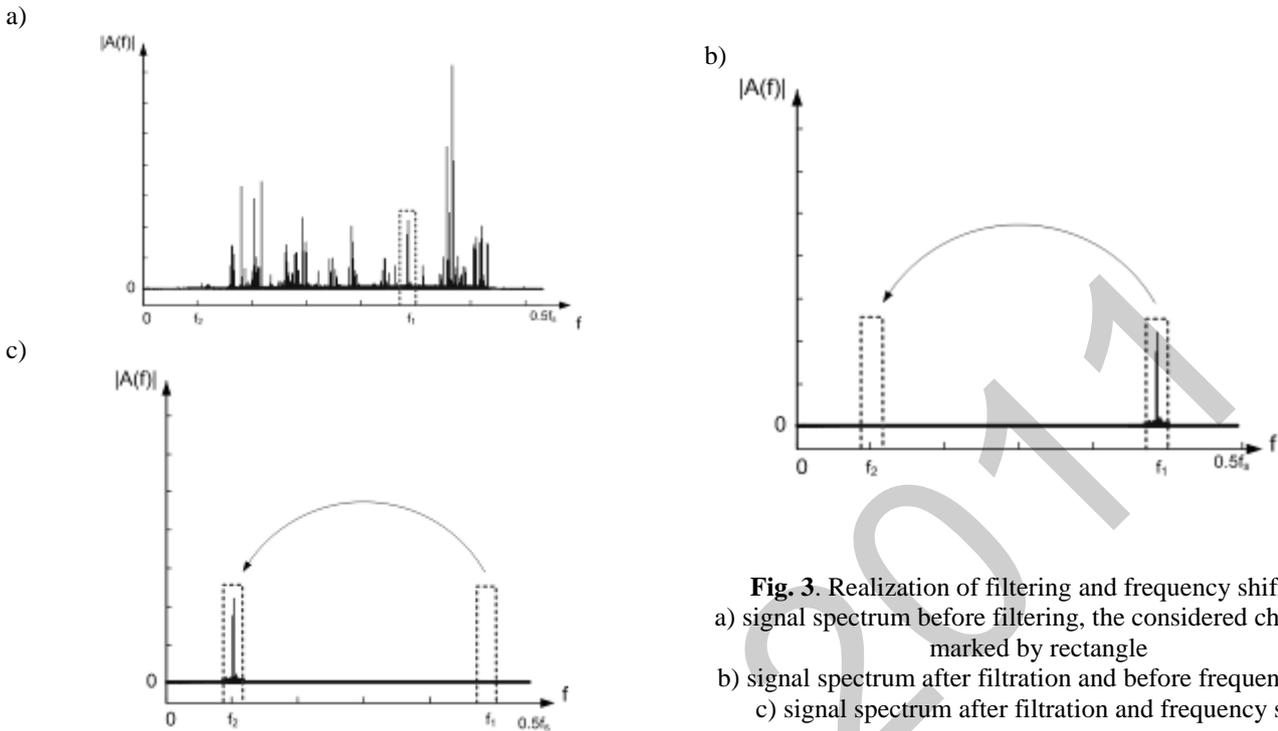
The stand shown in Fig. 1 may be used to receive information from one of the satellite communication systems. It can be made simultaneously, because radio signals are acquired in wide spectrum. The stand allows to record almost all downlink frequency channels used in the considered system. The band of single frequency channel in this system is less then 10 kHz. The functional scheme of signal processing used to receive transmitted information is shown in Fig. 2.



**Fig. 2.** Functional scheme of signal processing procedures used to receive signals

While signal registration is performed in the wideband (20 MHz) and channel band is less than 10 kHz, the first operation is a band pass filtering which suppresses the impact from other systems and channels. Moreover, to decrease frequency sampling the digital down conversion to frequency 50 kHz is required. For the frequency shifting two solutions can be implemented. In the first one, traditional frequency shifting, useful signal is combined with the signal from heterodyne to obtain the desired frequency. After this operation unwelcomed new frequency components are also generated and to suppress them another band pass filter is needed. It makes this method both time and resources consuming. The second solution uses a filter which values are 1 in the band pass and 0 beyond it which allows to carry out a frequency shifting from frequency  $f_1$  to  $f_2$  by changing the index of suitable spectrum components as shown in Fig. 3. The last solution has been used in the project.

After this operation the decimation is enabled. We reduce the number of samples 64 times, what changes the sampling frequency value to 781,25 kHz. This value significantly decreases the size of processed data and simultaneously keeps the gain achieved of cumulating when noise is integrated in detector. Such prepared signal is used in synchronization and demodulation operations. For demodulation, it is essential to know the exact carrier frequency of the signal, it means phase and symbol timing.



**Fig. 3.** Realization of filtering and frequency shifting:  
 a) signal spectrum before filtering, the considered channel is marked by rectangle  
 b) signal spectrum after filtration and before frequency shift  
 c) signal spectrum after filtration and frequency shift

In the considered system in every frame there are bits provided for synchronization processes. These bits are especially used while finding the beginning of symbols and phase of the signal.

Because in discussed system the OQPSK modulation is used, the frequency synchronization is made by finding in the spectrum of signal raised to 4<sup>th</sup> power a component of carrier frequency  $4f_c$ . For example, when the OQPSK signal frequency is 50 kHz, then the component on frequency 200 kHz will be distinctive in spectrum of signal raised to the 4<sup>th</sup> power. As it is shown in Fig. 2, after decimation the preliminary frequency synchronization is performed. For the correlation part we need to know only approximately the signal frequency. It is managed by computing the spectrum of signal raised to 4<sup>th</sup> power from fewer of number samples then when signal frequency is computed precisely. When the frequency signal is known, the model of signal is prepared for correlation. The unique word modulates the carrier which frequency is equal to the found one. Then the signal model is correlated with acquired signal to find the symbol and frame synchronization. If the signal is found the precise frequency synchronization is performed. In the end the phase synchronization must be achieved. It is accomplished because the unique word is known. As we know what symbols to expect, we can compute the difference between the angle of predicted point in the constellation diagram and the point achieved by demodulating signal without phase synchronization. The difference between these angles is the phase correction which should be taken in account during actual demodulation. When all signals parameters are known the demodulation processes can be performed.

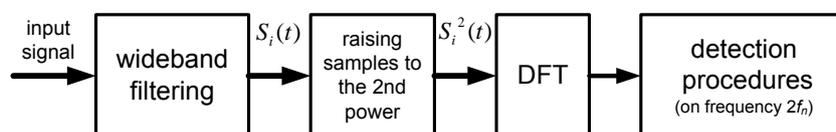
**THE DS SS SIGNALS DETECTION**

The method of the DS SS signals detection is based on rising the value of signal samples to the power of  $n$ , where  $n$  depends on the type of used digital angle modulation. In spectrum of raised signal in  $n*f_n$  appears a sufficiently large value, where  $f_n$  is a frequency of discussed signal.

If the input signal is squared, then in accordance with trigonometric relationship:

$$\cos^2 \alpha = \frac{\cos 2\alpha + 1}{2} \tag{1}$$

the appearance of a spectrum component at frequency two times higher than the signal carrier frequency can be observed (Was et al, 2008.; Katulski et al, 2008). The scheme of signal processing is presented in the Fig. 4.

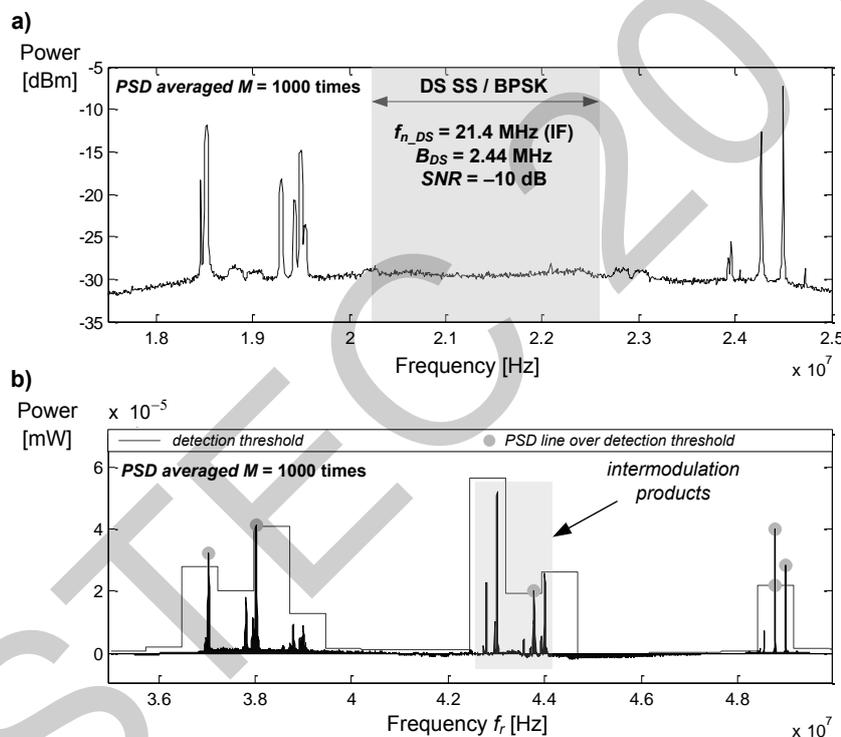


**Fig. 4.** The simplified scheme of signal processing used to detect of DS SS transmissions with BPSK modulation

An experiment was performed to detect the wideband transmission of the DS SS with BPSK modulation with negative SNR values, carried out in the vicinity of real and relatively strong signals which is narrowband interference for the detection algorithms. Results for procedures performed with an inactive and active block for detection and elimination of narrowband signals are presented below.

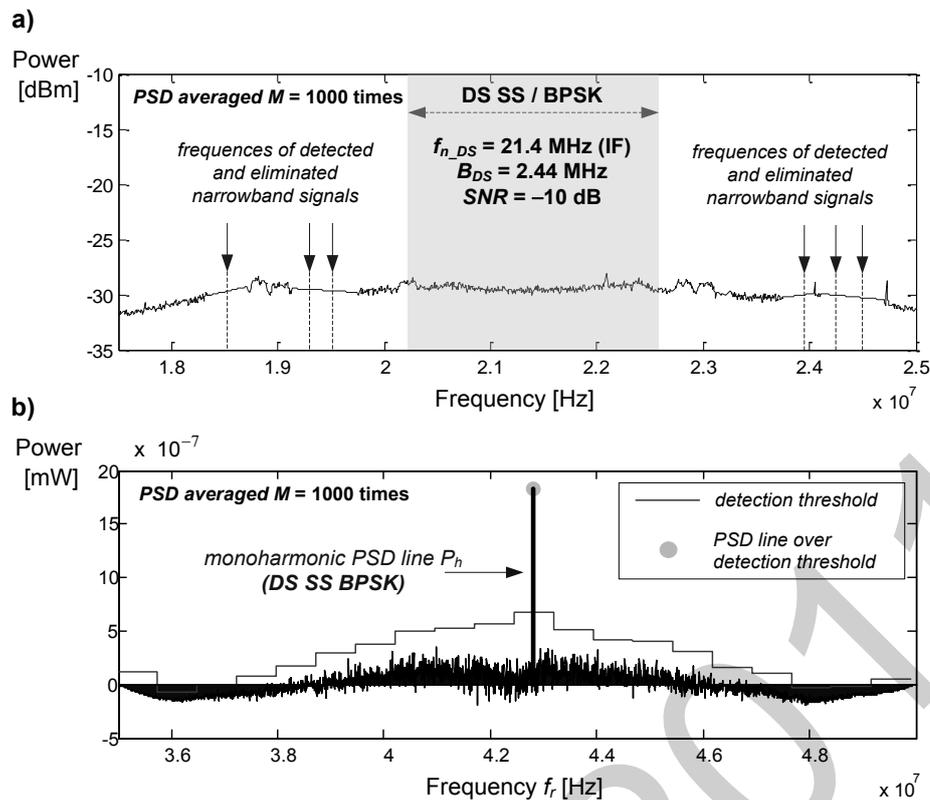
The aim of the experiment was to explore the possibilities of the DS SS signal with BPSK modulation detection in the presence of the real signals. The satellite signals received in the frequency range 1525 MHz to 1560 MHz were used as the background. The range of frequency band was chosen in such a way that there was relatively strong narrowband interference in the vicinity of the sought signal. The ratio of the maximum levels of the carrier power to the level of noise ranged from 10 to 20 dB (see Fig. 5a). The parameters of generated the DS SS signal with BPSK modulation were selected in such a way to get a negative ratio of wanted signal to the noise power  $SNR = -10$  dB at the input of the acquisition card. The frequency range covered by the presence of the wideband direct-scattering spectrum indicated in Fig. 5a and Fig. 6a in a shaded box ( $B_{DS} = 2.44$  MHz,  $f_n = 21.4$  MHz on the IF). The results of the experiment in the form of spectrum power density characteristics of the analyzed signal bandwidth and signal PSD of squared signal samples (in terms of twice the frequency) is shown in Fig. 5b and 6b. In the presented spectral characteristics the FFT of size  $N = 2^{14}$  was used.

Analyzing obtained results, it can be concluded that when the narrowband signals have not been subjected to elimination (see Fig. 5b), the detection condition has been met for the six components of the spectrum. As it can be seen, none of the components exceeding the detection threshold does not come from the DS SS signal hidden in noise. Moreover, in the middle of the band appeared some unwelcome "false" components indicating the possibility of hidden signals in noise. These components are the products of intermodulation, arising from the squaring of signal samples.



**Fig. 5.** Demonstration of PSD for signal samples on the input of the acquisition card (a) and results of the DS SS transmission in the absence of procedures for the elimination of narrowband signals

To sum up the carried out experiments, it can be concluded that the detection process has been disturbed by narrowband signals, and the obtained results give an erroneous impression of the existence, in the analyzed band, the wideband DS SS signals with negative SNR values. Therefore, detection procedures were repeated on the same set of samples, but this time with the active block for detection and elimination of narrowband signals. As a result of implementation of appropriate procedures six narrow-band signals were detected and eliminated. The PSD which figure in the band analysis is presented in Fig. 4a. Such a prepared signal was processed in accordance with the signal detection algorithm for the DS SS transmission with BPSK modulation using the spectral analysis of the squared samples put in the time domain. A result in a graphic form and the selected detection threshold is shown in Figure 6b. The experiment RF center frequency for input circuits of the receiver corresponded to the carrier frequency of generated spread spectrum signal, which in turn should lead to the emergence of  $P_h$  component (harmonic coming from searching for DS SS signal) on the frequency 42.8 MHz, exactly twice the IF carrier of 21.4 MHz.



**Fig. 6.** PSD of the signal of fig. 5a after the elimination of narrowband signals (a) and the results of the procedures for detecting the DS SS transmission with BPSK modulation (b)

Proposed procedures of detection DS SS signals were used to detect the GPS signals (for more details see Studanski et al., 2011).

## CONCLUSION

The development of electronic parts and computational components enables to use digital signal processing in wider variety of applications. Therefore, the thorough technical analysis of registered signal is possible.

It is manageable to receive narrowband signals from a real radio satellite system acquired in the wideband. Such approach enables to register signals from many frequency channels and store them on a hard drive.

The conducted experiments have confirmed the effectiveness of signal processing methods developed for the detection of the DS SS transmission with BPSK modulation and the power of signal lower than noise power. Using the method for testing the squared signal PSD, it is imperative to carry out the elimination of narrowband signals present in the analysis. Unwanted narrowband signals can disturb the proper operation of the detection algorithms by generating ambiguous and "fake" results.

## ACKNOWLEDGMENT

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# LAND USE AND LAND COVER (LULC) CLASSIFICATION USING SPOT-5 IMAGE IN THE ADAPAZARI PLAIN AND ITS SURROUNDINGS, TURKEY

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## Abstract:

The objective of the study is determination of land use and land cover patterns of Adapazari plain and its surroundings by image classification. The study area is located in northwest of Turkey between coordinates of 40°37'- 40°57' N and 30°12'- 30°46' E and approximately 140 km east of Istanbul. Plain has become by the accumulation of sediments carried by Sakarya River and its tributaries. Adapazari Plain is a fertile agricultural area because of its favourable natural conditions. However, because of its closeness to Istanbul, population stress has gradually increased, so industrialization and urbanization has been accelerated in the plain. In this study, SPOT-5 satellite image is used to determination of land use and land cover characteristics of research area. The image is analyzed by using data images processing techniques in ERDAS Imagine© 10.0 and ArcGIS© 10.0 software. Land cover nomenclature is classified according to the CORINE (Coordination of Information on the Environment) Level 2 Classification (1-Urban fabric, 2-Heterogeneous agricultural areas, 3-Forests and 4-Inland wetlands) and Level 3 Classification (1-Industrial units, 2-Roads) . Furthermore, the image analysis results are confirmed by the field research.

**Keywords:** Land use and land cover (LULC), CORINE, SPOT 5, The Adapazari plain.

## 1. INTRODUCTION

Land use and land cover (LULC) classes characterize important information of natural landscape and human activities on the Earth's surface (Gong et al. 2011). In recent decades, remotely sensed data have been widely used to provide the land use and land cover information such as degradation level of forests and wetlands, rate of urbanization, intensity of agricultural activities and other human-induced changes. More recently, imagery from high spatial resolution satellite systems such as IKONOS, QuickBird, and SPOT-5 has become available. High resolution satellite imagery offers new opportunities for potentially more accurate identification and area estimation than traditional satellite imagery (Yang et al. 2010). In this study we used SPOT-5 data with 10 meter spatial resolution. Land use/land cover classification is a time-consuming and expensive processes. There are various methods that can be used in the collection, analysis and presentation of resource data but the use of remote sensing and geographic information system (RS/GIS) technologies can greatly facilitate the process (İkiel and Ustaoglu, 2011). In remote sensing technology, classification as a common image processing technique is implemented to derive data regarding land cover types. In classification process, supervised classification with the maximum likelihood method which is also used in this study has been widely used in remote sensing applications (Yuksel et al. 2008). In this study, land use and land cover classification standards of Coordination of Information on the Environment (CORINE) Land Cover were used in the process classification system. The study area, Adapazari Plain, is located in northwest of Turkey approximately 140 km east of Istanbul (Figure 1). The plain has become by the accumulation of sediments carried by Sakarya River and its tributaries (Bilgin, 1984: 2). Adapazari plain has an intensive and varied agriculture because of its favorable natural conditions (Erinç and Tunçdilek, 1952) and the largest plain in the Marmara region (Tuncel, 2005). The research area is involved in Euxine province of Euro-Siberian phytogeographical region. This region is the most important area with its forest formation (Humid-Mild Deciduous Forests) (Kilic, 2011). However, because of its closeness to Istanbul, population stress has gradually increased, so industrialization and urbanization has been accelerated in the plain. In recent years, change has been observed in the natural land use and land cover. The objective of the study is determine the land use and land cover (LULC) patterns of Adapazari plain in 2010 using an integrated approach of remote sensing and GIS.

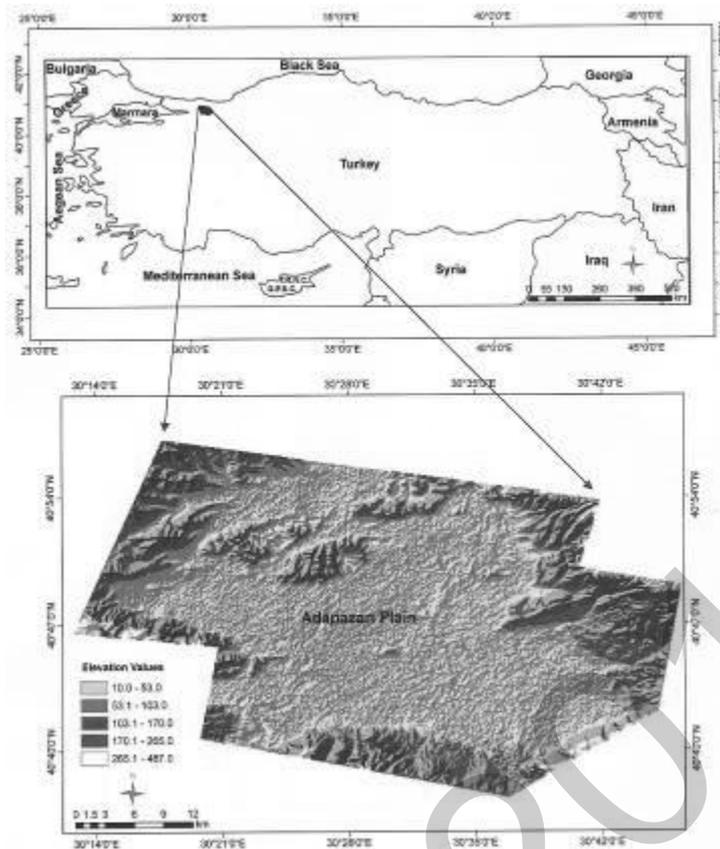


Figure 1: The Location map of study area.

## 2. DATA AND METHOD

### 2.1 Data

A Spot 5 image acquired on December 7, 2010 with 10 meter spatial resolution and four spectral bands: B1 (green: 0.50–0.59  $\mu$  m), B2 (red: 0.61–0.68  $\mu$  m), B3 (near infrared NIR: 0.79–0.89  $\mu$  m) and B4 (short-wave infrared SWIR: 1.58–1.75  $\mu$  m) was used to classify the land use land cover (LULC) in our study area. The image was provided by a commercial data provider. The image was also required to have less than 20 % cloud cover. With this criteria the image was cloud cover of 0 %. The characteristics of the image data are presented in Table 1. The other data used in this study for reference and analyses mainly include: (1) topographic maps at a scale of 1/100.000; (2) detailed vegetation map obtained from TR Forestry and Water Affairs Minister belongs to 2002; (3) detailed environment plan obtained from Sakarya Metropolitan Municipality; (4) ground reference data obtained from land survey with hand held GPS (5) demographic data of Sakarya from 1990 to 2010 which obtained from TurkStat, Turkish Statistical Institute (6) ERDAS Imagine© 10.0 and ArcGIS© 10.0 software were used for image classification and data analyses.

Type of imagery	Date	Spatial resolution (m)
Spot 5	07.12.2010	10

Table 1: Characteristics of the satellite data used for land cover change mapping in the study area.

### 2.2 LULC classification and mapping

LULC classification and mapping was performed in four stages: 1) Preprocessing of the images 3) Determination of land cover types 3) Supervised classification of the image into LULC classes 4) Accuracy assessment. These applications were performed using ERDAS Imagine 10.0 software. This research primarily used theory and methodology from geography, remote sensing and geographic information science to analyze the land cover dynamics in the study area.

#### 2.2.1 Preprocessing of the images

Image was clipped out according to the location map by using subset function (Figure 2). The radiometric corrections, systematic errors and SPOT 5 geometric correction were carried out by data set providers. The image was geo-referenced into the Universal Transverse Mercator-UTM, WGS-84.

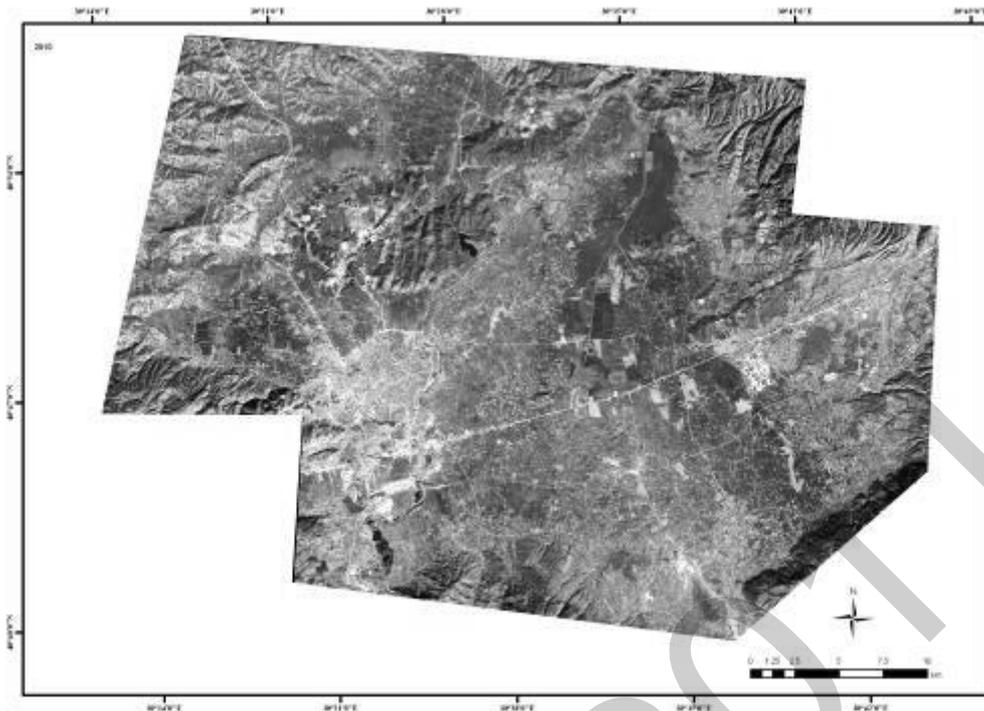


Figure 2: SPOT 5 satellite image with 10 meter resolution (07.12.2010)

### 2.2.2 Determination of land cover types

The CORINE land cover nomenclature/ classification system was chosen and referred for the classification system for this study. The field work supported the image interpretation of land cover types defined in the classification. The Coordination of Information on the Environment (CORINE) land cover determination program, which is mainly operated by member countries of the European Union, was started by the European Commission of the Union and can be summarized as ‘environmental knowledge formation’. The legend of the CORINE land cover nomenclature/ classification is standard for the whole of Europe, which as a result is quite extensive with 44 classes describing land cover (and partly land use) according to a nomenclature of 44 classes organized hierarchically in three levels (Sonmez et.al, 2009). In this study land cover legends include six classes. Some of those are classified at level 2 (1-Urban fabric, 2-Heterogeneous agricultural areas, 3-Forests and 4-Inland wetlands) and others are classified at level 3 (1-Industrial units, 2-Roads).

### 2.2.3 Supervised classification of the image into LULC classes

A good knowledge of the study area was achieved by a suitable image enhancement and related literature. Furthermore Richards and Jia (1999) suggest fieldwork that develops knowledge of the area with interviews, photography of characteristic surfaces, ground truth data in order to validate a classification. In this study, all images were independently classified using the supervised classification method of maximum likelihood algorithm. Although many different methods have been devised to implement supervised classification, the maximum likelihood is still one of the most widely used supervised classification algorithms (Jensen, 1996). In supervised classification, spectral signatures are collected from specified locations in the image by digitizing various polygons overlaying different land cover types. The spectral signatures are then used to classify all pixels in the scene. “user defined polygon” were selected from the whole study area by drawing area of interest (aoi). In supervised classification process, .aoi function reduces the chance of underestimating class variance since it involved a high degree of user control. After the classification process, all signature sample points were grouped as a class by “recode” function according to the determined land cover classification types in this study. In this study, the supervised classification method detected over 50 homogeneously distributed sample areas from 6 classes in total according to the maximum likelihood algorithm (aoi).

### 2.2.4 Accuracy assessment

Accuracy assessment tool was performed to evaluate the accuracy of the classified images. It is based on random sampling method which selected the points from referenced map. After the application, obtained a report which show error matrix of the results. Error matrix is in the most common way to present the accuracy of the classification results. Overall accuracy, user’s and producer’s accuracies, and the Kappa statistic were then derived from the error matrices. The overall accuracy and a KAPPA analysis were used to perform classification accuracy assessment based on error matrix analysis. Using the simple descriptive statistics technique, overall accuracy is computed by dividing the total correct (sum of the major diagonal) by the

total number of pixels in the error matrix. KAPPA analysis is a discrete multivariate technique used in accuracy assessments. KAPPA analysis yields a Khat statistic (an estimate of KAPPA, equation 1) that is a measure of agreement or accuracy (Jensen, 1996, Guler et al, 2007). The Khat statistic is computed as:

$$\frac{N \sum_{i=1}^r x_{ii} - \sum_{i=1}^r (x_{i+} x_{+i})}{N^2 - \sum_{i=1}^r (x_{i+} x_{+i})} \tag{1}$$

Where r is the number of rows in the matrix,  $x_{ii}$  is the number of observations in row i and column i,  $x_{i+}$  and  $x_{+i}$  are the marginal totals for row i and column i respectively and N is the total number of pixels. Independently classified images were compared with each other to determine the changes of land cover types. Accuracy levels of more than 80 % are considered adequate enough for reliable classification of land cover types (Sabins, 1997).

### 3. RESULTS AND DISCUSSIONS

The supervised classification method detected over 50 homogenously distributed sample areas from 6 classes in total according to the maximum likelihood algorithm (aoi). Accuracy analysis was applied to the classified satellite image (2010) with an aim to confirm the accuracy of the classification. To do this, over 50 random reference control points were identified on the study area map for 6 classes. The point distributions were made in proportion to the field distributions of the classes. Total accuracy rate (total number of accurate pixels / number of pixels taken as reference) was detected 94.00% and kappa statistics value was 92.30%. Both Producer’s accuracy and User’s accuracy (accuracy rate generated by the user) are over 80% in all classes (Table 2). According to the high accuracy assessment results up to 80%, LULC classification is correct statistically.

Class Name	Reference Totals	Classified Totals	Number Correct	Producers Accuracy (%)	Users Accuracy (%)	Kappa (%)
Heterogenous agricultural areas	20	20	19	95,0	95,0	91,6
Forests	5	5	4	80,0	80,0	77,7
Urban Fabric	6	5	5	83,3	100,0	100,0
Industrial Units	5	5	5	100,0	100,0	100,0
Inland Wetlands	5	5	5	100,0	100,0	100,0
Roads	4	5	4	100,0	80,0	100,0
Totals	50	50	47			78,2
Overall Classification Accuracy: 94.00 %			94,00%	Overall Kappa Statistics =		92,30%

Table 2: Results of accuracy assessment of the 2010 land use and land cover classification map produced from SPOT 5 data.

The highest classification accuracy was obtained in industrial units and inland wetlands due to their homogenous character. Structural character of the land (homogeneous-heterogeneous) and spatial resolutions of the satellite image put a direct effect on the obtained result. According to LULC classification results, land cover distributed as heterogeneous agricultural areas 78.4 %, forests 14.8%, urban fabric 5.1%, industrial units 0.3%, inland wetlands 0.5% and roads 0.9%. Based on the results, heterogeneous agricultural area is the largest land use and land cover classes in the plain (Table 3). Major agricultural areas and industrial units are located around the settlements according to the map (Figure 3).

Class Name	Area (hectare)	Area (%)
Heterogenous agricultural areas	145798	78,4
Forests	27476	14,8
Urban Fabric	9419	5,1
Industrial Units	609	0,3
Inland Wetlands	1014	0,5
Roads	1671	0,9
Totals	185987	

Table 3: Results of the land use and land cover classification table for 2010 image showing area of each class.

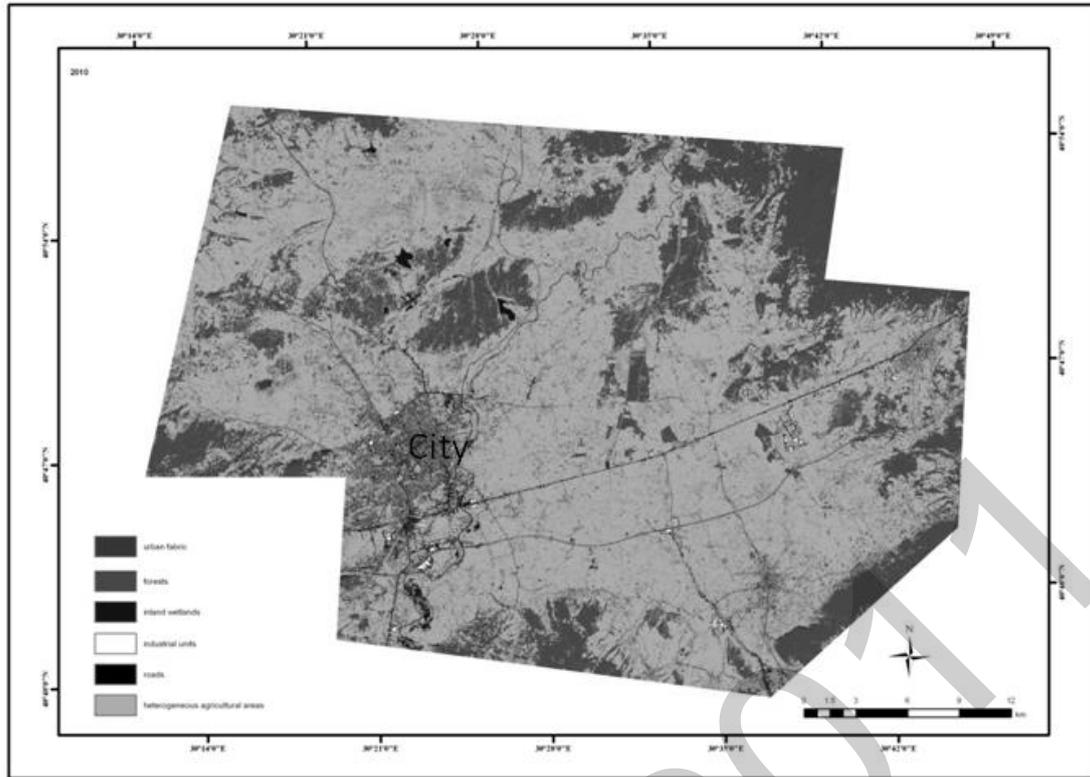


Figure 3: Land use and land cover (LULC) classification map (2010) derived from SPOT -5.

Adapazari plain is close to major roads every period of history. Because of this advantage geographic position, settlements on the plain have developed up to now (Doldur, 2006). Today the city of the Adapazari consisted of the expansion of settlement around the old Adapazari area. Other settlements are Hendek and Akyazı which are the town center in the plain.

Years	Total Population	Accrual	Population Growth Rate (%)
1990	683,061		
2000	756,168	73,107	10,7
2007	835,222	79,054	10,5
2008	851,292	16,070	1,9
2009	861,570	10,278	1,2
2010	872,872	11,302	1,3

Table 4: Population growth of the Sakarya city between 1990 and 2010 according to TurkStat 2011.

Therefore, the population is increasing in Adapazari which has become a center of attraction for the near and far around (Table 4). Particularly urban population has greater share increasing in this population. For example, while the central town of Adapazari according to 1955 census, 74% of the population living in villages (İnandık, 1956), this ratio decreased 5.1% while the urban population ratio increased % 94.9 according to the results the 2010 census calculation of the data obtained from TurkStat, Turkish Statistical Institute (Table 4). Therefore, urban fabric is changing and urban settlements area is growing continuously.

#### 4. CONCLUSIONS

We obtained classified land use and land cover classification in the Adapazari Plain, Turkey (2010) with analysing SPOT-5 satellite image. According to LULC classification results, land cover distributed as heterogeneous agricultural areas 78.4 %, forests 14.8%, urban fabric 5.1%, industrial units 0.3%, inland wetlands 0.5% and roads 0.9%. Based on the results, heterogeneous agricultural area is the largest land use and land cover classes in the plain. Although industrialization and urbanization is increasing in the study area, the Adapazari Plain is still an important agricultural area in Turkey. As a results of this study, high accuracy of land use and land cover classification map was obtained. Relatively homogeneous structural character of the plain and high spatial resolutions of the SPOT-5 with 10 meter put a direct effect on the obtained result. Accurate LULC maps can play an important role in aiding land use and land cover management as well as helping in deciding what sort of lands are best suited for sustaining land use and land cover and in what manner this land use and land cover should be practiced.

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# LANDSCAPE VALUE-BASED MICRO-REGIONAL DEVELOPMENT IN NORTHEASTERN-HUNGARY

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## ABSTRACT

In this study the connection between landscape values and tourism is analysed in the micro-region of Abaúj-Hegyköz. It is one of the most disadvantaged areas in Hungary, but it has great potential due to its variable natural and cultural values. Based on the diverse landscape values the main profile of development shall be tourism.

I have registered the landscape values, and explored the natural and cultural history of the region. I have elaborated a unique evaluation system, which helped to find the most important landscape values and determined what kind of tourism is suitable in certain settlements. The other method of evaluation was a questionnaire survey which revealed the recent conformation of tourism and the attitude of inhabitants. The synthesis of the two evaluations' results substantiated the development proposals. Based on the groups of landscape values a thematic route and a green way were proposed. Elemental aspect in the course of planning protection of landscape values was the.

## INTRODUCTION

The research area is located in the northern part of the Abaúj-Hegyköz micro-region in Hungary. The region, which constitutes of ten settlements, is located in the North-Hungarian Region, in Borsod-Abaúj-Zemplén county. The micro-region, thus the settlements belong to the most backward areas of the country. This is manifested in low living standards of local residents, in high proportion of unemployment and other negative social processes. Despite all of this, much potential lies in this micro-region owing to the rich natural, landscape and cultural values. The main development direction, the breakout opportunity could be clearly the tourism based on landscape values.

The main goal of the research is the familiarization and the development of a peripheral micro-region region, as well as enhancing its economic and cultural life. All of these can be realized by sustainable tourism. Existing capabilities and landscape based system-oriented planning is necessary to achieve the desired goal by which the settlements could develop through a deliberate framework.

## 1. PRESENTATION OF THE RESEARCH AREA

In the research the micro-region is presented through the defining aspects of tourism development. The largest portion of the research area is located in the upper valley of the Hernád river and the northwestern side of the mountains of Zemplén. Parts of some settlements' areas lie on the north-eastern hills of Cseréhat. The research area covers the northern half of Abaúj-Hegyköz micro-region, so the direct influential area of Gönc (which is also the center of the whole micro-region). The subject area consists of town Gönc and nine villages grouped around the micro-regional centre (Abaújvár, Hernádszurdok, Hidasnémeti, Göncruszka, Kéked, Pányok, Telkibánya, Tornósnémeti and Zsujta). The method of the delimitation is also justified by the crucial role of the Slovak-Hungarian border which has a direct influence on the settlements of the research area. The total research area is 171 km<sup>2</sup> (Figure 1).



Figure 1: The research area

The structure of the area (settlement network and infrastructure network) is determined by the landscape and geographical (topography, hydrography) conditions. The most important transport route is the main road nr. 3 which runs along in the valley of the Hernád, west of the river. Nearly parallel to this main road runs the railway line linking Miskolc and Kosice. The transport links of the settlements east from the Hernád-river are significantly worse than the previous area. The roads between the river and the mountains of Zemplén meet in Gönc. The nearest significant centre is Encs. It is important to note that the wider region's largest center, Kosice (in Slovakia) is half as far from Gönc as Miskolc, the county seat. The Slovak-Hungarian border runs along the northern perimeter of the research area. After the Schengen's border opening the proximity of the second largest city in Slovakia, Kosice with a population of 300,000 was appreciated.

### 1.1. Natural values

The Landscape Protection Area of Zemplén is of national importance as a nature conservation area. The Landscape Protection Area is one of the most undisturbed and undetected region in Hungary. For several years there have been efforts to declare the area as a national park. The Landscape Protection Area was established in 1984 on 26,496 acres. Certain parts of Nagy-Sertés Mountain, which belongs to Telkibánya, are also forest reserves (*F. Nagy, 1996*). About 85% of the Landscape Protection Area's territory is covered by forest, which determines its character. The planned Green Corridor Landscape Protection Area of Hernád, which is currently under preparation, affects a significant part of the research area. This protected area will also include parts of the following settlements that lie along the river: Abaújvár, Hernádszurdok, Hidasnémeti, Gönc, Göncruszka, Kéked and Zsujta. Some of the major potential and attraction of the research area are the beauty and the relative virginity of the landscape and the special relationship between the settlements and the nature. The area can be divided into two distinct, separate units based on landscape conditions: the mountain and the valley along Hernád (*Figure 2*).



Figure 2: Abaújvár and the gallery forests along Hernád from the Sáfrány-hill

### 1.2. Landscape history

At the time of the foundation of the state Hungarians settled in the area creating the historical Abaúj county. The main source of living was farming for the folk of the Hernád Valley and the Cserhát at all times. In addition, grape production was strongly revived in the 14<sup>th</sup> century (particularly in the area of Gönc). The vast forests of the area were sparsely populated in the 11-13<sup>th</sup> century. Greater immigration began in the 14<sup>th</sup> century, and the importance of mountain regions dramatically increased. After that time, the exploitation of the occurring precious metal deposits began (Telkibánya). In the foundation of the historical Abaúj county it was of decisive importance that a very important north-south military and trading route led through the region. That allowed Košice to become a town, and helped it become the center of the region till the end of the Middle Ages. In the 18-19<sup>th</sup> century there were extensive vineyards on the hillsides around Gönc and Göncruszka which are nowadays orchards. In the 19<sup>th</sup> century the railway line was built beside Hidasnémeti and Tornynosnémeti. The areas west from Hernád-river have become important from the point of view of transportation. The new frontier created in 1920 significantly influenced the further life of the area (Kosice, which had been the center of the region, became a part of Slovakia). The area has become for a good time a peripheral area of Miskolc, and Borsod industrial region which gained increasing importance. In the 20<sup>th</sup> century the vineyards of Gönc and Göncruszka were taken over by orchards.

### 1.3. Landscape values

The survey of landscape values was carried out in the total area. The landscape value definition created by the Corvinus University of Budapest, Department of Landscape Planning and Regional Development was used during the survey. We consider all natural and cultural landscape elements as landscape values which at all times determine the positive character of the landscape for the local residents, tourists and professionals (*Sallay 2009*). The following four steps were carried out during the survey of landscape values: the basic information collection (maps, monographs, and personal stories), site visit, register organization, data processing (*Csemez-Mócsényi, 1983*). In total, 489 landscape values were assessed. This landscape values register forms the basis for development proposals. All surveyed landscape values were given a code, furthermore, in the register exact name, type, location, main characteristics, age, condition and vulnerability. *Figure 3* shows the amount of measured landscape values in each settlement.

Settlements	The number of measured landscape values
Abaújvár	39
Gönc	63
Göncruszka	44
Hernádszurdok	30
Hidasnémeti	47
Kéked	34
Pányok	43
Telkibánya	119
Tornynosnémeti	47
Zsujta	23

Figure 3: The number of measured landscape values in the settlements

## 2. LANDSCAPE EVALUATION

During the evaluation process two main methods were applied: one is landscape value based in which a special system of criteria and scoring was worked out; and the other was based on questionnaires. These assessments helped to determine the most valuable landscape values, furthermore, to point out the settlements with the highest number of values. Recent developments in tourism were analyzed by a questionnaire method and the locals' attitudes to the subject were also explored.

### 2.1. Landscape value based evaluation

Evaluation was carried out on different levels using the registered landscape values. First, the individual values were separately scored according to the own system of criteria. In the next phase the points of the landscape values were summarized for each settlement. The first level of evaluation is necessary to decide what are exactly the landscape values, which should be involved in the planning. In addition, using this method it was possible to determine which values, should not become the basis of the suggestions, but optional, will appear as supplementary items. The system of criteria includes seven aspects, which are as follows:

- specialty, rarity,
- importance of tourism, awareness,
- landscape, urban visual significance,
- originality, influence,
- status and vulnerability,
- degree of protection,
- accessibility.

During the selection of these system components the aim was to provide a wide angle of view in the evaluation. Each of first five criteria was divided into four categories. Because of simplicity and transparency an evaluation aspect can be given up to 4, and minimum 1 point. So the landscape values are available between 5 and 20 points. The "degree of protection" aspect was introduced for the highly valuable and specially protected landscape values. In this category 6 and 3 extra points can be given according to the level of the protection. For scoring accessibility points between -1 and 2 were used. Overall, a surveyed landscape value can gain a maximum of 28, a minimum of 4 points. The total score determines the level of value, in which four categories were identified:

- 28-20 points: highly valuable,
- 19-16 points: very valuable,
- 15-12 points: valuable,
- 11-4 point less valuable.

According to the evaluation results 47 pieces of landscape values are in the category of highly valuable in the area. All the villages have at least one of them except Hernádszurdok and Hidasnémeti. In the following these values are summed up for each settlement.

*Abaujvár*: Reformed fortified church, fortress (earthwork), Kátyú-valley

*Gönc*: Pauline church and monastery ruins, Lookout point on Nagy-Amadé Hill, Amadé castle ruins, Roman catholic church, Hussite house (Kossuth Street 83.), Pálffy palace, Town Hall building, Bible Museum, Reformed church, Károlyi statue

*Göncruszka*: Bárczay-Patay mansion, Kornis-Kazinczy mansion, old gravestones in the garden of the Reformed Church, Reformed fortified church

*Kéked*: Oak trees of King Matthias, Former spa's main building, Female figurine shape at the spring of the spa, Roman catholic church, Melczer-castle, Melczer-castle garden

*Pányok*: Valley of Hasdát-creek

*Telkibánya*: Károlyi's hunting lodge, Hotel Silver Pine, Reformed fortified church, double trenches of a former earthwork, wooden headboards in the cemetery, rocks at the western foot of the Nagy-Ork Hill, rocks on the eastern side of the Szalonnás-Bérc, Medieval water barrage dam, abandoned perlite mine, Abauj Museum, sculpture park, Szép Ilonka grave, ice cave, King Matthias Fountain, Memorial tunnel of Királykút, Vörösvízi-creek, Koncfalva ruins, Collapses on the northern side of the Jó Hill, Old pines in Gúnyakút, lookout point on the northern side of Kecskehát Vineyard, Teresa tunnel

*Tornyosnémeti*: Reformed fortified church

*Zsujta*: Reformed church, People's house, old inn (Fő Street 46.)

The landscape values were evaluated on the level of settlements as well. This is not just based on the number of values, but on their score. Therefore, this method is more suitable for the ranking of the settlements, because there may be settlements in which many landscape values can be located, but none of them are too valuable. First of all every settlements value's score is summed. *Figure 4* shows that Telkibánya is above the rest of the settlements in aggregate landscape value score. Gönc is in second place, but only with half as many points as the first settlement.

Overall, in terms of landscape values clearly Gönc and Telkibánya are the settlements which pull the area. For the rest of the settlements, however, the situation is more complicated. There are settlements that have a lot of landscape values, but none of them are very significant (Hidasnémeti, Tornyosnémeti). However, the diversity and richness of the values can still be attractive. There are also settlements that have less landscape values, but these are all valuable and in themselves also constitute a good potential in terms of tourism (Abaujvár, Kéked). Finally, there are settlements that have fewer and less significant values, but they can have an important complementary role in connecting to the other settlements in the future and can help to create a tourism system of the settlements (Hernádszurdok, Pányok, Zsujta).

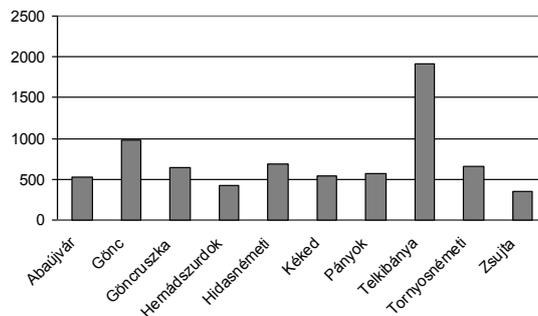


Figure 4: Aggregate score of the settlements' landscape values

## 2.2. Questionnaire-based evaluation

In those questionnaires which were filled in settlements provide assistance for evaluation, and also for the proposal. The questionnaires are based on the theme of tourism. Two types of questionnaires were created: one for the local population and tourists, the other for organizations, associations, businesses, institutions which are related to tourism to some extent. The questionnaires were distributed in proportion to the size of the individual settlements, and their importance. In total, 57 residential and 37 organizational forms were collected. The local population agrees that the priority of the development must be tourism. The majority of respondents highlighted the economic impact of tourism. In the responses, however, many people pointed out that tourism has a positive impact on social life, it "shakes up" the locals. Many responses also included that tourists encourage locals to decorate and keep clean the villages and to preserve the values. The landscape value based and the questionnaire evaluations show similar results, the villages with more sights are clearly Telkibánya and Gönc. The main attractions determined by the respondents' answers are the same as the "highly valuable" qualified landscape values.

## 3. DEVELOPMENT OF TOURISM

The results of the landscape values based evaluation show that the region is very rich in values, but they show a different distribution in certain settlements, and most of the landscape values alone are not great attractions. According to the questionnaire-based evaluation it can be said that the locals support and consider the development of tourism useful. The responses meant on appropriate control for the landscape value based evaluation. Building on these, the surveyed and evaluated landscape values are organized into a system by a thematic trip and a greenway.

### 3.1. "Pilgrimage of Zemplén" thematic trip

Those tourism products are called thematic trip, which attach natural and man-made attractions to a specific theme. These attractions use different forms of transport. The routes offer at the same time learning, entertainment, recreational activities, and in addition they take the principles of sustainability fully into account. Natural and other value-based routes are distinguished. The traversal of the routes is possible with or without organized leader. Out of these the last option was applied in the proposed thematic trip. The advantages of this method is that it mitigates the negative effects of the visit, distributes the traffic due to smaller groups, and tourists can go at their own pace along the route.

The planned route is appropriate for a cultural trip, connecting cultural values, heritage items, cultural attractions (*Puczko-Rátz, 2000*). Geographically we can distinguish local routes, regional, country and international routes. The proposed thematic route has a regional role, because it links the values of several settlements.

Traveling is possible in several ways: different modes of transport can be combined, as I have combined several means of transportation in the frames of the planned route. This way the visitors have free choice according to their own needs. The grouping of the values indicates that the settlements are all suitable for cultural tourism. The most of the highly valuable landscape elements are connected to religious, sacred life. For these reasons, the North-Abauj ecclesiastical values were chosen as the base of the thematic trip. My goal was with the project of "Pilgrimage of Zemplén" to make tourists discover other cultural, natural and landscape values in addition to the ecclesiastical values. This helps to create a positive image of the whole region. Creating this thematic route the attractions of the individual settlements are connected in a system, thus enhancing their value. The goal was also to allocate supplementary income for the local people, overall to increase the living standards.

Besides the attractions the most important element of the thematic trip is the route itself. It blends together a variety of attractions, station points, in fact, this is the base of the organization of the system, and creates a new, more complex attraction. The route aligns the stations in their recommended traversal order, as well as it gives specific instructions on how to approach the sights and how to get from one point to another using different means of transportation. The time of visit spent on the various stations and the travel time between two attractions are determined in the time plan. The route plan and the time plan are very important in terms of perspicuity and predictability. The proposed thematic trip has 11 main stations, some of them include more attractions (for example, the Bible Museum and the Reformed Church in Gönc are located directly next to each other), these stations are as follows:

- 1st. station: Reformed fortified church, Göncruszka
- 2nd. station: Bible Museum and Reformed church, Gönc
- 3rd station: Roman Catholic church, Gönc
- 4th station: Pauline church and monastery ruins, Gönc
- 5th station: Reformed fortified church and wooden headboards cemetery, Telkibánya
- 6th station: St. Catherine's chapel and ruins, Telkibánya
- 7th station: Szép Ilonka grave, Telkibánya

8th station: Reformed fortified church, Abaújvár

9th station: Roman Catholic church, Kéked

10th station: Reformed church, Zsujta

11th station: Reformed fortified church, Tornyosnémeti (final station)

For completing the route estimated times are 6.5 hours by car, 10.5 hours by bike and 22.5 hours on foot. By bike and on foot the route can be traveled through only in several days.

In addition to the planning and designation of the route and station points a number of formal and design planning task is required for the appropriate visual appearance of the route. For the construction of the architecture elements natural materials, form-fitting design should be used with and the position should fit into the surroundings, and stability should be an important aspect as well. Special attention should be paid on information panels, which help visitors to find the stations, and also provide additional information. The information panels should be built carefully to create a uniform, aesthetically pleasing color scheme and layout. The quality of work is very important in these cases, because the tables have a significant role in the experience of the visitors and they increase satisfaction. The planning, preparation and placement of the following information boards are necessary to create a thematic trip: starting table (Figure 5), direction table, board located at station points.

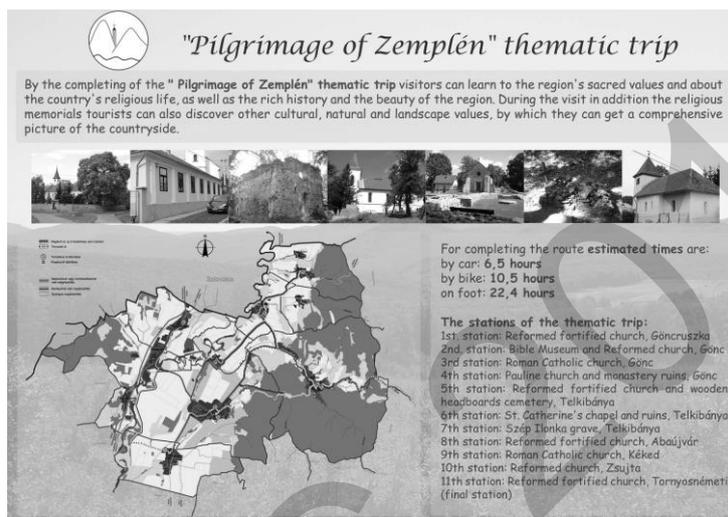


Figure 5: Thematic trip – plan of the starting table

### 3.2. "Hernád Zemplén" Greenway

The previously described thematic trip connects the main cultural values in the region. The area, however, has got many other natural treasures and cultural attractions as well. Creating a greenway is a good way to enhance the reputation of this rural region through the landscape values. Such routes usually run in nature, and they link environmentally friendly solutions and sustainability. Greenways mean not only physical routes, but also psychologically formulable routes (Ökotárs Foundation, 2009).

Greenways can be found in many parts of the world, but they carry a different meaning in different places. In Hungary they are natural corridors, trails, paths, which are used for sport, tourism, recreation and everyday transport while taking into account their ecological functions (Ökotárs Foundation, 2009 p. 8). These types of routes provide assistance in sustainable resource management, as well as they are important in terms of nature conservation, cultural heritage, health maintenance and strengthening of local identity. Greenways are suitable for three different modes of transport: walking, biking and riding. The "Hernád-Zemplén Greenway" was planned for bicycle transport. The choice is justified by the properties of the area (topography, distances between settlements) and the local needs (to supplement car traffic and public transport). Like the thematic trip a greenway also can help in familiarizing the area and connecting of values, and thus deepening the cooperation between individual settlements and local interest groups.

The "Hernád-Zemplén Greenway" would provide a connection between the neighboring settlements, the benefits of which would be enjoyed mainly by the local population. The greenway was investigated in several sections. Particular attention was paid to the safety, the quality of route (pavement, drainage, condition) and the terrain conditions. The division of the route was conducted with the previous conditions in mind, ie a new section begins, where at least one feature changes substantively. This type of analysis is important for utilization by the local people, as well as for utilization for tourism. Mainly because of the tourism aspect the "highly valuable" and "very valuable" landscape values were highlighted in each section.

For eliminating the problems of each part, and also for the development of the greenway short landscaping proposals were made. It is important to emphasize that the planned route takes into account the landscape values (it append the most valuable values) and the technical background (existing economic and agricultural routes, relatively small changes and low costs). The total length of the planned greenway is 78,3 km, which was divided into 36 distinct sections. Similarly to the thematic route here as well different design tasks have to be carried out. It is important to achieve an appropriate visual impact, and to convey the information. The creation of a greenway should not adapt to such strict rules as a thematic route, but some architectural elements are essential for the effective operation. There are two information items absolutely necessary to operate a greenway: signposts and information boards, which also have been designed during the planning work.

### SUMMARY

The landscape values of the ten settlements were researched during the survey, and a register was created from them. The major strengths from the aspect of tourism were overviewed. These strengths were such as conservation areas, landscape characteristics (especially the unique view of the landscape) and cultural values. During the landscape evaluation two methods – which complement each other - were used for the basis of the suggestions. An own system of criteria was developed for the landscape values-based evaluation which determines the most valuable landscape values, and which settlement has the most values. Another method of evaluation was the questionnaire survey. Two types of questionnaires were created: one for the local population and tourists, the other for organizations, associations, businesses, institutions which are related to tourism to some extent. The questions concerned the sights of the settlements, the landscape values of the region and the potential kinds of tourism. By the questionnaire method the recent developments in tourism and the local's attitudes to the subject were explored.

When adding proposals it was a key factor that the landscape values and their surroundings should not deteriorate. The protection has also significant importance, because much of the research area is still pristine, where natural conditions prevail. The "Pilgrimage of Zemplén" thematic trip and the "Hernád-Zemplén Greenway" comply with these requirements, they serve pre-defined goals. The region's landscape values reinforce each other through the routes, so they will attract much more tourists to the area. This disadvantaged region can develop and catching up as a result of the systematic and rational planning.

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# LETHAL EFFECT OF SOME SALTS ON THE TERRESTRIAL SNAIL *MONACHA CANTIANA*

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## ABSTRACT

The lethal effect of ten salts, on the terrestrial snail *Monacha cantiana*, was examined in laboratory. Tested salts were: sodium chloride, potassium sulphate, ferrous sulphate hepta hydrate, magnesium sulphate hepta hydrate manganese sulphate tetra hydrate, zinc sulphate hepta hydrate, ammonium sulphate, calcium nitrate, di ammonium phosphate and ammonium nitrate.

LC<sub>50</sub> values of the previous salts after 72 hours were; 2.09 %, 3.70 %, 0.27 %, 11.65 %, 3.38 %, 0.13%, 1.36 %, 1.85 %, 0.90 % and 0.20 %, respectively.

LC<sub>90</sub> values of the previous salts after 72 hours were ; 10.27 %, 4.82 %, 0.67 %, 25.45 %, 5.00 %, 0.18 %, 5.87%, 7.59 % , 4.68 % and 0.83 %, respectively.

Each of LC<sub>50</sub> and LC<sub>90</sub> values correlated negatively with E.C. values of 1 % solutions of the tested salts but correlated positively with pH values of 50 % solutions of the examined salts. In other words each of LC<sub>50</sub> and LC<sub>90</sub> values correlates negatively with each of salinity and acidity of salts.

Each of LC<sub>50</sub> and LC<sub>90</sub> values were found to be correlated positively with the molecular weights of the examined salts.

**Key words:** Lethal salts terrestrial snail *Monacha cantiana*

## INTRODUCTION

Slugs are a serious pest in floriculture, horticulture and agriculture in many parts of the world. *Deroceras reticulatum* is generally the most destructive species (Grewal *et al.*, 2001).

Different investigators examined different agents to be used to control snails; Bullock *et al.*(1992) found that control of terrestrial slugs and snails can be achieved by some common metals as contact-action poisons acquired passively by crawling animals and they were acting more efficiently than the currently used bait-delivery method.

Trent *et al.* (1997) tested thirteen molluscicides containing metaldehyde, three molluscicides containing metaldehyde plus carbaryl, one molluscicide containing metaldehyde plus methiocarb and one molluscicide containing methiocarb alone for their efficacy against the brown slug, *Vaginula plebeia* Fischer, and the two-striped slug, *Veronicella cubensis* (Pfeiffer). With the exception of corry's liquid slug, snail and Insect killer against *V. plebeia*, all the tested molluscicides caused significant mortalities against both species. In a separate study, physical barriers composed of copper or fiberglass screens repelled both slug species.

David *et al.* (2001) stated that feeding inhibition by diluted tuber peel extracts of the variety Homeguard was greater than that elicited by comparable authentic glycoalkaloid solutions suggesting additional inhibitory compound(s) in the peel of this variety.

Grewal *et al.* (2001) found that the beneficial nematode, *Phasmarhabditis hermaphrodita*, has potential for the biological control of slugs and application rates of  $3.0 \times 10^9$  infective juveniles (IJs)/ha are usually required for effective plant protection.

Schuder *et al.* (2003) tested certain products that have irritant, antifeedant, physical barrier, chemical repellent, or molluscicidal effects or a combination of more than one effect against slugs. Garlic, ureaformaldehyde and cinnamamide were the three best products for controlling snails. In 7 day bioassay trials, these products had mortality rates between 20% and 95% which was significantly higher than the untreated.

Shmuel *et al.*( 2004) tested two formulations of water dispersible granules contained 61.4% and 53.8% of copper hydroxide. The 0.1% concentration of either formulation was sufficient for the management of the land snails *Monacha syriaca* and *Theba pisana* populations.

Der *et al.* (2005) stated that morpholine which is a solvent of apple wax was very effective in suppressing hatching of the snail *Pomacea canaliculata* eggs at a concentration of 60%.

Ravindra *et al.* (2008) proofed that saponin concentration in rice water at 9 and 11 ppm gave seedling protection of 93% and 95%, respectively after 48 h against different sizes of the snail *Pomacea canaliculata*.

Youssef (2011) tested four plant species used as a dry powder of their leaves against *Biomphalaria alexandrina* snails. The bioassay tests revealed that the plants *Datura stramonium* and *Sesbania sesban* were more toxic to the snails than the other two tested ones.

Snails are found tremendously beside irrigation or drainage canals where moisture is abundant .They are more active after irrigation. Snails destroy the vegetative parts of plants therefore, the aim of the present study is to determine the most suitable substance to ban snails from passing through. These substances may be useful and can be used to surround fields to protect them from snails for their molluscicidal effects as contact-action poisons.

## MATERIALS AND METHODS

### Residual film bioassay

The effect of ten common and available salts on the terrestrial snail *Monacha cantiana* was examined in laboratory. All the chosen salts are chemical fertilizers except sodium chloride. The elemental composition and molar mass of the used salts are presented in Table 1.

Table 1: The tested salts and their composition and molar mass.

Salt	composition	Molar mass (molecular weigh) (g/mol)
Sodium chloride: Na Cl	39.3 % Na + 60.7 % Cl	58.4430
Potassium sulphate: K <sub>2</sub> SO <sub>4</sub>	44.9 % K + 18.4 % S + 36.7% O	174.2598
Ferrous sulphate hepta hydrate: Fe SO <sub>4</sub> . 7 H <sub>2</sub> O	20.1 % Fe + 11.5 % S + 63.3% O + 5.1 %H	278.0157
Magnesium sulphate hepta hydrate: Mg SO <sub>4</sub> . 7 H <sub>2</sub> O	9.9 % Mg + 13 % S + 71.4 % O + 5.7 % H	246.4755
Manganese sulphate tetra hydrate: Mn SO <sub>4</sub> . 4 H <sub>2</sub> O	24.6 % Mn + 14.4 % S + 57.4 % O + 3.6 % H	223.0626
Zinc sulphate hepta hydrate: Zn SO <sub>4</sub> . 7 H <sub>2</sub> O	22.7 % Zn + 11.2 % S + 61.2 % O + 4.9 % H	287.5799
Ammonium sulphate: (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	21.2 % N + 6.1 % H + 24.3 % S + 48.4 % O	132.1402
Calcium nitrate: Ca (NO <sub>3</sub> ) <sub>2</sub>	24.4 % Ca + 17.1 % N + 58.5 % O	164.0884
Di ammonium phosphate: (NH <sub>4</sub> ) <sub>2</sub> H PO <sub>4</sub>	21.2 % N + 23.4 % P + 48.5 % O + 6.9 % H	132.0564
Ammonium nitrate: NH <sub>4</sub> NO <sub>3</sub>	35 % N + 5 % H + 60 % O	80.0435

Distilled water was used to prepare different diluted concentrates of each salt. Each concentration was replicated three times. Three milliliters of each prepared concentration was spread distributed in a jar (1 liter) to form a thin film on the inner surface . All jars were left for an hour to dry. Ten alive snails of the same weight (0.6 g) were put in each jar. For control, similar snails were put in three replicates of jars previously treated with distilled water only.

Snails were banned from escape by covering the jars with plastic screens to be in contact with the tested concentrations and kept in the normal room temperature and humidity (25± 2 °C &70± 5% R H).

The number of dead snails , that doesn't react to excitation , were counted and recorded after three days of the treatment .

Electrical conductivity values of 1 % solutions of the examined salts and Ph values of 50 % solutions of the examined salts were estimated in laboratory.

**Statistical analysis**

Ten concentrations of each examined salt that caused response percentages between 0 % and 100 % were considered for creating the regression equations (Y= a + bx). LC<sub>50</sub> values (median lethal concentration), LC<sub>90</sub> values (lethal concentration for 90 % of the population) and their confidence limits, probit/ log concentration regression equations and slope were calculated by the method described by Finney (1971). Toxicity index and the relative toxicity were also calculated according to Sun (1950).

Simple correlations coefficient between LC<sub>50</sub> and LC<sub>90</sub> values and each of electrical conductivity values of 1% solutions, pH values of 50% solutions and the molecular weights of the examined salts were calculated and discussed.

**RESULTS AND DISCUSSION**

**1 - Bioassay**

The regression equations (Y= a + bx) resulted from plotting the response percentages against the different used concentrations of each tested salt are presented in Table 2.

Table (2): Toxicity parameters of different tested salts against the snail *Monacha cantiana* after 72 hours bioassay.

Salt	Regression equation Y= a + b x	Slope (±S.E)	LC <sub>90</sub> (%)	LC <sub>50</sub> (%) (Confidence limits) Lower-Upper	rank	T.I*	R.T**
ZnSO <sub>4</sub> .7 H <sub>2</sub> O	Y= - 8.272 + 9.354 x	9.354 (± 3.737)	0.18	0.13 (0.120- 0.141)	1	100	89.61
NH <sub>4</sub> NO <sub>3</sub>	Y= 1.447+ 2.086 x	2.086 (± 0.244)	0.83	0.20 (0.148 - 0.273)	2	65	58.25
FeSO <sub>4</sub> .7 H <sub>2</sub> O	Y= 1.841 + 3.298 x	3.298 (± 0.475)	0.67	0.27 (0.226- 0.337)	3	48.14	43.14
(NH <sub>4</sub> ) <sub>2</sub> H PO <sub>4</sub>	Y= 0.107+ 1.955 x	1.955 (± 0.174)	4.68	0.90 (0.521- 1.255)	4	14.44	12.94
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Y= - 0.271 + 2.020 x	2.020 (± 0.247)	5.87	1.36 (0.966 - 1.867)	5	9.55	8.56
Ca (NO <sub>3</sub> ) <sub>2</sub>	Y= -0.593 + 2.275 x	2.275 (± 0.219)	7.59	1.85 (1.262 - 2.512)	6	7.02	6.29
Na Cl	Y= - 0.598 + 1.858 x	1.858 (± 0.230)	10.27	2.09 (1.470- 2.922)	7	6.22	5.57
MnSO <sub>4</sub> .4H <sub>2</sub> O	Y= - 3.980 + 7.521 x	7.521 (± 2.098)	5.00	3.38 (3.103 - 3.684)	8	3.84	3.44
K <sub>2</sub> SO <sub>4</sub>	Y= - 6.737+ 11.850 x	11.850 (± 6.162)	4.82	3.70 (3.486- 3.931)	9	3.51	3.14
MgSO <sub>4</sub> .7H <sub>2</sub> O	Y= - 4.430 + 4.161 x	4.161 (± 0.750)	25.45	11.65 (9.755-13.786)	10	1.11	1.00

\*\*T.I = Toxicity index      \*\*R.T = Relative toxicity

The LC<sub>50</sub> values (median lethal concentration), LC<sub>90</sub> values (lethal concentration for 90 % of the population) and their confidence limits, slope, toxicity index (T I) and the relative toxicity (R T) were also displayed. The LC<sub>50</sub> values of the ten

tested salts were 2.09, 3.70, 0.27, 11.65, 3.38, 0.13, 1.36, 1.85, 0.90 and 0.20 % respective to sodium chloride, potassium sulphate, ferrous sulphate hepta hydrate, magnesium sulphate hepta hydrate, manganese sulphate tetra hydrate, zinc sulphate hepta hydrate, ammonium sulphate, calcium nitrate, di ammonium phosphate and ammonium nitrate, consequently after an exposure period of 72 hours.

According to the LC<sub>50</sub> values, zinc sulphate hepta hydrate was proved to be the most toxic salt (TI=100) followed by ammonium nitrate (TI=65), ferrous sulphate hepta hydrate (TI=48.14), diammonium phosphate (TI=14.44), ammonium sulphate (TI=9.55), calcium nitrate (TI=7.02), sodium chloride (TI=6.22), manganese sulphate tetra hydrate (TI=3.84) and potassium sulphate (TI=3.51). On the other hand, the least toxic tested salt was magnesium sulphate hepta hydrate (TI=1.11).

The strong lethal effect of zinc sulphate agrees with the results of MacInnes and Thurberg (1973) who found that oxygen uptake of distressed and retracted snails was found to be lower than that of controls after exposure to zinc metal.

Also, the relative toxicity (RT) was calculated considering the least toxic salt (magnesium sulphate hepta hydrate) having a figure of toxicity equal to 1.00 and therefore, the toxicity of the tested salts can be arranged in an ascending order as follows: potassium sulphate which showed more toxicity than magnesium sulphate hepta hydrate by 3.14 fold), manganese sulphate tetra hydrate (RT=3.44 fold), sodium chloride (RT=5.57 fold), calcium nitrate (RT=6.29 fold), ammonium sulphate (RT=8.56 fold), di ammonium phosphate (RT=12.94 fold), ferrous sulphate hepta hydrate (RT=43.14 fold), ammonium nitrate (RT=58.25 fold) and then the most toxic one; zinc sulphate hepta hydrate which was more toxic than magnesium sulphate hepta hydrate by 89.61 fold.

Figures 1-5 illustrated the concentration / mortality regression lines (Ld-p lines) of the tested salts against the terrestrial snail *Monacha cantiana*. The toxicity of the tested salts can be arranged as the following descending order: zinc sulphate hepta hydrate > ammonium nitrate > ferrous sulphate hepta hydrate > diammonium phosphate > ammonium sulphate > calcium nitrate > sodium chloride > manganese sulphate tetra hydrate > potassium sulphate > magnesium sulphate hepta hydrate.

The effect of ammonium sulphate was assured by the results of Tchounwou *et al.* (1991) who found that LC<sub>50</sub> value after 24-h was 701 mg/L for the snail snails *Helisoma trivolvis* while that concentration killing 100% of snails was 1250 mg/l.

In contrast the results of the lethal effect of calcium nitrate disagree with the results of Johannessen and Solhoy (2001) who found that adding calcium to the forest floor causes a significant increase in both individual populations and species numbers of snails.

The effect of nitrate was previously proofed by Norah *et al.*(2006) who examined short-term acute impacts of nitrate in laboratory against adult and juvenile snail. LC<sub>50</sub> values after 96 h could not be determined due to low mortality rates despite nitrate concentrations > 500 ppm. Snail growth was affected with LEC<sub>50</sub> values of 622 ppm nitrate. The authors suggested nitrate pollution in springs in Florida could be as a possible reason for declining populations of the Florida apple snail, *Pomacea paludosa* (Say).

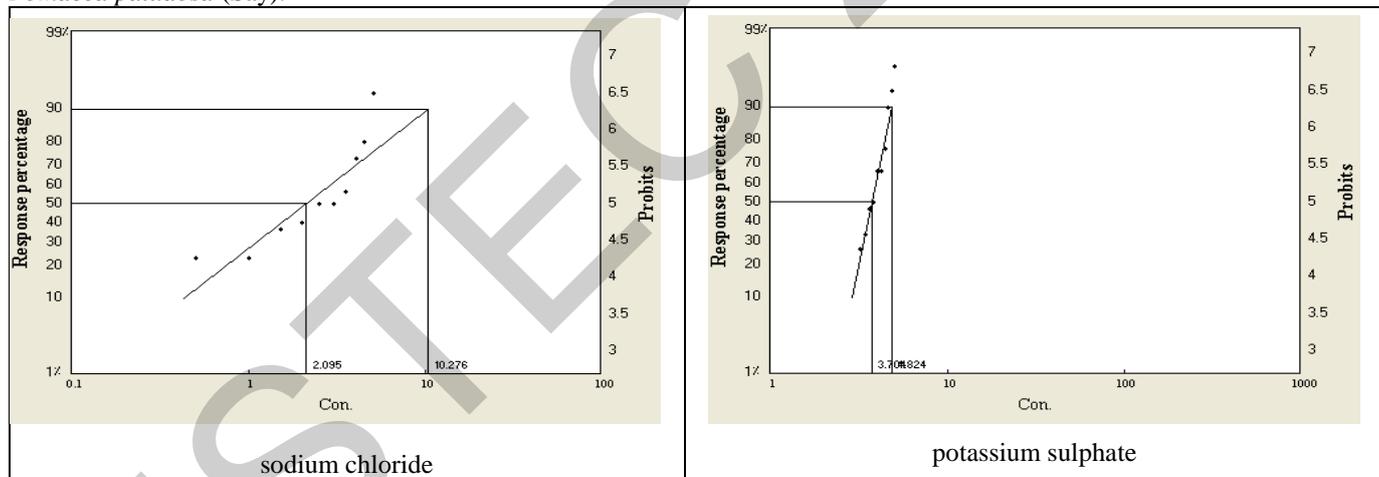


Fig. 1: L-d p lines of sodium chloride and potassium sulphate after 72 hours bioassay against the terrestrial snail *Monacha cantiana*.

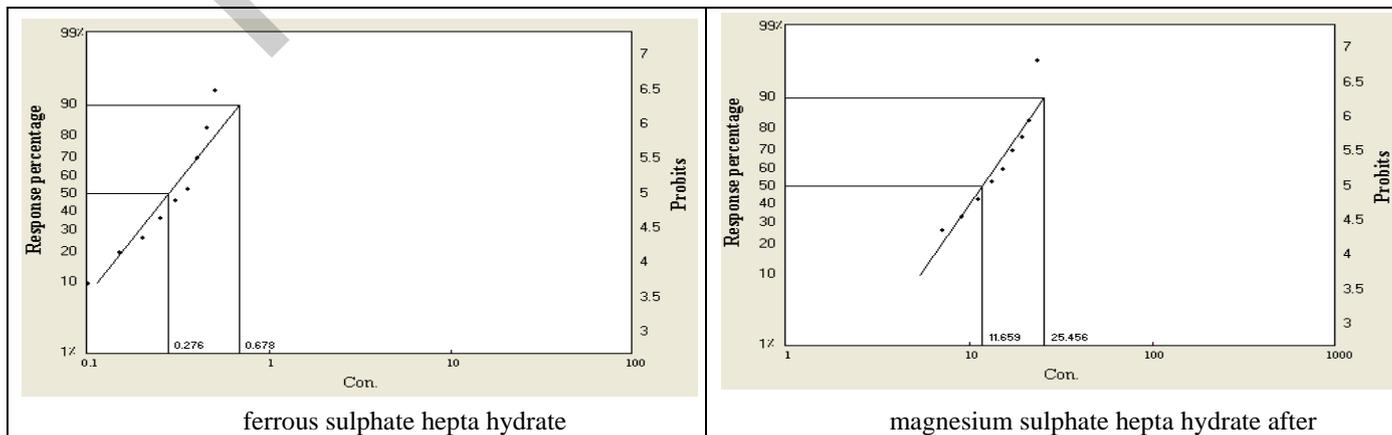


Fig. 2: L-d p lines of ferrous sulphate hepta hydrate and magnesium sulphate hepta hydrate after 72 hours bioassay against the terrestrial snail *Monacha cantiana*.

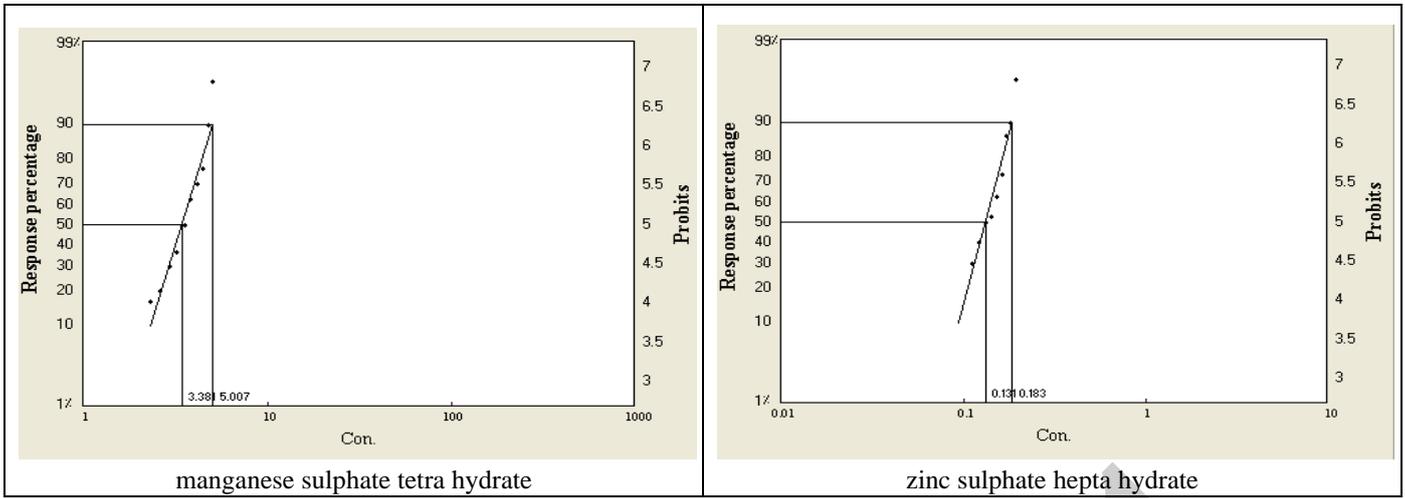


Fig.3: Ld-p lines of manganese sulphate tetra hydrate and zinc sulphate hepta hydrate after 72 hours bioassay against the terrestrial snail *Monacha cantiana*.

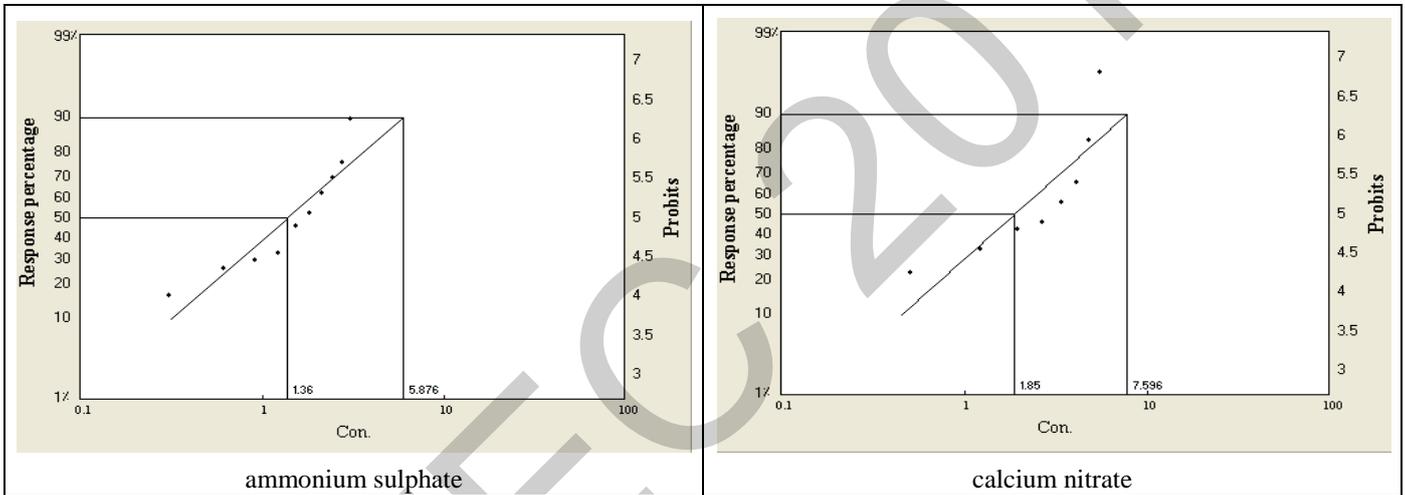


Fig. 4: Ld-p lines of ammonium sulphate and calcium nitrate after 72 hours bioassay against the terrestrial snail *Monacha cantiana*.

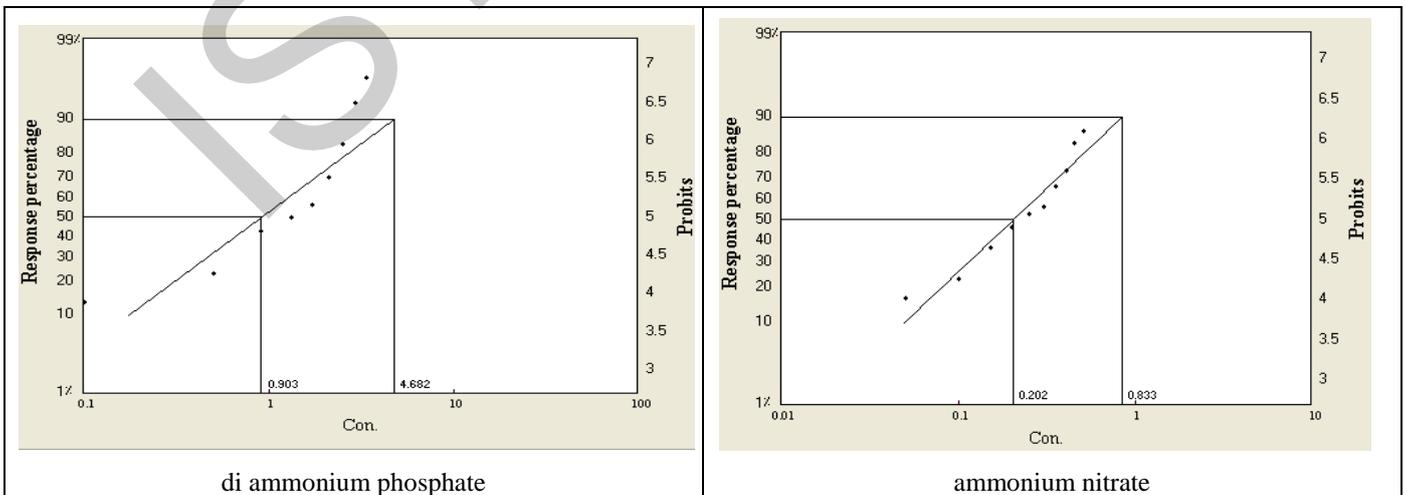


Fig. 5: Ld-p lines of di ammonium phosphate and ammonium nitrate after 72 hours bioassay against the terrestrial snail *Monacha cantiana*.

## 2 - Correlation between mortality and certain properties of the tested salts

E.C. ( electrical conductivity ,  $\text{dsm}^{-1}$  ) , pH ( - log. Hydrogen ions concentration) and molecular weight (the mass of one mole of a substance) of the tested salts as indicators for salinity , acidity and molar mass, respectively are recorded in Table 2.

Table (3): E.C. , pH and Molecular weight of the tested salts.

Salt	E.C.*	PH**	M.W.***
Zn SO <sub>4</sub> . 7 H <sub>2</sub> O	5.6	3.72	287.5799
NH <sub>4</sub> NO <sub>3</sub>	19.3	6.18	80.0435
Fe SO <sub>4</sub> . 7 H <sub>2</sub> O	4.6	1.66	278.0157
(NH <sub>4</sub> ) <sub>2</sub> H PO <sub>4</sub>	15.2	8.37	132.0564
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	18.4	6.00	132.1402
Ca (NO <sub>3</sub> ) <sub>2</sub>	9.9	5.74	164.0884
Na Cl	20.0	6.96	58.4430
Mn SO <sub>4</sub> . 4 H <sub>2</sub> O	5.3	7.01	223.0626
K <sub>2</sub> SO <sub>4</sub>	17.3	7.72	174.2598
Mg SO <sub>4</sub> . 7 H <sub>2</sub> O	5.40	7.02	246.4755

\* E.C. = Electrical conductivity of 1 % solution of the salt

\*\* Ph = acidity of 50% solution of the salt

\*\*\*M.W.= Molecular weight

Data presented in table (4) demonstrate that each of  $LC_{50}$  and  $LC_{90}$  values of the examined salts correlates negatively with E.C. values of salts but correlates positively with pH values of salts. In other words each of  $LC_{50}$  and  $LC_{90}$  values of the examined salts correlates negatively with each of salinity and acidity of salts.

Moreover , each of  $LC_{50}$  and  $LC_{90}$  values of the examined salts has a non-significant positive correlation with the molecular weights of salts.

In short,  $LC_{50}$  and  $LC_{90}$  values of the examined salts has no significant correlation with E.C. values , pH values or molecular weights of the examined salts. Hence , the variation in the lethal effect of the different tested salts may refer to another factor according to Fenchel (1975) who studied the distribution patterns of four species of mud snails (Hydrobiidae) in a complex. The species show habitat selection with respect to salinity but the tolerance ranges of the species overlap and it is shown that this factor alone cannot predict the distribution in the field. The lethal effect may refer to the presence of a specific element in the salt composition according to Ondina *et al.* (1998) who found that some snail species were more sensitive to aluminium and magnesium than others.

The lethal effect of salinity agrees with the results of Vaidya and Nagabhushanam (1979) who observed the survival and osmotic regulation following transfer of snails from freshwater to different salt concentrations .They found that the lethal salinity was at 0.5% salt concentration. They suggested that in hypertonic media snails lose considerable weight due to loss of water.

However, Donnelly *et al.* (1983) found that the survival of the snails *Bulinus africanus* (*Physopsis*) was unaffected in salinities < 3.5 ‰, while further increases in salinity resulted in significant reductions in survival up to a lethal salinity of 8.7 ‰, which caused 100% mortality within 24 h.

In addition, Bagarinao and Lantin-Olaguer (2000) found that snails were killed within a week by salinities of 48–70‰, but within 3 days by ammonium phosphate at 10 g / l.

Table(4) :Simple correlation coefficient among lethal concentrations and some chemical properties of salts.

Properties of salts	Correlation coefficient with	
	LC <sub>50</sub>	LC <sub>90</sub>
E.C.	- 0.2938 ns*	- 0.1468 ns
PH	0.3722 ns	0.3982 ns
M. w.	0.2390 ns	0.0307 ns

\* ns = not significant at 5 % level.

## CONCLUSION

The above mentioned results could suggest the use of the tested effective salts to surround fields for banning snails cracking from the adjacent irrigation or drainage canals. All the tested salts , except sodium chloride , are nutritious salts used for fertilization so, they may be considered useful as control agents for plants. The effective salts may be used to surround or coat certain areas like tree trunks to ban snails instead of harmful traditional molluscicides. However, in case of those plants infested with snails , it is not recommended to spray these high concentrations of salts on the vegetative parts of plants because they may cause phytotoxicity.

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# MEDICAL EDUCATION PROGRAM DEVELOPMENT APPLICATION OF KOCAELI UNIVERSITY

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## ABSTRACT

Today, a very fast changing conditions and new varieties of the disease occurs. However, the technology also introduces new methods of treatment to disease progression. Therefore, faculties of medicine need to keep up-to-date and form the core training program for changing health problems and practices of medicine education at graduate medical education. The core training program consists of learning objectives of graduate education, courses which will be given the degree of disease-state-symptom correlation matrix and learning outcomes ( knowledge, skills, attitudes ) which bring lessons to students. Kocaeli University Medical Education Program Development Application, which is a web-based application, aims to build up-to-date and online national core training program.

**Keywords-** medicine, core training, web application

## 1. INTRODUCTION

Nowadays, the number of newly appeared disease increases. At the same time, the methods of treatment are changing (Ozuah,2002). So faculty of medicine creates core training program to be able to graduate students who have enough information, skills and attitude to disease.

## 2. CORE TRAINING PROGRAM

Core training program aims to form a common base among students of faculties of medicine. So, it gathers topics under certain titles and comes to a specific standard.

Core training program is based on:

- Disease, status, symptoms
- Degree: TT, T, B, A, K
- Systems

For example: disease, status, symptoms such as angina pectoris. Systems such as circulatory system.

TT : Graduates should be able to know diagnosis, differential diagnosis of diseases, treatment and observe the whole process of the disease.

T : Graduates should be able to make the necessary preliminary attempts and redirect to expert.

B : Graduates should be able to have information about diseases and redirect to expert.

A : Graduates should be able to do emergency attempts in these cases.

K : Graduates should be able to know the methods of protection.

In application, core training program is created by instructors of faculty of medicine. In this paper, main modules of application are explained.

## 3. KOCAELI UNIVERSITY MEDICAL EDUCATION PROGRAM DEVELOPMENT APPLICATION

### 3.1 DESIGN AND IMPLEMENTATION

In the development of application, at server side, coldfusion markup language(CFML) language was used. CFML was chosen as programming language at this project because CFML tags have a similar format to HTML(Hyper Text Markup

Language) tags. So programmers can develop web programs, including internet and intranet programs, in a much shorter time. Also Java developers can call all their Java objects from within a ColdFusion application ([www.adobe.com/support/documentation/en/coldfusion/](http://www.adobe.com/support/documentation/en/coldfusion/)).

As seen on figure 1, Coldfusion server takes .cfm pages which come to the Web server, makes dynamic data operations which are insert, update, retrieve, delete based on the ColdFusion Markup Language (CFML) in the .cfm file, and returns pure HTML to the Web server, which forwards it to the browser ([www.flylib.com/books/en/1.324.1.274/1/](http://www.flylib.com/books/en/1.324.1.274/1/)).

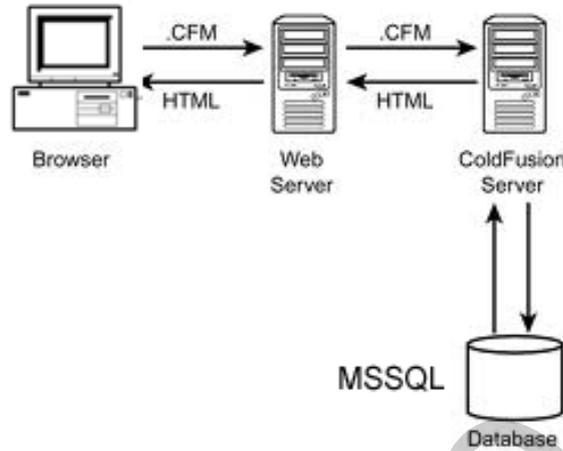


Figure 1. Coldfusion architecture

### 3.2 APPLICATION

Kocaeli University medical education program development application's login screen as shown figure 2. Users of application use their institutional register number and passwords. Only instructors of faculty of medicine have authority to enter the application. When the users enter the application, The welcome page is seen as figure 3. In application, there are defined roles on instructors. So each instructors see different menu of application due to their roles.

The roles are:

- The dean of faculty of medicine
- The chairman of education committee
- The vice chairman of education committee
- The term coordinators
- The heads of departments
- The heads of assembly
- The instructors



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Figure 2. The login page of application

**Kocaeli Üniversitesi**  
**Tıp Fakültesi**  
**Tıp Eğitimi Program Geliştirme Uygulaması**

Dahili Tıp / Radyoloji > Prof.Dr. Ali DEMİRÇİ ÇIKIŞ

AMAÇ/ÖĞRENİM HEDEFLERİ  
MESAJ (0)  
Dekan  
ANABİLİM DALI BAŞKANI  
VI. Kurul Başkanı  
ÖĞRETİM ÜYESİ

KURUL BAŞKANI ANABİLİMDALI BAŞKANI ÖĞRETİM ÜYESİ BİLGİSİ

Sayın Öğretim Üyemiz,

2011-2012 Eğitim Öğretim Dönemi Mezuniyet Öncesi Tıp Eğitimi Programı 15 Ağustos günü kesinleşmiştir. Program kitapçıkları öğretim yılı başında dağıtılacaktır. Programlara <http://tip.kocaeli.edu.tr> adresinden ulaşabilirsiniz.

Öğretim üyelerinin üstlendikleri derslerin bilgi, beceri ve tutum bakımından hedefleri, ÇEP ile ilişkisi, önerdikleri kaynaklar bakımından gerekli bilgileri hazırlamaları ve programa girmeleri gerekmektedir. Üniversitemizin içinde bulunduğu eğitim çalışmaları nedeniyle bu bilgilerin aynı zamanda İngilizce olarak görünür olmaları istenmektedir. Bu kayıtlar için yazılım programında gerekli düzenlemeler yapıldıktan sonra bu bilgileri girmeniz için hatırlatma yapılacaktır.

Değerli katkılarınız ve katılımınız için teşekkür eder, iyi çalışmalar dileriz.

Prof. Dr. Kürşat Yıldız  
Mezuniyet Öncesi Tıp Eğitimi Komisyonu Başkanı

Figure 3. The welcome page of application

### 3.2.1 COMMON MENU

All users have common menu sections which are:

- Purpose / The learning objectives
  - Program
  - Term
  - Assembly/Internship
- Message
  - From
  - To
  - Sent
- Instructor
  - Create Course
  - Your Course
  - Active Course

#### 3.2.1.1 Purpose / The learning objectives

Sub-menu shows purpose and the learning objectives of program(yearly), term(each terms of six years program) and assembly(each assembly of each term of year).

#### 3.2.1.2 Message

Users of application can communicate each other by messaging. Users can send easily message to other users

#### 3.2.1.3 Instructor

Sub-menu of instructor part is important module of application. Instructor creates program details of year due to terms.

##### 3.2.1.3.1 Create Course

Instructor creates courses by using form as shown figure 4. Form consists of information of course which are name of course, conditions, type, purpose, content, resources, amounts of theoretic and practice hours.

DERS OLUŞTUR	
ADI	<input type="text"/>
NAME	<input type="text"/>
ÖN KOŞULU	Yok ▾
TÜRÜ	Zorunlu ▾
SORUMLUSU	Prof.Dr. Demir Kürşat YILDIZ
AMACI	Font Size... Font Family. Font Format
PURPOSE	Font Size... Font Family. Font Format
İÇERİĞİ	Font Size... Font Family. Font Format

Figure 4. The form of Course Create

### 3.2.1.3.2 Your Course

The courses created by instructor are shown at this page. Instructors have the authority to delete courses, edit courses, enable courses and enter learning outcomes as shown figure 5.

**Enable courses:** Instructor can create many courses. Each year, when a new program starts, instructor can enable courses to add active program.

**Learning outcomes:** Instructor enters learning outcomes which are information, skills and attitude of courses as shown figure 6. Also edit and delete operations can be used on page.

AÇIKLAMALAR							
	DERS DETAYLARINI DÜZENLEYEBİLİRSİNİZ.						
	OLUŞTURDUĞUNUZ DERSİ TAMAMEN SİLEBİLİRSİNİZ.						
	DERSİNİZİN AKTİF PROGRAMDA YER ALMASINI SAĞLAYABİLİRSİNİZ.						
	DERSİNİZİN ÖĞRENİM ÇIKTILARINI(BİLGİ, BECERİ, TUTUM) OLUŞTURABİLİRSİNİZ.						

NO	DERS ADI	TEORİK	PRATİK	DÜZELT	SİL	AKTİF ET	ÖĞRENİM ÇIKTISI
1	Patoloji Pratik 3						
2	Melanositik Hastalıkların Patolojisi						
3	Üriner Sistemin Taşları						
4	Böbreği etkileyen sistemik hastalıklar: Damar hastalıkları, Diabetes Mellitus, SLE ve Amiloidoz						
5	Nevuslar ve Melanositik Hastalıklar	1	0				
6	Üriner sistem taşları	1	0				
7	Böbreği Etkileyen Sistemik Hastalıklar: Diabetes Mellitus, SLE ve Amiloidoz	1	0				
8	karsinojenik Etkenler						
9	Patoloji Pratik 2 (Beyin tümörleri ve melanom)	0	4				
10	Patoloji Pratik 1 (Sinir sistemi doğumsal gelişim bozuklukları)	0	4				
11	Nörokutanöz Sendromlar	1	0				
12	Merkezi Sinir Sistemi Tümörleri	1	0				
13	Merkezi Sinir Sistemi Enfeksiyonları	2	0				
14	Çevre Sinir Sistemi Hastalıkları	1	0				

Figure 5. Created Courses Page

### Patoloji Pratik 2 (Beyin tümörleri ve melanom)

ÖNCE DEN GİRDİĞİNİZ ÖĞRENİM ÇIKTILARINIZIN (BİLGİ, BECERİ VE TUTUM) İNGİLİZCELERİNİ GİRMEK İÇİN DÜZENLE İŞLEMİNİ KULLANINIZ.

#### ÖĞRENİM ÇIKTILARI

BİLGİ		
1	Başlıca beyin tümörlerinden örneklerin mikroskopik örneklerini inceleyerek öğrenecekler,	SİL DÜZENLE
2	Meninkslerden kaynaklanan tümörler hakkında bilgi sahibi olacaklar,	SİL DÜZENLE
3	Retinablastom ve medullablastom gibi embriyonal tümör örneklerini inceleyerek bilgi edinecekler,	SİL DÜZENLE
4	Nörofibromatozise ait makroskopi ve mikroskopi örneklerini inceleyerek nörokutanöz sendromlar hakkında bilgilerini pekiştireceklerdir.	SİL DÜZENLE
BİLGİ		EKLE
INFO		

BECERİ		
1	Mikroskop kullanma becerilerini geliştirecekler,	SİL DÜZENLE
2	Çıplak gözle veya mikroskopta gördükleri tümörleri tanımlayarak ve çizerek ayrıntılandırabileceklerdir.	SİL DÜZENLE
BECERİ		EKLE
SKILLS		

TUTUM		
1	Laboratuvarda çalışma disiplini kazanacaklar,	SİL DÜZENLE
2	Dokuya saygılı olmayı öğreneceklerdir.	SİL DÜZENLE
TUTUM		EKLE
ATTITUDE		

Figure 6. Learning Outcomes Page

### 3.2.1.3.3 Active Course

Courses which are added to active program by instructor are shown on this page as figure 7. Instructor performs correlations between courses learning outcomes and core training program created by the head of department. Each learning outcomes which are information, skills and attitude of courses are set relationships with core training items as figure 8.

DÖNEM	KURUL	KURUL ADI	TEORİK	PRATİK		
III. Dönem	I. Kurul	HASTALIKLARIN BİYOLOJİK TEMELLERİ	6	4		
<b>AKTİF DERSİNİZ YOKTUR.</b>						
DÖNEM	KURUL	KURUL ADI	TEORİK	PRATİK		
III. Dönem	IV. Kurul	ÜRİNER SİSTEM	9	8		
NO	DERS ADI	İLİŞKİ	DÜZELT	SİL	TEORİK	PRATİK
1	Böbrek patolojisine giriş, böbreğin doğumsal gelişme bozuklukları ve kistler	↔	📄	🗑️	1	0
2	Glomerül Hastalıklarının Patolojisi	↔	📄	🗑️	3	0
3	Tübüler ve interstisyel Hastalıkların Patolojisi	↔	📄	🗑️	2	0
4	Böbreğin Damar Hastalıkları	↔	📄	🗑️	1	0
5	Böbreği Etkileyen Sistemik Hastalıklar: Diabetes Mellitus, SLE ve Amiloidoz	↔	📄	🗑️	1	0
6	Üriner sistem taşları	↔	📄	🗑️	1	0
7	Üriner sistemin Tıkaçıcı Hastalıkları	↔	📄	🗑️	1	0
8	Böbrek Tümörlerinin Patolojisi	↔	📄	🗑️	1	0
9	Patoloji Pratik 2 (Böbrek tümörleri, böbrek ve üreter taşları, hidronefroz)	↔	📄	🗑️	0	4
<b>TOPLAM</b>					<b>11</b>	<b>4</b>

Figure 7. Active Course Page

Nörokutanöz hastalıkların temel özelliklerini öğrenecek			
HDS	SİSTEM	DERECE	SEÇ
Addison hastalığı	Endokrin Sistem	T	<input type="checkbox"/>
Adrenal hiperplazi, konjenital	Endokrin Sistem	T	<input type="checkbox"/>
Akciğer hastalığı, kronik obstrüktif	Solunum	TT,A,K	<input type="checkbox"/>
Akciğer hastalıkları, interstisyel	Solunum	B	<input type="checkbox"/>
Akciğer kanseri	Solunum	T,K	<input type="checkbox"/>
Akut apandisit	Acil, yoğun bakım	T,A	<input type="checkbox"/>
Alkol, ilaç ve madde bağımlılığı, yoksunluk ve intoksikasyonu	Sinir,Duyu	T,A,K	<input type="checkbox"/>
Anafilaksi	Acil, yoğun bakım	TT,A	<input type="checkbox"/>
Angina pectoris	Dolaşım	TT,K	<input type="checkbox"/>
Aort anevrizması	Dolaşım	T	<input type="checkbox"/>
Artrit (reaktif, septik)	Hareket Sistemi	T	<input type="checkbox"/>
Ateroskleroz	Dolaşım	B,K	<input type="checkbox"/>

Figure 8. Core Training Program of Department

#### 4. CONCLUSION

Web-based Kocaeli University Medical Education Program Development Application brings a standard to graduate training program of faculty of medicine. Because there are more than five hundred instructors in faculty of medicine. To be able to gather all staff to create program of year. But by using application, all members of faculty enter individually information about courses and education, communicate and offer information without depending on platforms. On the other hand, there are management information panels that the chairman of education committee controls easily situations of the tasks doing by instructor. At the end of program, we can get many reports forms about topics and relations each others: created courses, active courses, learning outcomes, core training program of department and yearly program of faculty of medicine. Also we can compare information of previous years.

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# MERKEZCİL KARIŞTIRICILI DÜZLEMSEL YÜZEYDE FAZ DEĞİŞİMİ SIRASINDA ISI TRANSFERİNİN DENEYSEL İNCELENMESİ

## AN EXPERIMENTAL INVESTIGATION ON HEAT TRANSFER DURING PHASE CHANGE ON PLANAR FACE WITH CENTRIPETAL AGITATOR

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### ÖZET

Bu çalışmada, karıştırıcı tanklarda kaynama sırasında ısı transfer hızının belirlenmesi hedeflenmiştir. Deneylerde sabit atmosfer basıncında farklı sıcaklıklarda kaynamakta olan şeker su çözeltileri kullanılmıştır. Taban yüzeyinden ısıtılan çözelti ve kanatlı bir karıştırıcı kullanarak değişik hızlarda ve farklı kanat taban arası mesafelerde deneyler yaparak bu parametrelerin ısı geçişine olan etkileri incelenmiştir. Isı geçiş hızının şeker konsantrasyonuna, karıştırıcı devir sayısına ve kanat ile taban arasındaki mesafeye bağlı olduğu görülmüştür.

**Anahtar kelimeler:** Isı geçişi, şeker su çözeltileri, karıştırıcı tanklar, havuz kaynaması.

### ABSTRACT

In this study, heat transfer rate under boiling in agitating tanks is aimed to determine. Constant pressure and different temperatures of boiling aqueous sugar solutions were used in experiments. Effects of different agitator speeds and different gaps between blade and surface on the heat transfer rate are investigated by using an agitator which has blades and solutions which are heating from surface experimentally. It was seen that how much heat transfer rate is depend on sugar concentration, agitator speed and gap between blade and surface.

**Keywords:** Heat transfer, aqueous sugar solutions, agitating tanks, pool boiling.

### 1. GİRİŞ

Şekerleme endüstrisinde şekerden üretilen gıdalara (bonbon vs.) şekil verilebilmesi ve katkı maddeleri (renk, aroma vs) ilave edilebilmesi için sakaroz ve/veya diğer şekerlerin sıvı fazda başka bir deyişle mayi durumda olması gerekmektedir. Toz şekerin ısı iletim katsayısı ise düşük olduğundan şekeri sıvı faza geçirmek için doğrudan ısı verilmesi oldukça güçtür. Bundan dolayı şekere bir miktar su ilave edilerek şeker su çözeltisi oluşturulmakta ve daha sonra bir kap içerisinde kaynatılarak su uzaklaştırılmaktadır. Bu şekilde yüksek sıcaklıkta sıvı-mayi durumda şeker elde edilebilmektedir.

Sulu şeker çözeltileri genellikle helva türündeki tatlıların üretiminde kullanılan esas bileşendir. Helva, Yunanistan, Türkiye ve Arap ülkeleri gibi birçok orta doğu ülkesinde yaygın olarak tüketilir. Sulu şeker çözeltilerinin kaynatılması sırasında şeker konsantrasyonu arttıkça ısı transferinin zorlaştığı bilinen bir gerçektir. Bunun doğal sonucu olarak şeker konsantrasyonu yüksek değerlere ulaştığında (%90-95) kaynama sıcaklığı da 130-150 °C sıcaklığa ulaşmaktadır (AL, 1936; Perez AM, 1997). Kaynamanın sürdürülebilmesi için ısıtıcı yüzey sıcaklığının daha yüksek sıcaklıklarda olmaması gerekmektedir. En büyük sorun ise şekerin (sakaroz) 150 °C üzerinde renk, 170 °C üzerindeki sıcaklıklarda ise kimyasal değişime uğrayarak lezzet değiştirmesidir. Bu yüzden çözeltinin içindeki suyun, maksimum 150 °C'nin altındaki bir sıcaklıkta mümkün olan en hızlı şekilde buharlaştırılması gereklidir. Bu işlem sonunda şeker kolay şekil verilebilir duruma gelir.

Yukarıdaki nedenlerden dolayı ısı transferini iyileştirmek için endüstriyel üretimde karıştırıcı kaplara oldukça fazla rastlanılmaktadır. Özellikle akide şekeri, helva ve birçok yöresel ve modern şekerleme üretiminde aynı teknolojiler kullanılmaktadır. Karıştırma sayesinde ısı transferinin iyileştiği iyi bilinmektedir. Buna rağmen bu özel konu ile ilgili çok az araştırma bulunmaktadır. Bu araştırmalar da ise saf maddelerin ısıtılması veya soğutulması sırasında karıştırmanın ısı transferine olan etkisi incelenmiştir. Bunlardan bazıları aşağıda sunulmuştur.

B. Triveni ve arkadaşları karıştırıcı tanklarda Newton ve Newton olmayan akışkanların ısı transferini çalışmışlardır. Deneysel olarak çapa ve türbin tipli kanatlar kullanarak serpantin borulu ısıtma ve soğutma yaparak kanat geometrisinin, hızının ve

aerasyonun ısı transferine etkilerini hint yağı ve onun metil esteri, sabun çözeltisi, CMC ve tebeşir çamuru için incelemiştir (B. Triveni, 2008).

B.Lakghomi ve arkadaşları, serpantin borulu ve ceketli tanklardaki ısı transferini incelemişler ve serpantin borulu tanklar daha verimli bulunmuş (B. Lakghomi, 2006).

Y. Kawase ve arkadaşları, ceketli karıştırma tanklarında Newton tipi olmayan değişik akışkanlar için farklı kanat tiplerinde ısı transferini deneysel ve teorik olarak çalışmışlardır (Y. Kawase, 2002).

Detaylı literatür araştırması sonunda yüksek şeker konsantrasyonuna sahip sulu şeker çözeltilerini havuz kaynaması esnasında karıştırmanın ısı transferine olan etkilerinin incelendiği özel bir çalışmaya rastlanmamıştır. Araştırmacılar karıştırma türlerinin etkinliği konusunda yeni bilgi ve bulgulara ulaşmakla birlikte bu araştırmanın konusu olan kaynayan şeker su çözeltileri için karıştırıcı kaplarda ısı transfer mekanizmalarını incelememişlerdir.

Saf maddelerin havuz kaynaması sırasında ısı transferi karakteristiğini ortaya koymak için 70 yıldan beri çalışmalar yapılmaktadır (Kays WM, 2005). Bu alandaki öncülerden birisi olan Rohesnow (Rohsenow, 1952) ve onun bazı temel hesaplamaları sonraki birçok çalışmada kullanılmıştır. Nukiyama (Nukiyama, 1934) havuz kaynamasını deneysel olarak çalışmaya odaklanmış ve kendi adıyla bilinen kaynama eğrisini bulmuştur. Fakat bu çalışmaların çoğu saf maddeler için uygulanabilirlerdir.

Çözeltiler için karıştırmanın olmadığı havuz kaynamasında şeker konsantrasyonuna bağlı kaynama noktası ve ısı transfer katsayısını hesaplayabilmek için M. Özdemir ve H. Pehlivan bir fonksiyon önermişlerdir (Mustafa Özdemir, 2008). Ancak elde edilen ilişkiler karıştırıcısız havuz kaynaması ile sınırlı olduğu için endüstriyel uygulamalarda kullanılan karıştırıcı tanklar için uygulanabilir değildir. Buradaki eksikliği gidermek amacı ile yapılmış olan bu çalışma önceki çalışmanın devamı niteliğinde olup söz konusu bilimsel boşluğu doldurmak amaçlanmıştır.

Merkezcil karıştırıcı bir kaptaki havuz kaynaması esnasında ısı transfer mekanizması deneysel olarak incelenmiştir. Deneysel sonuçlar, farklı devir sayıları ve değişik konsantrasyonlardaki şeker su çözeltileri kullanılmıştır.

## 2. HAVUZ TİPİ KAYNAMADA ISI TRANSFER MEKANİZMASI

Havuz kaynaması sırasında oluşan buhar fazı baloncukları ısı transfer edilen yüzeyde büyürler ve sıvı ile ısıtıcı yüzey arasındaki teması engelledikleri için ısı transferini zorlaştırırlar. Ancak kaldırma kuvvetinin etkisiyle de buhar baloncukları yüzeyden ayrılırken sıvının hareketine dolayısıyla sıvının bir miktar karışmasına neden olurlar. Bu durum ısı transferini de bir miktar iyileştirir.

Bu birbirine zıt iki olayın ısı transferine olan birleşik etkileri, ısıtıcı yüzeyin yapısı, baloncukların büyüklüğü, çözeltilerin yüzey gerilimi ve viskozitesi ile ilişkilidir (Hahne E, 2006; Kotthoff S, 2006). Şekerli su çözeltilerinde bu fiziksel özellikler şeker konsantrasyonuna bağlı olarak da değişmektedir. Doğal olarak yüksek şeker konsantrasyonlu çözeltilerde oluşan kabarcıklar daha büyük ya da daha uzun ömürlü olmaktadır. Isı transferi için olumsuz etki yapan bu durumu karıştırmak suretiyle kısmen ortadan kaldırmak mümkündür. Ayrıca sıvı fazının hareketlendirilmesinin ısı transferini hızlandırdığı da bilinmektedir.

Isı transferinin iyileştirilmesi amacıyla yapılan karıştırma işlemlerinde karıştırıcı kanatları iç cidarı sıyracacak şekilde (menteşeli oynar sıyrıcı kanat) imal edilirler. Ancak sıyrıcının yüzeye temas etmesini sağlayan menteşeler şeker vb. birçok gıda maddesinde olduğu gibi katılaşma sonrası görevini yerine getiremezler. Bu yüzden tank imalatı sırasında karıştırıcı kanatlar üretim hatalarını da karşılayabilmek için kanat ile yüzey arasında 0-12 mm arası boşluk kalacak şekilde imal edilmektedirler. Özetle şeker oranı yüksek şekerli su çözeltilerinde viskozitenin yüksek olmasından dolayı sıyrıcı kanatlar kullanılması gerekli olmasına rağmen uygulamada yaşanan problemler nedeni ile sıyrıcısız, boşluklu (4-12 mm) karıştırıcı kanatlar kullanılmaktadır.

### 2.1 Karıştırıcısız Havuz Kaynamasında Isı Transfer Mekanizması

Genel olarak kaynama, akışkan ile katı yüzey arasında, akışkanın sıvı fazdan gaz fazına geçmesi prosesidir. Proses, yüzey sıcaklığının sıvının belli bir basınçtaki doyma sıcaklığını aştığı anda başlar. Yüzeyden sıvıya transfer edilen ısı Newton'un soğuma kanunu gereği aşağıdaki gibi,

$$\dot{q} = h(T_w - T_{sat}) \quad (1)$$

ifade edilir. Baloncuk oluşum bölgesinde ise saf akışkanlar için ısı transferi aşağıdaki gibi ifade edilebilir (Jeschar R., 1990).

$$\dot{q} = c(T_w - T_{sat})^n \quad (2)$$

Yukarıdaki eşitliklere benzer olarak kaynamakta olan farklı konsantrasyonlardaki şekerli su çözeltileri için ise aşağıdaki denklem kullanılabilir (Mustafa Özdemir, 2008).

$$\dot{q} = k \cdot (1 - c_s)(T_w - T_b)^{1,3} \quad (3)$$

Karıştırıcısız durum için  $k=1$  [ $\text{kW}/\text{m}^{20}\text{C}^n$ ] ve  $(1 - c_s)$ 'de su konsantrasyonu olmak üzere yeni bir mühendislik yaklaşımıyla ısı akısı (3) nolu denklemden hesaplanabilmektedir. Ayrıca konsantrasyonu bilinen bir şekerli su çözeltisi için kaynama sıcaklığı ise aşağıda verilen eşitlik kullanılarak hesaplanabilmektedir (Mustafa Özdemir, 2008).

$$T_b = T_{sat} + (c_s T_{sat}/2,1)^{c_s^{2,1}} \quad (4)$$

(4) numaralı denklem (1) numaralı denklemde yerine konulursa,

$$h = k(1 - c_s)(T_w - (T_{sat} + (c_s T_{sat}/2,1)^{c_s^{2,1}}))^{0,3} \quad (5)$$

ısı taşınım katsayısı  $h$  yukarıdaki eşitlikten hesaplanabilir.

## 2.2 Karıştırmalı Havuz Kaynamasında Isı Transfer Mekanizması

Karıştırmalı kaynama sırasında ısı transfer hızı karıştırmasız duruma göre daha yüksek olmaktadır. Bu durumda  $\dot{q}_{toplam} = \dot{q}_{karıştırmasız} + \dot{q}_{karıştırıcı}$  etkisi yazılabilir. Bu ve denklem (1) esas alınarak,

$$\dot{q}_{toplam} = \dot{q}_{(0)} + \dot{q}_{(k)} \quad (6)$$

yazılabilir. Burada  $\dot{q}_{(0)}$  ve  $\dot{q}_{(k)}$  ise aşağıdaki gibi ifade edilebilir.

$$\dot{q}_{(0)} = h_{(0)} \cdot \Delta T \quad (7)$$

$$\dot{q}_{(k)} = h_{(k)} \cdot \Delta T \quad (8)$$

Isı akısı için geçerli olan bu durum ısı taşınım katsayısı  $h$  ve toplam ısı transfer katsayısı  $U$  için de geçerlidir. Dolayısıyla toplam ısı taşınım katsayısı  $h$ ,

$$h_{toplam} = h_{(0)} + h_{(k)} \quad (9)$$

şeklinde yazılabilir.

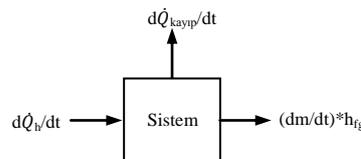
## 3. UYGULAMA

Saf maddeler için atmosfer basıncında yani tek bir basınçta tek doyma sıcaklığı olduğundan dolayı karıştırıcı ve karıştırıcısız kaynatıcılarda ısı transferinin farklı sıcaklıklarda denenmesi mümkün değildir. Bundan dolayı sabit basınçta fakat sıcaklığa bağlı olarak değişen malzeme özelliklerinin ( $\mu, \rho, c_p$  ve  $k$ ) ısı transferine olan etkilerinin incelenmesi mümkün olamamaktadır. Karıştırıcı kaplarda sızdırmazlık sorunundan dolayı yüksek basınçlarda deney yapmak çok kolay olmamaktadır. Bundan dolayı malzeme özellikleri çok iyi bilinen şeker su çözeltilerinde yaklaşık 30 °C'lik bir sıcaklık penceresinde şeker konsantrasyonuna bağlı olarak ısı transfer mekanizmasının ortaya konulması mümkün olmaktadır.

Deneylerde kullanılan kanat uzunluğu 168 mm ve kanat genişliği ise 16 mm'dir. Deneyler 40, 80 ve 120 devir olmak üzere 3 farklı sabit devirde, 12 ve 4 mm olmak üzere 2 farklı kanat-taban arası mesafede yapılmıştır. Sıcaklıklar her 5 s de bir ölçülerek 12 ölçümün aritmetik ortalama değeri olarak belirlenmiştir.

## 4. KÜTLE VE ENERJİ DENKLEMLERİ

Şeker su çözeltisinin enerji ve kütle dengesi Şekil 4.1'de gösterildiği gibidir.



Şekil 4.1 Kütle ve enerji denkliği

Burada kayıp ısı güç transfer edilen ısı güçlere göre çok küçük olduğundan ihmal edilmiştir. Kütle denkleğini kullanarak şekerin ( $c_s$ ) ve suyun ( $c_w$ ) konsantrasyonları yazılacak olursa;

$$c_s = \frac{m_s}{m_s + m_{wt}} \quad (10)$$

$$c_{wt} = \frac{m_{wt}}{m_s + m_{wt}} \quad (11)$$

dolayısıyla,

$$c_s + c_{wt} = 1 \quad (12)$$

olur. Buharlaşma süresince şeker miktarı sabit olacağından;

$$\frac{dm_t}{m_t} dt = -\frac{dc}{c} dt \quad (13)$$

Denklem (13)'in integrali alınır,

$$\int_1^2 \frac{dm_t}{m_t} dt = -\int_1^2 \frac{dc}{c} dt \quad (14)$$

elde edilir. Buradan,

$$\frac{m_2}{m_1} = \frac{c_1}{c_2} \quad (15)$$

ve dolayısıyla

$$m_1 - m_2 = m_1 \left(1 - \frac{c_1}{c_2}\right) \quad (16)$$

elde edilir. Burada ilk ve son kütle farkını aşağıdaki şekilde ifade edersek,

$$\Delta m = m_1 - m_2 \quad (17)$$

Birim zaman değişimi için kütle analizine dayanarak şekerin kütle konsantrasyonu hesaplanabilir. Her bir zaman adımı için enerji dengesi sürekli rejimde kaynama için aşağıdaki şekilde ifade edilir.

$$\frac{dQ}{dt} = \frac{dm}{dt} h_{fg} \quad (18)$$

ya da ısı transfer edilen yüzey bilindiği için ısı akışı,

$$\frac{d\dot{q}}{dt} = \frac{dm}{dt} \frac{h_{fg}}{A} \quad (19)$$

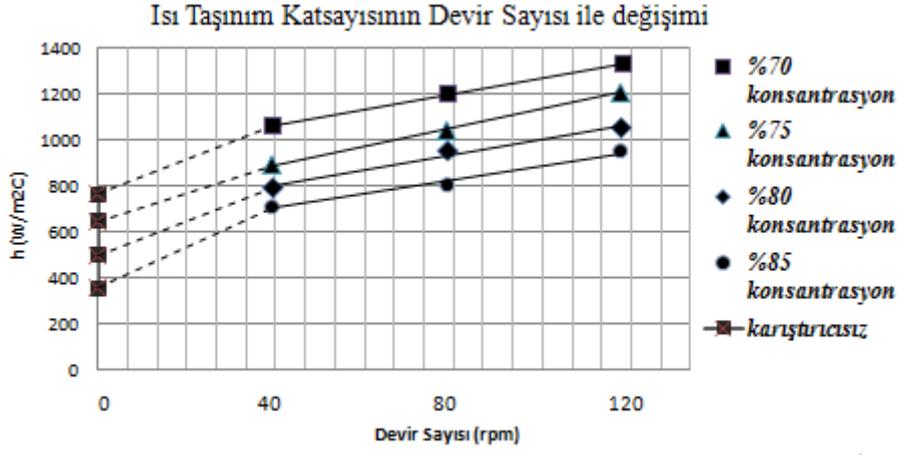
denklemleri kullanılarak hesaplanabilir.

## 5. DENEYSEL SONUÇLAR VE TARTIŞMA

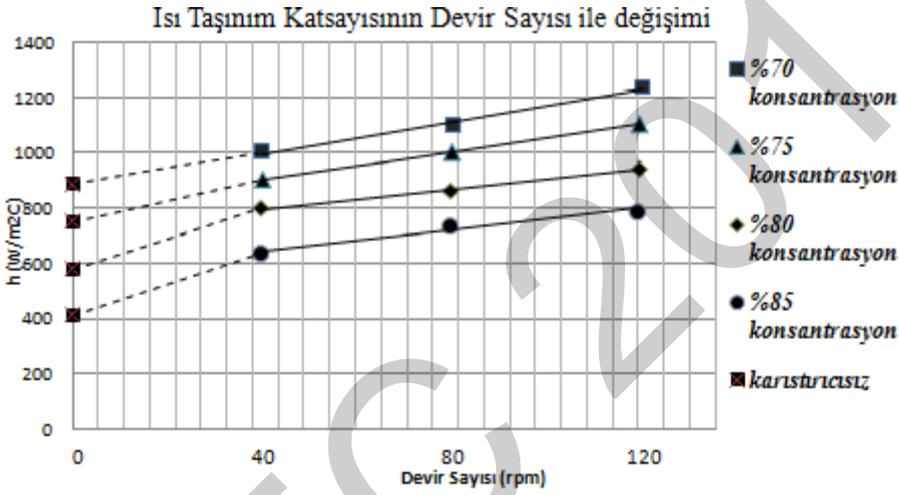
Şekil 5.1 ve Şekil 5.2'den görüldüğü üzere karıştırmanın olmadığı durumda doğal olarak ısı transfer hızı belli bir değerdedir. Bunun nedeni çözelti ile ısıtılan yüzey arasında kaynama sırasında oluşan kabarcıkların yüzeyden ayrılıp yükselirken çözeltinin karışmasına neden olmasıdır. Böylelikle devir sayısının sıfır olduğu başka bir deyişle zorlanmış akışın olmadığı durumda ısı taşınım katsayısının belirli bir değeri vardır. Bu değer (5) numaralı formül yardımıyla hesaplanabilmektedir.

Karıştırmanın etkisiyle ısı taşınım hızı karıştırıcının devir sayısına bağlı olarak artmaktadır. Isı taşınım hızı çözültideki şeker konsantrasyonunun artışına bağlı olarak da azalmaktadır. Kanat ile taban arası mesafe arttığında ısı transfer hızı bir miktar azalmaktadır. Bu durum tüm devir sayıları için geçerlidir.

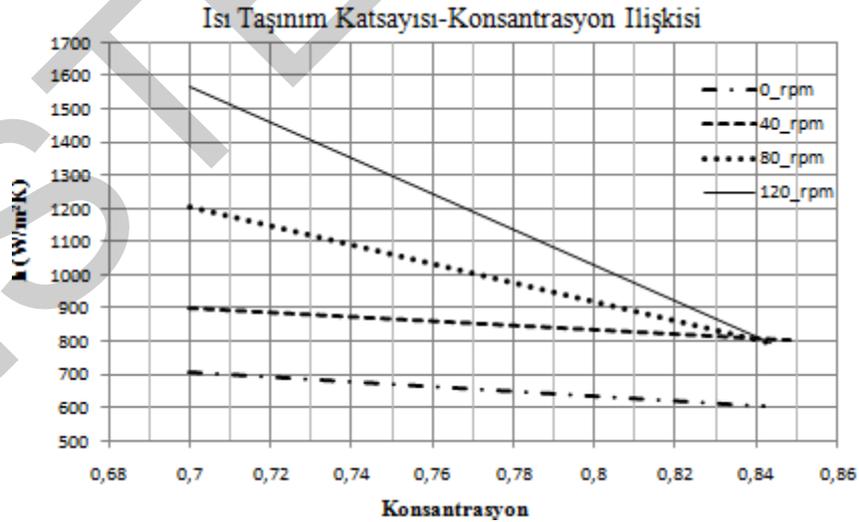
Şekil 5.3 ve Şekil 5.4'de kanat taban arası mesafenin 4 mm ve 12 mm olduğu durumlar için çözültideki şeker konsantrasyonunun ısı transfer hızı ile doğrusal bir ilişkide olduğu görülmektedir. Karıştırıcı devir sayısının sıfır olduğu durum için ısı transfer hızı ile şeker konsantrasyonu ilişkisi her iki kanat-taban arası mesafe içinde aynıdır. Ancak kanat-taban mesafesi karıştırıcı devir sayısı arttıkça ısı transferini etkilemektedir. Bu etkileşim yüksek şeker konsantrasyonlarında daha belirgin olarak görülmektedir. Taban-kanat arası mesafenin azalması ısı transferini arttırmaktadır.



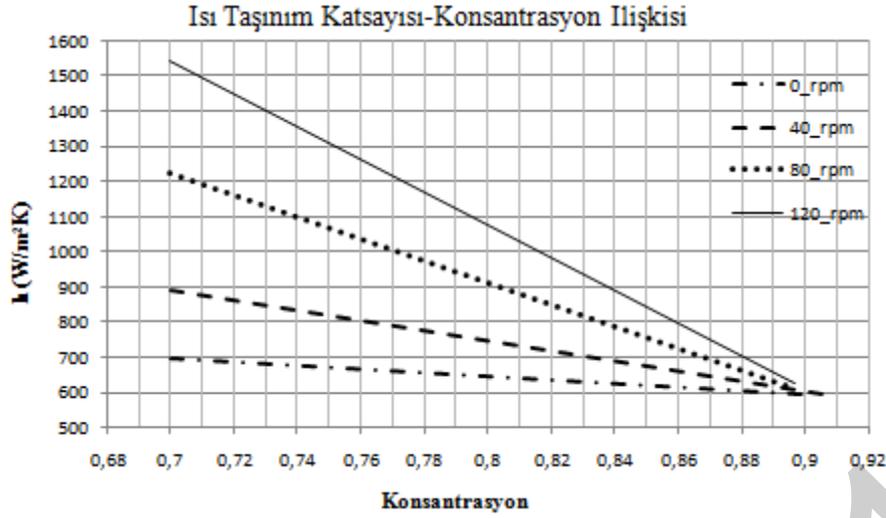
Şekil 5.1 Konsantrasyona bağlı devir sayısı- ısı taşınım katsayısı grafiği 4 mm boşluklu



Şekil 5.2 Konsantrasyona bağlı devir sayısı- ısı taşınım katsayısı grafiği 12 mm boşluklu



Şekil 5.3 Karıştırıcı hızına bağlı konsantrasyon - ısı taşınım katsayısı grafiği 12 mm boşluklu



Şekil 5.4 Karıştırıcı hızına bağlı konsantrasyon - ısı taşınım katsayısı grafiği 4 mm boşluklu

## 6. SONUÇLAR

Şekerli su çözeltilerinde kaynama sırasında ısı transfer katsayısı şeker konsantrasyonuna ve doyma basıncına bağlı olarak değişmektedir. Karıştırıcının olmadığı durumda ısı transfer yüzeyinde oluşan kabarcıkların yüzeyden ayrılıp yükselmeleri esnasında doğal bir karışmanın olduğu bilinmektedir. Çözelti mekanik bir karıştırıcı ile karıştırıldığında ısı transfer hızı bilinen veya hesaplanabilen bir değerden başlayarak, karıştırıcı devir sayısına bağlı olarak artmaktadır. Kanat ile taban arasındaki mesafenin küçük olduğu durumda daha iyi ısı transfer hızı elde edilmiştir. Özellikle gıda sektöründe şekerli su başka bir deyişle şerbet hammadde olarak oldukça fazla kullanılmaktadır. Şerbetli ürünlerin imalatında kullanılan karıştırıcı tanklarda ise taban-kanat arasındaki boşluğun minimum olması gerekmektedir. Aksi halde azalan ısı transfer hızı yüzeye temas eden ve yer değiştiremeyen sınır tabakadaki sıcaklık artışına neden olarak önce karamelleşmeye daha sonra da şekerin kimyasal yapısının bozulmasına neden olmaktadır.

## TEŞEKKÜR

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# MEVCUT BİNALARIN DEPREM HASAR GÖREBİLİRLİĞİNİ HIZLI BELİRLEYEN SİNİRSEL BULANIK AĞ TABANLI DEĞERLENDİRME SİSTEMİ

## A NEURO – FUZZY BASED QUICK ASSESSMENT SYSTEM TO DETERMINATION OF EARTHQUAKE VULNERABILITY FOR EXISTING BUILDINGS

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### ÖZET

Ülkemizin büyük bir bölümü aktif fay hatları üzerinde bulunmakta olup bu faylardan birçoğu büyük depremler oluşturmaktadır. Bu nedenle yerleşim alanlarının büyük bölümü deprem riski altında bulunmaktadır. 1999 Marmara depremi önemli fiziksel, sosyal ve ekonomik kayıplara yol açmış ve sonuçları, depremin önlenemeyen bir doğa olayı olduğunu göstermiştir. Deprem tehlikesi altındaki yerleşim alanlarında olası depremlerde oluşacak zararları azaltmak için öncelikle mevcut binaların deprem güvenliği açısından hızlı bir şekilde değerlendirilmesi, bu verilerle yapı stoku oluşturularak, gerekli yapısal tedbirlerin alınması gerekmektedir. Bu çalışmada, oluşturulacak yapı stoku veri tabanına veri sağlamak üzere özellikle yapı denetimine tabi olmadan inşa edilmiş mevcut betonarme binaların deprem hasar görebilirlik risklerinin belirlendiği bir karar destek sistemi geliştirilmiştir. Sinirsel-Bulanık Ağ yapısı ile oluşturulan sistem mevcut binaların, yapının taşıyıcı sistemi ve zemin özelliklerini dikkate alarak, depremde hasar görebilirlik risklerini yüksek, orta ve düşük olarak sınıflandırmaktadır. Çalışma birinci derece deprem bölgesinde yer alan Erzincan ilinde, 1992 depreminden en çok etkilenen Fatih Mahallesiindeki betonarme konutlar üzerinde sınanmış, elde edilen sonuçların 4 uzman görüşü ile çok büyük oranda örtüştüğü gözlenmiştir.

**Anahtar Kelimeler:** Deprem, Hasar Görebilirlik, Hızlı Tarama, Sinirsel Bulanık Ağ

### ABSTRACT

Large part of our country's on active fault lines and most of them can produce big earthquake. So that most of the settlement always is in the risk of earthquake. In 1999 a big earthquake occurred in The Marmara. This earthquake has caused physical, social and economic loss and these results showed us that the earthquake is an inevitable natural event. In order to minimize the damages of possible earthquakes in the residential area where there is a danger of earthquake, firstly evaluation of seismic performans of existing buildings and making up a build stock by using some data. In this study, to obtain data for the build stock database, a decision support system was developed to determine the risk of earthquake vulnerability of existing reinforced concrete buildings that are built without checked by building control. The neuro-fuzzy based decision support system, classifies the earthquake vulnerability of existing buildings as high, medium and low by taking into account their structural system and the characteristics of the ground. The study was tried on reinforced concrete buildings in Fatih neighborhood, the most affected part of the city in 1992 earthquake, in Erzincan located in the first degree seismic zone, it was observed that the obtained results mostly matched up with the four experts' opinion.

**Key Words:** Earthquake, Vulnerability, Quick Assessment, Neuro-Fuzzy Networks

### I. GİRİŞ

Topraklarının %93'ü, nüfusunun ise %98'i çeşitli derecelerde deprem etkisi altında olan ülkemizde, 1992 Erzincan, 1999 Marmara ve sonrası yaşanan 2011 Van depremi nedeniyle ortaya çıkan fiziksel, sosyal ve ekonomik kayıplar, hala depreme uygun bir yapılaşmaya sahip olmadığımız gerçeğinin yanı sıra çok ciddi tedbirlerin alınması gerektiğini de göstermiştir. Bu yönde yerleşimlerde alınacak önlemlerle zaman içinde sismik risklerin azaltılması, öncelikle yeni ve kentsel dönüşümlerle yenilenen yapıların depreme dayanıklı yapılması ve mevcut yapıların belirli bir program çerçevesinde

güçlendirilmesi şeklinde olabilecektir (Şengezer 1999). Yeni yapılacak ya da yenilenen yapılar yürürlükte olan yönetmeliklerde tanımlanan ölçüt ve performans düzeylerine göre tasarlanıp inşa edildiğinden, depreme dayanıklı yapı grubunda değerlendirilebilirken (Çelik 2007) asıl problemi mevcut yapılar oluşturmaktadır. Çünkü bu yapıların çoğu eski yönetmeliklere göre tasarlanıp inşa edilmiş olup büyük bir kısmı hala kullanılmakta ve olası şiddetli depremlerde de göçme riskleri taşımaktadır (Ghobarah 1998). Dolayısıyla deprem riski taşıyan yerleşim alanlarında can ve mal kaybını en aza indirmek için mevcut yapıların deprem davranışlarının hızlı bir şekilde bugünden değerlendirilmesi, bu verilerle yapı stoku oluşturularak (Memari 2001), gerekli yapısal tedbirlerin alınması gerekmektedir.

2002 Deprem Konseyi raporunda mevcut yapılar üzerinde gerçekleştirilecek deprem güvenliği değerlendirme çalışmaları iki ana grupta toplanmıştır: Kapsamlı, deneysel ve analitik inceleme (değerlendirme) ile hızlı ve basit değerlendirme yöntemi(tarama). 2007 Yılında yürürlüğe giren “Afet Bölgelerinde Yapılacak Yapılar Hakkında Yönetmelik” de mevcut yapıların deprem güvenliğinin belirlenmesi yönünde önerilen yöntemler kapsamlı ve analitik çalışmalara dayanmaktadır. Ancak bu tür analizlerin uygulanabilmesi uzun ve maliyeti yüksek bir çalışma gerektirmektedir (Karasu 2007). Solomon (2008) analitik incelemelerin özellikle yapı stoku fazla olan yerleşim bölgeleri için uygun olmadığı, benzer şekilde Tezcan’da (2005) yönetmeliğin öngördüğü “Sıfır Can Kaybı” yaklaşımı ile deprem riski altındaki tüm yapıların detaylı değerlendirilmesinin zaman ve ekonomik kısıtlar nedeniyle gereksiz olduğu fikrini savunmaktadır. Önerilen hızlı ve basit tarama yöntemleri, mevcut binalardan hangisinin ya da hangilerinin daha riskli olduğunun belirlenmesi ve kapsamlı bir değerlendirme için de öncelik sıralaması yapılması amacına yöneliktir. Bu doğrultuda NRCC (Kanada Ulusal Araştırma Birliği) ya da FEMA (Federal Acil Durum Yönetim Teşkilatı) tarafından geliştirilmiş pek çok hızlı değerlendirme yönteminden söz edilebilir (Çelik 2007). FEMA’nın önerdiği yöntemde yapının tipi, düşey süreksizlik, planda süreksizlik, yapım yılı ve yapı kalitesi gibi faktörler dikkate alınarak, mevcut betonarme yapıların sismik davranışları hızlı bir şekilde belirlenebilmektedir. Hızlı tarama yönteminde gerekli veriler yapının varsa projesinden, projesi olmayanlarda gözleme dayalı olarak ve sokak taraması şeklinde elde edilebilmektedir. Özcebe vd. (2006) gözlem ve 4-5 parametreye dayalı olarak mevcut yapıların deprem riskinin %80 doğrulukta tespit edilebileceğini ifade etmektedir. Bayındırlık İskan Bakanlığı Deprem Şurasının (2004), Mevcut Yapıların İncelenmesi ve Yapı Denetim Komisyon Raporunda da ülkemizde mevcut yapıların deprem risklerine karşı envanterinin oluşturulmasında kademeli değerlendirme yöntemleri önerilmektedir. Yüksek deprem riski taşıyan ülkemizde, hızlı tarama yöntemiyle mevcut yapıların deprem güvenliği açısından değerlendirilmesi ve sonrasında anlamlı bir öncelik sıralaması içinde depreme karşı güvenli duruma getirilmesi gerekmektedir.

Bu çalışmanın amacı, bina ölçeğinde, mevcut betonarme yapıların depremde hasar görebilirliklerini belirlemeye yönelik bir karar destek sistemi geliştirmektir. Geliştirilen sistem, afet yönetimi kapsamında yerel yönetimler ve İl Afet ve Acil Durum Müdürlükleri tarafından kullanılabilir bir bilgi tabanı oluşturacaktır. Çalışmada oluşturulan karar destek sistemi, ülkemizdeki yapı stokunun büyük çoğunluğunun betonarme yapılar olması nedeniyle bu hedef kitleye yönelik olarak geliştirilmiştir. Değerlendirme yalnızca bina türü yapılar için geçerli olup, köprü, kule gibi özellik gösteren yapılar araştırmanın dışında tutulmuştur. Değerlendirme yöntemi yapının hızlı ve basit tarama ile gözden geçirilmesi ve yapının deprem sırasındaki davranışını olumsuz yönde etkileyecek parametrelerin;

- Bina yerleşim alanı zemin özellikleri
- Bina yapısal özelliklerinin kontrolüne dayanmaktadır.

Değerlendirme yönteminde yer alan hasar görebilirlik parametreleri, yurt içi ve yurt dışında önerilen değerlendirme yöntemleri (Akbulut 2004, Çelik 2007, Temur 2006, Karasu 2007, FEMA 154, NRCC) ile 1997 “Afet Bölgelerinde Yapılacak Yapılar Hakkında Yönetmeliğe” dayalı olarak oluşturulmuştur. Çalışma kapsamında hasarların üç farklı düzeyde oluştuğu kabul edilmiştir:

- “Yüksek” düzey hasar riski
- “Orta” düzey hasar riski
- “Düşük” düzey hasar riski

Kontrolü yapılan yapılardan, deprem riski “yüksek” çıkanlara yıkım, ”orta” çıkanların ise detaylı ve analitik bir inceleme sürecine alınması gerekmektedir. Bu inceleme sonrasında güçlendirme ya da yıkım kararı verilmelidir. Deprem riski “düşük” çıkması durumunda ise kapsamlı analitik incelemeye zaman ve ekonomik şartlara göre karar verilmeli, bu grup içinde yer alan bir bina üzerinde yapılacak detaylı inceleme ve analitik hesaplamalar ile ortaya çıkacak sonuç, diğer binalar içinde emsal kabul edilebilir. Dolayısıyla çalışmada geliştirilen karar destek sistemi, çok aşamalı bir incelemenin ilk aşaması olarak düşünülmekte ve her bir binanın depremden hasar görebilirliğinin ön değerlendirmesini içermektedir. Değerlendirme yapıldıktan sonra öncelik sırasına göre daha kapsamlı bir çalışma mutlaka yapılmalıdır.

Çalışmada Visual Basic 5.0 Programlama dili ile hazırlanmış bir arayüz programı tarafından kontrol edilen Sinirsel Bulanık Ağlar ile hızlı tarama sonucu elde edilen bulguları kullanarak binaların deprem hasar görebilirlik riskleri tespit edilmektedir. Oluşturulan sistem, birinci derece deprem bölgesinde yer alan Erzincan ilinde, 1992 depreminden en çok etkilenen Fatih Mahallesindeki betonarme konutlar üzerinde denenmiş, elde edilen sonuçlar 4 farklı uzmanın görüşleri ile karşılaştırılmış ve sistemin elde ettiği sonuçlarla uzmanların görüşlerinin % 95.5 oranında örtüştüğü hesaplanmıştır.

## II. SİNİRSEL BULANIK AĞLAR

Yapay Sinir Ağları ve Bulanık Mantığın kombinasyonu olan Sinirsel Bulanık sistemler her iki metodun sınırlamalarından arındırılmış olmakla beraber her iki metodun avantajlarını kapsayan melez bir yapay zeka modelidir (Jang 1993). Sinirsel bulanık sistemler, yapay sinir ağlarının paralel hesaplayabilme ve öğrenme kabiliyeti ile bulanık mantığın uzman bilgisini kullanarak karar verme özelliklerine sahiptirler (Demirel vd. 2010) Sinir ağı içerisine bulanık kavramları yerleştirerek ya da bulanık modelleme için sinir ağları kullanılarak gerçekleştirilen çeşitli sinirsel bulanık sistem modelleri bulunmaktadır (Ballı vd. 2009).

Bulanık sistem ve Sinir ağlarının birlikte kullanıldığı en iyi örneklerinden biri olan ANFIS (Adaptive Network Based Fuzzy Inference System) 1993 yılında Jang (Jang 1993) tarafından geliştirilmiştir. Sugeno tipi çıkarım sistemi, En küçük Kareler Yöntemi ve Geri Yayılmalı Öğrenme algoritmalarının bir arada kullanıldığı melez öğrenme algoritmasına sahip olan ANFIS, Adaptif ağlar ve doğrudan bağlanmış düğümlerden oluşmaktadır (Jang vd. 1997).

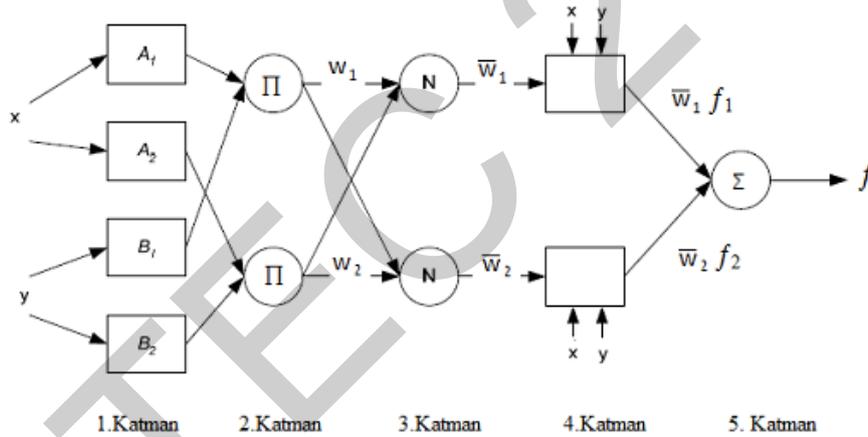
Düğümün bir işlem birimini temsil ettiği bu tür adaptif ağlarda, düğümler arası bağlantılar bu düğümlerin birbiriyle ilgisini göstermektedir. Bulanık denetleyici tasarımının en temel sorunlarından biri olan kural-tabanı oluşturma ve var olan kural tabanının optimizasyon sorununu çözen ANFIS, bir probleme yönelik tüm kuralları oluşturabildiği gibi kuralların uzmanlar tarafından da atanabilmesine imkan sağlamaktadır. Yapay sinir ağlarından farklı olarak sisteme uzman görüşlerini de kattığı için bir çok alanda sinir ağlarından daha iyi tahmin yapabilen ANFIS, 5 katmanlı bir yapıya sahiptir ve her bir katman bulanık çıkarım sürecindeki bir basamak ile ilgilidir (Nauck ve Kruse 1995).

X ve y olmak üzere iki giriş ve z olmak üzere bir çıkışlı kural kümesi,

$$\text{Kural 1: Eğer } x=A_1 \text{ ve } y=B_1 \text{ ise } f_1=p_1x+q_1y+r_1$$

$$\text{Kural 2: Eğer } x=A_2 \text{ ve } y=B_2 \text{ ise } f_2=p_2x+q_2y+r_2$$

Aynı katmandaki düğüm fonksiyonlarının eşit olduğu ANFIS yapısı Şekil 1’de verilmiştir.



Şekil 1. ANFIS Yapısı

### 1. Katman

Bulanıklaştırma katmanıdır. Bu katmanda yer alan her bir  $i$  düğümü adaptif bir düğümdür ve düğümlere ait çıkışlar aşağıdaki gibi tanımlanır.

$$O_{1,i} = \mu_{A_i}(x) \quad i = 1, 2 \text{ veya}$$

$$O_{1,i} = \mu_{B_{i-2}}(y) \quad i = 3, 4$$

Burada  $x$ (veya  $y$ )  $i$ . düğümün giriş değeri ve  $A_i$ (veya  $B_{i-2}$ ) ise bu düğüme ait bulanık kümeyi ifade etmektedir. Bu nedenle  $O_{1,i}$ , bir düğümün ilgili bulanık kümeye üyelik derecesini ( $\mu$ ) verirken bu değer seçilen üyelik tipi fonksiyonundan hesaplanır. Tipik bir üyelik fonksiyonu aşağıdaki gibi verilebilir:

$$\mu_{A_i}(x) = \frac{1}{1 + \left[ \frac{x - c_i}{a_i} \right]^2 b_i} \quad (2)$$

Burada  $a_i$ ,  $b_i$  ve  $c_i$  öncül parametreler olarak adlandırılır ve bu parametrelerin alacağı değere göre  $\mu$  değerleri yani düğüm çıkışları hesaplanır.

### 2. Katman

Bulanıklaştırma katmanı olarak isimlendirilen bu katmanda her bir düğüm  $\Pi$  ile etiketlenmiş sabit düğümlerdir. Bu katmandaki her bir düğümün çıkışı birinci katmandan gelen üyelik derecesi çarpımlarına eşittir.

$$O_{2,i} = w_i = \mu_{A_i}(x) \cdot \mu_{B_i}(y) \quad i=1,2 \quad (3)$$

Her düğüm çıkışı bir kuralın gerçekleşme derecesini oluşturur.

### 3.Katman

Normalizasyon katmanıdır. Bu katmandaki her bir düğüm, kural katmanından gelen tüm düğümleri giriş değeri olarak kabul etmekte ve her bir kuralın normalleştirilmiş değerini hesaplamaktadır. Bu katmanda yer alan her bir düğüm Nile etiketlenmiş sabit bir düğümdür. Katmandaki  $i$ . düğüm  $i$ . kuralın gerçekleşme derecesinin, bütün kuralların gerçekleşme dereceleri toplamına oranını hesaplar.

$$O_{3,i} = \overline{w}_i = \frac{w_i}{w_1 + w_2} \quad (4)$$

Bu katmanın çıkışları, normalize edilmiş gerçekleşme dereceleri olarak isimlendirilir.

### 4.Katman

Durulaştırma katmanıdır. Bu katmandaki her bir düğüme, verilen bir kuralın ağırlıklandırılmış sonuç değerleri hesaplanmaktadır. Düğüm çıkışları aşağıdaki gibi ifade edilmektedir:

$$O_{4,i} = \overline{w}_i f_i = \overline{w}_i (p_i x + q_i y + r_i) \quad (5)$$

Burada  $\overline{w}_i$  3. Katmanın çıkışı,  $\{p_i, q_i, r_i\}$  ise bu katmanda bulunan düğümlerin parametrelerinden oluşan sonuç parametreleri kümesidir.

### 5.Katman

Toplam katmanıdır. Bu katmanda sadece bir düğüm vardır ve  $\sum$  ile etiketlenmiştir. Burada 4. Katmandaki her bir düğümün çıkış değeri toplanarak, sistemin sonuç değeri elde edilir.

$$O_{5,i} = \sum_i \overline{w}_i f_i = \frac{\sum_i w_i f_i}{\sum_i w_i} \quad (6)$$

Bu şekilde elde edilen ANFIS yapısı fonksiyonel olarak Sugeno tipi bir FIS yapısıdır ve matematik modeli tam belli olmayan sistemler için oldukça iyi sonuçlar vermektedir (Barışçı ve Müldür 2003).

## III. MEVCUT BİNALARIN DEPREM HASAR GÖREBİLİRLİK RİSKİNİ BELİRLEMeye YÖNELİK BULANIK SİNİRSEL AĞ TABANLI BİR KARAR DESTEK SİSTEMİ

Bu çalışmada mevcut binaların deprem hasar görebilirlik risklerini belirlemek amacıyla Visual Basic 5.0 Programlama dili ile hazırlanmış arayüz tarafından kontrol edilen bir karar destek sistemi geliştirilmiştir. Sistemde kullanılan arayüzün ekran çıktısı şekil 2’de verilmiştir. Bu arayüze değerlendirilmesi yapılacak binanın kimlik bilgileri ile deprem hasar görebilirlik riskinin belirlenmesinde kullanılan parametrelere ilişkin veriler girilmektedir.

Deprem hasar görebilirlik riskinin belirlenmesinde kullanılan 7 parametreden 3 parametre bina yerleşim alanı zemin özellikleri diğerleri ise binanın yapısal özellikleri ile ilgilidir. Tablo1’de verilen değerlendirme kriterleri için uzman değerlendirmeleri, arayüzde scrollbar’lar aracılığı ile girilmektedir.

**Tablo 1.** Deprem Hasar Görebilirlik Riskinin Belirlenmesinde Kullanılan Kriterler

Ölçütler	
K1	Zeminin sınıfı ve yer altı suyunun varlığı
K2	Arazi eğimi
K3	Binanın yırtılan faya olan uzaklığı
K4	Yapıda yanal ötelenmeyi önleyecek miktarda perde duvar varlığı
K5	Gevrek kırılma oluşturacak kuvvetli giriş zayıf kolon durumu
K6	Yapının deprem davranışını olumsuz etkileyecek dikey süreksizlik durumu
K7	Yapının deprem davranışını olumsuz etkileyecek yatay süreksizlik durumu

Dinamik data değişimi yöntemi ile full-dublex veri iletişimi sağlanan sistemde uzmanlar tarafından yapılan değerlendirmeler MATLAB programının ANFIS tollbox’ına gönderilmektedir. 5 Uzman tarafından Erzincan ili Fatih mahallesinde 70 binada yapılan ölçümlerin %70’i oluşturulan sinirsel bulanık ağı eğitimi, %30’u da sistemin testi için kullanılmıştır. Sistemde eğitim algoritması olarak melez altküme ve eğitim adımları için melez algoritma kullanılmıştır. Sistem girişleri deprem hasar görebilirlik riski belirlenmesinde kullanılan parametreler olup, bu girişlerden K1 ve K2 kriterleri için oluşturulan üyelik fonksiyonları 3 parçalı diğer parametreler için de 2 parçalı olup Şekil 3’te gösterilmişlerdir. Bütün parametreler için Gaussian Üyelik Fonksiyonları kullanılmıştır.

Deprem Hasar Görebilirlik Belirleme Sistemi

Binanın Kimlik Bilgileri

Yapın Yılı: 1983  
Kat Adedi: 3  
Yapının Kullanım Amacı: Konut  
Beton Sınıfı: C20  
Çelik Sınıfı: S420  
Tayyaç Sistemi Tipi: Betonarme Çerçeve  
Paltı No: 20K3  
Ada No: 2171  
Parsel No: 20  
Temel Tipi: Radye

Değerlendirme Sonucu: Orta Düzey Risk

Deprem Hasar Görebilirlik Değerlendirme Kriterleri

Bina Yerleşim Alanı Zemin Özellikleri

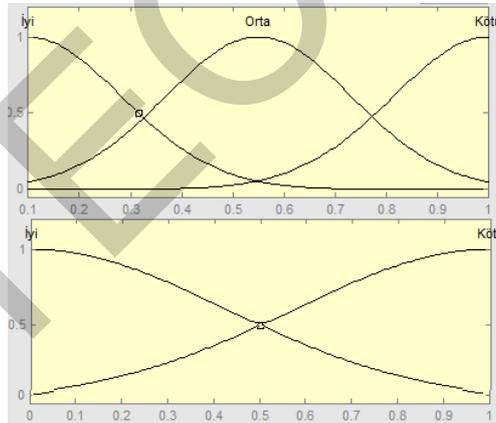
(K1) Zemin Durumu: İyi / Kötü  
(K2) Arazi Eğimi: İyi / Kötü  
(K3) Fay Hatline Olan Uzaklık: İyi / Kötü

Binanın Yapısal Özellikleri

(K4) Yapıda İki Yönlü Sismik Etkiyi Karşılayacak Eleman Varlığı: İyi / Kötü  
(K5) Kuvvetli Kaç Zayıf Kolon: İyi / Kötü  
(K6) Düşey Süreksizlik Durumu: İyi / Kötü  
(K7) Yatay Süreksizlik: İyi / Kötü

KAYDET DEĞERLENDİR

Şekil 2. Deprem Hasar Görebilirlik Belirleme Sistemi Arayüzü



Şekil 3. Deprem Hasar Görebilirlik Riskinin Belirlenmesinde Kullanılan Kriterlere Ait Üyelik Fonksiyonları

Eğitim aşamasında etki oranı 50, sıkıştırma faktörü 1,25 kabul oranı 0,5 red oranı 0,15 ve epoch sayısı 50 olarak belirlenmiştir. Çalışmada oluşturulan sinirsel bulanık sistemde 618 düğüm bulunmakta ve 288 kural kullanılmaktadır. Kuralların çalıştırılması sonucunda elde edilen deprem hasar görebilirlik değerleri sistem arayüzüne {Düşük Düzey Risk, Orta Düzey Risk, Yüksek Düzey Risk} şeklinde sözselleştirilmiştir. Sisteme ait örnek kurallar Tablo 2'de verilmiştir.

Tablo 2. Örnek Kurallar

K1	K2	K3	K4	K5	K6	K7	Çıkış
İyi	İyi	Orta	İyi	İyi	Kötü	Kötü	Orta Düzey Risk
Kötü	Kötü	Orta	Kötü	Kötü	İyi	Kötü	Yüksek Düzey Risk
İyi	Orta	İyi	İyi	Kötü	İyi	İyi	Düşük Düzey Risk
Kötü	İyi	Orta	Kötü	İyi	Orta	Kötü	Yüksek Düzey Risk
Kötü	İyi	Kötü	Kötü	İyi	İyi	İyi	Yüksek Düzey Risk
İyi	Orta	İyi	İyi	Orta	Orta	Orta	Düşük Düzey Risk
İyi	Kötü	Orta	Orta	Kötü	Orta	Orta	Orta Düzey Risk

Eğitim sonunda elde edilen hata ( $e < 10^{-8}$ ) düzeyi oldukça düşük olan sistemin elde ettiği sonuçlar 4 uzmanın görüşleri ile karşılaştırılmış, karşılaştırma sonuçları Tablo 3'te verilmiştir.

**Tablo 3.** Uzman Görüşleri ile Sistemin Uyuşma Yüzdeleri

	U1	U2	U3	U4
<b>Uyuşma (%)</b>	98	94	93	96
<b>Ortalama Uyuşma (%)</b>	95.5			

Geliştirilen sistem ayrıca değerlendirme sonuçlarını gerektiğinde bir veritabanına kaydederek oluşturulacak bina stoku için alt yapı sağlamaktadır.

#### IV. SONUÇ

Mevcut yapılarımızın çoğu eski yönetmeliklere göre tasarlanıp inşa edilmiş olduklarından, büyük bir kısmı olası şiddetli depremlerde de göçme riskleri taşımaktadır. Depremlerde can ve mal kaybını en aza indirmek için deprem riski taşıyan yerleşim alanlarında mevcut yapıların deprem davranışlarının hızlı bir şekilde bugünden değerlendirilmesi ve bu verilerle yapı stoku oluşturularak, acilen yapısal tedbirlerin alınması gerekmektedir. Bu çalışmada binaların depremlerde hasar görebilirlik risklerini belirlemek için sinirsel bulanık ağ tabanlı bir karar destek sistemi geliştirilmiştir. Geliştirilen sistem uzmanlarca belirlenmiş parametrelere göre binaların depremde hasar görebilirlik risklerini {Düşük Düzey Risk, Orta Düzey Risk, Yüksek Düzey Risk} olarak belirlemektedir.  $10^{-8}$ 'den daha düşük hata düzeyi ile sonuç üreten sistemin elde ettiği sonuçlar 4 farklı uzman görüşü ile karşılaştırılmış ve %95.5 oranında uyum tespit edilmiştir. Ayrıca elde edilen sonuçları bir veritabanında saklayan sistem, oluşturulacak bina stokları için alt yapı sağlayabilecektir.

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# MODELING AND CONTROL OF DOUBLY FED WIND GENERATOR WITH SUPER-CAPACITOR ENERGY STORAGE SYSTEMS

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## ABSTRACT

When very low voltage conditions appear at or near the terminals of a doubly fed induction generator, the converters in the rotor circuit fail to perform properly. Under the low voltage condition the grid fails to transfer adequate reactive power to support the generator terminal voltage. As a consequence, total voltage collapse may occur. This article demonstrates that the situation can be improved by injecting appropriate reactive and real power from a STATCOM supercapacitor combination. The STATCOM makes up for the unbalance in reactive power while the supercapacitor caters for real power need. Simulation studies show that decoupled P-Q control can hold the generator voltage to a reasonable level and help restore normal operation rapidly following severe low voltage conditions

## 1. INTRODUCTION

Doubly fed induction generator (DFIG) has gained popularity because of its advantages over other variable speed wind turbine generator systems [Datta & Ranganathan, 2002; Nunes, *et al*, 2004; Morren & Haan, 2005]. With such a drive system, it is possible to obtain a wide variable speed range with a reduced converter size, and a good performance in terms of active and reactive power control [Aguglia, *et al*, 2008]. In the DFIG concept, the induction generator stator terminals are directly connected to the grid and the rotor is grid-connected through variable frequency converter (VFC) which needs to handle a fraction of the total DFIG power to achieve full control of the generator. The VFC consists of a rotor-side and a grid-side converter connected back-to-back by a dc-link capacitor [Qiao, *et al*, 2009]. The DFIG design process needs suitable compromises between the wind turbine performance and the respective characteristics of the DFIG, the gearbox, the static converters and the associated control strategy [Aguglia, *et al*, 2008].

The massive employment of DFIG machines has led to motivate the modeling of such doubly fed induction generators, mainly in the issues related to power quality and ride-through capability [Junyent-Ferre, 2010]. Since the DFIG converters are designed by the slip power to achieve full control of the generator, there is not enough capacity to provide reactive power when the voltage dips below the tolerable grid voltage level at the point of common coupling [Chun, *et al*, 2009]. In the case of a weak power network and during a grid fault, the grid side converter cannot provide sufficient reactive power and voltage support due to its small power capacity, and there can be a risk of voltage instability. As a result utilities, typically, immediately disconnect the wind turbines from the grid to prevent such a contingency and reconnect them when normal operation has been restored. Therefore, voltage stability is the crucial issue in maintaining uninterrupted operation of wind turbines equipped with DFIGs during grid faults [Qiao, *et al*, 2009].

Different modeling approaches are presented for grid integration of doubly fed generators. In [Hansen & Michalke, 2007; Morren & Haan, 2005; Petersson, *et al*, 2005] their ride-through capability has been reported. The behaviour of doubly-fed machines in large wind farms, along with the general reactive and active power control of wind farms have been investigated [Hansen, *et al*, 2005; Rodriguez-Amenedo, *et al*, 2007]. Improvement of voltage instability has been addressed by using dynamic reactive compensation. Shunt flexible AC transmission system devices, such as the static var compensator and the static synchronous compensator (STATCOM), have been widely used to provide high-performance steady state and transient voltage control at the point of common coupling [Saad-Saoud, *et al*, 1998]. Use of energy storage systems have been reported to smoothen wind power fluctuations. The methods reported are flywheel energy storage, superconducting magnetic energy storage and battery energy storage. Use of energy capacitor systems for variable speed permanent magnet synchronous generator and fixed speed induction generators have been reported in the literature [Muyeen, *et al*, 2009; Alam, *et al*, 2010]. This article proposes to use of supercapacitor energy storage to supplement the real and reactive power unbalance following low voltage conditions of a variable speed DFIG system. Decoupled P-Q control strategies realized through a STATCOM interface has been shown to ride through very low voltage conditions satisfactorily.

## 2. SYSTEM MODEL

Fig.1 illustrates the DFIG wind power generation system consisting of a wound rotor induction generator and a back-to-back converter between the rotor slip rings and the grid. A so-called crowbar is inserted between the rotor slip rings and the rotor-side converter, which short-circuits the rotor windings in case of large external grid voltage sag or swell to protect the converter from over voltage and over current. The wound-rotor induction generator is grid-connected at the stator terminals, but the rotor terminals are fed with variable frequency voltage through a set of voltage source controllers. The system model,

given in the following, includes the wind turbine, the wind system, the induction generator, and the converter circuits, the transmission line and load. A STATCOM is connected at the generator end of the transmission line.

**2.1 Wind Turbine and the Wind System**

The mechanical power output of a wind turbine is related to the wind speed  $V_\omega$  by [Rahim & Habiballah, 2011],

$$P_m = \frac{1}{2} \rho A C_p(\lambda, \beta) V_\omega^3 \tag{1}$$

Here,  $\rho$  is the air density and  $A$  is the swept area by the turbine blades. The power coefficient  $C_p$  is expressed as a function of tip speed ratio  $\lambda$  and the blade pitch angle  $\beta$  through,

$$C_p(\lambda, \beta) = 0.5176 \left( \frac{116}{\lambda_i} - 0.4\beta - 5 \right) e^{\frac{-21}{\lambda_i}} + 0.0068\lambda \tag{2}$$

$$\frac{1}{\lambda_i} = \frac{1}{\lambda + 0.08\beta} - \frac{0.035}{\beta^3 + 1}$$

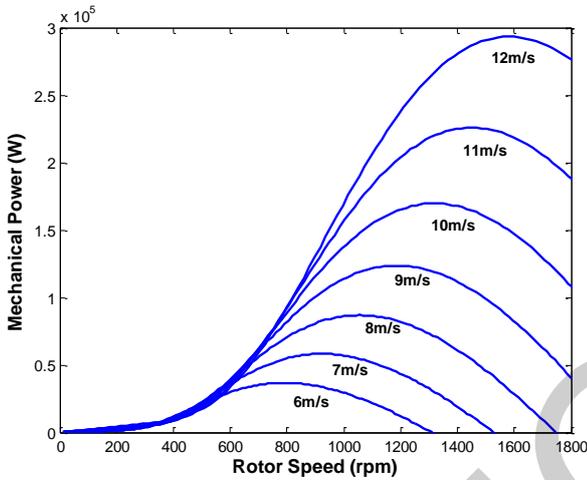


Fig.1 DFIG system configuration

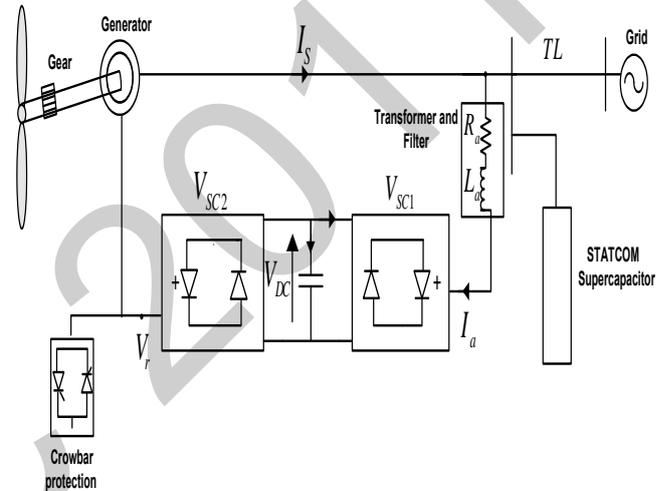


Fig. 2 Turbine output power for various wind speed

Fig.2 shows the variation of turbine power output for different wind speeds. The blade pitch angle  $\beta$  was considered to be zero in all these cases. Wind speed changes continuously and its magnitude are random over any interval. The average wind speed is usually considered constant for some intervals.

**2.2 The Doubly-Fed Generator Model**

The induction generator voltage current relations along the d-q axes of the stator and rotor circuits, respectively, can be expressed as,

$$\frac{1}{\omega_o} \dot{\psi}_{ds} - \frac{\omega_e}{\omega_o} \psi_{qs} - R_s \dot{i}_{ds} = v_{ds} \tag{3}$$

$$\frac{1}{\omega_o} \dot{\psi}_{qs} + \frac{\omega_e}{\omega_o} \psi_{ds} - R_s \dot{i}_{qs} = v_{qs}$$

$$\frac{1}{\omega_o} \dot{\psi}_{dr} - s\psi_{qr} - R_r \dot{i}_{dr} = v_{dr} \tag{4}$$

$$\frac{1}{\omega_o} \dot{\psi}_{qr} + s\psi_{dr} - R_r \dot{i}_{qr} = v_{qr}$$

The stator and rotor flux linkages and currents are related through,

$$\psi_{ds} = -x_s i_{ds} - x_m i_{dr} \tag{5}$$

$$\psi_{qs} = -x_s i_{qs} - x_m i_{qr}$$

$$\psi_{dr} = -x_r i_{dr} - x_m i_{ds} \tag{6}$$

$$\psi_{qr} = -x_r i_{qr} - x_m i_{qs}$$

In the doubly fed mode, active power is always supplied from the stator terminals to the power grid, independent of the value of rotor slip. At super synchronous speed rotor circuit supplies power to the grid, while under sub synchronous operation the grid supplies the rotor.

A two-mass model for the turbine generator system is adopted as higher inertia wind turbine rotor is connected to the low inertia IG rotor with a relatively soft shaft. The dynamic equations of the two-mass representation are expressed as,

$$2H_t \frac{d\omega_t}{dt} = P_m - K_s \theta_s - D_t \Delta \omega_t \tag{7}$$

$$2H_g \frac{d\omega_r}{dt} = K_s \theta_s - P_e - D_g \Delta \omega_r \tag{8}$$

$$\frac{d\theta_s}{dt} = \omega_b (\omega_t - \omega_r) \tag{9}$$

Here,  $\theta_s$  is the shaft torsion angle,  $K_s$  is the shaft stiffness, and  $D_t$  and  $D_g$  are the damping coefficients of turbine and generator respectively. The subscript  $t$ ,  $g$  and  $s$  refer to the turbine and generator and shaft quantities respectively;  $P_e$  is the generator output power given as,

$$P_e = x_m i_{qr} i_{ds} - x_m i_{dr} i_{qs} \tag{10}$$

Two back-to-back converters, one on the grid side (VSC1) and the other on the rotor side (VSC2) are connected to a capacitor on a common DC link as shown in Fig.1. The d-q components of grid side converter current is expressed through the dynamic relationships,

$$\frac{di_{ad}}{dt} = -\frac{\omega_0 R_a}{L_a} i_{ad} + \omega_0 \omega_e i_{aq} + \frac{\omega_0}{L_a} v_{ds} - \frac{\omega_0}{L_a} e_{ad} \tag{11}$$

$$\frac{di_{aq}}{dt} = -\frac{\omega_0 R_a}{L_a} i_{aq} - \omega_0 \omega_e i_{ad} + \frac{\omega_0}{L_a} v_{sd} - \frac{\omega_0}{L_a} e_{aq} \tag{12}$$

From power balance, the DC capacitor voltage equation is

$$\frac{dV_c}{dt} = \frac{1}{C} [m_1 \cos \alpha_1 i_{ad} + m_1 \sin \alpha_1 i_{aq} + m_2 \cos \alpha_2 i_{dr} + m_2 \sin \alpha_2 i_{qr}] \tag{13}$$

The symbols  $m$  and  $\alpha$  represents the modulation index and phase angle of the grid side and rotor side converters, respectively. The dynamic relations are integrated with the equations of the transmission line and load to give a complete state model of the DFIG.

### 3. THE ENERGY STORAGE SYSTEM

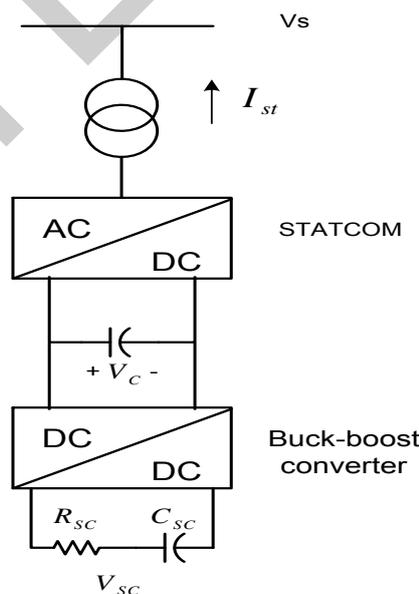


Fig. 3 STATCOM with supercapacitor energy storage system

Fig. 3 shows the configuration of a supercapacitor energy storage system, which is connected to the AC system through a voltage source converter. The storage system comprises of the supercapacitor, and a bi-directional DC-DC buck-boost converter to control the charge and discharge of the supercapacitor module [Camara, *et al*, 2008]. The supercapacitor is modeled by an ideal capacitance and an equivalent series resistance,  $R_{sc}$  as shown in Fig. 3. The control circuit of the supercapacitor is shown in Fig.4. From power balance, the dynamic equation of the DC capacitor voltage is,

$$\frac{dV_{dc}}{dt} = -\frac{m}{C_{dc}}(i_{std} \cos(\psi + \theta_s) + i_{stq} \sin(\psi + \theta_s)) - \frac{D_r I_{sc}}{C_{dc}} \tag{14}$$

Here,  $I_{sc}$  is the supercapacitor current and  $D_r$  is the duty ratio of the buck-boost converter, and  $\theta_s$  is the angle of bus voltage  $V_s$ . Supercapacitor voltage  $V_{sc}$  is related to  $I_{sc}$  through,

$$V_{sc} = E_{sc} + R_{sc} I_{sc}; \quad I_{sc} = C_{sc} \frac{dE_{sc}}{dt} \tag{15}$$

The voltage –current relation of the VSC can be expressed as,

$$L_{st} \frac{dI_{st}}{dt} + R_{st} I_{st} = V_{st} - V_s \tag{16}$$

Here  $V_{st}$  is the C voltage output of the VSC. By transforming the STATCOM current through the relation,  $I_{st} = I_{st}^{orig} e^{-j\theta_s}$  and breaking it along d-q axes a set of decoupled relationships for P and Q are obtained. The modulation index (m) and phase angle ( $\psi$ ) of the VSC of the supercapacitor can be generated as shown in Fig. 5. The command values of P and Q are generated through two sets of PI controllers whose inputs are phase angle and voltage magnitude of the AC bus voltage, respectively.

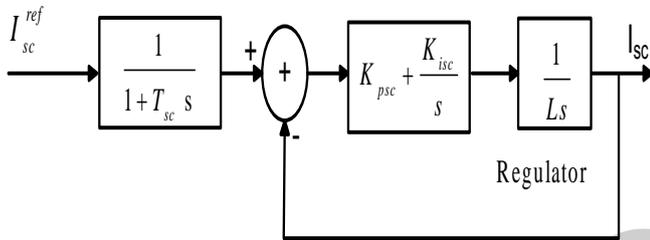


Fig. 4 The current control circuit of DC-DC converter

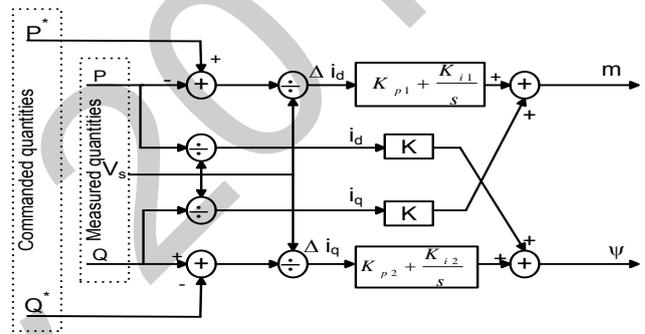


Fig. 5 Decoupled P – Q STATCOM control strategy

**4. SIMULATION RESULTS**

The dynamic performance of the DFIG system is investigated through symmetrical three phase faults of various durations at the grid bus. The nominal power output of the generator is 0.9pu. At this load, the system is stable for durations up to 100ms. For longer duration faults at the PCC, the generator voltage collapses, the rate of collapse depending on the level of low voltage conditions. Figures 6-9 show the record of various variables of the DFIG wind system for a 200ms three-phase fault at the grid bus. Plots labelled 'a' in the figures show the responses in the absence of any control.

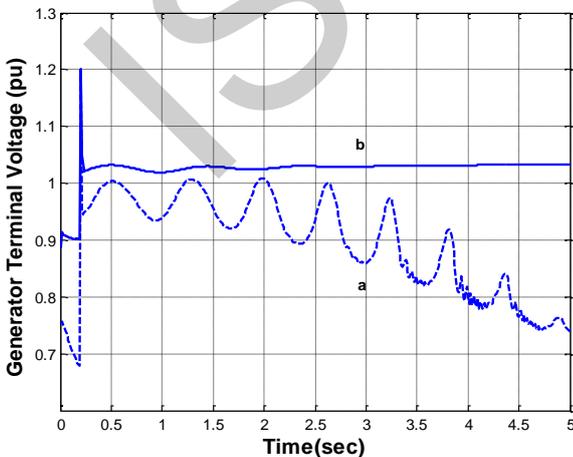


Fig.6 The doubly fed induction generator stator terminal voltage following a 0.2s fault with, a) no control and, b) with STATCOM and supercapacitor control

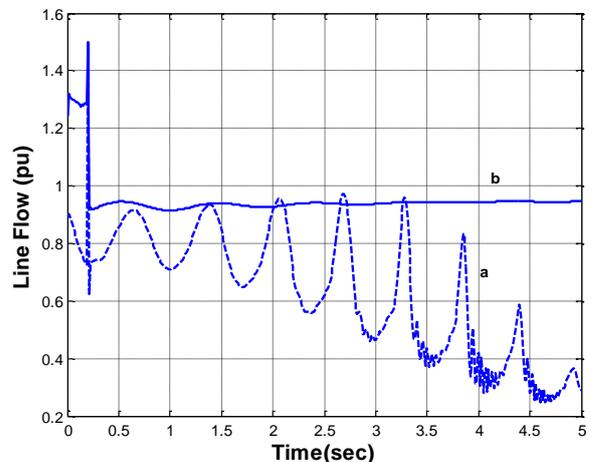


Fig. 7 Power flow variations of DFIG following the symmetrical three phase fault condition of Fig. 6

Fig. 6 shows the variations of stator terminal voltage variations of the doubly fed machine. Following the fault, the stator terminal voltage and current in converter (rotor) circuit fall into unstable oscillations, eventually causing voltage collapse which results in much reduced real and reactive line flows. The acceleration of the generator rotor causes the machine to slip heavily, as shown in Fig.8, and the speed goes up exorbitantly. The real and reactive power flows are shown in Figs.9 and 10, respectively.

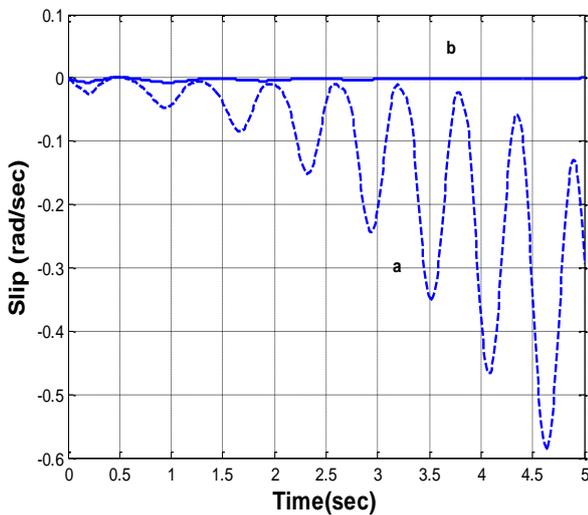


Fig. 8 DFIG slip variation following the fault condition of Fig. 20 with and without STATCOM based P-Q control

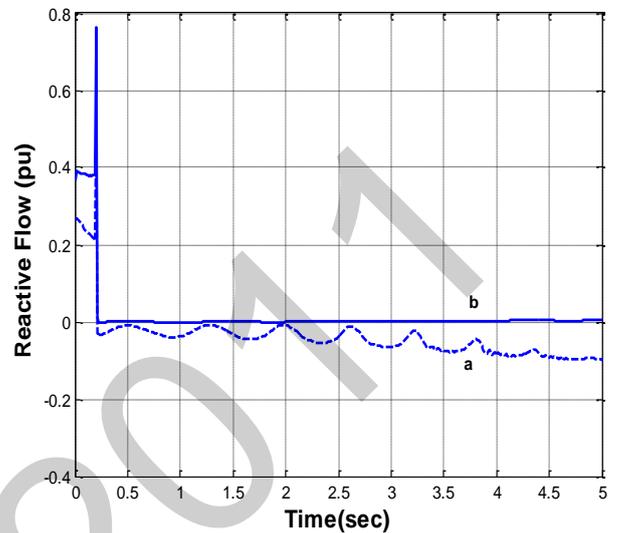


Fig. 9 Reactive flow following a 0.2s three phase fault at the grid with and without P-Q control

The responses with the decoupled P-Q control strategy are shown in curve ‘b’ in all the plots of Figs 6-9. The unbalances in real and reactive power in the system caused by the low voltage condition are compensated by the supercapacitor and STATCOM controller. It can be observed that even when the fault is on, the controllers try to raise the depressed terminal voltage hence allowing reactive flow to the generator. The recovery of the terminal voltage helps maintain the DC capacitor of the DFIG converters restoring normal condition fairly quickly.

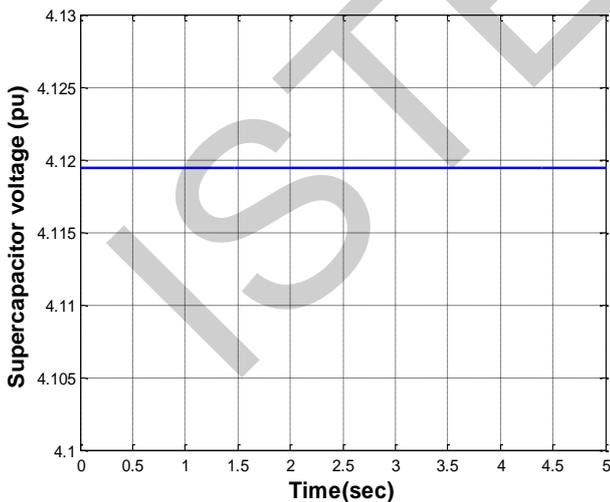


Fig. 10 Supercapacitor voltage profile following a 0.2s duration three phase fault at the grid bus

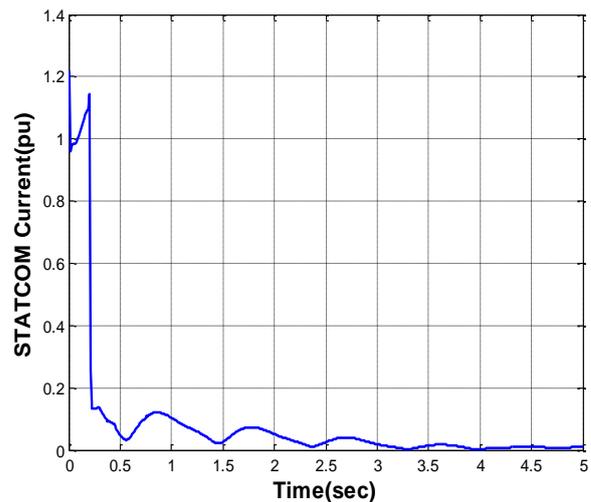


Fig. 11 magnitude of the current supplied by the STATCOM following the 0.2s duration fault corresponding to Fig 9

The effectiveness of the decoupled P-Q control depends on maintenance of the supercapacitor voltage at desired value. Fig. 10 depicts that the proposed strategy keeps it almost at a constant level. Expectedly, the amount of current supplied by the STATCOM is high while the fault is on. The current returns to very small value quickly when the fault is cleared as is shown in Fig. 11.

## 5. CONCLUSIONS

A control strategy to implement independent control of real and reactive power through a STATCOM supercapacitor combination is proposed for a doubly fed induction generator wind system. Voltage collapse of the DFIG resulting from severe low voltage conditions near the generator terminal can be halted by injecting reactive as well as real power appropriately. The STATCOM voltage magnitude and phase angle controls are derived to control the STATCOM d-q current components, which in turn control P and Q output of the supercapacitor STATCOM combination independent of each other. Appropriate choice of signals to create reference values in the controller and also on proper tuning of PI controller gains are essential for getting the desired dynamic response of the system.

## ACKNOWLEDGEMENT

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# MODELING OF RESIDUAL STRESSES IN TBC COATED GAS TURBINE BLADES

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## ABSTRACT

Ceramic thermal barrier coatings have been developed for advanced gas turbine and diesel engine applications to improve engine reliability and fuel efficiency. Blades and vanes of the high-pressure turbine stages of aero-engines are the most highly stressed parts in engineering components. The blade geometry was objected to airflow at the temperatures about 800°C. These high gas turbine temperatures can only be maintained through advanced cooling techniques like electro-beam physical vapor deposition (EB-PVD) and thermal barrier coatings (TBCs). Such TBCs consist of thin ceramic layers of low thermal conductivity, yttrium stabilized zirconia (YSZ) which are applied on the blade surface. The coating imparts good adhesion of the ceramic to the substrate.

In this study, 3-D finite element structural and thermal analyses were carried out on both uncoated (without coating) and ceramic-coated turbine blade using ANSYS code. A 150 micron super alloy bond coating (NiCrAlY) was first applied to the turbine blade. Then, the blade was covered by 350 micron thickness of Mullit ( $3Al_2O_3 \cdot 2SiO_2$ ) as a top coating. These analysis were performed for detecting the possible thermally problem spots. Finally, the blade's thermal stressed problematic areas were determined by the finite element simulations which were important for the improving blade and TBC.

**Keywords:** TBC, Turbine Blade, Finite Element Analysis, Residual Stresses, Modeling

## INTRODUCTION

For the protection of the blade in hot working conditions by thermal stresses and other effects, TBC was applied on to the geometry. Different types of coating technologies widely used on the turbine blades. Thermal barrier coating (TBC) systems, consisting of yttria partially stabilized zirconia (YSZ), thermally grown oxide (TGO) and a metallic bond coat are used in applications for thermal protection of hot-section parts in gas turbine engines. (R.A. Miller 1987, D.J. Wortman at all 1989, S.M. Meier at all 1991, R.T. Jones at all 1996, R.D. Jr. Sisson at all 1995, J Y.H. Sohn at all 2001)

When the turbine blades are considered, some affects are more important than the others. The important research areas related to heat transfer of a gas turbine blade include external and internal heat transfer coefficient predictions, metal temperature distributions, blade cooling methods, rotation effects, and ceramic coatings amongst others. External convection depends upon the development of the boundary layer on the blade surface, which is a complex phenomenon, and there is considerable uncertainty associated with both numerical predictions and experimental measurements (J N. Asok Kumar , S.R. Kale 2001).

The thermal barrier coating provides a temperature drop of up to 200°C, due to its low thermal conductivity, which is enhanced further by the intentionally porous microstructure (Marcin Białas 2008).

Although the composition of the TBC was created many protective abilities for the blades, some insufficient and troubled behaviors are still alive. A major weakness of TBC systems is the interface between the metallic bond coat and the ceramic TBC. At this interface an in-service degradation is observed often leading to a macroscopic spallation of the ceramic layer (R.A. Miller, C.E. Lowell 1982). The interface regions undergo high stresses due to the mismatch of thermal expansion between BC and TBC. Additionally, growth stresses due to the development of thermally grown oxide (TGO) at the interface and stresses due to interface roughness are superimposed. Stress relaxation leads generally to reduce stress levels at high temperature, but can give rise to enhanced stress accumulation after thermal cycling resulting in early crack initiation at the bond coat/alumina interface and spallation failure afterwards (A.G. Evans at all 2001, G. Fleury at all 1997, F. Schubert at all 2000)

In this study, finite element simulations of uncoated turbine blade model and also thermal barrier coated turbine blade geometry were performed with the ANSYS code. For the TBC used geometry, the turbine blade was covered with a super alloy bond coating (NiCrAlY). Over the bond coating layer, Mullit ( $3Al_2O_3 \cdot 2SiO_2$ ) was used as a top coating. For the coated turbine blade; hot air flow was applied to the all top coating layer surfaces and for the uncoated geometry; hot air flow was applied to the turbine blade surfaces. The results of the thermal simulations were compared, initially with the temperature distribution of the coated and uncoated turbine blades. Then the equivalent stress profiles of coated and uncoated turbine blade were matched and evaluated. As a final decision, TBC for the blade geometry is a supporting material for reducing the blade's temperature and equivalent stress value.

## MATERIALS

For the base blade material, steel substrate was used. As a bond coating material NiCrAlY was preferred. Mullit was selected for the top coating layer. See table 1 for materials' details. Up to the selected materials, thermal and structural properties affect the turbine blades behaviors. For an appropriate protection; which was originated from the selected materials, chemical and structural behaviors, coating material types and usage will differ.

For the TBC used geometry, the turbine blade was covered with a 150 micron thickness of a super alloy bond coating (NiCrAlY). For over the bond coating layer, 350 micron thickness of Mullit ( $3Al_2O_3 \cdot 2SiO_2$ ) was used as a top coating.

Table 1. Material properties of substrate, bond coat and top coating

Material	Thermal conductivity [W/m°C]	Thermal expansion $10^{-6}$ [1/°C]	Density [kg/m <sup>3</sup> ]	Specific heat [J/kg°C]	Poisson's ratio	Young's modulus [GPa]
Steel Substrate	16,2	17,2	7850	434	0,3	200
NiCrAlY	16	15	7710	520	0,25	16,8
Mullit	1,2	5,2	2608	760	0,25	21

### MODELING AND ANALYSIS

For the thermal and structural simulations of the turbine blades, solid CAD models were used. Solid models of the two different finite element models of the uncoated and coated turbine blades were modeled in Pro\_Engineer CAD program. Simplified solid models of the turbine blades were sent to ANSYS code directly, for easy control of finite element model. To prepare the fine meshed and simple based finite element models, unchanging one section area was applied to the turbine blades.

Two types of solid elements were used for the thermal and structural analysis in ANSYS code. Each solid element has 20 nodes. "Solid 90" element for the thermal analysis and "Solid 186" element was applied for the structural analysis. In figure 1, the meshed model of the coated turbine blade can be observed. For the uncoated turbine blade 2900 elements and 13428 nodes; for the coated model 1100 elements and 5959 nodes were used.

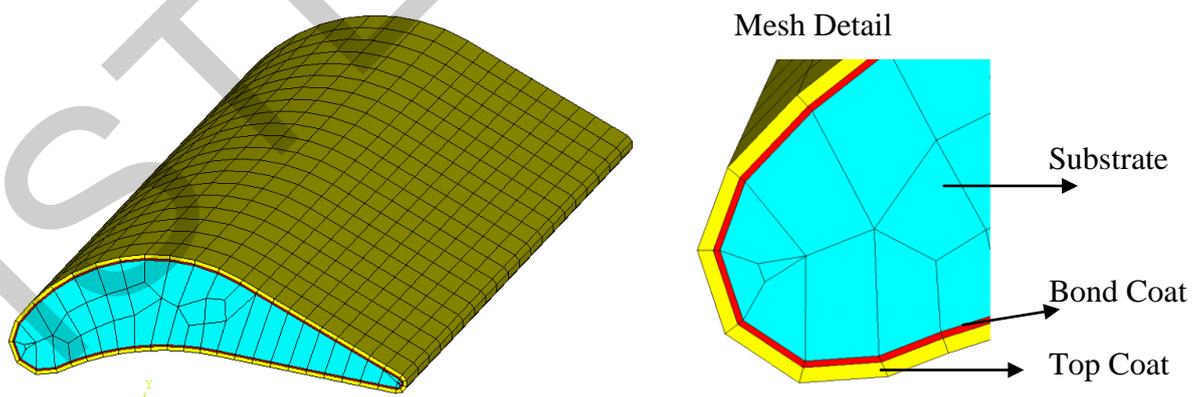


Figure 1. Meshed model of the coated blade

Initially, thermal analysis was processed for each turbine blade. During the thermal analysis, 800°C air flow was applied to the top coating surface for a while. For comparing the blades, in the uncoated model, same 800°C air flow was applied on to the turbine blade surfaces. The simulations were solved under these circumstances. The results of the thermal simulations were imported into the structural analysis set up data of the turbine blades.

During the structural analysis preparation process, transferred data of all the thermal simulation results was adapted to the structural finite element models. The thermal element "solid 90" was switched in to the structural element "solid 186" in ANSYS; but the mesh structure and distribution were not changed. Not changed mesh structure gives valuable advantage for the comparison between coated and uncoated turbine blades. All the comparisons were made from the same attitude of the

elements and nodes of the mesh structure. The results of the analysis can be matched between the same node and the same element numbers for the base turbine blade geometry.

In the structural analysis, thermally simulated models were held in All DOF from one flat side surface of the turbine blade geometry. The imported temperature distributions in the turbine blades and the coatings were reflected to the material behavior to find the stresses of the thermal simulation results. For the imported thermal simulation data, of the coated and the uncoated turbine blades, were solved. Finally, stress results for the thermally originated structural analysis can be determined for each turbine blade.

**RESULTS AND DISCUSSION**

After the analysis, results are satisfactory for the evaluation and comparison for the uncoated and coated turbine blades. The thermal simulation results for the models can be determined from the figure 2. Evaluation of the figure 2 is showed that coating material was decreased the turbine blade surface temperature from 440°C to 360°C during the process of 800°C air flow. For the last steps of the analysis of, about 80°C profit was held. Using Mullit as a top coating material, 18% thermal protection was received for the turbine blade.

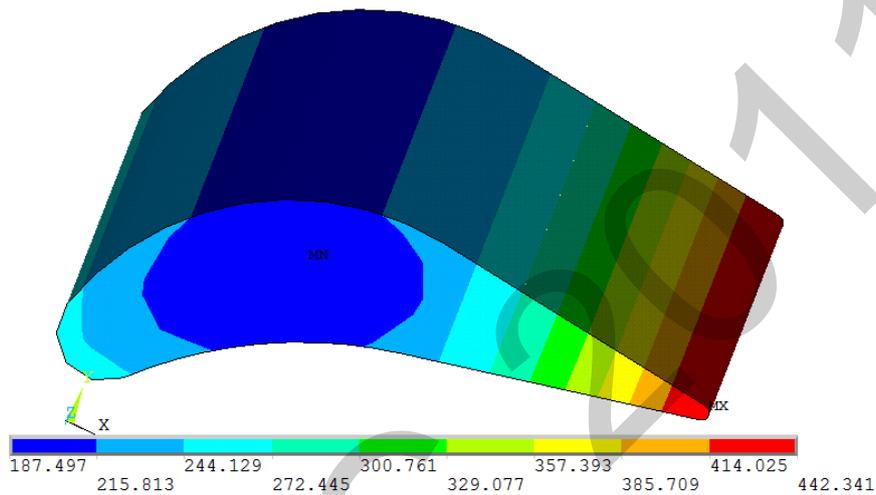


Figure 2.a. The thermal simulation results in temperatures (°C) for the uncoated blade

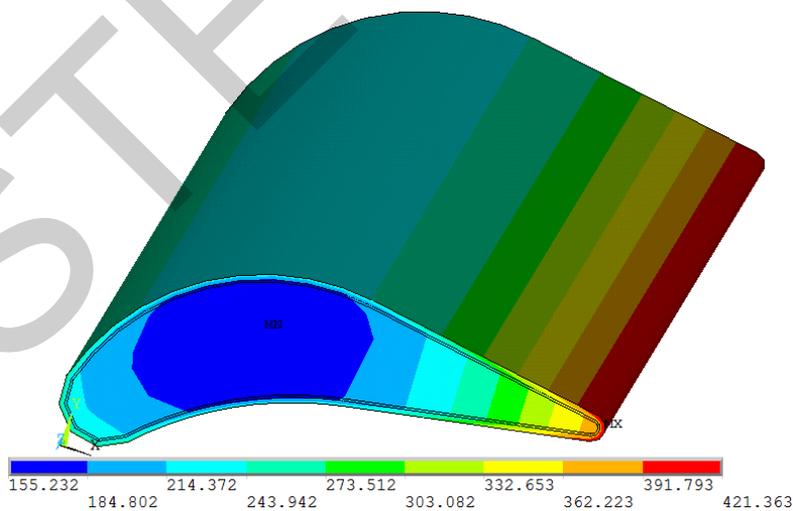


Figure 2.b. The thermal simulation results in temperatures (°C) for the coated blade

For the evaluation of the Temperature-Distance and Equivalent Stress-Distance curves, a distance profile was defined on the edge of the blade. The distance profile is started at the point which is defined in the figure 3 and 5, below the curves. As it is mentioned on the figure 3 and 5, arrows define the distance's trajectory.

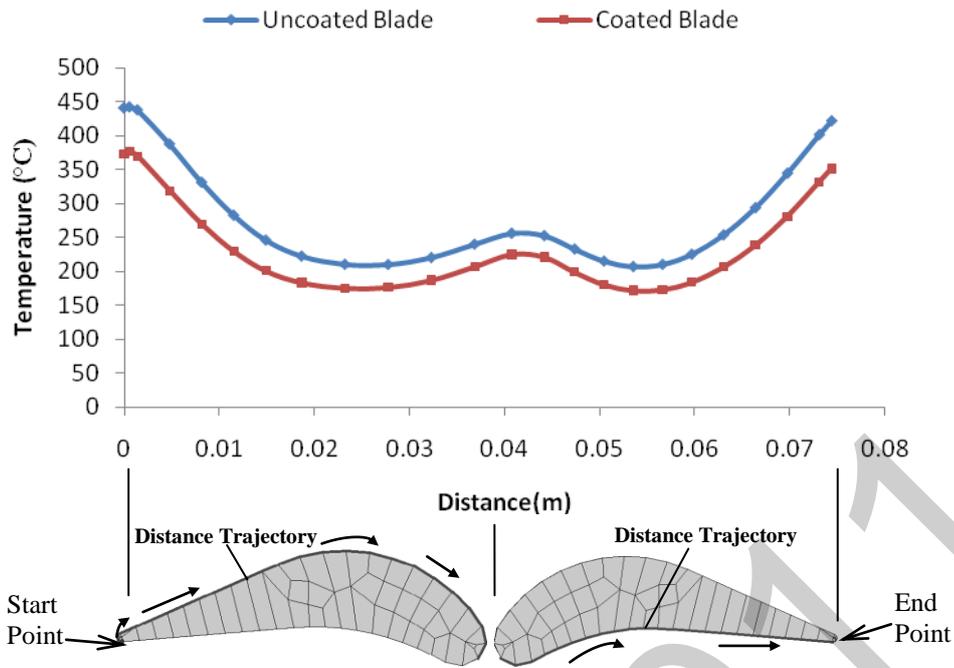


Figure 3. The temperature distribution (°C) of the uncoated and coated blades

In the figure 3, the temperature distribution could be observed through the whole process. During the thermal process coated turbine blade temperature is always smaller than the uncoated one, as it is wanted from the coated turbine blade geometry. For the critical trajectory, TBC was reduced the blade's mean temperature about 48°C. To understand the general thermal behavior of the blades, maximum, minimum and the mean temperature values for the distances of the uncoated and coated turbine blades are given in table 2.

Table 2. The maximum, minimum and mean temperature values for the trajectory distances of the uncoated and coated blades

	Max. Temp. (°C)	Min. Temp. (°C)	Mean Temp. (°C)
Uncoated Blade	442,29	206,68	290,88
Coated Blade	376,35	171,93	242,93

When the figure 4 is considered, stress curves of the uncoated and coated turbine blades can be compared. The uncoated turbine blade's maximum equivalent stress value was 3270MPa and the coated one's maximum equivalent stress value was 2550MPa. Used TBC was reduced the blade geometry's stress distribution in considerable values as 720MPa which was given the 22% equivalent stress reduction. More detailed evaluation of the stress behaviors of the uncoated and coated turbine blades' stress curves can be observed in figure 5.

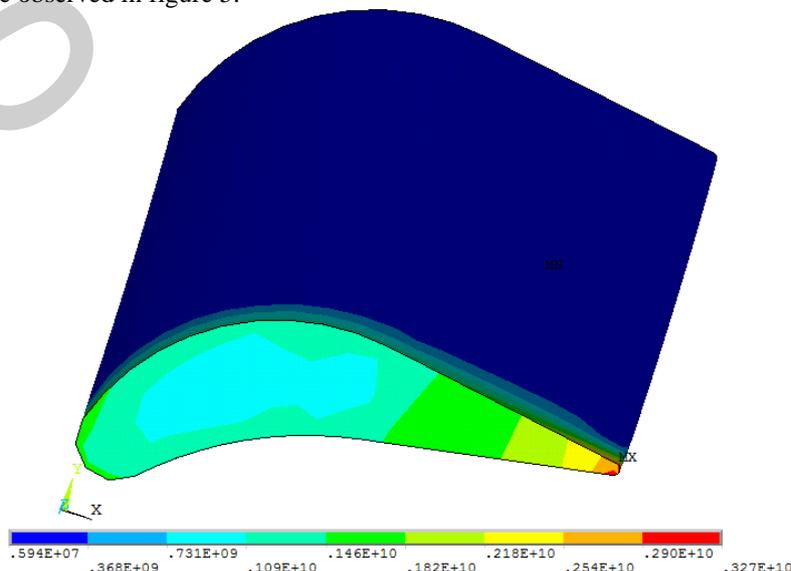


Figure 4.a. The structural simulation of equivalent stress results (Pa) for the uncoated blade

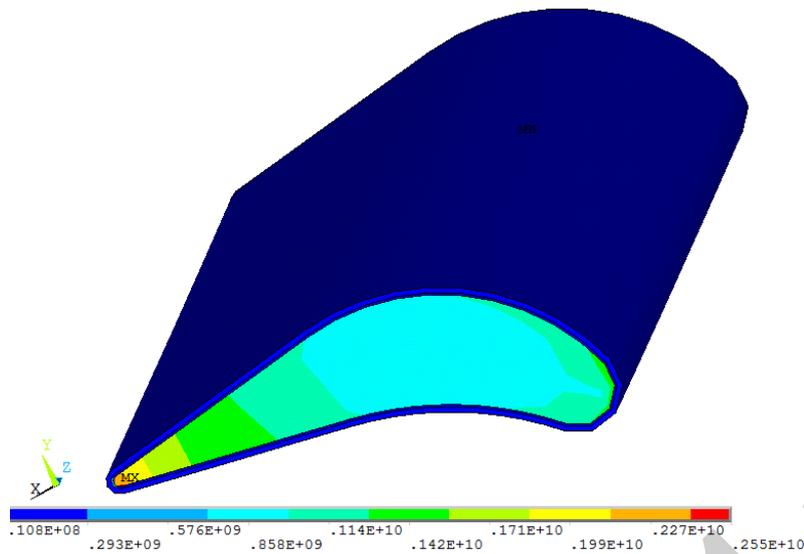


Figure 4.b. The structural simulation of equivalent stress results (Pa) for the coated blade

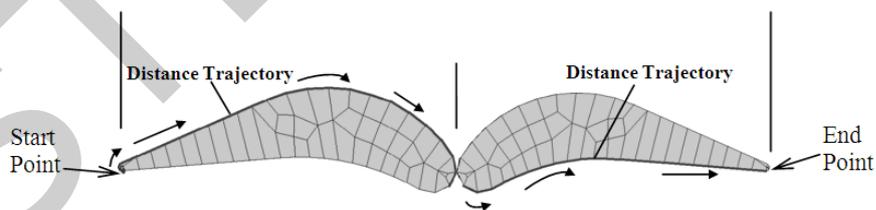
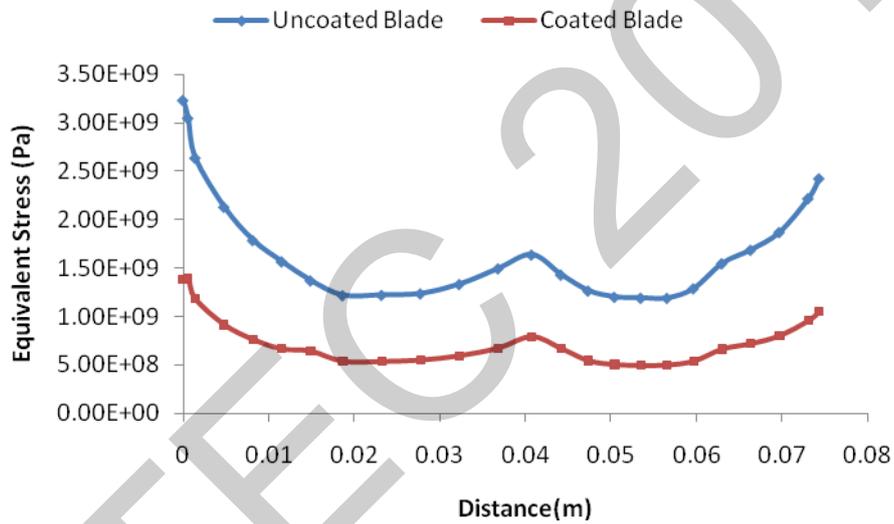


Figure 5. The equivalent stress distribution (Pa) of uncoated and coated blade for trajectory distance

As in the figure 3, figure 5 shows that the equivalent stress distribution of the coated turbine blade is always smaller than the uncoated turbine blade during the process. Little fluctuations can be observed from the curves. For the critical trajectory of the thermal barrier coated blade was reduced only blade's mean stress about 963MPa (29.4% equivalent stress reduction). To determine the stress distribution of the blades, maximum, minimum and mean stress results for the distances of the uncoated and coated turbine blades are shown in table 3.

Table 3. The maximum, minimum and mean equivalent stress values for the trajectory distances of the uncoated and coated blades

	Max. Stress (Pa)	Min. Stress (Pa)	Mean Stress (Pa)
Uncoated Blade	3,24e9	1,19e9	1,72e9
Coated Blade	1,4e9	4,95e8	7,53e8

Finally, in this study, used thermal barrier coated blade geometry, with the help of finite element technique, is proved that the coating decreases the temperatures and the stresses of the turbine blade.

### CONCLUSIONS

From the present study following results can be drawn:

- In the present study, used TBC reduced the whole blade geometry's mean temperature about 80°C. Using Mullit as a top coating material, 18% thermal protection is received for the turbine blade.
- For the critical trajectory, TBC was reduced the blade's mean temperature about 48°C.
- TBC used blade geometry's reduced mean stress value of 720MPa was given 22% equivalent stress reduction. The indicated level of stress reduction is considerable and protects the blade from the thermal stress more than expected.
- For the critical trajectory of the thermal barrier coated blade was reduced only the blade's mean stress about 963MPa (29.4% equivalent stress reduction).
- This study showed that; after thermal and structural finite element simulations for the uncoated and coated turbine blade, the reduction of the temperatures and stresses are satisfactory and can be determined easily.

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# MUNICIPAL SOLID WASTES GASIFICATION/POLYMER ELECTROLYTE MEMBRANE FUEL CELL INTEGRATED CHP SYSTEM

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## ABSTRACT

Secured, cheap and clean energy sources are very vital for economic growth and development. The current fossil fuel dominated energy scene is not sustainable. There is increasing interest in biomass as a sustainable energy source to arrest the fast depletion of the global fossil fuel reserves and the attendant environmental challenge posed by its end uses. Municipal Solid Wastes (MSW) is continuously generated with no threat of depletion. Over 70% of MSW is composed of combustible materials ideal for energy production. Gasification of the MSW via the refuse derived fuel (RDF) route will generate heat for power generation and synthesis gas rich in hydrogen as feed to fuel cell in a combined heat and power (CHP) systems. This study proposed a MSW treatment and processing strategy for energy and hydrogen production. It explores waste-to-energy approaches to eliminate the environmental footprints of the current MSW treatments and disposal methods in South Africa.

**Keywords:** municipal solid wastes; biomass; gasification; hydrogen; fuel cell.

## 1. INTRODUCTION

In South Africa, the steady economic growth and development has resulted in a steady rise in energy consumption and municipal solid waste (MSW) production necessitating more investment in the power industry on one hand and sustainable approach to management of the MSW on the other hand. The energy sector in South Africa is dominated by coal and nuclear, with approximately 93% of the electricity produced from coal-fired plants (Eskom, 2011). The over reliance on fossil fuels as primary energy source worldwide is not sustainable. It is essential not only to search for new energy carriers but also for new material sources. In this respect, virgin biomass and municipal solid wastes will become more important in the search for alternatives for fossil fuels alongside other alternatives such as solar, wind, tidal and nuclear energy. Supply of biomass unlike the other renewable sources of energy, is not intermittent or site-dependent, and can be used to produce not only energy, but also chemicals and materials (Deswarte *et al.*, 2008). Processes that recover materials and energy from the MSW and hence solved the problem of energy production and waste conversion same time, have been suggested and are currently at various stages of implementation worldwide.

South Africa for the first time runs out of surplus energy in 2007 resulting in power shortage and load shedding. With a reported reserve margin of around 8%, load shedding will be implemented at peak demand and supply falls due to some generating units taken offline for maintenance or repairs. There is need therefore urgent need to address this problem for sustained growth and development. To increase the generation capacity by constructing more coal-fired power plants has huge environmental consequences and hence not a way out. At the moment, South Africa is among the top 20 emitters of greenhouse gases (GHSs) in the world and is the largest emitter in Africa. So there is a need to use cleaner sources of fuel. An energy security strategy formulated by the Department of Minerals and Energy (DME) seeks to implement measures that will guarantee adequate supplies of energy in the short term; ensure accessible, affordable and reliable energy, especially for the poor and to diversify the primary energy sources to reduce the high dependency on coal. To achieve these objectives, it is imperative to put in place a mix of energy sources. Alternative sources of power from renewable and sustainable sources are currently being considered. These include biomass, geothermal, wind and solar powered plants. Of these sources, an integrated system of fuel cell coupled to a biomass gasification plant look very promising and is receiving more interest.

The Department of Science and Technology is presently promoting hydrogen and fuel cells as priority technologies under the national framework for hydrogen and fuel cell technology (DST, 2010). With the potential to produce hydrogen from biomass and the largest reserve of platinum (used in fuel cells), the country has a significant competitive advantage in developing hydrogen fuel cell-based applications. South Africa's rich platinum reserves (about 78% of the world's platinum along with 39% of the world's palladium production) could make it a key player in the development of fuel cell technology regarded as the future energy source. This will enable South Africa to extract more value from its platinum group metals (PGM) resources; diversify her energy industry, and reduce the environmental impacts of coal-fired plants. Most fuel cells use platinum-group-metals (PGM) as the electrode catalysts to convert hydrogen into electricity. The PGMs are also essential to achieve low-temperature reforming to improve the efficiency of CHP systems.

On a parallel front, the management and disposal of MSW has been a recurring problem in South Africa as elsewhere experiencing similar social and economic growth. In Cape Town, about 550-600 tons/day of MWS is produced in 2007. In sub-Saharan Africa, existing waste management practices are inadequate thus affecting human health, the environment, air quality, and the landscape. MSW supply is very much sustainable with no threat of depletion. A recent report published by the USDOE and the USDA (2005) reported that the US alone could sustainably supply more than one billion dry tons of biomass per annum by 2030. 70% of the MSW are combustible materials that could be thermo-chemically converted to energy, fuels and chemicals thereby solving the two problems simultaneously. MSW are combustible and non-combustible wastes that come from household, municipal, commercial, and industrial sites. For technical and economic reasons, the indirect conversion of the combustible materials in the MSW to energy and materials has been suggested. Refuse derived fuel (RDF) is produced

from dried combustible portions of MSW. The gasification of the RDF to produce clean and energy-carrying hydrogen gas as fuel for high temperature polymer electrolyte membrane (HTPEM) fuel cell for cogeneration (heat and electricity) plants will be an ideal energy source. The use of MSW avoid competition with the food sector and unlike virgin biomass is not to be cultivated. The major impediment to biomass use is the development of economically viable methods (physical, chemical, thermochemical and biochemical) to separate, refine and transform it into energy, chemicals and materials (European Commission, 2005). The options for economic conversion and integration of RDF gasification and HTPEM fuel cell CHP systems for domestic and industrial application is the focus of this article.

## 2. CURRENT MUNICIPAL SOLID WASTES MANAGEMENT CAPE TOWN

MSW is a mixture of wastes from households, commercial activities, industrial wastes, farm wastes, and educational institutions. Generally, MSW compositions include paper, plastics, sawdust, wood wastes, leather, glass, rubber, e-wastes, ceramics or debris, metals, textiles, bones, ashes, putrescible, food wastes, yard wastes, inert (Parfitt and Bridgwater, 2008; Burnley *et al.*, 2011). Table 1 shows composition of MSW from a number of regions.

Table 1: The Municipal Solid Waste Composition on Regional Basis

Regions	Combustible (Weight %)	Non-Combustible (weight %)	Others (Weight %)
<b>Asia</b>			
Eastern Asia	67.30	5.80	26.90
South Central Asia	69.20	7.30	23.50
South Eastern Asia	77.10	7.30	15.60
West Asia and Middle East	78.70	4.50	16.80
<b>Africa</b>			
Eastern Africa	76.90	7.30	15.80
Middle Africa	73.70	8.00	18.30
Northern Africa	66.60	8.00	25.40
Southern Africa*	77.20	20.30	2.50
Western Africa*	88.00	3.10	8.90
<b>Europe</b>			
Eastern Europe	71.70	13.60	14.70
Northern Europe	79.40	15.00	-
Southern Europe	64.50	-	-
Western Europe	62.70	-	-
<b>Oceania</b>			
Australia and New Zealand	90.00	-	-
Rest of Oceania	76.00	-	-
<b>America</b>			
Northern America	76.10	12.00	11.90
Central America	82.10	6.30	11.57
Southern America	80.80	6.20	13.00
Caribbean	83.20	10.70	6.10

Source: IPCC Guideline for National Greenhouse Gas Inventories (2006)

The variation in the waste composition has been linked to the economic level of countries, geographical location, energy resources, climate, living standards and cultural habits. The typical composition of Cape Town MSW is presented in Figure 1.

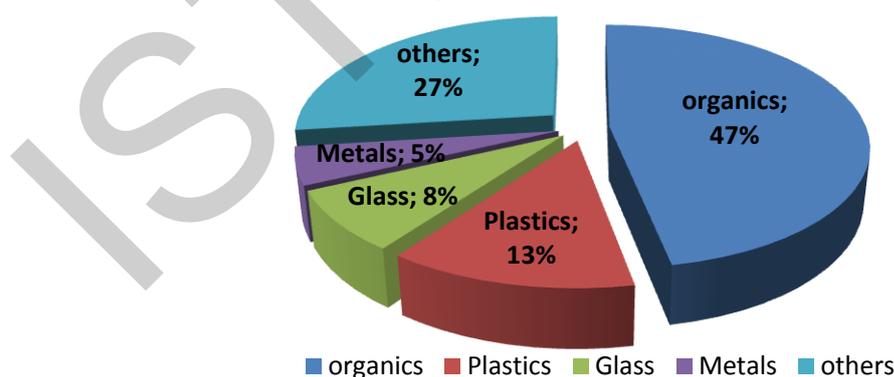


Figure 1: Typical composition of Cape Town MSW

In South Africa, current solid waste management systems include waste collection and sorting, followed by one or more of, recovery of secondary materials by recycling, biological treatment of organic waste for production of marketable compost, thermal treatment by incineration to recover energy in the form of heat and electricity and landfilling. In Cape Town alone, about 2.1 million tons of waste was landfilled in the city's three landfill sites in 2007. Despite the waste-to-wealth policies put in place, the figure is still about 1.6 million tons in 2010. The problem is further compounded by the fact that one of the landfill sites will be closed by 2013 and the last by 2022 at most.

Landfilling of MSW releases GHGs and volatile organic compounds along with leachable toxic heavy metals to the surrounding environment. Soil is contaminated by the heavy metals and radionuclides content and leachate. In a study on a dumpsite, trace metal concentrations in soil within a 50 meter radius of land fill sites had been contaminated by trace metals, lead, iron, copper, zinc, and phosphorus (Mangizvo, 2008; Chifamba, 2007). Leachates collected from various dumpsites revealed level of *coliforms*, cadmium, iron, lead, and nitrates above the water quality guideline (Ikem *et al.*, 2006). Okonkwo and Mothiba (2004) attributed the high concentration of lead in the Madanzhe and Mvudi Rivers in Thohoyandou, South Africa to the nearby waste dumping site.

Incineration to generate energy has become the most common method of dealing with combustible waste as it decreases the volume and mass of MSW. But, it has many drawbacks, particularly releasing hazardous emissions ( $\text{NO}_x$ ,  $\text{SO}_x$ , HCl), harmful organic compounds (Gordon, 2002; Zhang, *et al.*, 2011) and harmful process residues (Floyd and Anthony, 1996). Globally, about 4.6 million tonnes of solid waste is being incinerated per annum. This has led to the generation of a large amount of solid residues including fly ash and bottom ash and emission of hazardous gases to environment (Kwak *et al.*, 2006). Incineration of MSW generates fly and bottom ashes which release leachable toxic heavy metals, dioxin, furans and volatile organic compounds. Stringent environmental regulations are being imposed to control the environmental impact of MSW and incinerator residues (Zhang, *et al.*, 2011).

### 3. REFUSE DERIVED FUEL (RDF)

MSW is heterogeneous consisting of combustible, non-combustible, organic, inorganic and inert materials. It also exhibits a low bulk density and relatively high water content. Processes must therefore be designed to reduce the cost of collection, transportation and storage for any MSW conversion technique to be competitive (Gravitis, 2007; Wright and Brown, 2007). This is achieved by densification of the MSW via pelletization or briquetting to form RDF. Density increase of up to a factor of three is obtained with the RDF (Deswarte *et al.*, 2007). Briquettes has a density of about 800–1300 kg/m<sup>3</sup> compared to loose biomass with a bulk density of 10–20 kg/m<sup>3</sup> (Hedman *et al.*, 2005). The RDF is more homogeneous and has higher heat content per unit mass than raw MSW (Dalai *et al.*, 2009). Untreated MSW typically has a heating value of around 5815 kJ/kg while processed (and dried) municipal solid waste has a fuel value as high 9304 -16282 kJ/kg. The economics of the thermo-chemical conversion processes therefore would be dramatically improved through the reduced volume and water content. The gasification of the RDF with higher carbon and hydrogen contents is advantageous.

Pelletization of MSWs involves the processes of segregating, crushing, mixing high and low heat value organic waste material and solidifying it to produce RDF. It is prepared by the pelletizing machine or compactor after it has been shredded to homogenous particles. Various qualities of RDF pellets can be produced, depending on the needs of the user. A high quality RDF would possess higher heating value, and lower moisture and ash contents.

### 4. PROPOSED PROCESS DESIGN

The process flow diagram for the proposed RDF gasification/PEM fuel cell co-generation plant is presented in Figure 2. The detail of each stage is discussed in detail in the following section.

#### 4.1 Characterization and pre-treatment of MSW

To determine the moisture content and hence the suitable drying method, a sample of the MSW was put in a specially designed oven set at 100°C. The weight and hence the moisture loss is recorded every one hour for 24 hours. After the period, the oven temperature was increased to 120°C and the same procedure repeated. A further reduction in mass of the MSW was noted implying that at 100°C, only the free water was removed and to remove more water higher temperature is required. To confirm these results, the method of Laurent *et al.* (2005) was used for the same sample. Based on this, a drum dryer or hot air contactor at 120°C for the required time is proposed to remove the free water and as much as the trapped water. Characterization of the composition of MSW by proximate and ultimate analysis of dried MSW and fly ash from the bomb calorimeter is carried out. Chemical compositions of these samples were analyzed with x-ray fluorescence spectroscopy, atomic absorption spectroscopy (AAS).

#### 4.2 RDF Production

Magnetic separation and Eddy current separations is proposed to separate the ferrous and non-ferrous metals while glass and plastics would be separated by optical scanning system, pneumatic and NIR sensor sorting system. The plastics content is suggested to be first removed during sorting and added backed to the MSW after drying. The presence of the plastics will increased the cost of shredding and pelletizing, but the plastics contents is expected to give higher heating value and hydrogen content (Wu and Williams, 2010a, 2010b; Ahmed and Gupta, 2009; Dalai, *et al.*, 2009).

The combustibles materials (plus plastics) after the separation are dried, shredded and pulverized to form a fluff, which is then pelletized to produce refuse derived fuel (RDF). The pelletizing process can be achieved by different techniques, by adding a binder or by direct compacting without any binder. In this work, used vegetable oil is proposed as a binder. Previous works done shown that emission of obnoxious compounds during gasification is not changed. The net calorific heat value of pellets is about 24 MJ/ kg. The pellets should be secured in close containers to prevent adsorption of water. The characteristics of the final pellets will depend on the gasifier design. An optimum gasification process depends on the pellets particle size, and particle size distribution, pellet density (measured and controlled by the pore volume and pore volume distribution), and hence need to controlled as desired.

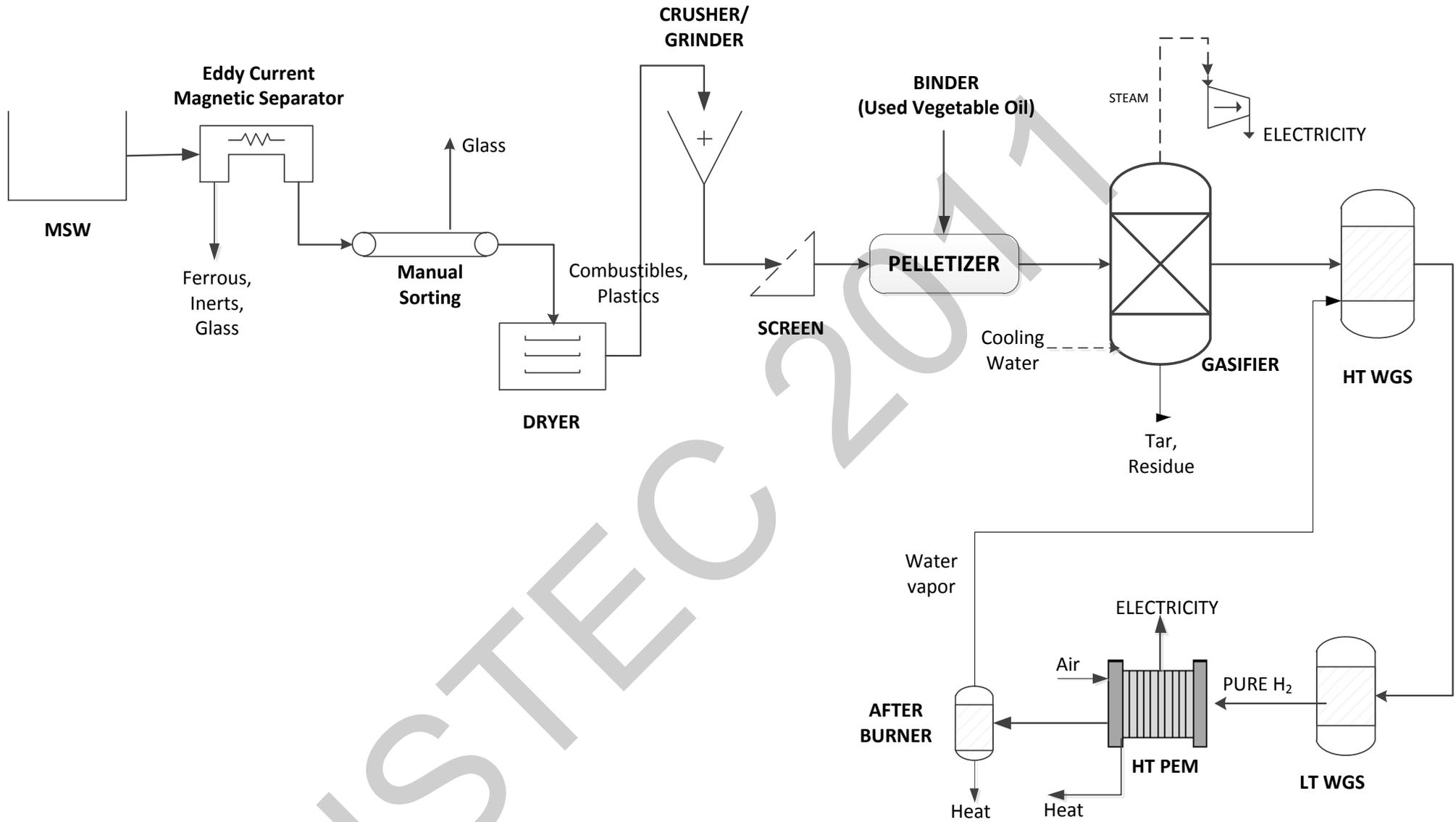


Figure 3: The Proposed Ideal Cogeneration System

### 4.3 Gasification of RDF

Gasification is the thermochemical conversion of a carbon-containing material through the addition of heat in an oxygen-starved environment (Basu, 2010) using air or oxygen and their mixtures to produce gaseous products, rich in hydrogen and carbon monoxide (or synthesis gas). RDF gasification reduces corrosion and emissions by retaining alkali and heavy metals particle size distribution, pellet density (measured and controlled by the pore volume and pore volume distribution), and hence need to be controlled as desired.

### 4.4 Gasification of RDF

Gasification is the thermochemical conversion of a carbon-containing material through the addition of heat in an oxygen-starved environment (Basu, 2010) using air or oxygen and their mixtures to produce gaseous products, rich in hydrogen and carbon monoxide (or synthesis gas). RDF gasification reduces corrosion and emissions by retaining alkali and heavy metals (except mercury and cadmium), sulphur and chlorine within the process residues (Chen *et al.*, 2011) and reduces thermal NO<sub>x</sub> formation due to lower temperatures and reducing (He *et al.*, 2009).

The hydrogen-rich gas would be directly used in the production of electrical power in fuel cells (Chaudhari *et al.*, 2003). The product yield during the gasification of MSW depends on temperature, pressure, time, reaction conditions and reactor type. RDF gasification processes have been studied using several different types of reactors such as fixed bed, fluidized beds, rotary kilns and plasma furnace (Xiao *et al.*, 2006; Min *et al.*, 2005; Galvagno, *et al.*, 2006; Mountouris, *et al.*, 2006). Basu (2010) reported that a survey of gasifiers in Europe, the United States, and Canada show that downdraft gasifiers are the most common, 75 % are downdraft, 20 % are fluidized beds, 2.5 % are updraft, and 2.5 % are of various other designs. The fixed bed gasifier air-blown downdraft is simple type gasifier compared to other fixed bed types. It is one of the simplest and cheapest biomass conversion technologies (McIlveen-Wright, *et al.*, 2011). Updraft fixed bed gasifier is proposed because of tar formation and removal.

### 4.5 Syngas Post Processing and Cleaning

The synthesis gas from the gasifier is sent to the Water Gas Shift (WGS) reactors to convert the CO into more hydrogen. This increases the total yield of hydrogen and also reduces the CO content of the gaseous products. During the WGS reaction, CO and H<sub>2</sub>O react in the presence of a catalyst to form CO<sub>2</sub> and H<sub>2</sub>. This is a reversible reaction and therefore steam is added in excess to shift the equilibrium towards the product side. The WGS reaction occurs in two temperature ranges: the high temperature reaction is carried out using Fe/Co supported on alumina at temperature between 350 and 500 °C. The low temperature WGS reaction is carried out over Cu-Zn oxide catalysts at 200-250 °C. The use of the high performance catalyst lowers the CO content to the less than 10 ppm level that can be safely fed to the high temperature PEM fuel cell. Otherwise an additional preferential oxidation (PROX) reactor may be necessary.

## 5. THE HIGH TEMPERATURE PEM FUEL CELL SYSTEM

The predominantly hydrogen products from the LTWGS reactor is fed to anode side of the fuel cells stack. A compressed air/oxygen is fed to the cathode. The stack is maintained at 160 °C which is tolerable by the phosphoric acid doped PBI membrane. A cooling loop of water/alcohol mixture is used to remove and recover the heat co-produced with power in the stack and so maintain the operating temperature. The stack exit containing unreacted hydrogen is fed to an afterburner to re-use the materials for heat production. The waste heat and H<sub>2</sub>O generated are integrated back into the system. The heat loop or the heat from the afterburner is used to pre-heat the air supply to the stack operating temperature, to lower the start-up time. The air compressor isentropic efficiency is 85 %. The fuel cell stack characteristics and performance is as described by Rabiou *et al.* (2011) to be presented in the next paper. The stack simulation study was implemented in EES.

## 6. CONCLUSION

The proposed design generates heat and electricity via the electrochemical conversion of hydrogen clean fuel for material (hydrogen) and energy (electrical and thermal) recovery. The system is made of three major sub-systems: the fuel processing sub-system, the fuel post-processing and cleaning and the high temperature PEM fuel cell stack sub-system. All these are shown in Figure 2. The HT PEM fuel cell-based CHP system produces little emission and gave high total system efficiency. Further studies are being conducted on the use of process integration technique to optimally integrate the various sub-systems and hence improve its overall economics. This system provides solution to the twin problem of waste management and energy security and with very little environmental footprint.

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# MYCO AND PHYTO REMEDIATION OF HEAVY METALS FROM AQUEOUS SOLUTION

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## ABSTRACT

Biosorption technique was applied to remove the Ni(II), Cu(II), Cr(III) and Cr(VI) from single metal solution. Seven fungal species viz., *Aspergillus niger*, *A. terreus*, *A. flavus*, *Trichoderma harzianum*, *Alternaria alternata*, *Rhizopus arrhizus* & *Cunninghamella echinulata*, three agricultural materials viz., *Oryzae sativa* straw (rice straw), *Cicer arietinum* dried seed (gram husk) & *Luffa cylindrical* dried fruit (luffa sponge), leaves of five trees i.e., Neem (*Azadirachta indica*), Dareek (*Melia azedarach*), Bohar (*Ficus benglensis*), Peepal (*Ficus religiosa*), sunflower (*Helianthus annuus*) and charcoal were chosen as adsorbent material. Laboratory biosorption experiments were performed with different concentrations of each of four metals. Results showed highly significant sequestering capacity of all selected biosorbents for both Cr(III & VI) in comparison to Cu(II) and Ni(II) ions. Removal efficiency of candidate biosorbents reached up to 80%, 58% and 52% for Cr(III & VI), Cu(II) and Ni(II) ions, respectively.

**Keywords:** Biosorption, Metals, Fungi, Agricultural waste, Tree leaves

## INTRODUCTION

Industrial wastewater is considered as most notorious source of heavy metal pollution in the surrounding environment (Sun et al., 2010). In Pakistan industrial wastewater pollution from the electroplating processing has become most serious issue. Volume of the wastewater produced by such processing units is comparatively much smaller but highly toxic in nature because of the high concentration of copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb), various acids and cyanide compounds as compared to prescribed limits of National Environmental Quality Standards (Javaid et al., 2010).

Now the attention is being focused on reducing reliance upon expensive chemical methods, and finding alternatives directing attention towards biological technique like Biosorption. Biosorption is ability of certain biological material to sequester contaminates like heavy metals from adjoining environment in economic and eco-friendly way. It occurs through bindings of metal ions with chemical groups present on the biosorbent cell wall surface. Biosorption technique offers several advantages over conventional treatment methods including cost effectiveness, efficiency, minimization of chemical/biological sludge, requirement of additional nutrients, and regeneration of biosorbent with possibility of metal recovery. A diversity of adsorbents like microorganisms (fungi, bacterial, algae and yeast), plant by-products (rice straw and husk, wheat straw and husk, chick pea husk) and waste material (fallen leaves and peels) have been utilized to remove heavy metals from aqueous medium (Javaid et al., 2010). Biomaterials like fungi have been proved efficient and economic for removal of metal ions from aqueous solution due to high percentage of cell wall material, which shows excellent metal binding properties (Das et al., 2008). Among the fungi, *Aspergillus*, *Trichoderma* and *Penicillium* are the most important group that degrades variety of polysaccharides in agricultural waste, soil and feces of cattle and sheep (Sun et al., 2010). So far, Ali et al. (2007) results showed *Trichoderma viride* is successful as biosorbents for the removal of Zn, Pb and Cd from the aqueous media. Rajender et al. (2008) examined tremendous ability of *Aspergillus niger*, *A. sydoni* and *Penicillium janthinellum* to remove Cr(VI) ions @ 91.03, 87.95 and 86.61% from aqueous solution as well as from electroplating effluent. Pal et al. (2010) showed cell surface functional groups of the fungus might act as ligands for metal sequestration and varied their findings with *Aspergillus niger* during Cd and with *R. arrhizus* during Pb biosorption from the aqueous culture media. Findings of Hmambika et al. (2011) indicted more than 60-95% metal ions like Cu, Cd and Pb were removed due to application of *Aspergillus* sp. *Penicillium* and *Cephalosporium* sp. from aqueous solution.

Apart from fungi, removal of heavy metals by lignocellulosic and plant waste material has been extensively investigated in past decades. The plant and agricultural waste material are good source of cheap, easily and locally available adsorbent with reasonable metal loading capacity. *Cicer arietinum* dried seed (gram husk) showed 99.9% removal of Cr(VI) (Ahalya et al., 2005), *Ficus religiosa* leaves powder was found to be a very good adsorbent for Cr(VI) and Pb (Qaiser et al., 2007) and sunflower (*Helianthus annuus*) exhibited 80% removal efficiency for Cr(VI) (Jain et al., 2009). Oboh et al. (2009) found 76.8, 67.5, 58.4 and 41.45 removal efficiency of neem leaves for Cu, Ni, Zn and Pb, respectively. Aslam et al. (2010) showed that *Ficus Religiosa* leaves are the suitable material for Ni(II) biosorption. The potential use of rice straw as an adsorbent for Ni and Cd was suggested El-Syed et al. (2010). Ohbo et al. (2011) stated that *Luffa cylindrical* seeds and sponge mixture is a good alternative biosorbent for Ni, Pb, Cu and Zn ions removal from aqueous solution.

Based on literature survey, present study was conducted to evaluate the Ni(II), Cu(II), Cr(III) and Cr(VI) removal potential of variety of fungal and natural adsorbent from single metal solution at various concentrations.

## METHODOLOGY

### Biosorbents

The pure cultures of fungal species viz., *Aspergillus niger* (FCBP 0074), *A. terreus* (FCBP 0058), *A. flavus* (FCBP 0064), *R. arrhizus* (FCBP 800), *A. alternata* (FCBP 0092), *T. harzianum* (FCBP 0139) and *C. echinulata* (FCBP 0104) were procured from First Fungal Culture Bank of Pakistan, Institute of Agricultural Sciences (IAGS), Punjab University. Mycelial biomass of the each fungal species was cultivated in 2% malt extract (ME) broth in 250 mL conical flasks. Inoculated flasks were incubated for 6-7 days under controlled temperature of  $25 \pm 1^\circ \text{C}$  in stationary phase. Prepared biomass of each candidate fungus was separated from culture broth by filtration and subjected to successive washings with double distilled deionized water followed by drying in oven at  $60^\circ \text{C}$  for 24 hours. The dried biomass of each test fungus of 0.5-1 mm was used in biosorption experimentation.

*O. sativa* straw, *C. arietinum* husk and luffa sponge were obtained from local market. *A. indica*, *M. azedarach*, *F. benglensis*, *F. religiosa*, *H. annus* leaves were collected from local environment of University of Punjab Lahore, Pakistan. Each biosorbent material was dried in oven at  $100^\circ \text{C}$  for 24 hours and homogenized in a blender to break the cell aggregates into smaller fragments of 0.5-1 mm diameter (mesh size 150  $\mu\text{m}$ ). Waste charcoal was acquired from Natural Product laboratory of Herbal Heritage Centre, IAGS, Punjab University and utilized for biosorption experiment after drying at  $100^\circ \text{C}$  for two hours. Each of the natural biosorbent material was kept in separate airtight bottles for later utilization in biosorption experiments. Table 2.1 shows list of biosorbens materials selected for current investigation.

Table I. List of biosorbent materials utilized in present work

No	Biosorbents	Metal			
		Ni(II)	Cu(II)	Cr(III)	Cr(VI)
	<b>Fungi</b>				
1	<i>Aspergillus niger</i>	+	+	+	+
2	<i>Aspergillus terreus</i>	+	+	-	-
3	<i>Aspergillus flavus</i>	+	+	-	-
4	<i>Alternaria alternata</i>	+	+	-	-
5	<i>Rhizopus arrhizus</i>	+	+	+	+
6	<i>Trichoderma harzianum</i>	+	+	+	+
7	<i>Cunninghamella echinulata</i>	+	+	-	-
	<b>Agricultural waste</b>				
8	<i>Oryzae sativa</i> straw	+	+	+	+
9	Dried seed of <i>Cicer arietinum</i>	+	+	+	+
10	Dried fruit of <i>Luffa cylindrica</i>	+	+	+	+
	<b>Tree Leaves</b>				
11	<i>Azadiracta indica</i>	+	+	+	+
12	<i>Melia azedarach</i>	+	+	+	+
13	<i>Ficus benglensis</i>	-	-	+	+
14	<i>Ficus religiosa</i>	-	-	+	+
15	<i>Helianthus annus</i>	-	-	+	+
16	Charcoal	+	+	+	+

+ indicates material utilized in biosorption experiments for aforementioned metal; - indicates material not utilized in biosorption experiment for above mentioned metal

### Metals

The stock solutions of Ni(II), Cu(II), Cr(III) and Cr(VI) ions were prepared from respective salts, included Ni  $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  by dissolving the exact quantity of salt in double distilled deionized water. Stock solution measuring  $1000 \text{ mg L}^{-1}$  of each metal ion was further diluted for composing various concentration regimes. On the basis of literature available, four concentrations 50, 100, 300 and  $500 \text{ mg L}^{-1}$  were prepared from standard solution of Cu(II) and Ni(II) five levels of 5, 15, 25, 35 &  $45 \text{ mg L}^{-1}$  were made from stock solution of Cr(III) & Cr(VI)

### Experiment

Biosorption experiments were performed by suspending 0.1g of fungal and 0.5g of natural biosorbent material in 100 mL of metal solution in 250 mL flask stirred at 150 rpm at pH 4.5 (0.5M NaOH and 0.5M HCl was used to adjust pH in each flask) for 3 hours. The change in working volume due to addition of NaOH and HCl was negligible. These chemicals were added to reaction mixture before the addition of biomass to avoid change in pH value. Different sets of experiments were carried out to appraise the maximum metal accumulating capacity of the biosorbents at different initial concentration of metal ions ranging between 50, 100, 300 &  $500 \text{ mg L}^{-1}$  for Cu(II) and Ni(II), and 5, 15, 25, 35 &  $45 \text{ mg L}^{-1}$  in case of Cr(III) & Cr(VI). After desired contact time, the mixture was filtered through Whatmann filter paper No.1 and the residual metal ion concentrations were determined using Atomic absorption spectrophotometer (AAS).

### Biosorption data evaluation

The efficiency of the biosorbent or its removal capability (E) was calculated using following equation:

$$E = \frac{C_i - C_f}{C_i} \times 100$$

Where,  $C_i$  = initial concentration of the metallic ion ( $\text{mg L}^{-1}$ );  $C_f$  = final concentration of metallic ion ( $\text{mg L}^{-1}$ );  $m$  = dried mass of the biosorbent in the reaction mixture (g) and  $V$  = volume of reaction mixture (mL).

## RESULTS AND DISCUSSION

Comparative analysis of data acquired, in general, exhibited significantly higher sequestering capacity of all selected biosorbents for both Cr(III & VI) in comparison to Cu(II) and Ni(II) ions. Removal efficiency of candidate biosorbents reached up to 80%, 58% and 52% for Cr(III & VI), Cu(II) and Ni(II) ions, respectively (Table 2, 3, 4 & 5). This may also be related to differential electrode potential of various metal ions, resulting in different biosorption affinities (White et al., 1979). Similar concept of stronger chemical and physical affinity for metal ion at greater electronegative bonds and ionic radii has been suggested in other studies (Tsezos & Volesky, 1981, Weast, 1988).

Data acquired on influence of initial concentration of metal ions revealed strong impact of this factor on uptake potential by the biosorbents, the effect being more conspicuous at higher concentrations. Accordingly, adsorption efficiency reduce up to 5-20% for Cu(II) and Ni(II) at 300-500 mg L<sup>-1</sup> and 2-35% in case of Cr(III & VI) at 35-45 mg L<sup>-1</sup> by the biosorbents. Over and above, this trend in metal uptake reduction was dominant in case of Cr(III & VI), as 10 amongst the twelve elected biosorbents exhibited this decline in efficiency. Whereas, in case of the Cu(II) and Ni(II) the reduction rate was recorded in half of the biosorbents (6). These results are similar to the observations made by Malkoc et al. (2006), Dubey and Krishna (2007) and Zvinowanda et al. (2010) with different biomaterials. However, the sorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. At low concentrations adsorption sites took up the available metal more quickly. However, at higher concentrations, more metal ions are left un-adsorbed in solution due to the saturation of binding sites (Lokeshwari & Joshi, 2009). For each metal different adsorbent were noticed that hold maximum metal adsorption efficiency. For **Cu(II) ions**, *C. arietinum* husk showed significantly greater biosorption efficiency 44-50% within concentration range of 50-500 mg L<sup>-1</sup>, respectively in comparison to rest of the 12 biosorbents. However, removal rate declined only up 20% in case of *R. arrhizus*, *A. niger*, *A. indica*, *M. azedarach*. Among rest of adsorbents, *O. sativa* straw, *L. cylindrica* dried fruit, *A. terreus*, *A. flavus*, *T. harzianum* and *A. alternata* showed up to half time reduction and *C. echinulata* and charcoal exhibited 75% decline in biosorption efficiency as compared to maximum recorded in *C. arietinum* husk (Table 2). *L. cylindrica* dried fruit showed the highest removal efficiency of 44-50% for **Ni(II)** ions followed by *T. harzianum*, *R. arrhizus*, *O. sativa* straw and leaves of *A. indica*, *M. azedarach* within concentration range of 50-500 mg L<sup>-1</sup>. Amongst remaining 6 biosorbents, efficiency was further reduced up to 50-60% in *C. arietinum* husk, charcoal, *A. niger*, *A. terreus*, *A. flavus*, *A. alternata* and *C. echinulata* in comparison to the highly efficient (44-50%) biosorbent (Table 3). In case of **Cr(III)**, four biosorbents viz. *O. sativa* straw, leaves of *F. bengalensis*, *F. religiosa* and *H. annus* hold the greatest biosorption efficiency (80%) at applied concentrations in comparison to rest of adsorbents (Table 4). On the other hand, *F. religiosa* was proved to be most efficient biosorbents (80%) for adsorption of **Cr(VI)** (Table 5).

Disparity in biosorption capacity of different adsorbents may be ascribed to the intrinsic ability of organism, its chemical composition of cell wall leading various types of interaction of metals with adsorbents (Gadd, 1993). This indicates adsorbent variability in metal ions binding affinities for the same or different functional groups (amino, carboxylate, phosphate, sulphhydryl, phosphate and thiol) on cell walls. Since in solution all the metal ions are in competition for the available binding sites, a metal that has a higher affinity for particular functional group would bind in greater concentration (Bayramoglu et al., 2003).

Generally we observed that agro-waste and plant leaves exhibited greater adsorption efficiency than fungi. Among the fungi, *T. harzianum* and *R. arrhizus* were found to be good adsorbents of metal ions. Difference among the different fungal species could be owing to marked variations in the wall composition between different fungal taxonomic groups (Siegel et al., 1990; Fourest and Roux, 1992). Generally, major constituents of fungal cell wall are carbohydrates, chitin, chitosan, polyuronide and polyphosphates and proteins that probably participated in metal binding. It has been stated that difference in the high chitin and chitosan content of the cell walls attributed differential metal uptake efficiencies in the fungal biomass (Tsezos & Volesky, 1981).

In case of agro-waste, *O. sativa* straw, *C. arietinum* husk & *L. cylindrica* are ligno-cellulose based. Most of the plant tissues are composed of structural carbohydrates as cellulose, hemicellulose, pectin, lignin, proteins, subreins, mineral salt and waxes (Rowell et al., 2002; Mazali and Alves, 2005). Carbohydrates of lingo-cellulosic mainly contributed in metal binding. Variation in adsorption efficiency of agro-waste materials could be due to the variation in number of fissures and holes. Presence of some fissures and holes indicated the existence of the macroporous structure. Previous findings reported that major contribution of the metal ions uptake is due to micro- and mesoporous structures (Oboh et al., 2009).

In present study leaves were found to be good biosorbents for Cr(III) than rest of metals. This could be due to difference in the metal-attracting groups of the cell walls of these leaves. Leaves of different trees are contained a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectins and lignin present in the cell wall are the most important sorption sites (Volesky, 2003). Leaves have chlorophyll, carotene, anthocyanin and tannin which contribute to metal biosorption. The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption (Kaiser et al., 2007).

Table 3.2: Comparative representation of biosorption efficiency of various biosorbents at selected concentrations.

Biosorption conditions: biosorbents concentration, 0.1 g 100 mL<sup>-1</sup>; pH, 4.5 (the solution pH was not controlled during the experiment); 150 rpm and 25°C for 3 hours.

#	Biosorbents	Efficiency (%)			
		50 mg/L	100 mg/L	300 mg/L	500 mg/L
1	<i>A. niger</i>	36	34	35	34
2	<i>A. terreus</i>	21	20	20	19.8
3	<i>A. flavus</i>	22	22	23	20
4	<i>T. harzianum</i>	24	24	24	24
5	<i>A. alternata</i>	20	20	19	18
Cu(II) 6	<i>R. arrhizus</i>	34	35	36	36
7	<i>C. echinulata</i>	20	18	16	12
8	<i>O. sativa</i> straw	30	30	30	25
9	<i>C. arietinum</i> husk	44	58	54	50
10	<i>L. cylindrica</i> dried fruit	20	25	20	18
11	<i>A. indica</i> leaves	30	29	31	31
12	<i>M. azedarach</i> leaves	30	30	33	33
13	Charcoal	6	7	8	10

#	Biosorbents	Efficiency (%)			
		50 mg/L	100 mg/L	300 mg/L	500 mg/L
1	<i>A. niger</i>	20	20	16.67	14
2	<i>A. terreus</i>	20	21	17	16
3	<i>A. flavus</i>	16	16	15	15
4	<i>T. harzianum</i>	46	45	43.33	43
5	<i>A. alternata</i>	20	19	15	15
Ni(II) 6	<i>R. arrhizus</i>	36	40	46.67	46
7	<i>C. echinulata</i>	20	20	18.67	18
8	<i>O. sativa</i> straw	36	38	41	43
9	<i>C. arietinum</i> husk	18	19	30	24
10	<i>L. cylindrica</i> dried fruit	44	50	51.67	48
11	<i>A. indica</i> leaves	32	30	46	45
12	<i>M. azedarach</i> leaves	36	35	48	46.6
13	Charcoal	28	27	26	26

Note: Highlighted rows indicate biosorbent with the maximum biosorption efficiency

Table 3.3 A&B: Comparative representation of biosorption efficiency of various biosorbents at selected concentrations.

Biosorption conditions: biosorbents concentration, 0.1 g 100 mL<sup>-1</sup>; pH, 4.5 (the solution pH was not controlled during the experiment); 150 rpm and 25°C for 3 hours.

#	Biosorbents	Efficiency (%)				
		5 mg/L	15 mg/L	25 mg/L	35 mg/L	45 mg/L
1	<i>A. niger</i>	50	50	51.2	51.43	48.89
2	<i>R. arrhizus</i>	70	70	68	66.86	66.67
3	<i>T. harzianum</i>	76	73.33	60	54.29	40
4	<i>O. sativa</i> straw	80	78.67	76	74.29	72.22
5	<i>C. arietinum</i> husk	80	73.33	64	57.14	48.89
6	<i>L. cylindrica</i> dried fruit	80	80	80	57.14	51.11
7	<i>A. indica</i> leaves	60	60	48	48.57	44.44
8	<i>M. azedarach</i> leaves	66	66.67	58	46.86	44.44
9	<i>F. benglensis</i> leaves	80	80	80	80	80
10	<i>F. religiosa</i> leaves	80	80	80	80	80
11	<i>H. annus</i> leaves	80	80	80	77.15	75.56
12	Charcoal	50	46.68	46	46	44.44

#	Biosorbents	Efficiency (%)				
		5 mg/L	15 mg/L	25 mg/L	35 mg/L	45 mg/L
1	<i>A. niger</i>	47.2	47.33	46	45.71	44.44
2	<i>R. arrhizus</i>	34	33.33	32	31.43	32.22
3	<i>T. harzianum</i>	70	68	65.2	65.14	65.11
4	<i>O. sativa</i> straw	57.6	56.67	56	55.71	55.55
5	<i>C. arietinum</i> husk	72	70	68	67.71	66.67
6	<i>L. cylindrica</i> dried fruit	30	26.67	24	20	17.78
7	<i>A. indica</i> leaves	66	56.67	48	45.71	40
8	<i>M. azedarach</i> leaves	40	33.33	30	28.57	28.89
9	<i>F. benglensis</i> leaves	52	42.67	39.6	35.14	33.33
10	<i>F. religiosa</i> leaves	80	80	80	80	80
11	<i>H. annus</i> leaves	60	46.67	46	45.14	44.44
12	Charcoal	52	66.67	72	72	73.33

Note: Highlighted rows indicate biosorbent with the maximum biosorption efficiency

### CONCLUSION

Perusal of results acquired on metal removal capability of the biosorbents revealed that among thirteen selected candidates for Cu(II) and Ni(II) half of them proved to be 30-50% efficient with concentration range of 50-500 mg L<sup>-1</sup>. For removal of Cu(II) from aqueous solution, *C. arietinum* husk, *A. niger* and *R. arrhizus* could be utilized. For Ni(II), six namely *T. harzianum*, *R. arrhizus*, *O. sativa* straw, *L. cylindrical* dried fruit, leaves of *A. indica* and *M. azedarach* were found as efficient adsorbents. Five biosorbents viz. *R. arrhizus*, *O. sativa* straw, leaves of *F. benglensis*, *F. religiosa* and *H. annus* hold the greater biosorption efficiency 80% for Cr(III). Four biosorbents, *T. harzianum*, *C. arietinum* husk, *F. religiosa* leaves and charcoal were recorded to be best option (75%± 5) as Cr(VI) sequestering agents at applied concentrations (5-50 mg L<sup>-1</sup>).

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# NOVEL CHIRAL COMPOUND: (*R*) AND (*S*) 1-(2-BENZYLOXY-3-METHOXYPHENYL)-2,2,2-TRICHLOROETHYL BENZENESULFONATE, SYNTHESIS AND CHARACTERIZATION

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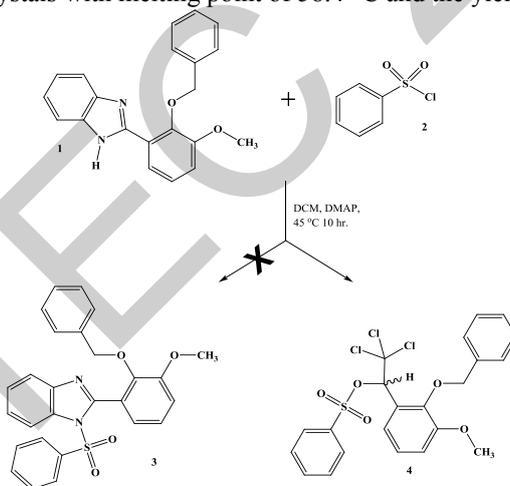
## ABSTRACT

The reaction between benzimidazole **1** and benzenesulfonyl chloride **2** in dichloromethane (DCM) at 45 °C for 10 hr in the presence of dimethyl aminopyridine (DMAP) as a catalyst was expected to obtain 2-(2-benzyloxy-3-methoxyphenyl)-1-(phenylsulfonyl)-1*H*-benzimidazole, **3**. Unfortunately, a novel chiral compound (*R*) and (*S*) 1-(2-benzyloxy-3-methoxyphenyl)-2,2,2-trichloroethyl benzenesulfonate **4** was obtained as a single crystal (59% yield) with melting point of 58.4 °C. However, the mechanism of this reaction still is under investigation. The molecular structure of this compound was confirmed by FTIR, HRMS, X-Ray crystallography, 1D and 2D NMR spectroscopy. The crystal of **4** is in the monoclinic space group  $P2_1/c$  with  $a = 8.1638$  (1) Å,  $b = 8.8536$  (1) Å,  $c = 30.7221$  (5) Å,  $\beta = 90.670$  (1)°,  $D_{\text{calc}} = 1.501 \mu\text{g m}^{-3}$ ,  $V = 2220.41$  (5) Å<sup>3</sup> and  $R_{\text{int}} = 0.059$ . The complete assignments of **4** were made using 1D and 2D NMR including APT, DEPT-135, COSY, HMQC and HMBC in CDCl<sub>3</sub>.

**Keywords:** <sup>1</sup>H NMR; <sup>13</sup>C NMR; 2D NMR; X-Ray Crystallography; 2,2,2-Trichloroethyl Benzenesulfonate.

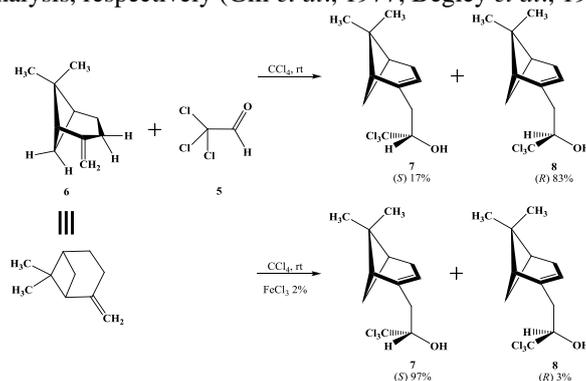
## INTRODUCTION

The reaction between benzimidazole **1** and benzene sulfonyl chloride **2** in DCM at 45 °C for 10 hr in the presence of DMAP as a catalyst was hoped to obtain 2-(2-benzyloxy-3-methoxyphenyl)-1-(phenylsulfonyl)-1*H*-benzimidazole **3** (Li *et al.*, 2006), but it was given (*R*) and (*S*) 1-(2-benzyloxy-3-methoxyphenyl)-2,2,2-trichloroethyl benzenesulfonate **4** (Al-Douh *et al.*, 2007, Scheme 1). It was obtained as single crystals with melting point of 58.4 °C and the yield was 59%.



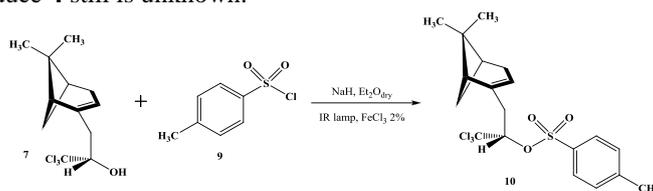
Scheme 1: Synthetic route towards the compound **4**.

The addition of chloral **5** to (–)-(1*S*,5*S*)-pin-2(10)-ene **6** was formed diastereoisomers (*S*) **7** and (*R*) **8** with ratio 17:83, while the ratio was enhanced in the presence of FeCl<sub>3</sub> 2% as a bulky Lewis acid catalyst to 97:3, which were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR experiments and X-ray analysis, respectively (Gill *et al.*, 1977; Begley *et al.*, 1978, Scheme 2).

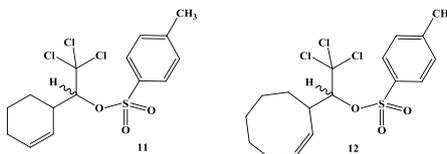


Scheme 2: Gill *et al.* method to prepare derivative of **4**.

Begley *et al.* (1978) were synthesized derivatives of **4** from the reaction of **7** with toluene-*p*-sulphonyl chloride or tosyl chloride **9** to produce **10** as (*S*) diastereoisomer (Scheme 3), while Gill *et al.* (1979) were synthesized other derivatives from the reaction of cyclohex-1-ene and cycloocta-1-ene with **9** to produce **11** and **12** as diastereoisomers (*R*) and (*S*), respectively (Scheme 4). Figure 1 shows the chemical structure and the numbering scheme of **4** for discussion purposes in the following sections. The mechanism of produce **4** still is unknown.



Scheme 3: Derivative **10** was prepared by Begley *et al.*



Scheme 4: Other derivatives of **4** were prepared by Gill *et al.*

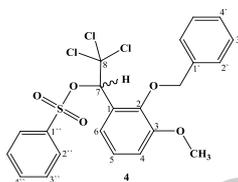


Figure 1: The chemical structure and the numbering scheme of **4**.

## EXPERIMENTAL PART

### General

All NMR experiments were performed on *Bruker Avance 400 Ultrashield*<sup>TM</sup> NMR for <sup>1</sup>H, operating at 400.132 MHz, and *Bruker Avance 300* NMR spectrometers for <sup>13</sup>C, operating at 71.478 MHz at 298 K using *Bruker XWINNMR* software equipped with a 5 mm BBI inverse gradient and QNP probes, respectively (Bruker, 1999; Berger and Braun, 2004). Chemical shifts were reported downfield in parts per million (ppm) from a tetramethylsilane (TMS) reference, and coupling constants (*J*) were measured in Hz. The concentration of solute molecule was 25 mg in 1.0 mL CDCl<sub>3</sub>.

High-resolution mass spectrum (HRMS) was recorded by a *Bruker Daltonics' micrOTOF-Q*<sup>TM</sup> mass spectrometer, operated in electrospray ionization source ESI mode. In DCM, the sample was prepared in 1.0 μL–1.0 mL/min. The crystal structure was determined by an *APEX2 Bruker* (APEX2, 2005) and *SHELXTL* (Sheldrick, 1998, 2008) crystallographic software packages for determining molecular structure, and Infrared spectrum was recorded on a *Perkin-Elmer 2000 FT* spectrometer and was expressed in cm<sup>-1</sup>. The compound was prepared using KBr cells. Melting point (uncorrected) was determined on Stuart melting point apparatus.

### Synthesis

The synthetic method of **4** was described previously (Li *et al.*, 2006; Al-Douh *et al.*, 2007).

## RESULT AND DISCUSSION

### FTIR Spectroscopy

The FTIR spectrum of **4** is depicted in Figure 2 and selected FTIR data are listed in Table 1. The bands with weak intensity observed of benzene rings at 3096, 3067 and 3028 cm<sup>-1</sup> are ascribed to the stretching of aromatic ν C=C–H. The bands observed at 2948 and 2873 cm<sup>-1</sup> are assigned to ν<sub>as</sub> and ν<sub>s</sub> CH<sub>3</sub> of methoxy group, respectively, while the bands observed at 2927 and 2855 cm<sup>-1</sup> assigned to ν<sub>as</sub> and ν<sub>s</sub> CH<sub>2</sub> of methylene group, respectively.

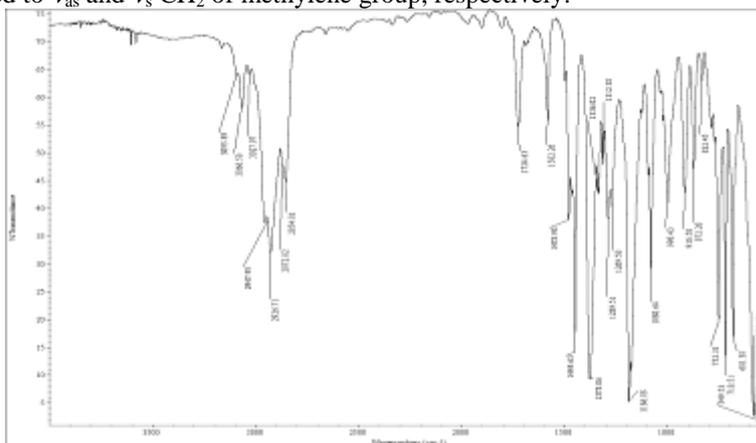


Figure 2: FTIR spectrum of **4**.

The asymmetrical bending vibration of  $\delta_{as}$  CH<sub>3</sub> occurred at 1479 cm<sup>-1</sup>, while the symmetrical bending vibration of  $\delta_s$  CH<sub>3</sub> appeared at 1336 cm<sup>-1</sup>, and the CH<sub>2</sub> scissoring vibration  $\delta_s$  CH<sub>2</sub> appeared at 1450 cm<sup>-1</sup>. The strong intensity bands appeared at 1378 and 1187 cm<sup>-1</sup> are assigned to  $\nu_{as}$  and  $\nu_s$  SO<sub>2</sub> sulfonic esters (Silverstein *et al.*, 2005). The free  $\nu$  N–H stretching band of benzimidazole **1** at 3354 cm<sup>-1</sup> was disappeared (Al-Douh, 2010).

Table 1: FTIR spectral data of compound **4** (cm<sup>-1</sup>):

$\nu$ C–H arom.	$\nu$ CH <sub>3</sub> aliph.	$\nu$ CH <sub>2</sub> aliph.	$\delta$ CH <sub>3</sub>	$\delta$ CH <sub>2</sub>	$\nu$ S=O ester	$\nu$ C–O–C aliph.	$\nu$ C–Cl aliph.	$\nu$ aromatic
3096	as 2948	as 2927	as 1479	as 1450	as 1378	as 1270	998	833, 752, 719,
3067	sy 2873	sy 2855	sy 1336		sy 1187	sy 1081	917	681, 577 & 550
3028							872	

### HRMS Spectra

Figure 3 shows the HRMS spectrum of **4**. The HRMS of **4** shows a molecular formula of C<sub>22</sub>H<sub>19</sub>Cl<sub>3</sub>NaO<sub>5</sub>S<sup>-</sup> at  $m/z$  522.9933 (M+Na<sup>+</sup>). The peaks at  $m/z$  523.9940, 524.9903, 525.9912, 526.9862, 527.9885 and 528.9830 for the isotopes of the benzenesulfonate **4**, M+2, M+4, M+6, M+8, M+10 and M+12, respectively, which it has three chlorine atoms (Silverstein *et al.*, 2005).

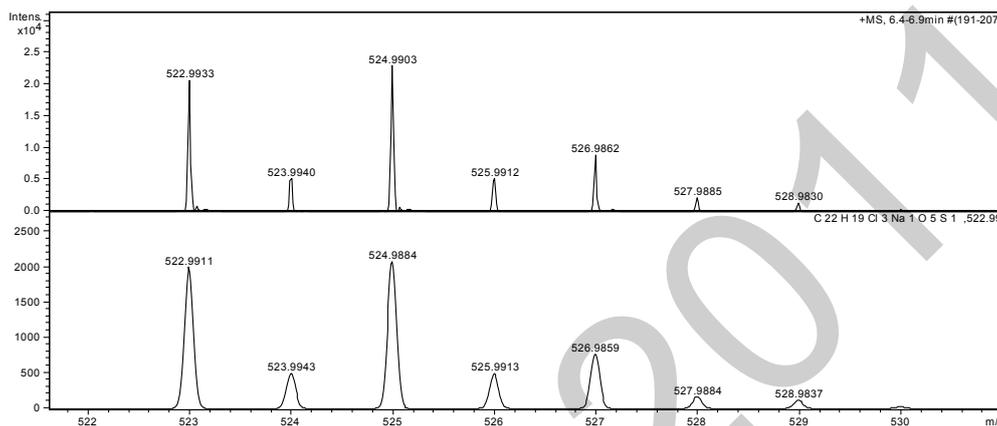


Figure 3: HRMS spectrum of **4**.

### <sup>1</sup>H NMR

The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of **4** was shown in Figure 4. The spectrum shows the chemical shift of the aromatic protons of the benzyloxy ring H<sub>2</sub> were observed signal as double doublet at  $\delta = 7.69$ – $7.66$  ppm ( $J = 8.46$  and  $1.19$  Hz), and H<sub>3</sub> were exhibited signal as a triplet at  $\delta = 7.36$ – $7.32$  ppm ( $J = 7.92$  Hz), while proton H<sub>4</sub> was displayed triplet at  $\delta = 7.52$  ppm ( $J = 1.05$  Hz), due to its coupled with H<sub>3</sub>. The signals as multiplet at  $\delta = 7.58$ – $7.54$ ,  $7.48$ – $7.43$  and  $7.41$ – $7.38$  ppm are proposed to be assigned to H<sub>2'</sub>, H<sub>3'</sub> and H<sub>4'</sub> in the benzenesulfonyl ring, respectively. The double doublet were overlapped with CDCl<sub>3</sub> peak and were observed at  $\delta = 7.28$ – $7.25$  ppm ( $J = 7.56$  and  $1.82$  Hz) was assigned to H<sub>6</sub> in the trisubstituted ring, while both protons H<sub>5</sub> and H<sub>4</sub> were observed two signals as triplet and double doublet at  $\delta = 7.06$ – $7.01$  and  $7.00$ – $6.96$  ppm ( $J = 7.92$ ,  $8.21$  and  $1.83$  Hz), respectively. The methoxy group OCH<sub>3</sub> of **4** was shown as singlet at  $\delta = 3.89$  ppm, and the methine H<sub>7</sub> was also observed signal at  $\delta = 6.46$  ppm as singlet.

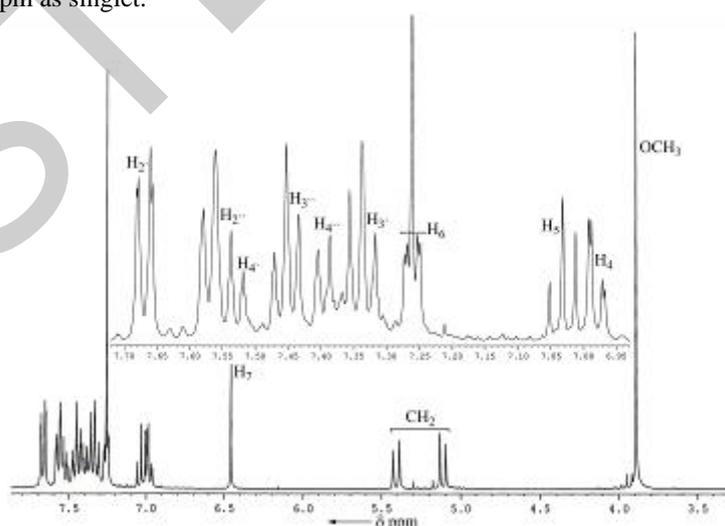


Figure 4: <sup>1</sup>H NMR spectrum of **4** in CDCl<sub>3</sub>.

On the other hand, the methylene group CH<sub>2</sub> was exhibited signal as double doublet at  $\delta = 5.41$ – $5.12$  ppm ( $J = 88.34$  and  $11.48$  Hz). These values of coupling constant are unexpected specially 88.34 Hz. We suggest the reasons of these values to be due to the configuration of those hydrogen atoms between benzyloxy ring and the 2,2,2-trichloroethyl benzenesulfonate group, which <sup>1</sup>H–<sup>1</sup>H COSY experiment was performed to further confirmed the assigned peak between the methine proton H<sub>7</sub> with one proton of methylene group CH<sub>2</sub> and one proton of benzene ring H<sub>2</sub> (see <sup>1</sup>H–<sup>1</sup>H COSY analysis, Figure 7), while <sup>1</sup>H–<sup>13</sup>C HMBC experiment was performed to further confirmed the assigned peak between the protons of benzene ring H<sub>2</sub> and the

protons of methylene group CH<sub>2</sub> (see <sup>1</sup>H–<sup>13</sup>C HMBC, Figure 11). Additionally, the crystal structure of **4** confirmed the posture of that groups (see X-ray analysis, Figures 5, 13 and 14).

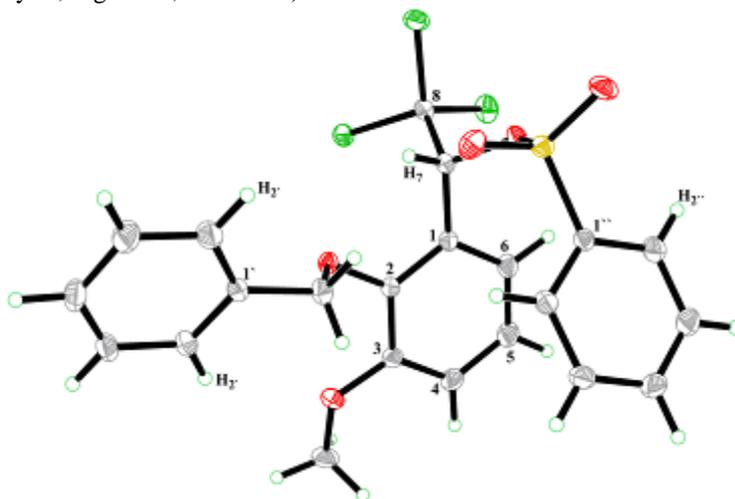


Figure 5: The crystal structure of **4**.

### <sup>13</sup>C APT NMR

The <sup>13</sup>C NMR spectrum of **4** was obtained with using APT NMR experiment and shown in Table 2 and Figure 6. The peak in CDCl<sub>3</sub> appears at  $\delta = 56.26$  ppm of **4** was assigned to the methoxy group OCH<sub>3</sub>, while methylene group CH<sub>2</sub> and methine carbon C<sub>7</sub> were showed at  $\delta = 74.79$  and  $82.70$  ppm, respectively. The quaternary carbon signals were observed at  $\delta = 152.42$ ,  $147.40$ ,  $138.35$ ,  $136.18$ ,  $126.84$  and  $98.35$  ppm for C<sub>3</sub>, C<sub>2</sub>, C<sub>1'</sub>, C<sub>1''</sub>, C<sub>1</sub> and C<sub>8</sub>, respectively. Other aromatic carbon signals of benzenesulfonyl ring were observed at  $\delta = 128.97$ ,  $128.56$  and  $127.62$  ppm for C<sub>4''</sub>, C<sub>3''</sub> and C<sub>2''</sub>, respectively, while C<sub>4</sub>, C<sub>6</sub> and C<sub>5</sub> at the trisubstituted aromatic carbon showed signals at  $\delta = 114.47$ ,  $121.13$  and  $124.08$  ppm, respectively. Aromatic carbons of benzyloxy ring observed signals of C<sub>2'</sub>, C<sub>3'</sub> and C<sub>4'</sub> at the respective  $\delta = 128.16$ ,  $129.31$  and  $134.30$  ppm. Table 2 summarizes the <sup>1</sup>H and APT NMR of **4** in CDCl<sub>3</sub>.

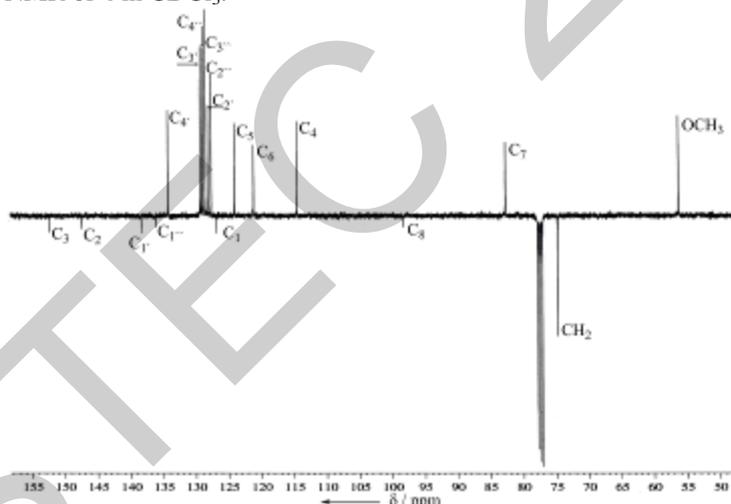


Figure 6: APT NMR spectrum of **4** in CDCl<sub>3</sub>.

Table 3.39: <sup>1</sup>H and <sup>13</sup>C APT NMR chemical shifts (ppm) and coupling constants (Hz) of **4** in CDCl<sub>3</sub>:

Atom No.	<sup>1</sup> H NMR		<sup>13</sup> C NMR
	$\delta$	<i>J</i>	
OCH <sub>3</sub>	3.89, <i>s</i>	–	56.26
CH <sub>2</sub>	5.41–5.12, <i>dd</i>	88.34, 11.48	74.79
1	–	–	126.84
2	–	–	147.40
3	–	–	152.42
4	7.00–6.96, <i>dd</i>	8.21, 1.83	114.47
5	7.06–7.01, <i>t</i>	7.92	124.08
6	7.28–7.25, <i>dd</i>	7.56, 1.82	121.13
7	6.46, <i>s</i>	–	82.70
8	–	–	98.35
1'	–	–	138.35
2'	7.69–7.66, <i>dd</i>	8.46, 1.19	128.16
3'	7.36–7.32, <i>t</i>	7.92	129.31
4'	7.52, <i>t</i>	1.05	134.30
1''	–	–	136.18
2''	7.58–7.54, <i>m</i>	–	127.62
3''	7.48–7.43, <i>m</i>	–	128.56
4''	7.41–7.38, <i>m</i>	–	128.97

### <sup>1</sup>H–<sup>1</sup>H COSY

Figures 7 and 8 were shown the <sup>1</sup>H–<sup>1</sup>H COSY NMR spectra of **4** in CDCl<sub>3</sub> and the most important correlations observed were shown in Figure 9. In COSY spectrum confirmed the correlation assignments of H<sub>4</sub> with methoxy group OCH<sub>3</sub> and one proton

of methylene group CH<sub>2</sub> in benzyloxy ring at  $\delta = 3.89$  and 5.41 ppm, respectively, but low correlation were observed with the second proton of CH<sub>2</sub> at  $\delta = 5.12$  ppm.

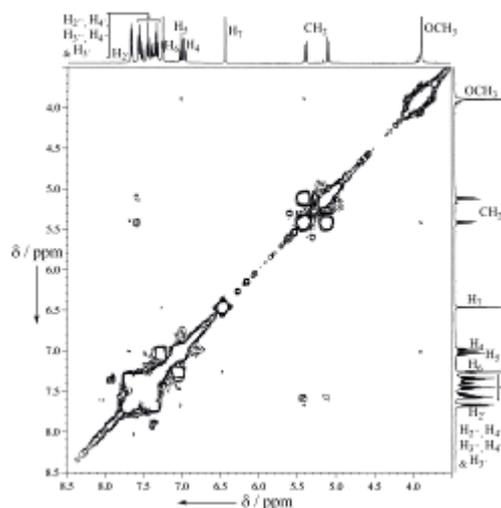


Figure 7: <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of **4** in CDCl<sub>3</sub>.

On the other side, both CH<sub>2</sub> protons were correlated with H<sub>3</sub> in the benzyloxy ring, but the second proton showed more correlated with H<sub>3</sub> than the other one. The methine proton H<sub>7</sub> was observed assignment with H<sub>6</sub> in the trisubstituted ring at  $\delta = 7.28$ – $7.25$  ppm. In the trisubstituted ring, proton H<sub>4</sub> in **4** showed <sup>3</sup>J with H<sub>5</sub> at  $\delta = 7.06$ – $7.01$  ppm, while proton H<sub>5</sub> was showed <sup>3</sup>J-correlation with both H<sub>4</sub> and H<sub>6</sub> protons at  $\delta = 7.00$ – $6.96$  and  $7.28$ – $7.25$  ppm, respectively. However, the correlations between H<sub>3</sub> with both protons H<sub>2</sub> and H<sub>4</sub> in benzyloxy ring were shown clearly at  $\delta = 7.69$ – $7.66$  and  $7.52$  ppm, respectively, while in the benzenesulfonyl ring, H<sub>3</sub> was observed <sup>3</sup>J-correlation with H<sub>2</sub> at  $\delta = 7.58$ – $7.54$  ppm (Figure 8).

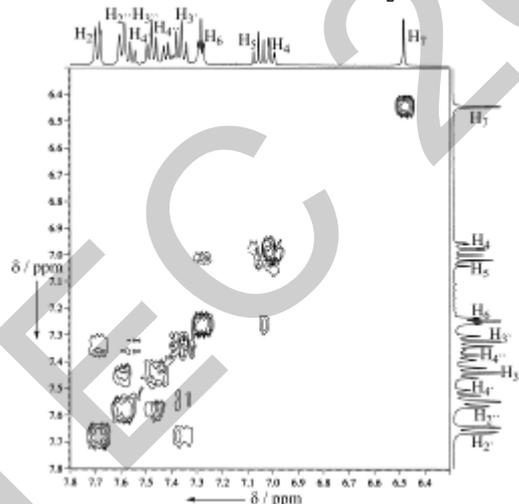


Figure 8: <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of the aromatic protons range of **4**.

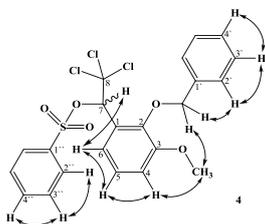


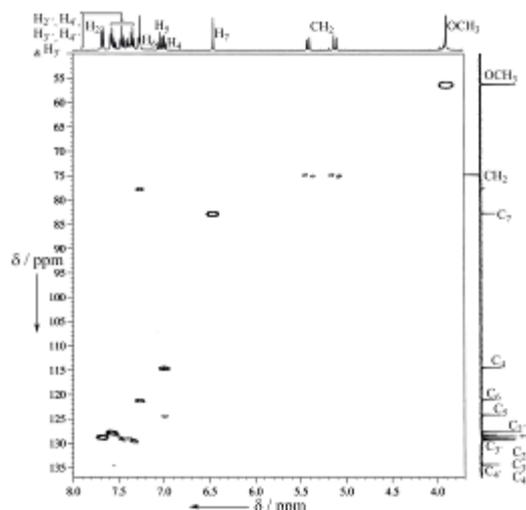
Figure 9: The most important correlations observed in COSY spectrum of **4**.

### <sup>1</sup>H-<sup>13</sup>C HMQC

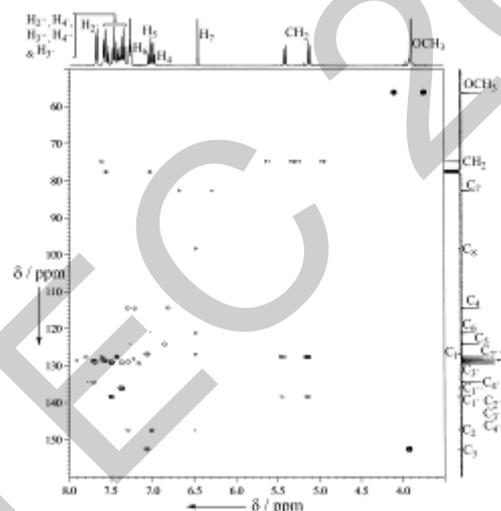
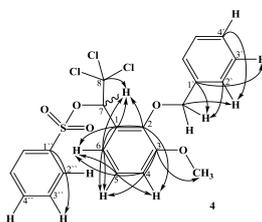
The HMQC NMR spectrum for **4** was shown in Figure 10 in CDCl<sub>3</sub>. The signals owing to C<sub>4</sub>, C<sub>3</sub>, C<sub>4</sub><sup>′</sup>, C<sub>3</sub><sup>′</sup>, C<sub>2</sub>, C<sub>2</sub><sup>′</sup>, C<sub>5</sub>, C<sub>6</sub> and C<sub>4</sub> atoms were observed at  $\delta = 134.30$ ,  $129.31$ ,  $128.97$ ,  $128.56$ ,  $128.16$ ,  $127.62$ ,  $124.08$ ,  $121.13$  and  $114.47$  ppm. The one bond <sup>1</sup>H-<sup>13</sup>C connectivities were also well observed for OCH<sub>3</sub>, CH<sub>2</sub> and C<sub>7</sub> atoms whereby the cross peaks appeared at the respective  $\delta = 56.26$ ,  $74.79$  and  $82.70$  ppm.

### <sup>1</sup>H-<sup>13</sup>C HMBC

The HMBC NMR spectrum for **4** was shown in Figure 11 and the most important correlations observed shown in Figure 12. The long-range HMBC cross peaks of the methylene group CH<sub>2</sub> protons with C<sub>2</sub> and C<sub>1</sub> in the benzyloxy ring were appeared at  $\delta = 128.16$  and  $138.35$  ppm, respectively. The HMBC cross peaks of the methoxy protons OCH<sub>3</sub> with C<sub>3</sub> was observed at  $\delta = 152.42$  ppm. On the other hand, the methine proton H<sub>7</sub> was correlated with C<sub>8</sub>, C<sub>6</sub>, C<sub>1</sub> and C<sub>2</sub>, at  $\delta = 98.35$ ,  $121.13$ ,  $126.84$  and  $147.40$  ppm, respectively.

Figure 10:  $^1\text{H}$ - $^{13}\text{C}$  HMQC NMR spectrum of **4** in  $\text{CDCl}_3$ .

Additionally, the correlation between  $\text{H}_5$  with both  $\text{C}_1$  and  $\text{C}_3$ , both protons  $\text{H}_4$  and  $\text{H}_6$  with  $\text{C}_2$ , and  $\text{CH}_2$  with  $\text{H}_2$  in the benzyloxy ring were observed clearly as  $^3J$ -correlation. The homonuclear connectivities were observed between protons in  $\text{C}_4$  with  $\text{H}_6$  and  $\text{C}_6$  with  $\text{H}_5$  as  $^3J$ -correlation, and  $\text{C}_5$  with both  $\text{H}_4$  and  $\text{H}_6$  as  $^2J$ -correlation. In addition,  $\text{C}_4$  was correlated with  $\text{H}_2$  in the same ring at  $\delta = 7.58$ – $7.54$  ppm, while  $\text{C}_1$  was correlated as  $^3J$ -correlation with  $\text{H}_3$  at  $\delta = 7.36$ – $7.32$  ppm. However, in the benzenesulfonyl ring, the homonuclear connectivities were shown between  $\text{C}_1'$  with  $\text{H}_3'$  as  $^3J$ -correlation. Other observed correlations between the aromatic protons and the carbons were showed in Table 3. All these correlation assignments were demonstrated and consistent with the crystal structure of **4**. Table 3 summarizes the values of COSY, HMQC and HMBC experiments in  $\text{CDCl}_3$ .

Figure 11:  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of **4** in  $\text{CDCl}_3$ .Figure 12: The most important correlations observed in HMBC spectrum of **4**.Table 3: 2D  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HMQC and HMBC correlations for **4** in  $\text{CDCl}_3$ :

Atom No.	COSY	HMQC		HMBC	
	$^1\text{H}$ - $^1\text{H}$	$^1J$	$^2J$	$^3J$	$^4J$
OCH <sub>3</sub>	CH <sub>2</sub> , H <sub>4</sub>	56.26	—	152.42, C <sub>3</sub>	—
CH <sub>2</sub>	OCH <sub>3</sub> , H <sub>2</sub>	74.79	138.35, C <sub>1</sub>	128.16, C <sub>2</sub>	—
H <sub>4</sub>	OCH <sub>3</sub> , H <sub>5</sub>	114.47	124.08, C <sub>5</sub>	147.40, C <sub>2</sub>	—
H <sub>5</sub>	H <sub>4</sub> , H <sub>6</sub>	124.08	121.13, C <sub>6</sub>	152.42, C <sub>3</sub>	—
H <sub>6</sub>	H <sub>5</sub> , H <sub>7</sub>	121.13	124.08, C <sub>5</sub>	114.47, C <sub>4</sub>	—
H <sub>7</sub>	H <sub>6</sub>	82.70	98.35, C <sub>8</sub>	147.40, C <sub>2</sub>	—
H <sub>2</sub>	H <sub>3</sub>	128.16	126.84, C <sub>1</sub>	121.13, C <sub>6</sub>	—
H <sub>3</sub>	H <sub>2</sub> , H <sub>4</sub>	129.31	— <sup>x</sup>	147.40, C <sub>2</sub>	—
H <sub>4</sub>	H <sub>3</sub>	134.30	— <sup>x</sup>	74.79, CH <sub>2</sub>	—
H <sub>5</sub>	H <sub>4</sub>	127.62	— <sup>x</sup>	134.30, C <sub>4</sub>	—
H <sub>6</sub>	H <sub>5</sub> , H <sub>7</sub>	128.56	— <sup>x</sup>	138.35, C <sub>1</sub>	—
H <sub>7</sub>	H <sub>6</sub>	128.97	— <sup>x</sup>	147.40, C <sub>2</sub>	—

<sup>x</sup>: is not observed

### X-Ray Crystallography

The previous results of **4** by FTIR, HRMS,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were consistent with the result of X-ray crystallography, which the golden single crystal of **4** was obtained and determined by X-ray crystallography, Figures 13 and 14. Bond lengths and angles in **4** have normal values, and are comparable with those in the related structures (Begley *et al.*, 1978; Gill *et al.*, 1979). The methoxy group at C9 is slightly twisted from the plane of the attached benzene ring C22–O2–C9–C10 with a torsion angle of  $-18.96$  ( $14$ ) $^\circ$ . The dihedral angle between the benzene rings [(C1–C6) and (C8–C13)] is  $22.64$  ( $5$ ) $^\circ$  whereas the torsion angle of C8–O1–C7–C6 is  $-157.96$ ( $7$ ) $^\circ$ . In the crystal structure, the intramolecular C7–H7B $\cdots$ O2 interaction generated an  $S(6)$  ring motifs, while other intramolecular C14–H14A $\cdots$ O1, C14–H14A $\cdots$ O3 and C21–H21A $\cdots$ O3 interactions generate  $S(5)$  ring motifs (Bernstein *et al.*, 1995), Table 4, Figure 13. The molecules of benzenesulfonate **4** are linked by short inter C12 $\cdots$ O4<sup>ii</sup> contact of  $3.0170$  ( $8$ )  $\text{\AA}$  (symmetry code: (ii)  $-x, -y, -z$ ) into cyclic centrosymmetric  $R^2_2$  ( $12$ ) dimers. These dimers are interlinked by the C3–H3A $\cdots$ O2<sup>i</sup> (symmetry code: (i)  $-x, y + 1/2, -z + 1/2$ ) intermolecular interactions, Figure 14. H atoms were placed in calculated positions and constrained to ride on their carrier atoms, with C–H distances in the range  $0.93$ – $0.98$   $\text{\AA}$ . Table 4 shows the summarized value for inter and intra hydrogen bonds of **4**. The crystal data of **4** was showed in Table 5 (Al-Douh *et al.*, 2007).

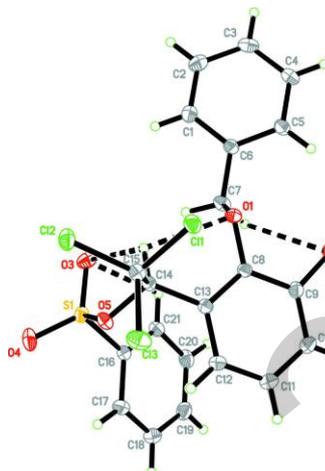


Figure 13: The crystal structure of **4** showing 50% probability displacement ellipsoids and the atomic numbering. The dashed lines indicate intramolecular hydrogen bonds.

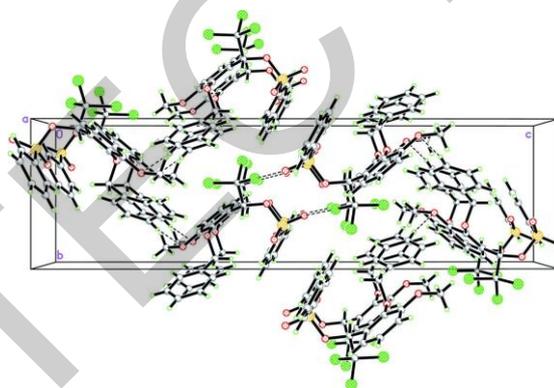


Figure 14: The crystal packing of **4**, viewed down the  $a$  axis. The intermolecular C–H $\cdots$ O hydrogen bonds and the short inter Cl $\cdots$ O contacts are shown as dashed lines.

Table 4: Hydrogen bond geometry of **4** ( $\text{\AA}$ ,  $^\circ$ ):

$D\cdots H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7–H7B $\cdots$ O2	0.97	2.56	3.040 (1)	110
C14–H14A $\cdots$ O1	0.98	2.38	2.820 (1)	107
C14–H14A $\cdots$ O3	0.98	2.34	2.838 (1)	111
C21–H21A $\cdots$ O3	0.93	2.55	2.919 (1)	104
C3–H3A $\cdots$ O2 <sup>i</sup>	0.93	2.49	3.414 (1)	172

Symmetry code: (i)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Table 5: Crystal data of **4**

Empirical formula, Formula weight	$\text{C}_{22}\text{H}_{19}\text{Cl}_3\text{O}_5\text{S}$ , 501.78
$T$ , $\lambda$	293(2) K, 0.71073 $\text{\AA}$
Crystal system, space group	$P2_1/c$ , monoclinic
Unit cell dimensions	$a = 8.1638$ (1) $\text{\AA}$ , $b = 8.8536$ (1) $\text{\AA}$ , $c = 30.7221$ (5) $\text{\AA}$ , $\alpha = 90^\circ$ , $\gamma = 90^\circ$ , $\beta = 90.670$ (1) $^\circ$
$V$ , Crystal size	2220.41(5) $\text{\AA}^3$ , $0.48 \times 0.30 \times 0.29$ mm
$Z$ , Calculated density	4, 1.501 $\mu\text{g}/\text{m}^3$
$\mu$ , $F(000)$ , $\theta$	0.54 $\text{mm}^{-1}$ , 1032, 1.33 to 40.00 $^\circ$
Limiting indices	$-14 \leq h \leq 14$ , $-16 \leq k \leq 16$ , $-54 \leq l \leq 54$
Reflections collected / unique	122837 / 13669 [ $R_{\text{int}} = 0.059$ ]
Data / restraints / parameters, $S$	11428 / 0 / 280, 1.08
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.040$ , $wR_2 = 0.108$
Largest diff. peak and hole	0.56 and $-0.55$ $\text{e}\cdot\text{\AA}^{-3}$

### CONCLUSION

We have reported the complete assignments of the novel chiral compound (*R*) and (*S*) 1-(2-benzyloxy-3-methoxyphenyl)-2,2,2-trichloroethyl benzenesulfonate **4** using  $^1\text{H}$ ,  $^{13}\text{C}$  APT, COSY, HMQC and HMBC NMR in  $\text{CDCl}_3$ . Compound **4** was

obtained as single crystal and it was studied by X-ray crystallography. Further, it using the compound in biologically important is in progress. The formation mechanism of **4** is in progress to identify.

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# NUMERICAL ANALYSIS ON THE CONVECTIVE VORTEX FLOW AND HEAT TRANSFER IN THREE-DIMENSIONAL CHANNELS

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## ABSTRACT

A numerical study is carried out to investigate the mixed convective vortex flow in three-dimensional horizontal rectangular channels. Finite volume method is employed for the discretization and PISO algorithm is used for calculating pressure term. The results are obtained for Reynolds number between  $10^{-3}$  and  $9.6 \times 10^{-2}$ , Aspect ratio from 2 to 12, Prandtl number 909. In the present study, it is found that mixed convective vortex flow can be classified into three flow patterns basically, and a new vortex flow structure containing inclined longitudinal rolls is found, which is affected by aspect ratio and Reynolds number.

## 1. INTRODUCTION

Mixed convective vortex flow in a bottom heated and top cooled horizontal rectangular channel can be significantly affected by the channel aspect ratio, Prandtl number, Reynolds number and Rayleigh numbers. The detailed understanding of the aspect ratio effect is relatively important in various technological processes such as solar energy collectors, heat exchangers, chemical vapor deposition, cooling of microelectronic equipments, and many others. Considerable research has been carried out to explore various characteristics of the buoyancy induced longitudinal vortex rolls in the mixed convective flow through a bottom heated and top cooled rectangular channel from experimental measurement [1]-[4] and numerical simulation [5]-[7] over wide ranges of the Reynolds and Rayleigh numbers covering the steady and time-dependent mixed convection for high or low aspect ratios. However, the systematic study on how the vortex flow characteristics in a bottom heated and top cooled horizontal rectangular channel are influenced by the aspect ratio was not conducted in the past. Also, most of previous studies used working fluid with low viscous fluids such as air ( $Pr=0.7$ ), nitrogen ( $Pr=0.72$ ) and water ( $Pr=6$ ). Very few results were obtained for high viscous fluid ( $Pr \geq 500$ ). In this study, three-dimensional numerical simulation was carried out to study the effects of the aspect ratio on the longitudinal vortex flow in a bottom heated and top cooled horizontal rectangular channel filled with high viscous fluid ( $Pr=909$ ). Attention was focused on the change of the longitudinal vortex flow structure with the aspect ratio ( $2 \leq A \leq 12$ ) for various Reynolds numbers ( $10^{-3} \leq Re \leq 9.6 \times 10^{-2}$ ).

## 2. NUMERICAL ANALYSIS

Under consideration was the forced flow of mean velocity  $U_{in}$  in a differentially heated rectangular channel, as schematically shown in Fig. 1. Initially at time  $t < 0$ , the flow in the channel was fully developed and at the uniform temperature,  $T_m$ . The bounding walls were insulated. At time  $t = 0$ , the bottom wall was heated to a high value  $T_h$  and the top wall was cooled to a low value  $T_c$  over a finite length  $L_0 \leq x \leq L_0 + L$  and both are maintained at these levels thereafter. In spite of this change other boundary conditions were assumed to be unaffected.

The numerical simulation was assumed to be governed by the three-dimensional Navier-stokes equations together with the following restrictions: steady state, laminar flow, constant physical properties, density variations relevant only Boussinesq approximation, negligible viscous dissipation. The corresponding set of differential equations may be written:

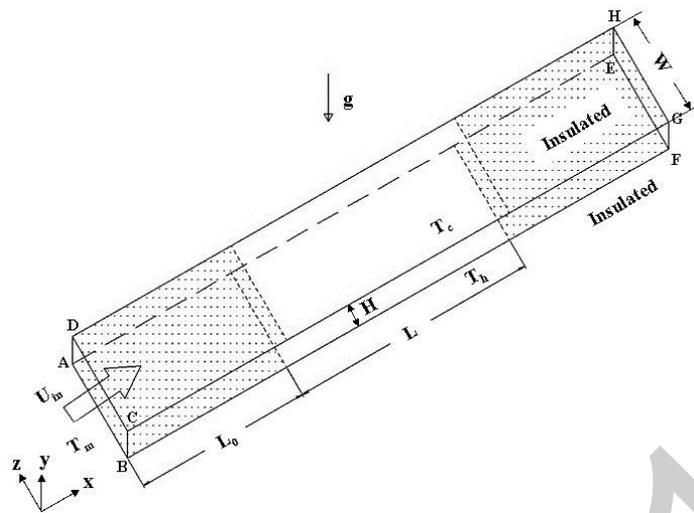


Fig.1 Schematic of the physical system

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \tag{ 1 }$$

$$\rho(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z}) + \frac{\partial p}{\partial x} = \mu(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}) \tag{ 2 }$$

$$\rho(u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z}) + \frac{\partial p}{\partial y} = \mu(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2}) + \rho g \beta \Delta T \tag{ 3 }$$

$$\rho(u \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z}) + \frac{\partial p}{\partial z} = \mu(\frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2}) \tag{ 4 }$$

$$\rho c_p (u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} + w \frac{\partial T}{\partial z}) = \lambda(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}) \tag{ 5 }$$

where  $\beta$  represents the thermal expansion coefficient,  $g$  the gravitational acceleration,  $\lambda$  the thermal diffusivity,  $\rho$  the density of fluid,  $t$  the time,  $u, v, w$  the velocity for  $x-, y-, z$ -direction,  $p$  the pressure,  $T$  the temperature,  $\Delta T$  the temperature difference between bottom and top walls,  $\mu$  the dynamic viscosity.

These equations are subject to the following initial and boundary conditions.

$$t < 0; \quad u = U_{in}, \quad v = w = 0, \quad T = T_m \tag{ 6 }$$

$$t \geq 0; \quad \begin{aligned} x=0: & \quad u = U_{in}, \quad v = w = 0, \quad T = T_m \\ y=0, L_0 \leq x \leq L_0+L: & \quad u = v = w = 0, \quad T = T_h \\ y=H, L_0 \leq x \leq L_0+L: & \quad u = v = w = 0, \quad T = T_c \\ y=0, 0 \leq x \leq L_0, x > L_0+L: & \quad u = v = w = 0, \quad \frac{\partial T}{\partial y} = 0 \\ y=H, 0 \leq x \leq L_0, x > L_0+L: & \quad u = v = w = 0, \quad \frac{\partial T}{\partial y} = 0 \\ z=0 \text{ \& \ } W: & \quad u = v = w = 0, \quad \frac{\partial T}{\partial z} = 0 \end{aligned} \tag{ 7 }$$

The governing equations were solved by the widely used commercial CFD package STAR-CD employing the PISO algorithm for the pressure correction process. For the discretization of

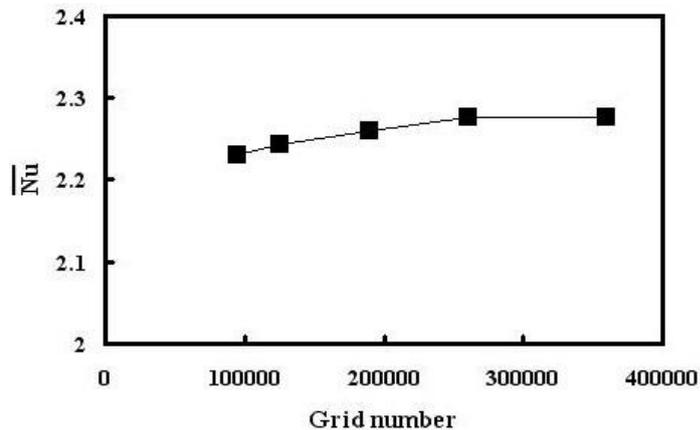


Fig. 2 Examination of grid independence of numerical solution at  $Pr=909$ ,  $A=4$ ,  $Re=2 \times 10^{-2}$ ,  $Ra=10^4$

convective-diffusive transport, the central-difference scheme was employed. Convergence was considered as being achieved when the residual values become less than  $10^{-4}$ .

To further validate the solution method, grid independence tests were conducted here. Fig. 2 shows the sample results for the case of  $Pr=909$ ,  $A=4$ ,  $Re=2 \times 10^{-2}$  and  $Ra=10^4$  using various numbers of grid. As shown in Fig. 2, when the numbers of grid were 260,000 and 360,000, the average Nusselt numbers were in error by less than 0.02635%. The numbers of grid used in this study were 260,000.

### 3. RESULTS AND DISCUSSION

In order to obtain the steady longitudinal rolls flow in horizontal rectangular channels with high viscous fluid ( $Pr=909$ ), in the present numerical simulation, the Reynolds number and aspect ratio were systematically varied over wide ranges at fixed Rayleigh number ( $Ra=10^4$ ).

Fig. 3 shows the velocity magnitude plots at the mid height of the channel ( $y=0.5$ ) for various Reynolds numbers at  $Pr=909$ ,  $A=4$  and  $Ra=10^4$ . At the very low inlet velocity relatively, with  $Re=10^{-3}$ , the vortex flow in the entire channel shows downstream moving transversal rolls flow [Fig. 3(a)]. At the higher inlet velocity, with  $Re=2 \times 10^{-3}$ , the moving transversal rolls disappear and four steady longitudinal rolls are formed in the upstream. But in the downstream, the vortex flow is still dominated by the moving transversal rolls [Fig. 3(b)]. Thus, we have mixed longitudinal/transversal vortex flow at this Reynolds number. As the inlet velocity was increased to  $Re=4 \times 10^{-3}$ , the transversal rolls completely disappear and four steady symmetric longitudinal rolls dominate the entire vortex flow [Fig. 3(c)]. Note that for an even higher inlet velocity with  $Re=1.6 \times 10^{-2}$ , the flow was still dominated by the steady symmetric longitudinal rolls in the most of the channel, but the numbers of rolls were increased to 6. Also, in the region of inlet, the flow was dominated by forced convection [Fig. 3(d)]. As the inlet velocity was increased further to  $Re=3.2 \times 10^{-2}$ , the forced convection occupy a bigger region gradually and six longitudinal rolls were still induced in the downstream [Fig. 3(e)]. As the inlet velocity was increased even further to  $Re=9.6 \times 10^{-2}$ , the effect of natural convection was completely neglected in the entire channel, the flow was only dominated by the forced convection [Fig. 3(f)].

Fig. 4 shows the velocity magnitude plots for various aspect ratios of even numbers at  $Re=4 \times 10^{-3}$ ,  $Ra=10^4$  and  $y=0.5$ . At the aspect ratio  $A \leq 6$ , the roll number is equal to the aspect ratio  $A$ . At the aspect ratio for  $A=8$ , and 12, the induced longitudinal rolls in the channel [Fig. 4 (d), (e)] resemble those for  $A=2$  given in Fig. 4(a), but, the roll number is increased to aspect ratio  $A+2$ .

Fig. 5 shows the velocity magnitude plots for various aspect ratios of even numbers at  $Re=1.6 \times 10^{-2}$ ,  $Ra=10^4$  and  $y=0.5$ . At the low aspect ratio  $A=2$  and 4, the vortex flow was dominated by the forced convection in the inlet region, and show the steady symmetric longitudinal rolls flow in the most of the channel. The roll number is increased from  $A$  to  $A+2$  with increasing Reynolds number [Fig. 5(a), (b)] as compared with Fig 4(a) and (b). At the higher aspect ratio  $A \geq 6$ , the steady longitudinal vortex flows move to the central portion of the channel in the downstream, and more rolls were formed with increasing Reynolds number [Fig. 5(c)~(e)].

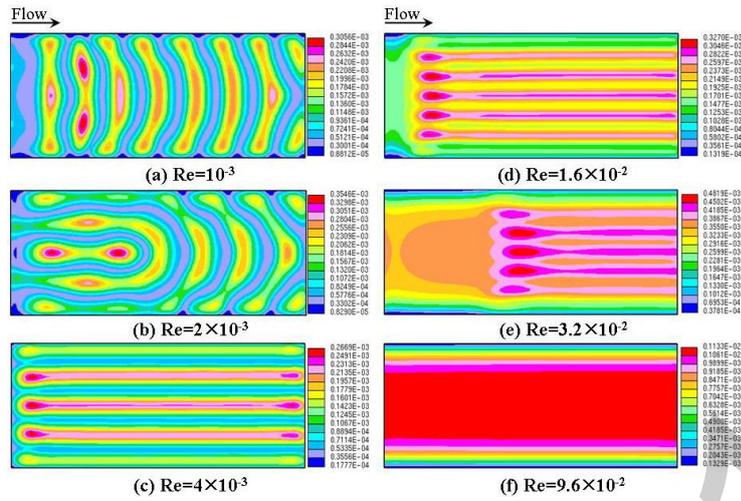


Fig. 3 Velocity magnitude plots for various Reynolds numbers at  $A=4$ ,  $Ra=10^4$ ,  $y=0.5$

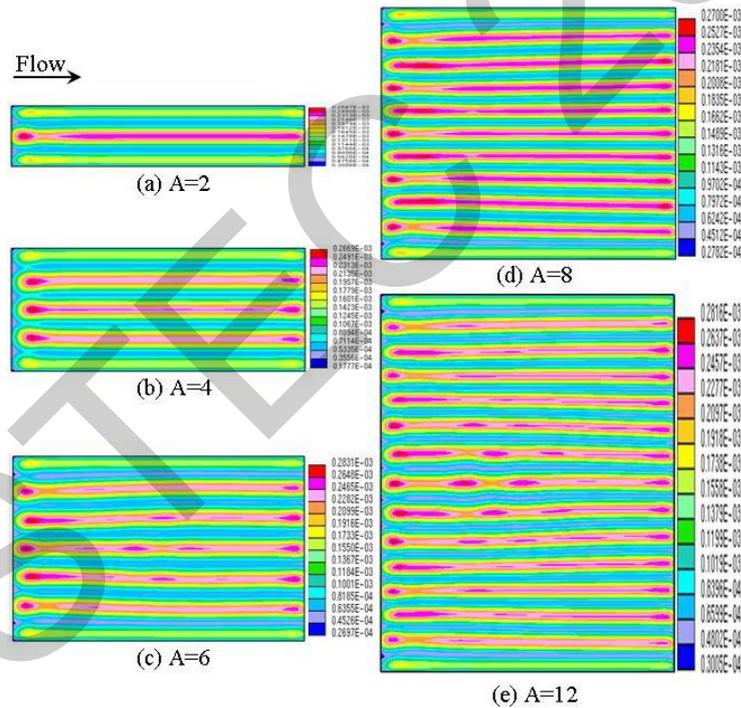


Fig. 4 Velocity magnitude plots for various aspect ratios at  $Re=4 \times 10^{-3}$ ,  $Ra=10^4$  and  $y=0.5$

Fig. 6 shows the velocity magnitude plots at the middle height in the channel for various aspect ratios of odd numbers for  $Re=4 \times 10^{-3}$ . As shown in Figure, when the aspect ratio is  $A=3$  two steady symmetric longitudinal rolls are formed [Fig. 6(a)], in case of  $A=5$  and  $7$  the numbers of roll are six and eight respectively [Fig. 6(b), (c)]. From these results, it is found that the numbers of roll induced in the channel are always even for both even and odd aspect ratios.

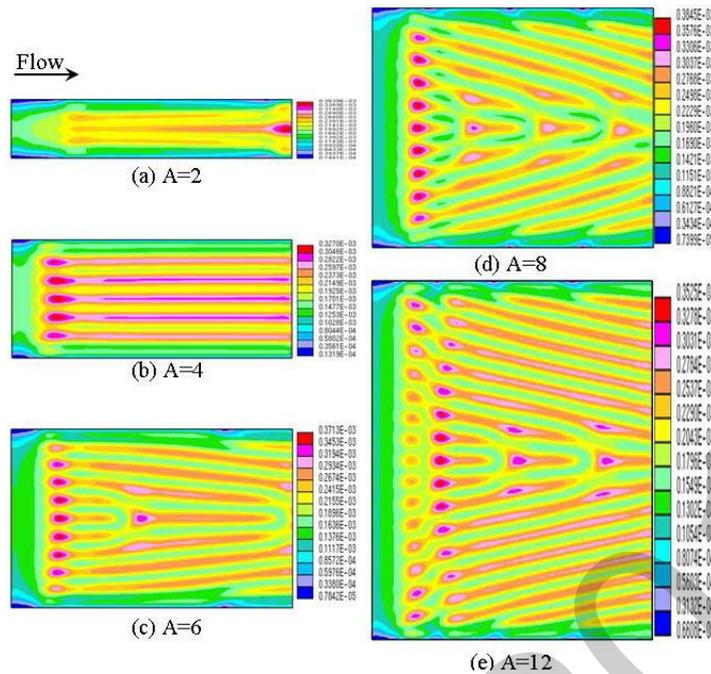


Fig. 5 Velocity magnitude plots for various aspect ratios at  $Re=1.6 \times 10^{-2}$ ,  $Ra=10^4$  and  $y=0.5$

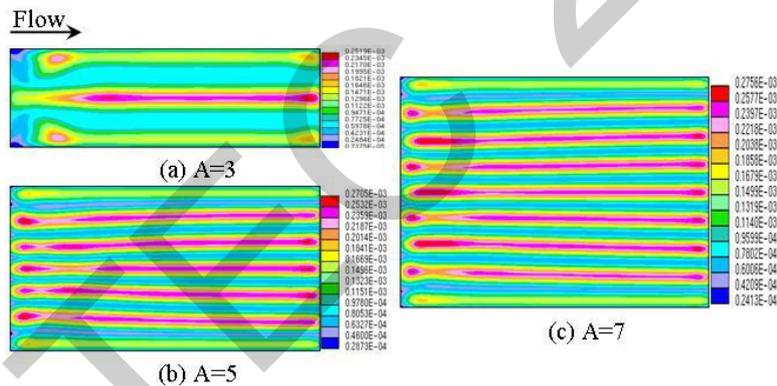


Fig. 6 Velocity magnitude plots for various aspect ratios at  $Re=4 \times 10^{-3}$ ,  $Ra=10^4$ ,  $y=0.5$

#### 4. CONCLUSIONS

Three-dimensional numerical simulation is carried out to study mixed convective vortex flow in horizontal rectangular channels with top-cooled and bottom-heated uniformly. The Prandtl number is 909, the Rayleigh number is  $10^4$ , the Reynolds number ranges from 0 to  $9.6 \times 10^{-2}$  and the aspect ratio  $A$  from 2 to 12. The following conclusions can be drawn from the present study.

- 1) Four flow patterns are obtained which affected by Reynolds numbers and aspect ratios:
  - a) The transversal rolls flow;
  - b) The mixed rolls flow;
  - c) The horizontal longitudinal rolls flow.
  - d) The inclined longitudinal rolls flow
- 2) In spite of the aspect ratio is an odd or an even number, the roll numbers induced in the channel are still even.
- 3) The roll numbers are increased with increasing aspect ratio.

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# NUMERICAL PROPERTIES OF STOCHASTIC LINEAR QUADRATIC MODEL WITH APPLICATIONS IN FINANCE

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## ABSTRACT

The aim of this paper is to consider the characteristics of the numerical equilibrium solution of the stochastic linear quadratic models (SLQ) along with possible applications in financial modelling. The purpose of this approach is to find feedback control function that maximizes the portfolio value keeping the condition that stock prices are modeled by stochastic differential equation.

Two iterations – the Newton iteration and the Lyapunov iteration for solving the generalized algebraic Riccati equation, associated with the stochastic linear-quadratic problem in an infinite time horizon are discussed. We compare these iterations with the approach based on the solution to a semidefinite programming problem. Finally, in order to demonstrate the efficiency of the proposed algorithms, computational examples are provided and numerical effectiveness of the considered algorithms is commented.

**Key Words:** Stochastic linear-quadratic control; Generalized algebraic Riccati equation; Positive definite solution; Linear matrix inequality. Portfolio optimization

## STOCHASTIC LINEAR QUADRATIC MODEL

Let us consider the following SLQ model (Yao, Zhang & Zhou, 2006):

$$\min E \int_{t_0}^{\infty} (y(t)^T Q y(t) + u(t)^T R u(t)) dt$$

$$(1) \quad dy(t) = [Ay(t) + Bu(t)]dt + \sum_{j=1}^n [C_j y(t) + D_j u(t)]dW_j(t),$$

$$y(0) = y_0.$$

In the above control problem  $Q, R, A, B, C_j$  and  $D_j$  for  $j=1, \dots, n$  are constant matrices with appropriate dimensions,  $y(\cdot)$  denotes the state variable, and  $u(\cdot)$  the control. The model is defined on a filtered probability space  $(\Omega, F, F_t, P)$  involving an  $n$ -dimensional standard Brownian motion  $W(t)$ .

The solution of the SLQ problem is related to a stochastic algebraic Riccati equation which is a result of the indefiniteness of the linear quadratic model.

Recently a computational approach to stochastic algebraic Riccati equation is developed based on a semidefinite programming problem over linear matrix inequalities (LMI). Many authors have considered a semidefinite programming problem as an unifying approach to stochastic linear quadratic problem in the absence of the positive definiteness (semidefiniteness) of the cost matrices  $R$  and  $Q$ .

The introduced model (1) can be directly related to portfolio optimization problem (Yao, Zhang & Zhou, 2006), where the control of a portfolio affects not only the average return of the portfolio but also its volatility.

Consider  $m$  listed stocks that are constituent of a market index. Assume that the price of each stock  $S_i(t)$ ,  $i = 1, 2, \dots, m$  follows the multi-dimensional GBM:

$$dS_i(t) = b_i S_i(t) dt + \sum_{j=1}^m \sigma_{ij} S_i(t) dW_j(t), \quad S_i(0) = S_{i0},$$

where  $W(t) = (W_1(t), \dots, W_m(t))^T$  is an  $m$ -dimensional standard Brownian motion (with  $t \in [0, \infty)$  and  $W(0) = 0$ ), defined on a filtered probability space  $(\Omega, F, F_t, P)$ .

Further assume that there is a risk less asset, the price of which is  $S_0(t)$ :

$$dS_0(t) = r S_0(t) dt, \quad S_0(0) = S_{00}.$$

Given a portfolio of  $n$  ( $n \leq m$ ) stocks out of the  $m$  constituent stocks, our objective is to control the investment of a given wealth initially values at  $x_0$ , among the  $n$  stocks and the bond, via dynamic asset allocation, in such a way that the performance of the investment follows as closely as possible a pre-specified, deterministic, continuously compounded growth trajectory,  $x_0 e^{\mu t}$  (where  $\mu > 0$  is a given parameter representing the growth factor) over a long time horizon. Here, the number of stocks in the portfolio  $n$  is a typically much smaller than  $m$ , the number of stocks in the market index. Thus we are

essentially dealing with a portfolio selection problem in an incomplete market. Assume that the first  $n$  of the  $m$  stocks have been selected for the portfolio.

Let  $\pi_i(t)$ ,  $i = 1, 2, \dots, n$  denote the wealth invested in stock  $i$  at time  $t$ . That is  $\pi(\cdot) = (\pi_1(t), \dots, \pi_n(t))^T$  is the composition of the stock portfolio at time  $t$ , and it is called a (continuous - time) portfolio. In control parlance,  $\pi(\cdot)$  is the control. We say the portfolio or control is admissible if  $\pi(\cdot)$  belongs to  $L^2_F(R^n)$ , the space of all  $R^n$ -valued,  $F_t$ -adapted measurable processes satisfying  $E \int_0^\infty \|\pi(t)\|^2 dt < +\infty$ .

It is well known that in a self-financed manner, the wealth process  $x(\cdot)$ , under an admissible control  $\pi(\cdot)$ , satisfies

$$(2) \quad dx(t) = [rx(t) + \sum_{i=1}^n (b_i - r)\pi_i(t)]dt + \sum_{j=1}^m \sum_{i=1}^n \sigma_{ij}\pi_i(t)dW_j(t), \quad x(0) = x_0.$$

In the control terminology  $x(\cdot)$  is the state process under the control  $\pi(\cdot)$ . Note that  $\pi_0(t) = x(t) - \sum_{i=1}^n \pi_i(t)$  is the amount invested in the bond, which is uniquely determined by  $\pi(\cdot)$  via the above equation. We define

$$b = (b_1 - r, \dots, b_n - r)^T, \quad \sigma = (\sigma_{ij})_{m \times n}, \quad \Gamma = \sigma\sigma^T.$$

Moreover, let  $\sigma_n$  denote the  $n \times m$  matrix which is identical to the matrix consisting of the first  $n$  rows of  $\sigma$ , and let  $\Gamma_n = \sigma_n\sigma_n^T$ .

The dynamics in (2) can be rewritten as follows:

$$dx(t) = [rx(t) + b^T \pi(t)]dt + \pi^T \sigma_n dW(t), \quad x(0) = x_0.$$

Our objective is

$$\min E \int_{t_0}^\infty e^{-2\rho t} [x(t) - x_0 e^{\rho t}]^2 dt,$$

where  $2\rho > 0$  is a discount factor. At this point we simply remark that  $\rho$  is introduced to guarantee the stabilizability of the control system, its actual value will have minimal impact on the result.

Applying a transformation of variables

$$y(t) = e^{-\rho t} [x(t) - x_0 e^{\rho t}], \quad \tilde{\pi}(t) = e^{-\rho t} \pi(t)$$

to turn the above control problem into the following equivalent form:

$$\min E \int_{t_0}^\infty |y(t)|^2 dt$$

subject to:

$$dy(t) = [(r - \rho)y(t) + b^T \tilde{\pi}(t) + (r - \mu)x_0 e^{(\mu - \rho)t}]dt + \tilde{\pi}(t)^T \sigma_n dW(t)$$

$$y(0) = 0.$$

The above is a control problem to minimize a quadratic cost functional, with the system dynamics being linear with a nonhomogeneous term with respect to the state and control variables. Moreover, the system dynamics are stochastic. Hence, this is a SLQ problem. In order to relate the above control problem in (1) we can follow Yao et al. (Yao, Zhang & Zhou, 2006). Yao et al. (Yao, Zhang & Zhou, 2001) have investigated the SLQ model (1) in case  $k=1$ . Further on, they have extended (Yao, Zhang & Zhou, 2006) such type models and they have proposed a new approach to tracking either a given fixed growth rate or a stochastic market index. Both problems have been formulated as SLQ models.

Consider the introduced canonical formulation (1) of the above indefinite SLQ problem. To solve the SLQ problem (1) it is necessary to solve the following Riccati equation (Yao, Zhang & Zhou, 2006):

$$(3) \quad R(X) := A^T X + XA + Q + \sum_{j=1}^n C_j^T X C_j - (XB + \sum_{j=1}^n C_j^T X D_j) [R + \sum_{j=1}^n D_j^T X D_j]^{-1} (XB + \sum_{j=1}^n C_j^T X D_j)^T = 0.$$

with the additional condition  $R + \sum_{j=1}^n D_j^T X D_j > 0$  (positive definite) for the unknown matrix  $X$ . The new equation has the inverse matrix depending on the unknown  $X$  and the additional strictly positive definiteness condition for the inverse one.

If  $\tilde{X}$  is the maximal positive definite solution of the above equation with  $R + \sum_{j=1}^n D_j^T \tilde{X} D_j > 0$ , then

$$\tilde{u}(t) = -(R + \sum_{j=1}^n D_j^T \tilde{X} D_j)^{-1} (\tilde{X} B + \sum_{j=1}^n C_j^T \tilde{X} D_j)^T \tilde{x}(t)$$

is an optimal state feedback control for (1). The optimal control  $\tilde{u}(t)$  depending on the matrix  $\tilde{X}$  which is the maximal solution to (3). There are few iterative algorithms for solving a generalized Riccati equation (3) under the assumption that R is a positive definite matrix. Very interesting the case where R is an indefinite symmetric matrix. We adapt the Newton-type algorithm for solving (3) and an algorithm that is called the Lyapunov iteration for (3) can be considered. Numerical simulations are used to demonstrate the performance of considered solvers.

Thus, following the classical linear quadratic theory we know that the following optimization problem is associated with the equation  $R(X) = 0$ , for example see Yao et al. (Rami & Zhou, 2000; Yao, Zhang & Zhou, 2006):

$$(4) \quad \begin{aligned} & \max \langle I_p, X \rangle \\ & \left( \begin{array}{cc} R + \sum_{j=1}^n D_j^T X D_j & (XB + \sum_{j=1}^n C_j^T X D_j)^T \\ XB + \sum_{j=1}^n C_j^T X D_j & Q + A^T X + XA + \sum_{j=1}^n C_j^T X C_j \end{array} \right) \succ = 0 \\ & R + \sum_{j=1}^n D_j^T X D_j \succ 0 \\ & X \succ 0, \end{aligned}$$

where  $\langle X, Y \rangle$  denotes the matrix inner-product. The above convex optimization problem is called a semidefinite programming problem. We use the existing MATLAB functions for solving the semidefinite programming problem. The solvability of  $R(X) = 0$  and the corresponding semidefinite programming problem and connections between the maximal positive definite solution to  $R(X) = 0$  and the positive definite solution to (4) are fully investigated in (Rami, Zhou & Moore, 2000; Rami & Zhou, 2000). The obtained results are related to  $R(X)=0$  where  $n=1$ . In this special case the equation  $R(X) = 0$  is solvable if and only if the LMI (4) ( $n=1$ ) with  $X \succ 0$  are feasible. We cite the following theorem (Theorem 10, Rami & Zhou, 2000) where it is claimed that if equation (3) ( $n=1$ ) has a maximal positive definite solution then it is the unique optimal solution to the related semidefinite programming problem. We can extend this conclusion to our consideration. The above conclusion stay valid in more general case, i.e. if rational matrix equation (3) with  $n>1$  has a maximal positive definite solution then it is the unique optimal solution to the related semidefinite programming problem (4). In practical, it is interesting to find the solvability margin  $r^*$  of (3). The solvability margin is defined as the largest the nonnegative scalar  $r \geq 0$  such that (3) has a solution for any symmetric matrix  $R$  with  $R \succ -r^* I$ . It is easy to extend Theorem 11 derived from Rami & Zhou (Rami & Zhou, 2000) for the equation (3) in general case ( $n>1$ ).

Theorem 1. The solvability margin  $r^*$  can be obtained by solving the following semidefinite programming problem:

$$\begin{aligned} & \min(-r) \\ & \left( \begin{array}{cc} A^T X + XA + \sum_{j=1}^n C_j^T X C_j + Q & XB + \sum_{j=1}^n C_j^T X D_j \\ (XB + \sum_{j=1}^n C_j^T X D_j)^T & \sum_{j=1}^n D_j^T X D_j - rI \end{array} \right) \succ = 0 \\ & \sum_{j=1}^n D_j^T X D_j - rI \succ 0 \\ & r > 0. \end{aligned}$$

The margin  $r^*$  (Rami & Zhou, 2000) has the properties:

If the smallest eigenvalue of  $R(\lambda_{\min}(R))$  is such that  $\lambda_{\min}(R) > -r^*$ , then (3) has a solution.

If the largest eigenvalue of  $R(\lambda_{\max}(R))$  is such that  $\lambda_{\max}(R) \leq -r^*$ , then (3) has no solution.

We have seen that the feasibility of LMIs is necessary and sufficient for the solvability of (3).

### NUMERICAL SOLUTION OF THE GENERALIZED RICCATI EQUATION

Yao et al. (Yao, Zhang & Zhou, 2006) have considered the application the LMI techniques for solving the SLQ model (1). This techniques is presented via LMI problem (4). Here we propose two recursive equations for solving equation (3). These iterations can be considered as an effective alternative to (4). First, the Newton method for solving equation (3) is considered. The Newton method to the rational matrix equation  $R(X)=0$  can be applied under the conditions that  $R(X)$  is stabilizable and that the inequality  $R(X) \geq 0$  is solvable in  $domR = \{X = X^T, R + \sum_{j=1}^n D_j^T X D_j > 0\}$ . Under these conditions,

Damm and Hinrichsen (Damm & Hinrichsen, 2001) have proved the convergence of Newton's method if the method starts at any stabilizing initial point  $X_0$ . The standard Newton-iteration for equation  $R(X) = 0$  has the following form

$$X_{i+1} = X_i - (R'_{X_i})^{-1}(R(X_i)), \quad i=0,1,2, \dots$$

where  $R'_{X_i}$  is known as the Frechet derivative of  $R(X)$  at  $X_i$ . The Newton algorithm becomes

$$(5) \quad (A + F_{X_i})^T X_{i+1} + X_{i+1}(A + F_{X_i}) + Q + F_{X_i}^T R F_{X_i} + \sum_{j=1}^n (C_j + D_j F_{X_i})^T X_{i+1} (C_j + D_j F_{X_i}) = 0,$$

where  $F_X = -(R + \sum_{j=1}^n D_j^T X D_j)^{-1} (XB + \sum_{j=1}^n C_j^T X D_j)^T$ . The following theorem is derived by Damm & Hinrichsen:

Theorem 2 (Theorem 6.1, Damm & Hinrichsen, 2001). Assume that there exist a solution  $\tilde{X} \in \text{dom}R$  to  $R(X) \geq 0$  and a stabilizing matrix  $X_0$  (i.e.  $R'_{X_0}$  has eigenvalues in the open left plane). Then the iteration scheme (5) defines a sequence  $\{X_i\}$  in  $\text{dom}R$  with the following properties:

- (i) for  $i = 1, 2, \dots$ :  $X_i \geq X_{i+1} \geq \tilde{X}$  and  $R(X_i) \leq 0$ ;
- (ii) for  $i = 0, 1, 2, \dots$ :  $R'_{X_i}$  is stable;
- (iii)  $\{X_i\}$  converges to a limit matrix  $X_\infty \in \text{dom}R$  that satisfies  $R(X_\infty) = 0$ ;
- (iv)  $X_\infty$  is the greatest solution of  $R(X) \geq 0$  and all eigenvalues of  $R'_{X_\infty}$  lie in the closed left plane.

In the last equation we replace  $X_{i+1}$  with  $X_i$  in the expression  $\sum_{j=1}^n (C_j + D_j F_{X_i})^T X_{i+1} (C_j + D_j F_{X_i})$  and we derive the new formula for the Lyapunov iteration to solve  $R(X) = 0$ , which is

$$(6) \quad (A + F_{X_i})^T X_{i+1} + X_{i+1}(A + F_{X_i}) + Q + F_{X_i}^T R F_{X_i} + \sum_{j=1}^n (C_j + D_j F_{X_i})^T X_i (C_j + D_j F_{X_i}) = 0.$$

The convergence properties of iteration (6) in case  $n=1$  is derived in the following theorem:

Theorem 3 (Theorem 2.10, Ivanov, 2007). Assume there exist Hermitian matrices  $\hat{X}$  and  $X_0$  such that  $R(\hat{X}) \geq 0$  and  $X_0 > \hat{X}$ ,  $R(X_0) < 0$  and  $A + F_{X_0}$  is stable. Then for the matrix sequence  $\{X_i\}$  defined by (6) are satisfied:

- (i)  $X_i \geq X_{i+1}$ ,  $X_i \geq \hat{X}$ ,  $R(X_i) < 0$ ,  $i = 0, 1, 2, \dots$ ;
- (ii)  $A + F_{X_i}$  is stable for  $i = 0, 1, 2, \dots$ ;
- (iii)  $\lim_{i \rightarrow \infty} X_i = \tilde{X}$  is a solution of  $R(X) = 0$  with  $\tilde{X} > \hat{X}$ . Moreover, if  $X_0 > X$  for all solutions  $X$  of  $R(X) = 0$ , then  $\tilde{X}$  is the maximal solution;
- (iv) the eigenvalues of  $A + F_{\tilde{X}}$  lie in the closed left half plane. In addition, if  $R(\hat{X}) > 0$ , then all eigenvalues of  $A + F_{\tilde{X}}$  lie in the open left half plane.

In our model of portfolio optimization the matrix  $R$  can be a negative definite or even a zero matrix. In such cases the expression  $R + \sum_{j=1}^n D_j^T X D_j$  depends on the unknown matrix  $X$  and can be singular, so  $(R + \sum_{j=1}^n D_j^T X D_j)^{-1}$  is not defined

and therefore the Newton iterations (5) and Lyapunov iterations (6) are not applicable. The only working method in such cases is the optimization problem (4), but reaching of the optimal solution is not guaranteed when  $R$  is negative definite (Rami & Zhou, 2000). Moreover in our previous works (Ivanov & Lomev, 2009), (Ivanov, Lomev & Netov, 2010) we demonstrated that methods (5) and (6) are faster when  $R$  is a positive definite matrix. Therefore if we can find a transformation of  $R(X)$  where instead of  $R$  we have new symmetric matrix  $\tilde{R}$  that is a positive definite matrix, then we might expect improvement of the numerical properties of the solution. There are many examples of such transform, for instance proposed in (Lin, Bao & Wei 1994). Let's introduce new variable  $X=Z+Y$  in (3):

$$R + \sum_{j=1}^n D_j^T X D_j = R + \sum_{j=1}^n D_j^T (Z + Y) D_j = R + \sum_{j=1}^n D_j^T Z D_j + \sum_{j=1}^n D_j^T Y D_j = \tilde{R} + \sum_{j=1}^n D_j^T Y D_j$$

The  $Z$  matrix can be selected in a way to assure that  $\tilde{R}$  is a positive definite matrix. After transformation we obtain new form of (4), where the unknown variable is  $(Y=Y^T)$ :

$$(7) \quad \begin{aligned} & \max \langle I_p, Y \rangle \\ & \left( \begin{array}{cc} \tilde{R} + \sum_{j=1}^n D_j^T Y D_j & (L^T + YB + \sum_{j=1}^n C_j^T Y D_j)^T \\ L^T + YB + \sum_{j=1}^n C_j^T Y D_j & \tilde{Q} + A^T Y + YA + \sum_{j=1}^n C_j^T Y C_j \end{array} \right) \succ= 0 \\ & \tilde{R} + \sum_{j=1}^n D_j^T Y D_j > 0 \end{aligned}$$

where  $\tilde{Q} = A^T Z + ZA + Q + \sum_{j=1}^n C_j^T Z C_j$  and  $L = B^T Z + \sum_{j=1}^n D_j^T Z C_j$ .

**NUMERICAL SIMULATIONS**

Our experiments are executed in MATLAB on 2,16GHz PENTIUM(R) Dual CPU computer. We denote tol - a small positive real number denoting the accuracy of computation,  $E_s = \|R(X_s)\|_2$ , It - number of iterations for which the inequality  $E_t \leq tol$ . The last inequality is used as a practical stopping criterion.

The coefficients of (3) will be generated as a pseudo-random numbers. All experiments will be carried out with negative definite matrix R and for different values of the dimension parameter p we shall generate series of 100 simulations. For each of the series the maximum number of iterations (mIt) and the average number of iterations (avIt) for finding of the solution are calculated. The details of the test simulation are :

$R = \text{diag} [-0.001, -0.5]$ ,  $q=2$ ;  $A = \text{randn}(p,p)/100 - 0.5 I_p$ ,  $B = 2 \text{randn}(p,2)$ ,  $C_j = \text{randn}(p,p)/10$ ;  $D_j = 2 \text{randn}(p,2)$ ;  
The selected transformation is:  $Z = 0.4 I_2$ . The results are presented in the following table:

Table 1: Maximum and average number of iterations for simulated 100 cases

	<b>LMI(4):</b>		<b>NI (5):</b>		<b>LI (6):</b>		<b>LMI(7):</b>	
<b>p</b>	<b>m It</b>	<b>av It</b>	<b>m It</b>	<b>av It</b>	<b>m It</b>	<b>Av It</b>	<b>m It</b>	<b>av It</b>
10	55	39.3	6	4.1	20	14.6	31	26.7
12	54	41.7	6	4.2	21	14.6	31	25.7
15	68	57.3	6	4.2	22	15.8	27	27.2
The total time for solving of 100 cases (in seconds)								
15	111.42		4.93		1.79		40.46	
20	320.46		118.06		20.4		118.46	

**CONCLUSION**

The obtained results confirm that the introduction of new variable leads to substantial improvement of LMI method. Again the Lyapunov approach (6) is the fastest method.

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# NUMERICAL STUDY ON THE HEAT TRANSFER CHARACTERISTICS AT THE MASTER JOINT IN AN ONDOL HEATING SYSTEM

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## ABSTRACT

Ondol is a traditional heating system in Korea. Nowadays, hot water floor heating systems have been used as ondol systems to improve the thermal comfort, convenient maintenance and energy efficiency. In a floor heating system using thermosiphons, the shape of the master joint plays an important role in heat transfer of this system. Numerical simulations were carried out to find out the flow patterns and temperature distributions in the present master joint. New master joint is proposed in this paper to increase the performance of the floor heating system and flow patterns and temperature distributions for both models are compared.

## 1. INTRODUCTION

A traditional Korean heating system<sup>1, 2)</sup> is an ondol, floor heating system, shown in Fig 1(a). Hot water flowing in the pipes under floors is used to heat the floors of living rooms, bed rooms, etc. These days, new system using heat pipes<sup>3,4)</sup> or thermal siphons is applied to the floor heating system. The schematic diagram of this system is shown in Fig. 1(b). It consists of pipes where water flows, heat pipes or thermal siphon, and master joint where thermal energy of water is transferred to the heat pipes of thermal siphons.

Fig. 2 shows the present master joint used for the floor heating system. The shape of master joint plays an important role in heat transfer in this system. To see the flow patterns and temperature distributions in this conventional present master joint, numerical simulations were carried out. After several trials and errors, a new master joint, which was shown in Fig. 3, was proposed to increase the performance of the floor heating system and flow patterns and temperature distributions are compared with the ones for the conventional master joint.

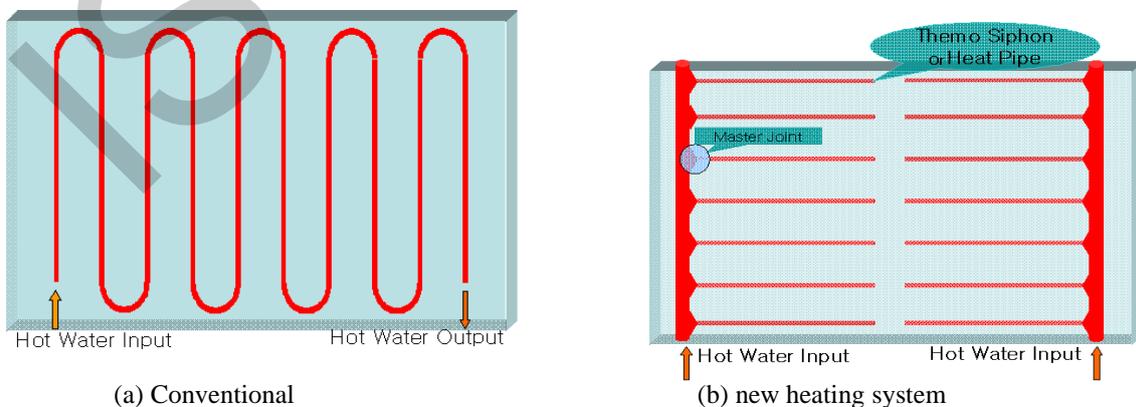


Fig. 1 Conventional and new floor heating system with thermo siphon or heat pipe

## 2. NUMERICAL SIMULATIONS

Numerical simulations were carried out to see the flow patterns, pressure distributions, and temperature distribution for two different master joints, a present master joint and a new master joint. The grids for the two master joints used in this numerical simulation are shown in Fig. 2. The diameter of main hot water pipe is 17.5mm and other dimensions are shown in the figure.

Total pressures were given at the inlet of main pipe and static atmospheric pressures were given at the outlet of main pipe. For temperature boundary conditions,  $80^{\circ}\text{C}$  for hot water is used at the inlet and adiabatic conditions are used at walls of master joint and isothermal conditions of  $54^{\circ}\text{C}$  for heat pipe walls are used in the numerical simulations.

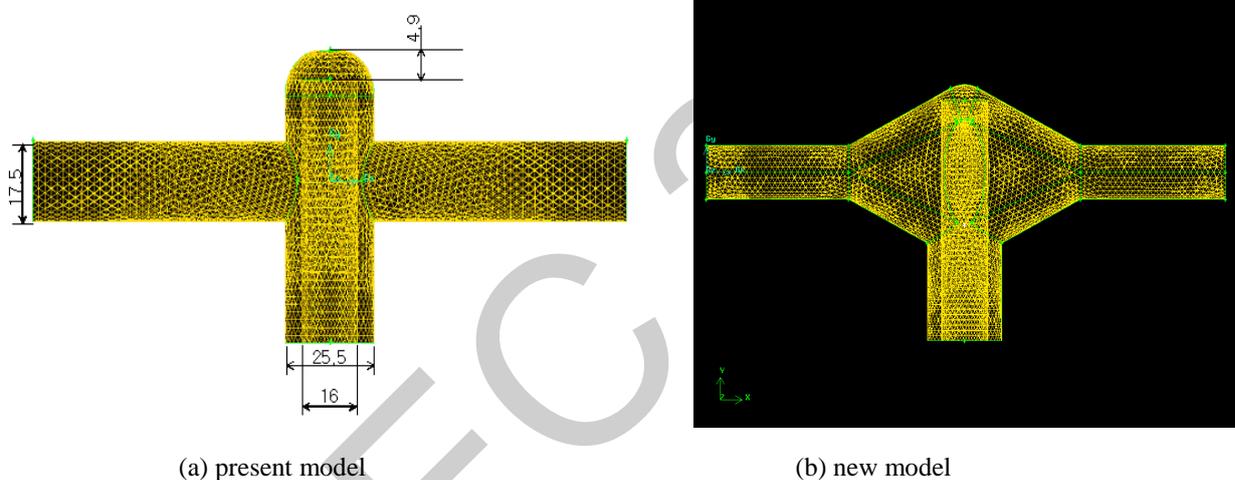
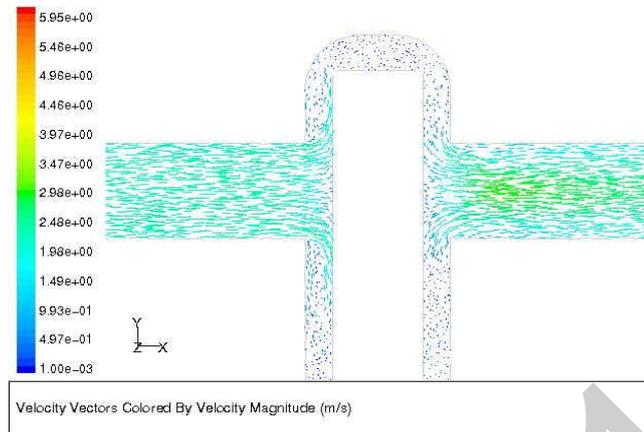


Fig. 2 Grids for numerical analysis

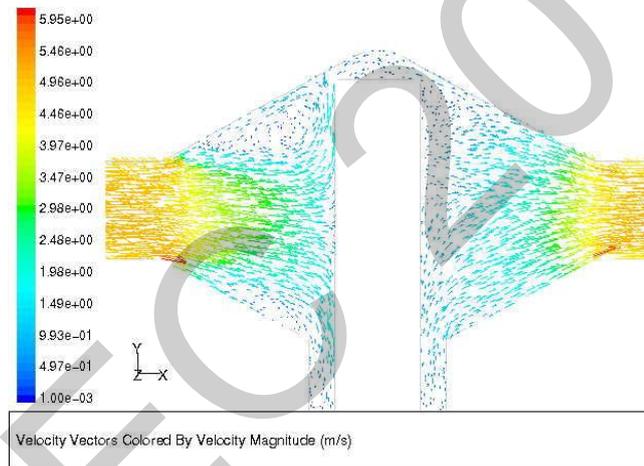
Fig. 3 shows velocity vectors at the central vertical sections of two master joint models, for the same inlet total gage pressure of 80kPa. As shown in Fig 3(a), the velocities at upper and lower part of the master joint are very small, while velocities only at center part of master are relatively large for the present model. Fig. 3 clearly shows the velocities for the new model are generally larger than those for the present model. Although separated flows are also observed for the new model, velocities are very large over the wide area of the master joint. Hence, the flow rate for the new model is generally larger than the flow rate for the present model for the same total inlet pressure, which can enhance heat transfer to the heat pipe of thermal siphon. Fig. 4 shows velocity vectors near the heat pipe at the central horizontal sections of the heating system, for the same inlet total gage pressure of 80kPa. As shown in Fig 4, the velocity around the heat pipe is very large due to the small passing area.

Fig. 5 shows temperature fields at the central vertical sections of two master joint models, for the same inlet total gage pressure of 80kPa. As shown in Fig 5(a) and 5(b), the heat pipe in the new model can contact more high temperature water than the pipe in the present model, hence the amount of heat transferred from the hot

water to the heat pipe for the new model is increased.

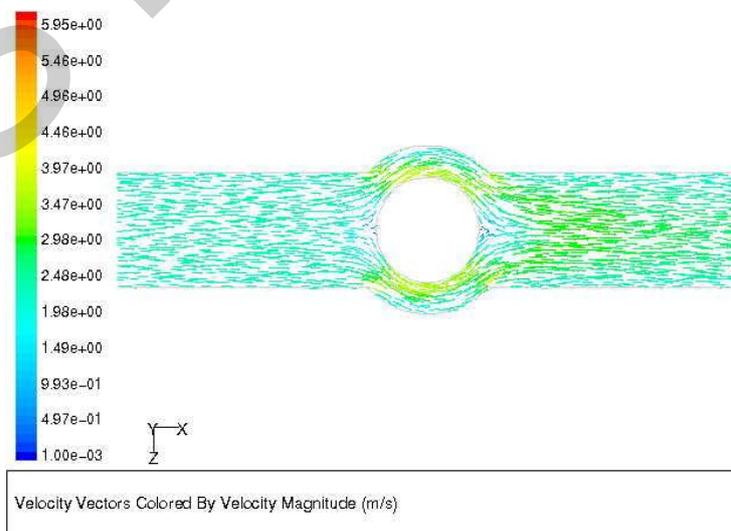


(a) present model

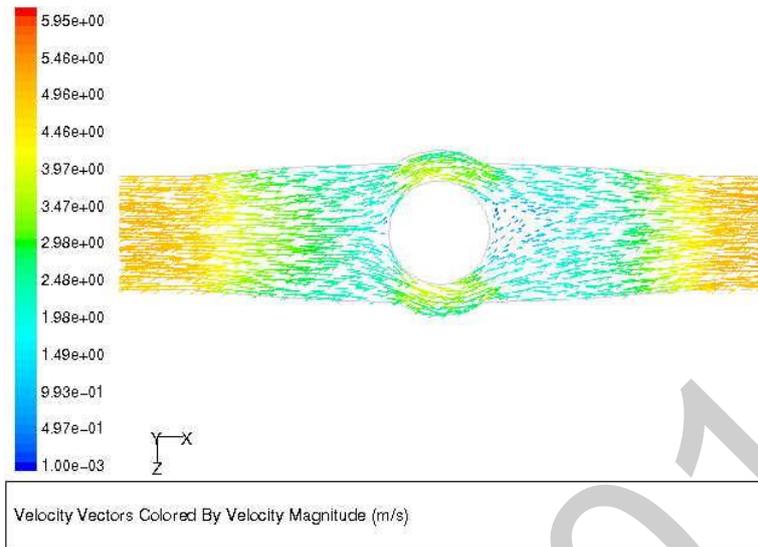


(b) new model

Fig. 3. Velocity vectors at the central vertical sections of two master joint.

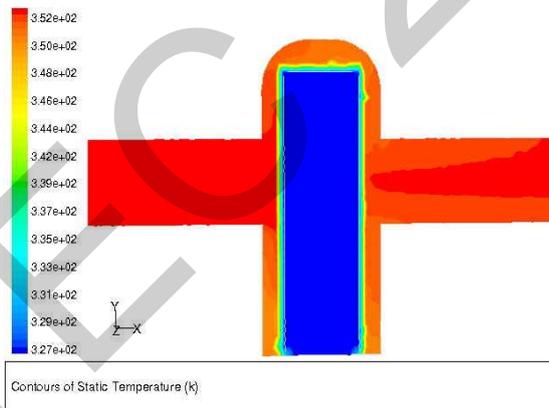


(a) present model

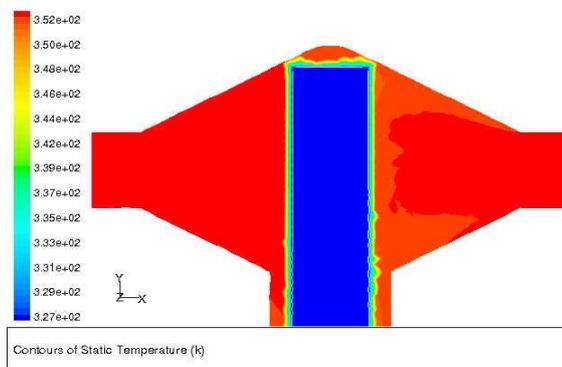


(b) new model

Fig. 4 Velocity vectors at the central horizontal sections of two master joint.



(a) at the central vertical sections, present model



(b) at the central vertical sections, new model

Fig. 5 Temperature fields at two master joint models (inlet total gage pressure : 80kPa)

Fig. 6 and Fig. 7 summarize the results calculated in the simulations. For a given pressure difference, the flow rate at the new model is much larger than the flow rate at the present model, as shown in Fig. 6. The heat transfer rate to the heat pipe at the new model is much larger than the heat transfer rate at the present model, for a given pressure difference, as shown in Fig. 7. Thus, we can conclude the new model enhances the performance of the master joint.

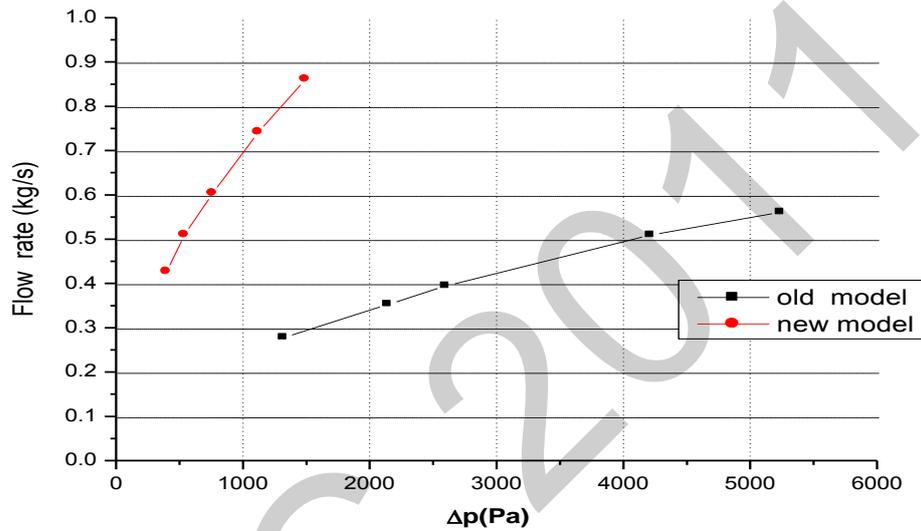


Fig. 6 Comparison of flow rates at the two master joint models

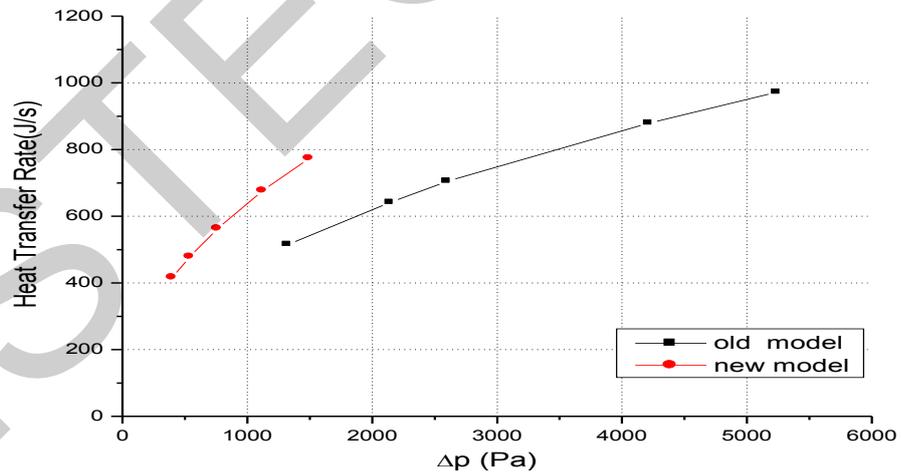


Fig. 7 Comparison of heat transfer rate at the two master joint models

### 3. CONCLUSION

A new floor heating system using heat pipes or thermal siphons was presented and discussed. Flow

characteristics and temperature distributions for several main pipe diameters are shown and discussed to see the effect of main pipe diameter. New master joint is proposed in this paper to increase the performance of the floor heating system and flow patterns and temperature distributions for both models are compared.

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# OIL PALM LEAVES EXTRACT IMPROVED THE MEMORY AND COGNITION OF ESTROGEN-DEFICIENT RATS

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## ABSTRACT

Estrogen deficiency in females (postmenopausal) often leads to decrease in memory and other cognitive functions. Catechins-rich green tea reportedly improves cognition. This study aims to evaluate the in vivo cognitive effects of phytoestrogenic oil palm leaves extract (OPL) in estrogen-deficient ovariectomized female rats as compared to green tea. The Sprague Dawley rats fed on normal rat chow, were divided into five experimental groups: (1) normal rats (control N); (2) ovariectomized rats (OVX control); and OVX rats supplemented with either (3) green tea (2.0% w/v); (4) 150 mg OPL/kg body weight (BW); or (5) 300 mg OPL /kg BW in the drinking water. Memory and cognitive functions were measured by the time taken to reach the hidden platform in the Morris Water Maze (MWM) test. The OVX control rats took the longest time, while the green tea rats took the shortest time compared to the other rats. Results showed that the phytoestrogenic OPL dose dependently improved the memory and cognition of estrogen deficient rats throughout the 3 months study period.

**Keywords:** Oil palm leaves; Water maze; Ovariectomy; Learning; Memory

## Introduction

The dramatic reduction in estrogen and progesterone levels at menopause may contribute to the accelerated cognitive decline observed in older women (Anderson, Fincham, Qin, & Stocco, 2008). There are a large number of studies, which report that the long-term consumption of catechins of in green tea would reduce the free radicals levels and hippocampal level of lipid peroxide (Nanjo et al., 1996; Nanjo, Mori, Goto, & Hara, 1999). On the other hand, several research studies also demonstrate that the oil palm leaf (OPL) is a major waste in industry (Rosalina Tan, Mohamed, Samaneh, Noordin, Goh, & Manap, 2011a). However, there is little or no knowledge on the antioxidant properties of OPL that can prevent oxidative stress in the brain and help improving cognitive function. Thus, this study reports an evaluation of the different concentrations of OPL extracts compared with GT in prevent oxidative stress in the brain and improve cognitive function in Sprague-Dawley rats.

## Materials and methods

- Female (Sprague-Dawley rats )fed with standard diet (2 weeks)
- Assigned randomly into different (5) groups
- 1- Control groups
  - a- Normal (N) without ovariectomy
  - b- Ovariectomy (OVX)
  - c- Green tea (G) (2% W/V)
- 2- Treatment groups
  - a- Oil palm leaves feed with high 300g/kg
  - b- Oil palm leaves feed with 150g/kg
- Perform ovariectomy for group (1)
- Return to the housing for 1 week
- Behavior test Morris Water maze
- Made an ovariectomy for oil palm leaf groups and green tea group
- Behavior test (Morris water maze)
- Feeding for 4 weeks
- At the end of the third month behavior test will be also carried out

Result

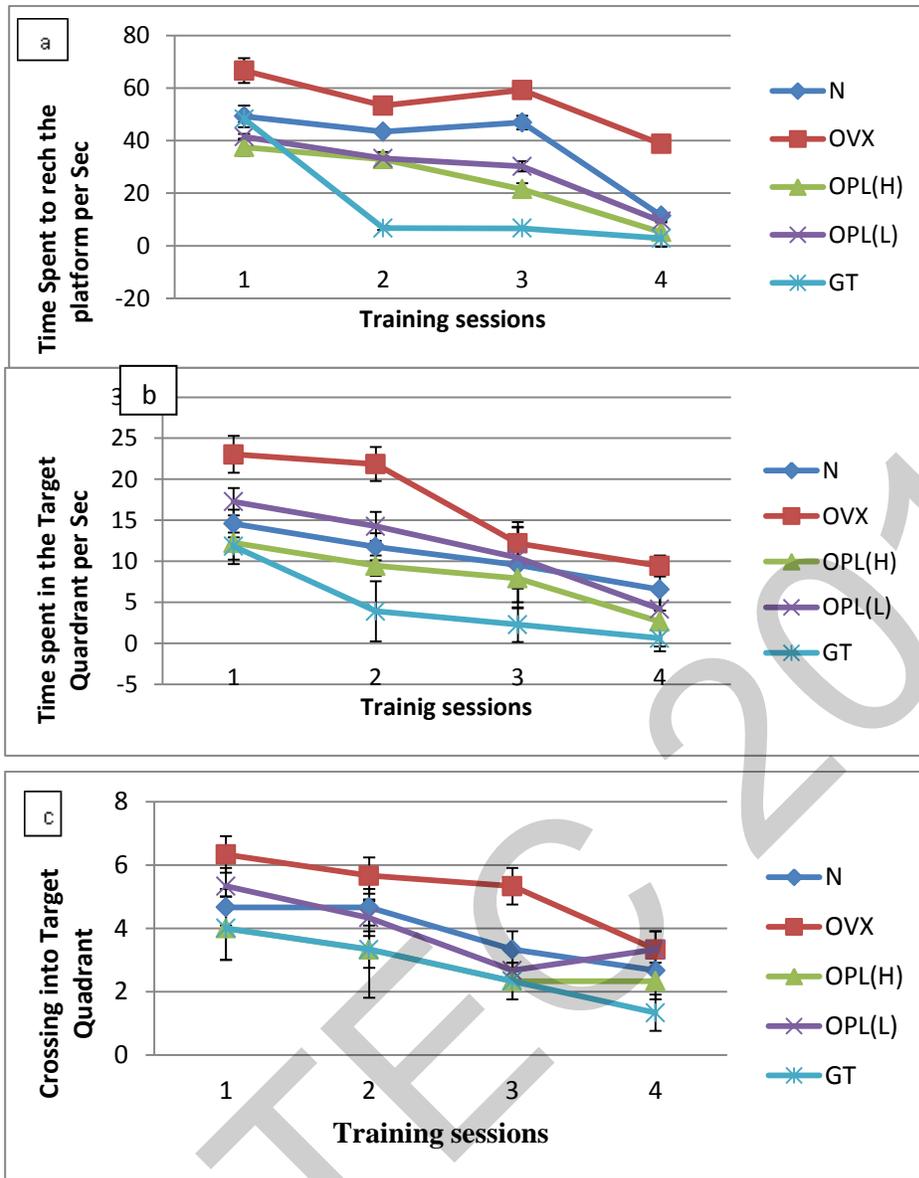


Figure1: Morris Water Maze (MWM) test after one month feeding. Normal Control (N), ovariectomy (OVX), and GT (2.0% w/v) considered as control groups. OPL with high (H) 300mg OPL/kg body weight (B/W) and low (L) 150 mg OPL/ kg (B/W) considered as treatment groups. (A) Time spent to reach platform per sec (speed); (B) Time spent in the target quadrant per sec (learning) (C) Crossing to target quadrant (processing). Values are the means± standard deviation of three replications.

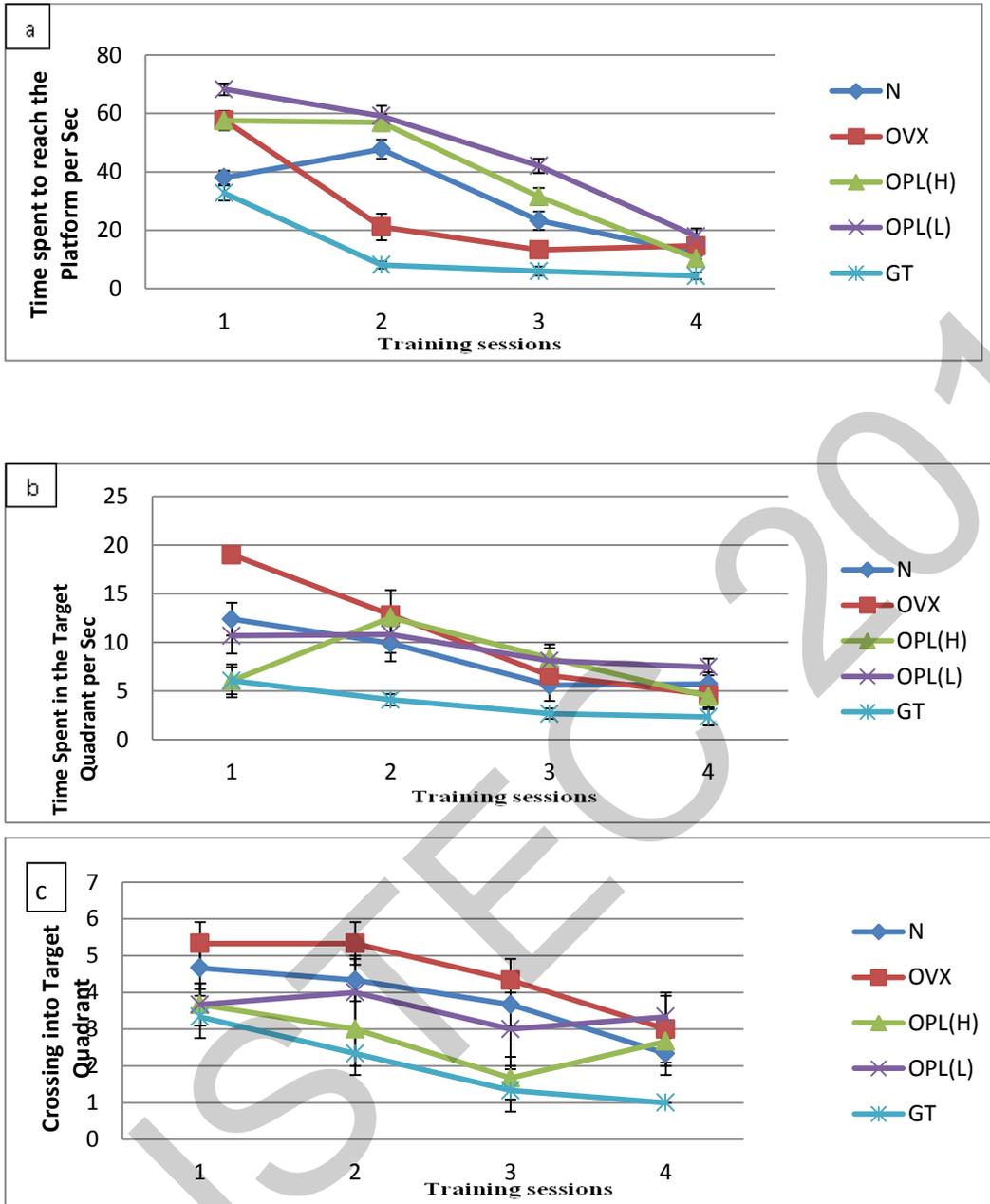


Figure 2: Morris Water Maze (MWM) test performance after three months to see the improvement in cognitive function of feeding with the treatment of oil palm leaves (OPL) and green tea (GT). Normal Control (N), ovariectomy (OVX), and GT (2.0% w/v) considered as control groups. OPL in high (H) 300mg OPL/kg body weight (B/W) and low (L) 150 mg OPL/ kg (B/W) considered as treatment groups. (A) Time spent to reach platform per sec (speed); (B) Time spent in the target quadrant per sec (learning) (C) Crossing to target quadrant (processing). Values are the means± standard deviation of three replications.

### Conclusion

The findings from this study support the hypothesis that the GT group affected the strategy during the performance of cognitive even than N group meanwhile, OPL had improvement before ovariectomy and had loss of CA1 synapses area after ovariectomy which affects the long term memory (LTM) but it showed better performance compared to OVX. This specifically suggests that the GT group had better thinking, expression, learning, and memory to reach the platform.

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# OPTIMIZATION STUDIES ON THE PERFORMANCE OF A HIGH TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELL

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## Abstract

High temperature polymer electrolyte membrane fuel cells (PEMFC) operating between 120-180 °C are currently of much research attention. The acid doped polybenzimidazole (PBI) membranes electrolyte are known for their tolerant to relatively high levels of carbon monoxide impurity in the feed. This study focussed on modelling the electrochemical behaviour of a high temperature PEMFC. A zero dimensional model was developed to express the cell voltage as a function of current density among others. Experimental results obtained from a test station were used to validate and improve on the models. The validated models were employed for the simulation of the stack performance in Engineering Equations Solver (EES) environment to investigate the effects of temperature, pressure, anode stoichiometry and the level of CO impurity in the synthesis gas, on the cell potential and overall performance. Good agreement was obtained from the simulation results and experimental data. The results showed that increasing temperature (up to 180°C) and acid doping level have positive effects on the cell performance. The results also show that the cell can operate with a reformat gas containing up to 2% CO without significant loss of cell voltage at elevated temperatures.

## 1. Introduction

A polymer electrolyte membrane fuel cell (PEMFC), also known as proton exchange membrane fuel cells, transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical (and heat) energy. PEMFC distinguishing features include wide operating temperature/pressure, high power density and low sensitivity to orientation. It uses solid polymer as an electrolyte and porous carbon electrodes containing platinum catalyst. PEMFC operates over a relatively wide temperature range, around 80°C - 200°C. The low temperature PEMFC operates between 30 °C - 80 °C and the high temperature PEM between 120 °C - 200 °C. The choice of the operating temperature depends on the purity of hydrogen and the desired durability of the stack (Andreasen and Koer, 2008). Low temperature operation allows quick start-up and results in less wear on system components, resulting in better durability. But it is more susceptible to CO poisoning and also poor heat recovery. At temperatures between above 120°C, better heat is recoverable and also better tolerance to CO content.

Membranes for high temperature operations are based on polybenzimidazole (PBI) doped with phosphoric acid and can operate at temperatures up to 220°C needing no humidification. However, an optimal operating temperature is around 160°C to prevent acid leaching (Sousa *et al.*, 2010). The high temperatures eliminate the problem of water management (Jiao and Li, 2010) and also allows for higher power densities, ease of cooling, reduced sensitivity to CO monoxide poisoning and better controllability. At the heart of the fuel cell is a solid (polymer) electrolyte sandwiched between two porous electrodes, a negative electrode (anode) and a positive electrode (cathode). The combination of the three layers (including the catalyst layer typically fused with the electrodes) is called the membrane electrode assembly (MEA). The electrochemical reactions occur on the catalyst layer surface. The MEA is sandwiched between two current collector plates for single cell configuration or between bipolar plates for multi-cell configurations. Figure 1 present the schematics of the typical operation of a PEM fuel cell.

In fuel cell systems there are multiple complex phenomena occurring. It would be quite costly and time consuming to experimentally investigate each parameter independently or all in combinations. Modelling can be an important research tool to study this. With a model, a better understanding of the fuel cells performance can be rapidly obtained. Fewer publications have been reported on modelling of PBI based PEMFC compared to the work published on Nafion® based PEMFC. The majority of the modelling studies on PBI-based HTPEM employed either 2-dimensional approach (Cheddie and Monroe, 2007; Sousa *et al.*, 2010) or 3-dimensional techniques (Jiao and Li, 2010; Bergmann *et al.*, 2010). These are theoretical and complex models that require heavy programming and computational platforms. The models presented by (Cheddie and Munroe, 2006) and Scott *et al.* (2007) are simple but are limited to prediction of conductivity at various stack temperatures. In this paper, the work of Scott *et al.* (2007) was extended to include the effects of acid doping and catalyst loading level on the cell performance. The purpose of the study is to develop models that will describe steady state operation of a single fuel cell. The validated models were used to investigate the dependence of the cell performance on different parameters. The effects of catalyst loading, acid doping level, fuel CO content and the operating temperature were reported.

## 2. Models Formulation

This paper used a one-dimensional model that focuses on the kinetics instead of transport phenomena inside the MEA. This approach is chosen because of its simplicity for implementation on Engineering Equation Solver (EES) modelling platform. The model framework is based on the isothermal model developed by Mumlouk and Scott (2007). In the model, the hydrogen oxidation and oxygen reduction reaction kinetics are expressed using Butler-Volmer equations, which allows for analysis of cell performance for different electrochemical surface area and catalyst loadings. The approach of Cheddie and Munroe (2007) using species solubility in phosphoric acid is used to predict the membrane conductivity activity. The model is

developed to calculate the cell voltage. In doing so, expressions to determine the electrode overpotentials (activation and ohmic) are presented.

### 2.1 Electrochemical Reaction Kinetics

The reactions occurring in a fuel cell is an exothermic reaction which means heat is liberated during the reaction. The heat produced is what makes fuel cells attractive for combined heat and power production. The reactions occur in two separate half reactions that take place simultaneously at the anode and cathode. The hydrogen fed continuously to the anode side of the MEA undergoes protonation assisted by the platinum catalyst layer. The anode-half reaction is called the hydrogen oxidation reaction (HOR) and is expressed as:



The protons permeate through the membrane to the cathode side while the electrons travel along an external load circuit, thus creating the current output of the fuel cell. At the cathode, oxygen (pure or in air) react with the protons to form water molecules. The cathode half reaction is called the oxygen reduction reaction (ORR):



The activation polarization at the cathode is expressed using the Butler-Volmer equation:

$$j = j_{o,c} \left[ \exp\left(-\frac{\alpha_{Rd,n}F}{RT}\eta_c\right) - \exp\left(-\frac{\alpha_{Ox,c}nF}{RT}\eta_c\right) \right] \quad (3)$$

where  $j$  represents the current density,  $j_{o,c}$  the cathode exchange current density,  $\alpha$  is the oxidation and reduction transfer coefficients and  $\eta_c$  is the cathode activation polarization.

The exchange current density is a function of catalyst layer parameters and is expressed as:

$$j_{o,c} = i_o^{ref} a_c L_c \left(\frac{C_{O_2}}{C_{O_2}^{ref}}\right)^\gamma \exp\left[-\frac{E_c}{RT}\left(1 - \frac{T}{T_{ref}}\right)\right] \quad (4)$$

where  $E_c$  is the activation energy,  $\gamma$  the reaction order.  $i_o^{ref}$  is the reference exchange current density measured at reference oxygen concentration on the catalyst surface  $C_{O_2}^{ref}$  and reference temperature  $T_{ref}$ .  $a_c$  is the catalyst specific area and  $L_c$  is the catalyst loading.

By assuming symmetry ( $\alpha_{Rd,c} = \alpha_{Ox,c}$ ) the Butler-Volmer equation can be expressed as:

$$j = 2j_{o,c} \sinh\left[\frac{anF}{2RT}\eta_c\right] \quad (5)$$

By rearranging equation 5 results in an expression for the cathode electrode polarization

$$\eta_c = \frac{RT}{anF} \sinh^{-1}\left[\frac{j}{j_{o,c}}\right] \quad (6)$$

Taking the natural logarithm results in a final expression for the electrode polarization

$$\eta_c = -\frac{RT}{anF} \ln\left[\frac{j}{j_{o,c}} + \sqrt{1 + \left(\frac{j}{j_{o,c}}\right)^2}\right] \quad (7)$$

Equation 3 through 7 also applied to the anode, with subscript  $c$  becoming  $a$ .

### 2.2 Ohmic losses

The proton conduction in the acid doped PBI membranes is a strong function of the acid doping level (X). The structure of PBI membrane allows for maximum doping level of X = 2, after which there would be an excess acid in the membrane (Ma *et al.*, 2004). The doping level dependence on the concentration of the acid is expressed by (Cheddie and Munroe, 2007) as:

$$X = 0.012M^3 - 0.211M^2 + 1.2363M + 0.7199 \quad (8)$$

where  $M$  is the acid concentration.

In this work the conductivity is considered to be a function of temperature and acid doping level. The expression to give the conductivity of the membrane is given by (Cheddie and Munroe, 2007) thus:

$$k = \frac{100}{T} \exp\left[8.0219 - \left(\frac{2605.6 - 70.1X}{T}\right)\right] \quad (9)$$

The final expression for ohmic polarization is:

$$\eta_{ohmic} = l j \left(\frac{1}{k^{eff}} + \frac{1}{k_a^{eff}} + \frac{1}{k_c^{eff}}\right) \quad (10)$$

where  $k_t^{eff}$  represents the effective conductivity in the anode catalyst layer and cathode catalyst layer respectively and  $k$  is the effective conductivity of the membrane.

**2.3 Reformate fuel**

Bose *et al.* (2011) studied the effect of CO poisoning on the hydrogen electrode and suggested the following equation to account for the exchange current density:

$$j_o^{CO} = j_{o,a} (1 - \theta_{CO})^2 \tag{11}$$

where  $j_o^{CO}$  is the exchange current density after CO poisoning,  $j_{o,a}$  is the current density without CO poisoning calculated using equation 17 and  $\theta_{CO}$  is the CO surface coverage.

Dhar *et al.* (1986) proposed  $\theta_{CO}$  relation to temperature as:

$$\theta_{CO} = 19.9 \exp(-7.69E - 3T) - 0.085 \ln \left[ \frac{CO}{H_2} \right] \tag{12}$$

**3 Results and Discussion**

Before the model was used for parametric analysis, simulations of the one dimensional model for base case parameters were done. The resulting simulation results were compared with experimental data reported by Sousa *et al.* (2010) (Figure 2). The deviation of model results from the experimental is visible in the two overpotential (OP) regions. The first deviation is observed in the activation OP region of the polarisation curve; therefore the parameters in this region need to be optimised to get good agreement. It is well known that the limiting reaction is the cathode oxidation reduction reaction as the anode hydrogen reaction proceeds fast over a Pt-catalyst (Iranzo *et al.* 2010). For this reason the cathode activation parameters were chosen to be optimised. The activation OP was observed to be sensitive to two parameters; the activation energy and the reference exchange current density, and for this reason the two are chosen to be optimised. The second deviation of model from experimental is observed in the slope of the ohmic over-potential region. Similarly to the activation OP region, parameters that affect the ohmic OP were chosen to be optimised. Figure 3 shows the model and experimental results after the model was optimised and a good fit can be observed.

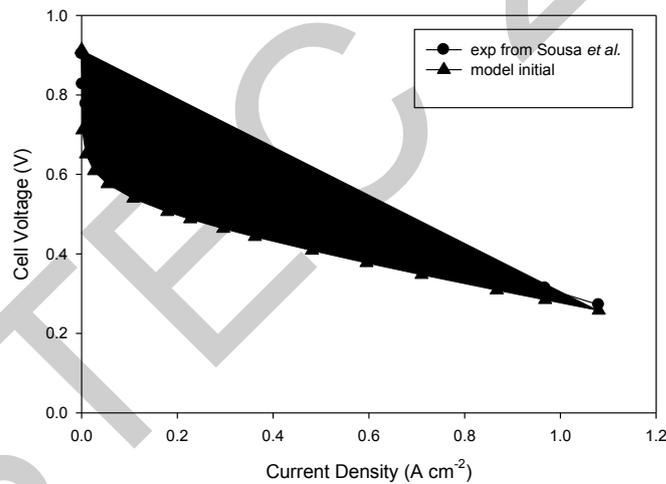


Figure 2: Polarization Curve - Model predictions and experimental data at 150 °C

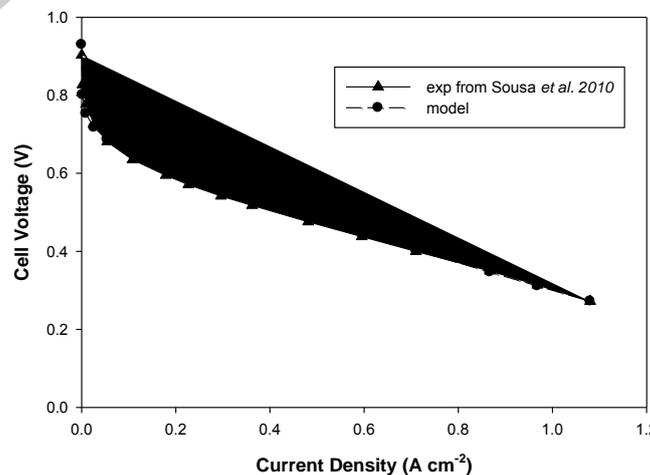


Figure 3: Comparison between model predictions and experimental data at 150 °C

### 3.1 Temperature Effects

Figure 4 shows the simulation results at three different operating temperatures (135 °C, 150 °C and 175 °C). O<sub>2</sub> and H<sub>2</sub> stoichiometric ratios of 2 and 1.25 respectively were used. The model showed that increasing the operating temperature results in increased performance. The reaction kinetics is enhanced due to improved reactant solubility and diffusivity that results in increased concentration of the reactant on the catalyst surface, therefore speeding up the rate of the reaction (Jiao and Li, 2010; Chen and Lai, 2010). Secondly the increased temperature results in increased membrane conductivity, which promotes faster electron transfer. Similar observations have been reported by (Ubong *et al.*, 2009; Jiao and Li, 2010).

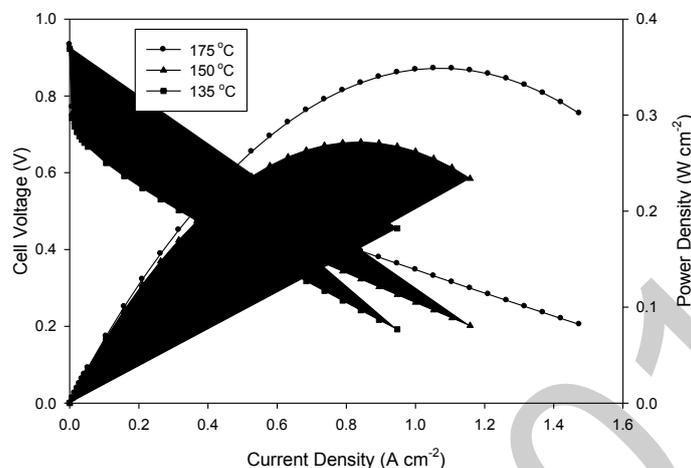


Figure 4: Temperature dependency of polarisation curve (with pure hydrogen and air)

### 3.2 Acid Doping Level

The performance curves at different acid doping levels of the membrane are shown in Figure 5. The results indicate that increasing phosphoric acid doping level of PBI membranes has significant improvements on the cell performance (Mamlouk and Scott, 2010). The increase performance is due to increased reactant activity as a result of excess acid in the electrolyte. The excess acid improves the membrane conductivity and the solubility of reactants. However, too much acid will result in poor mechanical properties and poor performance (Liu *et al.*, 2004; Ma *et al.*, 2004).

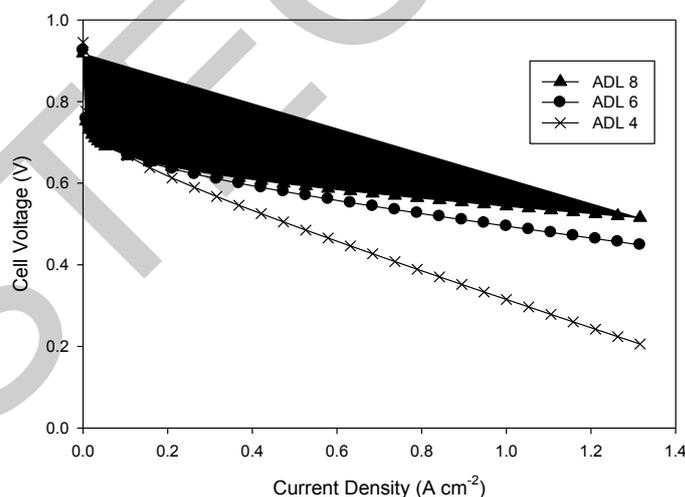


Figure 5: Effects of phosphoric acid doping level on the cell performance

### 3.3 Catalyst loading

The effect of platinum loading is shown in Figure 6 and 7. It was observed that when both the anode and cathode catalyst loadings were decreased, the cell performance also decreased due to the increase in activation polarization caused by decrease in rate of reaction or catalytic activity (Cho *et al.*, 2007). For the cathode, decreasing the catalyst loading from 0.2 to 0.025 mg/cm<sup>2</sup> resulted in a drop in voltage of 2.5 mV at a current density of 1 A/cm<sup>2</sup>, which is a same order of magnitude as values reported by Gasteiger *et al.* (2004) and Cho *et al.* (2007).

### 3.4 Effect of CO content

The influence of CO at different operating temperatures is shown in Figure 7. 2% CO is added to the hydrogen feed gas. The decreased performance is due to CO adsorption on the catalyst active sites, thus blocking sites that would be otherwise available for hydrogen protonation (Das *et al.*, 2009). The worse performance at low temperatures compared to high temperatures is

because of high energy of adsorption of CO on the platinum surface (Modestov *et al.*, 2010). High temperature reduces CO adsorption whilst it does not affect the hydrogen adsorption on the catalyst surface.

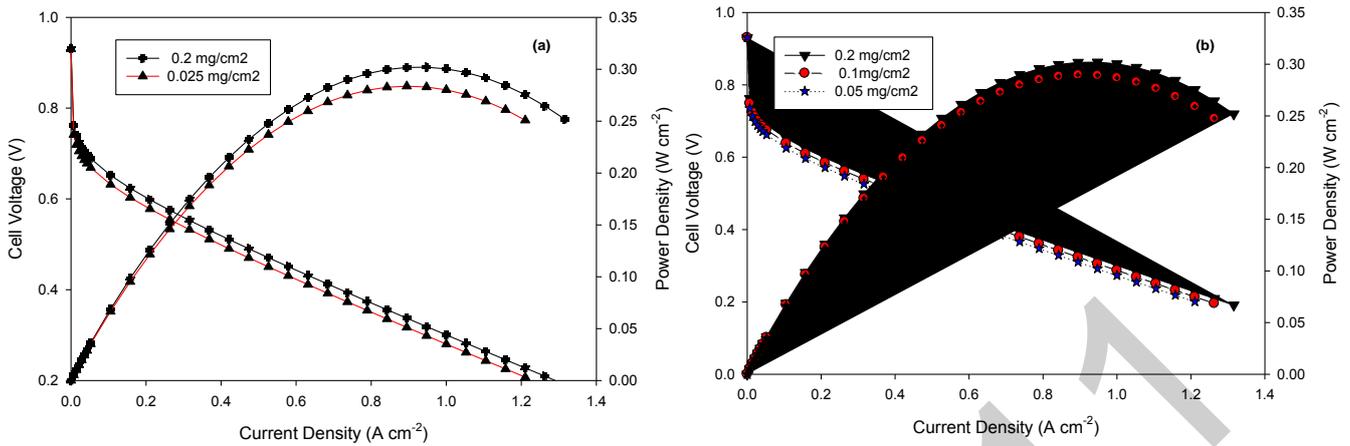


Figure 6: Polarization curves for the different platinum loading (a) Anode, (b) Cathode

### 3.5 Reformate

Figure 8 shows the results comparing the use of pure hydrogen and a reformate gas composed of (2% CO, 19% CO<sub>2</sub>, 3% CH<sub>4</sub> and 76% H<sub>2</sub>). There is a huge loss in cell voltage when the cell was simulated with reformate feed. This can be explained by the combined effect of CO poisoning and the reduced H<sub>2</sub> partial pressure.

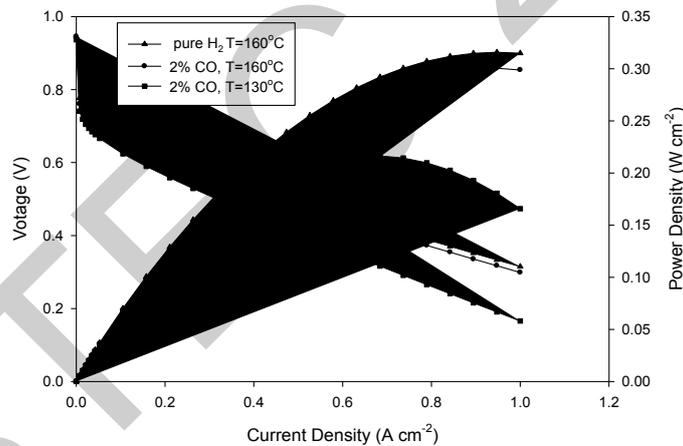


Figure 7: Effects of CO poisoning on the cell performance fed with pure hydrogen

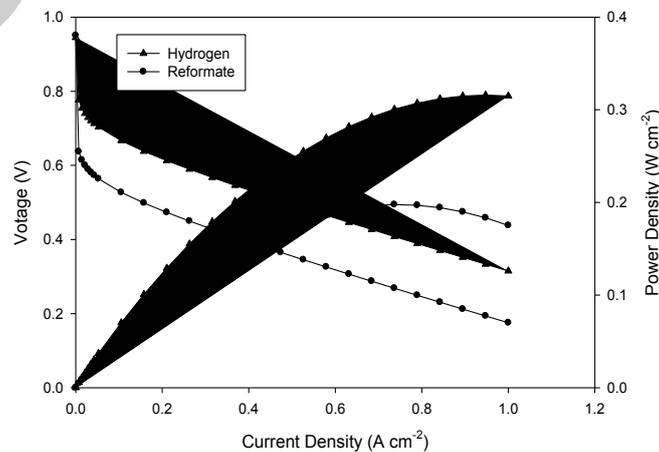


Figure 8: Predicted effects of hydrogen vs reformate on the cell perform

#### 4 Conclusion

Modelling provides alternatives to physical testing and hence speeds up the screening of design alternatives and eventually eases the task of integrating engineering design process. In order to optimize the overall design (with respect to cost and efficiency) and operation (in terms of lifetime or durability), it is necessary to develop laboratory scale prototype CHP-systems and accurate modelling tools. HySA Systems, a competence centre for hydrogen and fuel cell technology established at the University of the Western Cape, will be developing prototypes to test and validate various CHP-system configurations. This study is closely aligned with this hardware development.

#### Acknowledgement

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## PLANT IMMUNE SYSTEM, PATHWAYS, AND SIGNAL ELICITORS

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### ABSTRACT

Crop yields loss due to pathogen attacks of economic crops is worth billions of dollars around the world annually. On the other hand using pesticides to fight those pathogens proved to be not effective degrading the quality of the crops and in many occasions causing serious health problems to humans on the long run if not on the short term. This paper presents a review on the theories behind plant immune system and the recent findings of all the steps along the signal pathways from the point the plant knows about the attack till the point the plant is actually in a defense status and able to fight the pathogen. A focus has been given to the viral pathogens.

### INTRODUCTION

Viruses and pathogens in general can cause dramatic damages to plants leading to major economic losses in agriculture. Billions of dollars worth of annual loss in crop yields around the world is caused by plant diseases. A considerable amount of this loss is due to viruses and specially the tobacco mosaic virus (TMV) (Dickinson, 2003). Also, in a recent research conducted by South Dakota State University, it has been reported that bean pod mottle virus (BPMV) and soybean mosaic virus (SMV) have a more serious effect when they infect the same soybean plant, and that they can cause up to 100% yield loss in infected soybean (Schwartz et al., 2008). On the other hand, Tomato spotted wilt virus (TSWV) represents a big risk on the production of many crops like tobacco, tomato, and pepper in Georgia (Woodward, 1999). Plants on the other hand, developed many ways to fight viral infection. Those defense mechanisms are induced in the plant as a result of a stress or a combination of different stresses applied on the plant. Depending on the type of stress and the time applied on the plant as well as the plant receptors and pathways the speed, intensity and persistence of the induced resistance differ. Plant virus resistance can cause one of two effects either inhibiting the growth of the virus inside the plant cells or increasing the plant tolerance to this virus by decreasing the virus damage to the plant cells (Lucas, 1998).

Plant stresses can be divided into biotic and abiotic. Biotic stresses include pathogens and plant growth-promoting rhizobacteria (PCPR). Abiotic stresses, on the other hand, include physical and climate stresses like heating, cooling, drenching, wounding, and so forth, and can also include synthetic chemicals (Vallad and Goodman, 2004), more information about plant-stress interaction comes in later sections of this paper. Finally natural plant extracts that serve as plant pathogen inhibitors can be considered resistance inducers that can be applied on the host plant prior to the infection by some period of time depending on the (virus-host-inhibitor-environmental conditions) combination, to induce plant resistance that will fight the virus whenever it attacks the plant. Research on the plant induced resistance started long time ago. It was first mentioned in the literature by Chester, (1933) and 33 years later; Ross reported, in his study on the tobacco plants, that infection with TMV makes the tobacco plants resistant to diverse viral pathogens (Ross 1966).

To better describe the plant mechanism to induce pathogen/viral resistance, let's start by describing the plant before and after the viral infection. There are many guards that the virus has to penetrate in order to infect the plant, those guards start with the plant surface, cell walls, and the plant immune system that includes many plant pathogenesis-resistance factors and mediators in the idle state with the ability to be activated whenever they get an activation signal. Plant immune system includes pathogenesis related proteins like defensins, and PR-1, antimicrobial chemicals like glucosides, antimicrobial enzymes like peroxidases, and finally the activators that activate all the mentioned antimicrobial compounds whenever they sense a penetration by a virus or a pathogen in general and the immune system activation signal pathway mediators. After the penetration happens, the receptors (activators) send signals to activate all parts of the plant immune system. As a result a reinforcement of the cell wall happens using cell wall proteins, antimicrobial chemicals like hydrogen peroxide gets induced as well as the induction of pathogenesis related proteins, and the antimicrobial enzymes (Lucas, 1998). Some plants have in addition to the regular plant immune system, a set of genes called resistance genes, that mediate a fast response to the virus penetration of the plant by making the infected cells of the plant committing a suicide to block the infected cells from the uninfected cells which blocks the virus in dead cells and end the risk (Métraux et al., 1991, van Loon et al, 1998, Banhamou and Nicole, 1999, Hammond et al., 2000 and Heil and Baldwin, 2002).

Now comes the question "what is the role of the different types of plant stresses in the above immune paradigm?" and the answer to this question is that the above model depends on the receptors to sense the infection and send the signal to the rest of the immune system to fight the already happening infection, so if those receptors send this signal earlier to the infection and the whole plant immune system is set in the steady state to fight the infection whenever it happens the losses will be much less because the plant now is already on the defensive state even before the infection happens, the cell walls are already reinforced and all the antimicrobial compounds are already there. The different types of stresses, called resistance elicitors, are the factors that can make this happens by simulating the attack state to the plant to enforce the receptors to send the attack signals

to the rest of the immune system and put the plant in the defensive mode (Hammond et al., 2000). Vallad and Goodman, (2004) divided plant resistance into two types, the systemic acquired resistance (SAR), and the induced systemic resistance (ISR). There are three main differences between the two types of resistance, the position in the plant where the application of the stress happens, the type of the stress, and the phyto hormone (the antimicrobial compound) that the resistance depends on. SAR is the resistance induced in the plant upon exposing the roots or the leaves to biotic or abiotic stresses and it depends on salicylic acid as its signaling pathway mediator. ISR, on the other hand, is the resistance induced in the plant by exposing the roots to biotic stresses like growth promoting rhizobacteria and it depends on ethylene and jasmonic acid as mediators to the signaling pathway (Vallad and Goodman, 2004). Recently, it was also shown that wounding and physical stresses of the leaves or roots can induce systemic resistance as well. This type of resistance is sometimes combined with the ISR because it is found to be mediated by jasmonic acid like the ISR, and sometimes is put under different name called wound induced systemic resistance (WSR) (Sato et al., 2009).

## INDUCED RESISTANCE ELICITORS

### Biotic Elicitors

Elicitors can be described as inducers of the defense response in plants. Those inducers have low molecular weight and get released from polymeric precursors during infection/stress (Mejia et al., 2010). When a plant gets infected by a biotic elicitor, like a pathogen, this infection causes responses in the infected host cells, leading to cell death showing as necrosis symptoms on the infected cells (Kombrink and Schmelzer, 2001). This cell death will keep the pathogen in a closed loop inside the infected cells that soon will be dead and not giving the pathogen the chance to spread to uninfected cells and surviving on the cost of host cells survival. As mentioned above, the cell wall composition itself is subject to changes, as a result of those responses initiated in the plant upon infection. This change in the cell wall composition will prevent the pathogen from penetrating the wall (Hammerschmidt, 1999). These local responses, or as called above the hypersensitive responses, compose a systemic signal that spreads throughout the whole plant including the uninfected cells to prepare the plant for future pathogen attacks (van Loon and van Strien, 1999). Examples on the above scenario include the tomato plants which when stimulated; by root infection with certain strains of the *Bacillus* bacteria induce ISR capable of fighting cucumber mosaic virus (CMV). Also when stimulated with certain *Bacillus* strains the tomato plants found to induce ISR capable of fighting the tomato mottle virus (Zehnder et al., 2001). Also, a strain of plant-growth-promoting rhizobacterium has shown to induce ISR in cucumber plants against CMV, TMV, and potato virus Y (PVY) (Park *et al.*, 2009). In this scenario, a plant growth promoting rhizo-bacteria applied to the roots of the plant induces the resistance, ISR in this case, which depends on jasmonate and ethylene as its pathways mediators (Yan et al., 2002). The induction of resistance scenario can be started however, artificially, by using some compounds that are known to elicit or stimulate systemic resistance in plants. Those elicitors can be natural and chemical synthetic compounds, as follows.

### Abiotic Elicitors: Physical Stress

Induced resistance can be initiated in the plant by physical stress, which includes leaves wounding, drenching, heating, cooling and treatment with lethal doses of UV irradiation. In this case, the scenario starts with the wounding of the plant, which stimulates the release of linolenic acid from membrane lipids, which is then transformed by enzymatic action into jasmonic acid (JA). JA then, activates the genes encoding a special set of inhibitors called the proteinase inhibitors (PIs) and defense compounds like phenolics, and nicotine (Boland et al., 1999). It has been shown that JA accumulates in the leaves of tobacco from wounding sites to systemic sites (Sato et al., 2009), and plants stressed with lethal doses of UV radiation acquired resistance against different pathogens (Sharma et al, 1996). Also, drought and UV radiation have been reported to induce resistance in pea and wheat plants (Alexieva et al., 2001). Wounding in tomato plants has been studied thoroughly and has been found to cause the mobilization of systemin, which is an 18-amino acid polypeptide hormone (Pearce et al., 1991). Wounding in tomato also found to induce other signaling peptides (Ryan et al., 2002).

### Abiotic Elicitors: Synthetic Chemical Compounds

Induced resistance can also be potentiated by external application of SA and synthetic chemical compounds (Hammerschmidt, 1999). The acquired resistance, SAR in this case, is not guaranteed to be induced however, unless the plant is further challenged by a pathogen (Gozzo, 2003). There is a big trend in the induced resistance research to find a synthetic chemical compounds that can work as external inducers to the SAR in plants (Lawton et al., 1996). A synthetic chemical acid was also used as an artificial elicitor to induce SAR in the tobacco plants. The resultant SAR reduced the symptoms of the TMV and the tobacco necrosis virus (TNV) significantly (Vernooij et al., 1995). On the other hand, a strobilurin fungicide was used in a trial to enhance the resistance of the tobacco plants against the TMV by infiltrating halves of the tobacco leaves with water and the other halves with aqueous suspension of the fungicide. TMV was applied 24 hours later to all the plant leaves. It was reported that infiltrating the tobacco leaves with the fungicide caused a reduction in the TMV lesions' size by almost 50% (Herms et al, 2002). Also, greenhouse application of acibenzolar-*S*-methyl prior to transplanting induced SAR in the tobacco plants against the TSWV (Csinos et al., 2001).

Aside from the tobacco plants, the SAR induced in *Arabidopsis* is effective against the turnip crinkle virus (TCV) (Uknes et al, 1992). Also, salicylic acid (0.5%) and potassium sulfate (3%) gave the highest effect in inducing SAR in cucumber plants which gave the plant 100% protection against zucchini yellow mosaic potyvirus (ZYMV) 25 days post inoculation

(Abo-Elnasr et al., 2004). Another synthetic chemical that is used as an artificial elicitor to induce broad-spectrum resistance in a range of crops is the nonprotein amino acid  $\beta$ -aminobutyric acid (BABA) (Jakab 2001). When BABA was applied to tobacco at 10 mM, it caused an increase in the SA content of leaves (Siegrist et al., 2000). BABA has also been reported to lead to induction of some set of proteins called the pathogenesis-related (PR) proteins, like PR-1a, chitinase, and glucanase in tobacco, tomato, and pepper (Jakab 2001)

#### Abiotic Elicitors: Natural Plant Virus Inhibitors

On the other hand, there is a huge trend in agriculture to use natural plant inhibitors as SAR inducers instead of using chemicals. Virus inhibition works by inoculating some of the leaves, sometimes the basal in particular, by aqueous extracts of the plant inhibitors before the inoculation. Examples include the aqueous leaf extract of *Bougainvillea spectabilis* which upon spraying it on the tomato, and melon plants, the symptoms of TMV, tomato yellow mottle virus (TYMV) and cucumber mosaic virus (CMV) have had a significant decrease (Verma and Dwivedi, 1983). Also, there exists a highly active virus inhibiting agent developed systemically in a number of plants after treating their basal leaves with the *Bougainvillea spectabilis* extract and that the amount of the inhibiting agent reached its maximum value 24 hours after treatment (Verma and Dwivedi, 1984). It was found that water extracts from *Pseuderanthemum atropurpureum* and *Bougainvillea spectabilis* inhibited several viruses when sprayed on the plant before inoculation (Verma et al., 1985). Later, in a study of several crude leaf extract from 46 plant species, plant virus inhibitors against TMV proved to exist. Those inhibitors triggered SAR into the tobacco plant as a local lesion host, and *Chenopodium annuum* as a systemic host plant (Peshney and Moghe 1990). Same results were reported by Neeta and Verma (1995), who stated that aqueous extract of fresh leaves of *Chenopodium mural* showed antiviral activity and induced systemic resistance in tobacco.

#### THE MECHANISM BEHIND THE INDUCED RESISTANCE: HOW DOES IT WORK?

As mentioned in the introduction the whole resistance paradigm depends on the following: Receptors to sense the attack status of the plant by a pathogen or some cell stress, and start the whole signaling process to put the plant in the defense status; The signaling mechanism itself; and The result of the signaling and activation of the plant immune system, the end of the signaling/resistance pathways (Fig 1).

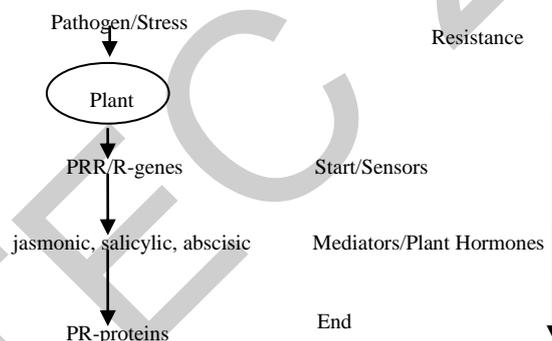


Figure (1): Plant Immune system

#### Induced Resistance – start of pathway

When the cells of a plant are put under attack by a pathogen or some stress some molecular patterns gets generated in the plant called pathogen-associated molecular patterns (PAMPs). Plant immune system expresses specific type of proteins called pattern recognition receptors (PRR) to detect those patterns and consequently detect the attack (Alisa et al., 2011, and Beutler, 2006). Pathogens on the other hand, have another type of proteins called the effector proteins that inhibit the plant defenses and increase the bad effect of the pathogen on the plant. To overcome the effect of those pathogen effector proteins, a specific set of genes have evolved in plants called the resistance genes (R-genes). R-genes products have the benefit of detecting the pathogens either via their markers (effectors), or via the effect they do on the plant cells (alteration, mutation, and so forth). Products of R-genes usually have a control on the resistance for a wide spectrum of pathogens, and usually stop the growth and adaptation of the pathogen inside the plant. In addition to that, the plant R-genes must have a match with the pathogen effector genes in order to trigger the plant immune system to induce the resistance (Friedman and Baker, 2007).

#### Induced Resistance - pathway mediators

Starting the signaling process requires increasing some chemical inside the plant to act like a plant hormone that upon its increase, the whole plant immune system changes its status to the defense status. So whenever the plant senses that it is under attack via the PRR, or R-genes, it increases the level of this plant hormone, which is considered the resistance pathway mediators, that in turn triggers the induction of the resistance. Some known plant hormones or resistance pathway mediators include ethylene, jasmonic acid, salicylic acid, and abscisic acid (Hammond and Parker, 2003). SA plays the lead role in the SAR signaling pathway (Cameron, 2000). Endogenous levels of SA in a plant starts to increase locally as the plant gets infected and spreads systemically in the whole plant to a certain level and this is when the plant SAR starts to get triggered in

the plant, and as the SA level in a plant increases the level of SAR induced in the plant increases as well which indicates a positive correlation between the SAR induced in a plant and the SA level (Cameron, 2000).

Now assuming that SA is the only or the lead key player in the signaling pathway of SAR in plants, this would mean that if we prevent the plant from accumulating its endogenous SA and increasing its level, the SAR will not be induced in the plant. Surprisingly, when this scenario was actually conducted in an experiment to prove that SA is the key player in the SAR induction by removing the infected leaves of the cucumber plants to cut the local signal of infection before the accumulation of the endogenous SA, the SAR was still induced in the cucumber plants against CMV (Rasmussen et al., 1991), suggesting that SA is one of other compounds comprising the signaling pathway leading to the induction of SAR in the plant (Sticher et al., 1997). JA on the other hand, is the compound in the plant that is analogous to SA. JA however, is the signaling molecule in response of herbivores or insects attacks (Wasternack and Parthier, 1997) and wounding. JA, upon a stress, activates the genes encoding PIs and some other defense related compounds like nicotine and phenolics (Wasternack and Parthier, 1997; and Sato et al., 2009).

### Induced Resistance - end of pathway

End of pathway represents the real mechanism of resistance the plant acquires and it depends on the kind of resistance induced. SAR end of pathway is represented by SAR proteins which found to belong to the class of PR-proteins. PR-proteins were discovered and defined, for the first time, as sets of proteins that do not exist in healthy plants and start to accumulate by large amounts after infection (van Loon and van Kammen, 1970). They were also detected and defined as proteins accumulating in tobacco plants upon infection by TMV (van Loon, 1985). Recently, around 13 families of PR-proteins were found, belonging to two main groups, namely the basic and the acidic PR groups. The main differences between the two groups are the molecular weights and the amino acid sequences (van Loon and van Strien, 1999). SAR end of pathway, referred to as SAR markers, found to consist of nine families in tobacco comprising acidic forms of PR-1,  $\beta$ -1,3-glucanase, class II chitinase, hevein-like protein, thaumatin-like protein, acidic and basic isoforms of class III chitinase, an extracellular p-1, 3-glucanase, and the basic isoform of PR-1 (Ward et al., 1991). As for SAR markers in wheat in response to infection by *Fusarium graminearum* causing the fusarium head blight (FHB), real-time quantitative reverse-transcription (Q-RT-PR) was used to validate the 51 genes encoding disease resistance. Out of the 51 genes, 18 genes showed to be defense-related genes.

Despite the fact that PR-proteins did not show to have any antiviral, or in general, antimicrobial, activity at all, it was widely believed that PR-proteins and specifically some set of genes named as the defense-related genes are the real markers of the induced resistance activation because of the correlation between their accumulation and the induction of the systemic resistance in the plant. Recently however, it has been shown that there is no relation between the expression of those defense-related genes like PR-1 and  $\beta$ -glucanase-2 and the activation of the induced resistance in plants (Greenberg et al., 2000). ISR markers on the other hand, include a PIs, and phenolics (Sato et al., 2009). It is also worth mentioning that in the case of virus attacks, plants induce virus specific genes that conduct a virus gene silencing blocking the virus replication inside the plant and eventually get rid of it (Baulcombe 2004).

### Antagonistic Interaction

Sometimes, plants develop strange systemic induced susceptibility due to the antagonistic interaction between two different signaling pathways. When the *Arabidopsis thaliana* was infected two consecutive times with *Pseudomonas syringae* it was supposed to develop ISR due to the first inoculation and have better resistance for the second infection. Surprisingly, the resistance was much less in the second infection than the first one, which introduces the systemic induced susceptibility due to the antagonistic interaction between the SA and JA different signaling pathways (Jianping et al., 2005). It has also been shown that using synthetic chemical compounds as elicitors to induce SAR in the plant decreases the plant ability to express wound inducible PIs. SA inhibits the synthesis of JA in tobacco and tomato, which inhibits the induction of wound related systemic resistance (Baldwin et al., 1997).

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# PRACTICAL STUDY ON THE OFF-LINE TRAINING OF THE INVERSE NEURAL CONTROLLER FOR ROBOTIC MANIPULATOR IN THE REAL TIME OPERATION

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## ABSTRACT

This paper presents a study on the off-line training of the inverse neural network controller also presents an efficient off-line training method for the neural network controller to be used as feed forward controller in the real time applications without need to the on-line training. This neural controller has been designed, trained, implemented and tested practically to control the operation of 6 Degree Of Freedom (DOF) robotic manipulator in the real time operation. Practical results show good performance of the proposed neural controller which were able to control the operation of all six joints of the 6DOF robotic manipulator also they were able to compensate the coupling effects between different joints in the robotic manipulator providing good system response.

**Keywords:** Neural networks, Neural Controllers, Feed Forward Controllers, Robotic Manipulator.

## INTRODUCTION

Since the neural networks have the ability to comprehend and learn about complex plant structures, disturbances, environment and different operating conditions, they (neural networks) are used in the artificial intelligent controllers. One of the most important features of the neural networks their ability to learn or model unknown systems even they are complex and non-linear systems. Updating of the neural network is the process of modifying the weights and biases of the neural network to minimize the error between its actual and desired outputs. Updating is done by using set of input data and the corresponding output data. Updating can be done by using off-line training which is done before using neural network controller in real time operation or on-line training which is done during real time operation of the neural network controller, however sometimes both off-line and on-line training are used to get better performance for the neural controller [4].

On-line training can map changes in the inputs with the outputs during the real time operation better than off-line training of the neural network controller [2, 4]. On the other, hand on-line training has heavy computations which require long time during real time operation and this is the main problem with the on-line training of neural network controller. This time becomes very critical when it is greater than sampling time of the system operation and sometime makes the system unstable. To avoid this problem efficient off-line training is used to train neural controller to model a system even it is non-linear system, this can be done by selecting efficient training algorithm, good training data and efficient controller scheme.

## INVERSE NEURAL NETWORK CONTROLLER (INNC) FOR 6DOF ROBOTIC MANIPULATOR

There are several controller schemes that use neural networks as an intelligent component. One of these controller schemes uses the neural networks as a FFC [2, 5]. In this control scheme the neural network is trained to identify (learn) the inverse of the plant dynamic with the aid of a set of training data then the trained neural network is used as FFC. In this paper an INNC has been designed, trained, implemented and tested practically to control the operation of the MA2000 robotic manipulator.

MA2000 is 6DOF articulated type robotic manipulator has six revolute joints; three of them are in the arm structure (major joints) these are base, shoulder, and elbow, the other three joints lie in the wrist structure these are pitch, yaw, and roll. Each joint of the six axes has a separated driver and controller which are used to drive and control the DC servo motor of that joint, figure 1 shows MA2000 robotic manipulator structure. The idea behind using INNC for the MA2000 manipulator can be summarized in the following words "Without using the mathematical model of MA2000 manipulator, a controller for this manipulator can be designed". Six INNCs are used to control the operation of the MA2000 manipulator. For each one of the six actuators of the MA2000 manipulator there is an INNC which is used to achieve fast response with minimum steady state error in that joint to reach its desired joint variable which is computed using the inverse kinematic of the manipulator system [1]. All the six INNCs have three layers but they differ in their inputs, number of hidden neurons and training data set. There are nine inputs to the INNCs of the minor joints in the wrist structure which are pitch, yaw and roll axes; while there is only one output from it which is the control signal of that joint in the MA2000 manipulator. The 1<sup>st</sup> input of the INNC of the  $i^{\text{th}}$  joint of the minor joints is its desired value  $\theta_{id}(k+1)$ . The 2<sup>nd</sup> to 7<sup>th</sup> inputs are the current and previous values of that joint variable i.e.  $\theta_{ia}(k)$ ,  $\theta_{ia}(k-1)$ ,  $\theta_{ia}(k-2)$ ,  $\theta_{ia}(k-3)$ ,  $\theta_{ia}(k-4)$  and  $\theta_{ia}(k-5)$ . The 8<sup>th</sup> input is the current change in the  $i^{\text{th}}$  joint variable, i.e.  $\theta_{ia}'(k) = \theta_{ia}(k) - \theta_{ia}(k-1)$ ; while the last input to the INNC is  $u_i(k-1)$  which is the previous value of the control signal of the joint  $i$ . In the major joints (Base, shoulder and elbow) the coupling effects between these parts become significant and they should be considered in the controller design. Thus for the first three joints (major joints) there are four extra inputs for their controllers these extra inputs are the previous joint variable and the pervious control signal of the other two major joints. The input signals to the six INNCs are given in table 1.

Where  $\theta_{id}(k)$ ,  $\theta_{ia}(k)$ ,  $\theta_{ia}'(k)$ , and  $u_i(k)$  are the desired value of the  $i^{th}$  joint variable at sample  $k$ , the actual value of the  $i^{th}$  joint variable at sample  $k$ , the change in  $i^{th}$  joint variable at sample  $k$ , and  $u_i(k)$  is the control signal of joint  $i$  at sample  $k$  respectively.

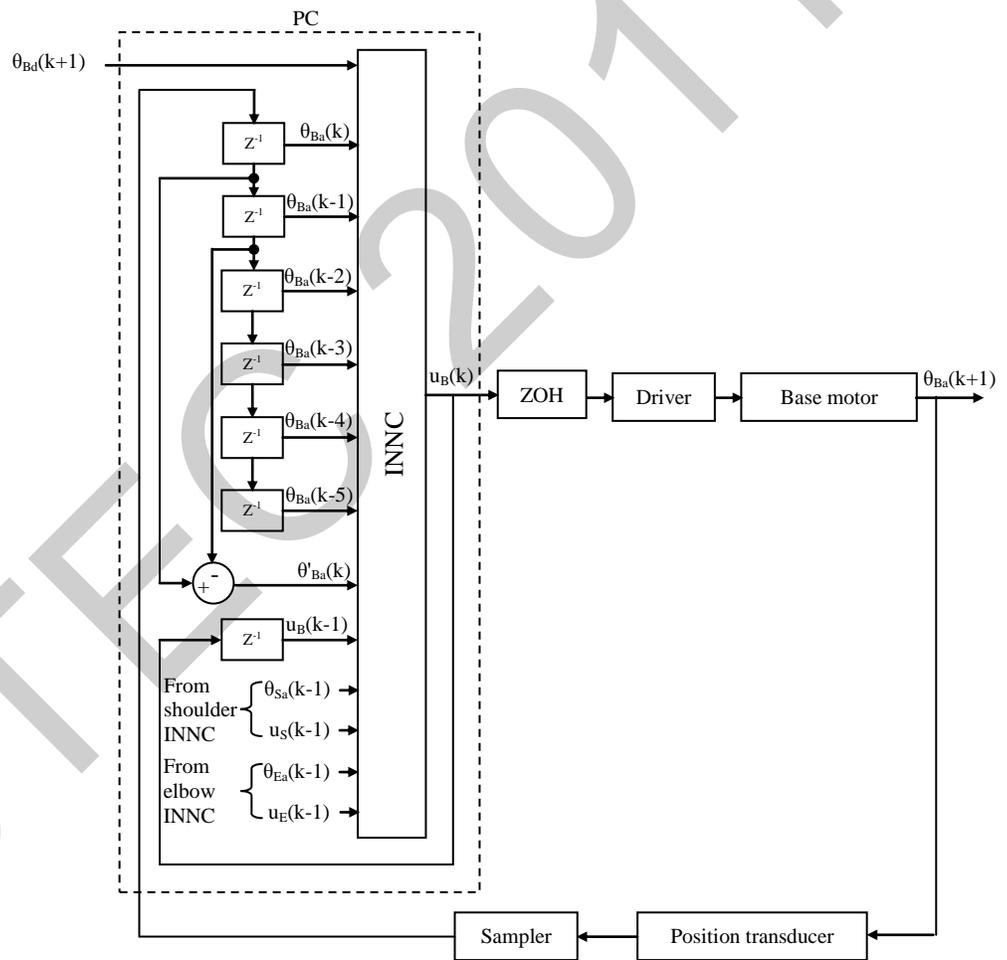
Figure 2 shows the INNC of the base joint of the robotic manipulator. There are thirteen inputs and one output. The same controller scheme is used for the shoulder and elbow joints but  $\theta_{Sa}(k-1)$ ,  $u_S(k-1)$  are replaced by  $\theta_{Ba}(k-1)$ ,  $u_B(k-1)$  in the shoulder controller and  $\theta_{Ea}(k-1)$ ,  $u_E(k-1)$  are replaced by  $\theta_{Ba}(k-1)$ ,  $u_B(k-1)$  in the elbow INNC. While the last four inputs  $\theta_{Sa}(k-1)$ ,  $u_S(k-1)$ ,  $\theta_{Ea}(k-1)$ ,  $u_E(k-1)$  are not used for the minor joints (pitch, yaw and roll) because their joints effects can be neglected.

**Table 1.** Input signals to the all six joints controllers

Joint	Input vector to the INNC
Role	$\theta_{Ra}(k+1), \theta_{Ra}(k), \theta_{Ra}(k-1), \theta_{Ra}(k-2), \theta_{Ra}(k-3), \theta_{Ra}(k-4), \theta_{Ra}(k-5), \theta_{Ra}(k) = \theta_{Ra}(k) - \theta_{Ra}(k-1), u_R(k-1)$
Yaw	$\theta_{Ya}(k+1), \theta_{Ya}(k), \theta_{Ya}(k-1), \theta_{Ya}(k-2), \theta_{Ya}(k-3), \theta_{Ya}(k-4), \theta_{Ya}(k-5), \theta_{Ya}(k) = \theta_{Ya}(k) - \theta_{Ya}(k-1), u_Y(k-1)$
Pitch	$\theta_{Pa}(k+1), \theta_{Pa}(k), \theta_{Pa}(k-1), \theta_{Pa}(k-2), \theta_{Pa}(k-3), \theta_{Pa}(k-4), \theta_{Pa}(k-5), \theta_{Pa}(k) = \theta_{Pa}(k) - \theta_{Pa}(k-1), u_P(k-1)$
Elbow	$\theta_{Ea}(k+1), \theta_{Ea}(k), \theta_{Ea}(k-1), \theta_{Ea}(k-2), \theta_{Ea}(k-3), \theta_{Ea}(k-4), \theta_{Ea}(k-5), \theta_{Ea}(k) = \theta_{Ea}(k) - \theta_{Ea}(k-1), u_E(k-1), \theta_{Sa}(k-1), u_S(k-1), \theta_{Ba}(k-1), u_B(k-1)$
Shoulder	$\theta_{Sa}(k+1), \theta_{Sa}(k), \theta_{Sa}(k-1), \theta_{Sa}(k-2), \theta_{Sa}(k-3), \theta_{Sa}(k-4), \theta_{Sa}(k-5), \theta_{Sa}(k) = \theta_{Sa}(k) - \theta_{Sa}(k-1), u_S(k-1), \theta_{Ea}(k-1), u_E(k-1), \theta_{Ba}(k-1), u_B(k-1)$
Base	$\theta_{Ba}(k+1), \theta_{Ba}(k), \theta_{Ba}(k-1), \theta_{Ba}(k-2), \theta_{Ba}(k-3), \theta_{Ba}(k-4), \theta_{Ba}(k-5), \theta_{Ba}(k) = \theta_{Ba}(k) - \theta_{Ba}(k-1), u_B(k-1), \theta_{Sa}(k-1), u_S(k-1), \theta_{Ea}(k-1), u_E(k-1)$



**Figure 1.** MA2000 robotic manipulator structure.



**Figure 2.** INNC of the base joint in the robotic manipulator.

**TRAINING OF THE INNC**

In this controller scheme the neural network is trained off-line to learn the inverse dynamic of the  $i^{th}$  joint in the MA2000 manipulator. The off-line training phase is done before using the neural network as Feed Forward Controller (FFC). The training of INNC of the base joint is shown in Figure 3 which provides a method to minimize the overall Mean Square Error (MSE) of the training data.

The off-line training of INNC of joint  $i$  is achieved by using hard training signal which is taken from the open loop response of joint  $i$ . The training data must be extended to fill all the range of the input and output variables of that joint. Otherwise the neural network cannot learn the inverse dynamic of joint exactly which may cause bad system response especially in the range of the output or input variables that were not included in the training signal even MSE of the training process is small.

In this paper only off-line training is used to train INNOC, so that it is important to use a hard and complex training signal to get good system response with the INNOC. The on-line training is not used in this controller because it is time consumption during the real time operation of MA2000 manipulator which sometimes makes system unstable due to heavy mathematical computations in the on-line training phase which take a time more than the sampling interval. However practical results show good off-line training of INNOC can give good system response. The off-line training of the INNOC is achieved by using batch training method [3]. This training technique gives better and faster convergence from single train step. In this training technique a batch of a training data is used, which includes input vectors and the corresponding output vectors. In the batch training, the output of the neural network is computed according to each input vector, then the MSE is computed which is equal to:

$$MSE = \sqrt{e_1^2 + e_2^2 + e_3^2 + \dots + e_n^2} \quad (1)$$

$$e_j(k) = u_j^{\wedge}(k) - u_j(k) \quad (2)$$

Where  $e_j(k)$ ,  $u_j^{\wedge}(k)$  and  $u_j(k)$  are the error due to the  $j^{th}$  vector in the training data at sample  $k$ , actual output of INNOC in the training phase at sample  $k$ , and desired output of INNOC in the training phase at sample  $k$ .

The new network weights are computed and updated in order to minimize the MSE. Then the batch training method applies the inputs to the new network, calculates outputs, compares them to the associated output values in the training data and calculates the MSE. If the error goal is satisfactory, then the training is stepped. Otherwise batch training goes through another training loop.

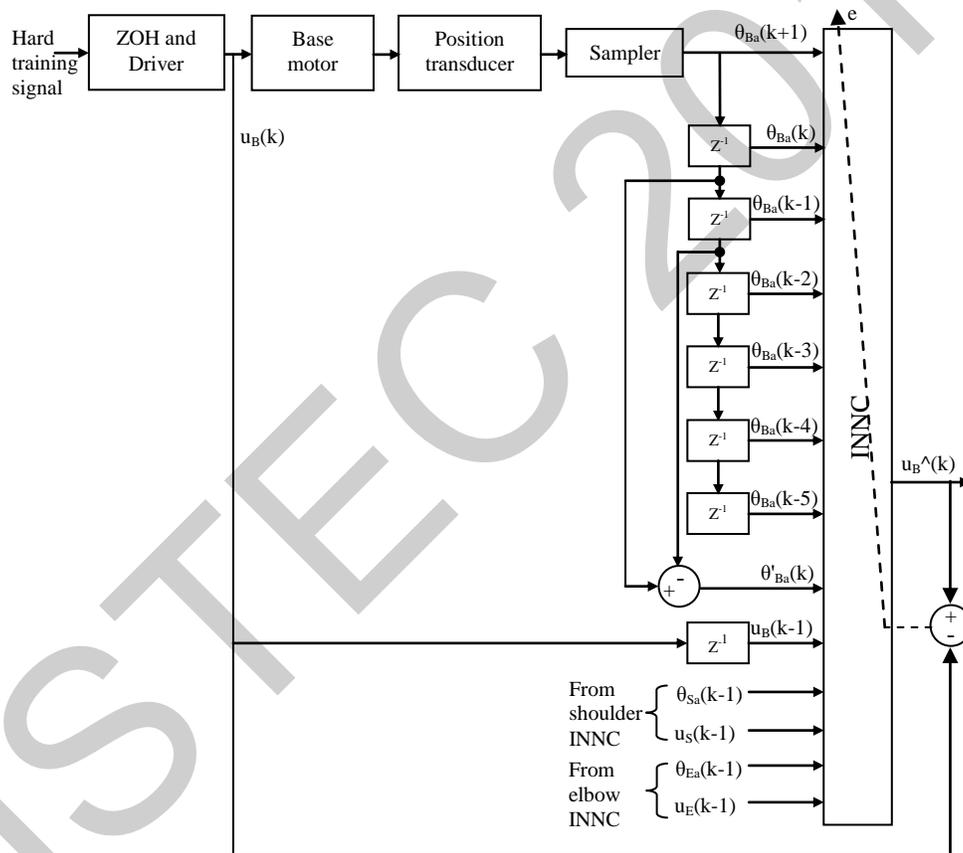


Figure 3. Training of the INNOC of the base joint.

**OPEN LOOP RESPONSE OF MA2000 MANIPULATOR**

Open loop response of a system can be obtained from the system under condition of no control action. Simply this can be done by applying an input signal to the certain joint in the MA2000 manipulator and read the corresponding joint variable of the joint without using any controller. Figure 4 illustrates the open loop response of the base joint of MA20000 manipulator due to a square wave ( $\pm 7.5$  Volt) as an input signal to the base motor. It is clearly that the open loop response of the system is nonlinear due to many factors like the effects of the gravity, friction, shape of the manipulator, coupling effects between the main parts (links or joints) of the manipulator structure... etc.

The base joint in the MA2000 manipulator is the largest joint in this manipulator structure, so it is the most critical link in the manipulator structure because it has largest effective mechanical time varying load (i.e. shoulder, elbow, pitch, yaw, roll, gripper, and load structures). Any change in the manipulator structure will directly effects on the base joint and link. The load inertia of the

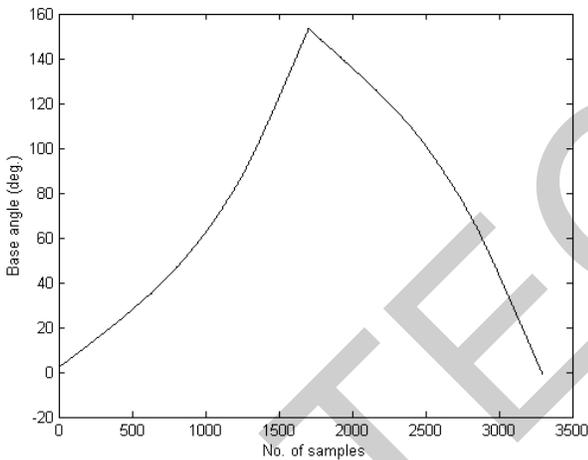
base motor may change at any time because it depends on the shape and the mass of the base effective load of manipulator. The shape of the effective load may change if any one of the other links in the manipulator changes its joint variable or if there is any change in the gripper's load, in this case, the mass of the effective load of the base joint will change too. For these reasons the base joint becomes the most sensitive joint in the manipulator so that the performance of INNc will be tested practically on this joint.

**TESTING MA2000 MANIPULATOR WITH THE INNc**

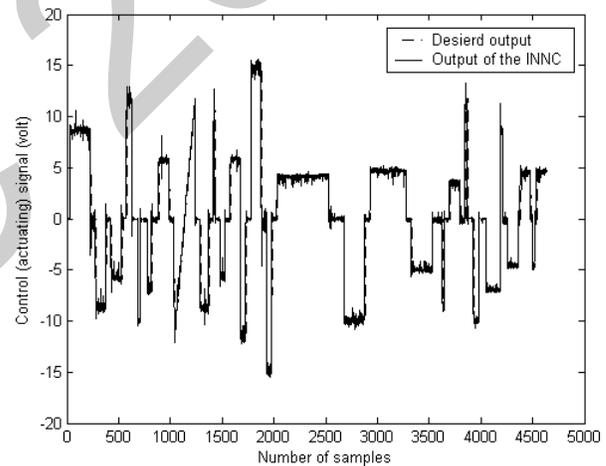
A multilayer neural network contains 23 neurons in the hidden layer is used as INNc for each joint in the MA2000 manipulator. First the neural network is trained off-line by using batch training technique with the input vectors given in table 1. Levenberg Marquardt [3] training algorithm is used to learn the inverse dynamic model of a certain joint in the MA2000 manipulator. Then it is used as a FFC for that joint. The neural network inverse model has been trained by using hard training signal taken from the open loop response of that joint of the manipulator. Figure 5 illustrates the hard training signal which is used to train the neural network to learn the inverse of the base joint.

The batch size of the training data (n) is 4700 input/output vectors. The neural network is trained using Levenberg Marquardt algorithm until an acceptable MSE is reached, which is equal to 161 and then the neural network is connected as INNc. Note that  $\theta_{Ba}(k+1)$  in the training phase is replaced by  $\theta_{Bd}(k+1)$ ; while other inputs to the INNc remain as they were used in the off-line training phase. The base step response using the INNc with thirteen inputs is shown in Figure 6; while Figure 7 illustrates the output of base INNc (control signal). It is clear that by using efficient off-line training for INNc, the system response reaches the desired value. It combines with low overshoot and decayed oscillation until the desired value is reached. The steady state system response with the INNc is good and the actual value reaches the desired value without (or with small) steady state error. Also the INNc can move the joint for small step change as it is shown in Figure 8. It is important to note that, in this figure, to explain the system performance for small change in the joint variables, the system response is drawn in steps of ADC (not as angle in degree or radian). Each step equals to:

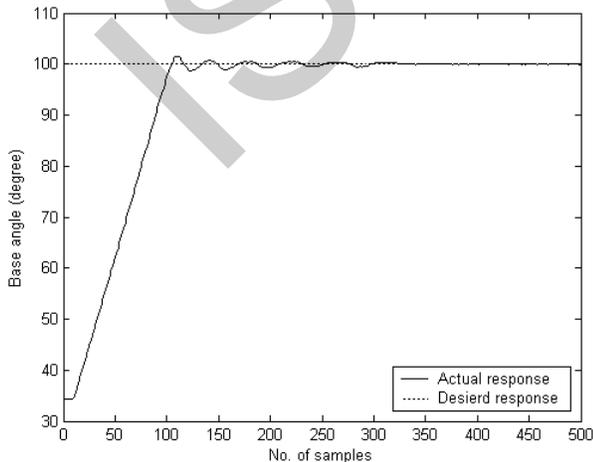
$$steps\ per\ degree = \frac{\text{no. of steps of ADC}}{\text{operating angle range of base}} = \frac{2^{12}}{270^\circ} = 15.17 \frac{steps}{degree} \quad (3)$$



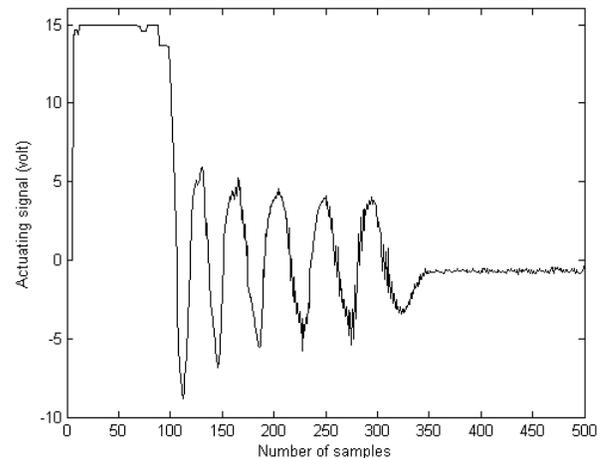
**Figure 4.** Open loop response of the base joint in MA2000 due to ( $\pm 7.5$ Volt) square input.



**Figure 5.** The training signal of the INNc to learn the inverse model of the base joint.



**Figure 6.** Step response of the base joint using INNc.



**Figure 7.** Control signal of base actuator using INNc.

The oscillation that appears in the system response in Figure 8 is not a mechanical oscillation in the base structure but it represents the noise due to the small step size of the analog to digital converter which is equal to 2.4mV.

There are two important points must be investigated during training INNc. The first one is MSE which is given in equation (1). For same INNc structure as the MSE decreases the INNc gives better performance in the real time operation. Figure 9 shows base step response using INNc with the same internal structure, number of the hidden neurons, and training data but they differ in their MSE, the first INNc has MSE of 161 while the second controller has MSE of 304. It can be shown that the system response with the first INNc (MSE=161) is better than the system response with the second INNc (MSE=304). In the first case the system response reaches the desired value with zero steady state error while with the second INNc there is a steady state error in the system response.

The second important point which effects on the performance of INNc is the number of neurons in the hidden layer. From practical results, it was found that, if two neural networks with different number of neurons in the hidden layer and same training data are trained to learn the INNc for a certain joint in the MA2000 manipulator until they reach the same value of the MSE, the INNc with the largest number of the neurons in the hidden layer gives better system response than that of smaller number of neurons in the hidden layer even the two INNc have the same MSE and same training data. This is due to that INNc with largest number of neurons in the hidden layer can map the input vectors with the output vectors in more details (due to the large number of the neurons in the hidden layer) than the other uses small number of neurons in the hidden layer. Figure 10 shows the base step response using INNc with the same MSE but differ in the number of the neurons in the hidden layer (23 and 9 neurons). As it is expected system response with the INNc of largest number of neurons in the hidden layer is better than that of small number of neurons in the hidden layer. However, there is a limit for the number of neurons in the hidden layer because if the number of neurons in the hidden layer becomes large this may push the system to be unstable. Figure 11 shows the response of the three major axes (base, shoulder, and elbow) in the MA2000 manipulator for several steps with using INNcs.

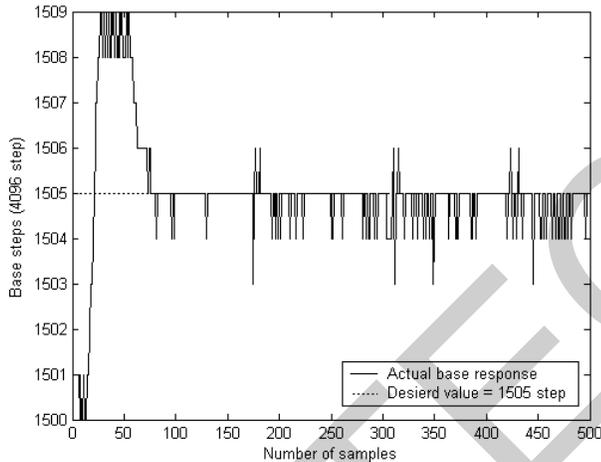


Figure 8. Base step response (small change) of the MA2000 robotic manipulator using INNc.

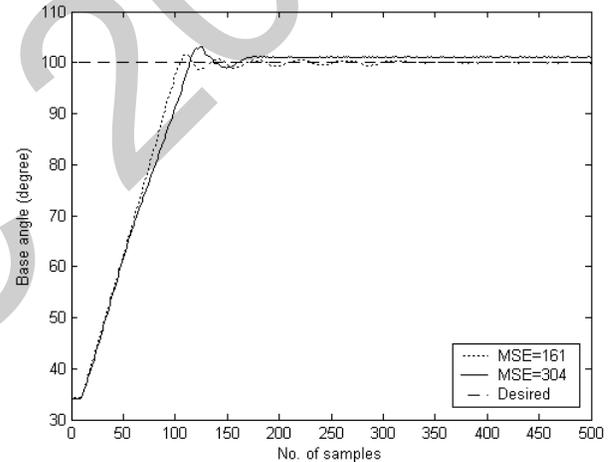


Figure 9. Step response of the base joint using two inncs with different MSE.

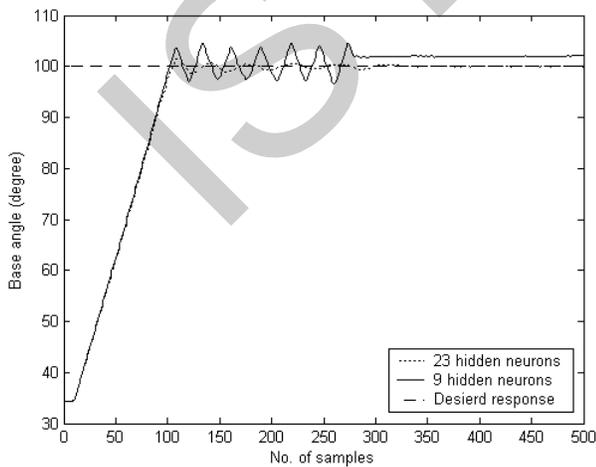


Figure 10. Step response of the base joint using two inncs with different number of neurons in the hidden layer.

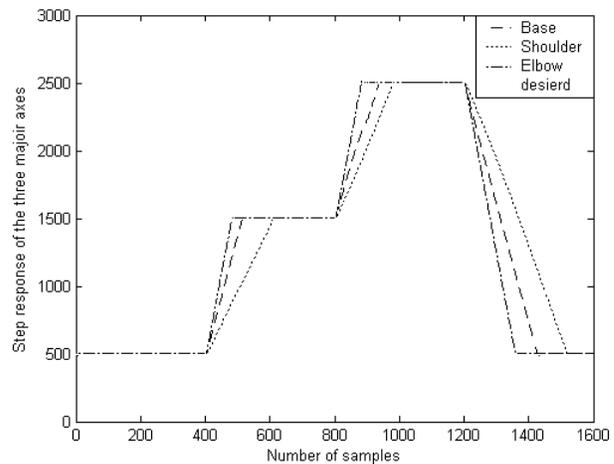


Figure 11. Response of the major axes of the MA2000 manipulator for different set points using INNc.

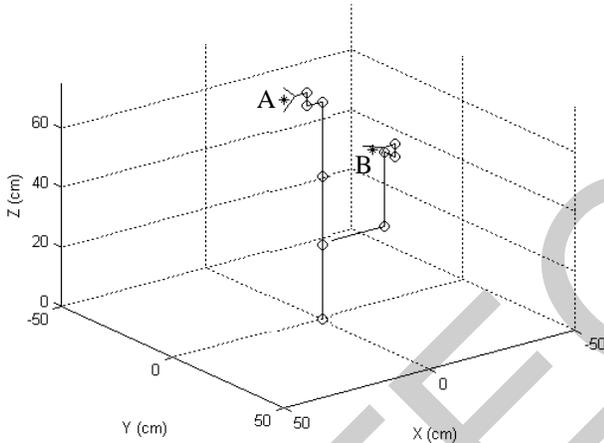
### PERFORMANCE OF MA2000 MANIPULATOR IN CARTESIAN COORDINATE

Assume the MA2000 manipulator has the following joints variables  $90^\circ, 90^\circ, 0^\circ, 90^\circ, 180^\circ, 90^\circ$  which make the central point of the gripper lies at point A[13,0,77.4]cm with respect to the global coordinate of the manipulator system and it is required to move the central point of the gripper to a new position which is given by point B[-15,5,54.4]cm as shown in Figure 12 by using INNCC. Figure 13 shows the error in Cartesian coordinate in the workspace of the MA2000 manipulator when gripper moves from point A[13,0,77.4]cm to point B[-15,5,54.4]cm. It is clearly that at the end of the motion the Cartesian error becomes zero and the central point of the gripper attains the desired position with the desired orientation with zero steady state error.

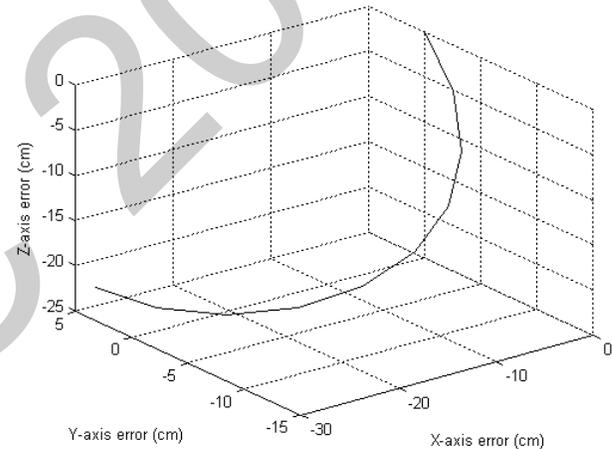
### CONCLUSIONS

The following guide points are concluded form practical design, implementation and results of INNCC trained by off-line training. The INNCC is used to control the operation of robotic manipulator in the real time operation:

- ✓ The off-line training signal for the INNCC must cover all ranges of the input and output variables of the system to get best training of the neural network in the off-line training phase.
- ✓ Increasing the number of neurons in the hidden layer (to certain value found by trial) that are used in the hidden layer of the INNCC gives better controller performance in the real time operation.
- ✓ Good off-line training of the neural network to learn inverse dynamic of complex plant structure by using good hard training signal which is taken from the open loop response of the system, lead to good learning of the neural network and on-line training is not required in the real time operation of the INNCC.
- ✓ System steady state error can be zero with the using of the INNCC.
- ✓ INNCC can be used for small step change in the system output.
- ✓ As MSE in the off-line training decreases the performance of the INNCC will be better in the real time operation.



**Figure 12.** Sketch of MA2000 manipulator with the central point of the gripper at points A[13,0,77.4]cm and point B[-15,5,54.4]cm.



**Figure 13.** Error in Cartesian coordinate due to movement of the MA2000 manipulator from point A[13, 0, 77.4]cm to point B[-15, 5, 54.4]cm.

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# PRECIPITATION PHENOMENA STUDY DURING AGEING OF CU-SN AND AL-AG ALLOYS.

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## Abstract:

Ageing study of supersaturated solid solutions Cu-13 wt. % Sn and Al-20 wt. % Ag has shown that the two types of precipitation (continuous and discontinuous) would occur for various temperatures and plastic deformation rates (thickness reduction by cold rolling following rapid quenching in iced water). The precipitated phases take place generally on the grain boundaries (discontinuous precipitation DP) and inside the grains (continuous precipitation CP). A detailed study of phases' development conditions and the growth controlling mechanisms has been carried out, for several ageing temperatures with and without plastic deformation of the supersaturated solid solution using various experimental techniques (optical microscopy, X-ray diffraction and microhardness measurements).

**Keywords:** *Discontinuous precipitation; Microstructure; Cu-Sn; Al-Ag.*

## 1. Introduction

The discontinuous precipitation shows a solid state reaction where a supersaturated solid solution  $\alpha_0$  is replaced by a cellular structure composed of two ( $\alpha + \beta$ ) phases. From scientific and commercial perspective, this reaction was considered of great interest for a long time; this interest is not only the mechanism of the reaction itself, but also the tremendous properties changes of materials that it induces. Since the discovery of the discontinuous precipitation by Agreew et al [1] in 1930 of Ag - Cu alloys, the understanding of this reaction has enormously changed [2-7]. Nevertheless, ambiguities still remain on many important issues related to it. For example, it is still impossible to predict which binary systems, precipitation may occur intermittently, or what are the actual reaction driving forces, or what is the nucleation and growth mechanism that is the most likely for each alloy system.

The continuous precipitation has a large influence on the progress of the decomposition process of some discontinuous supersaturated solutions [8-10]. The discontinuous precipitation is generally controlled by the grain boundary diffusion while the continuous precipitation is controlled by volume diffusion. The grain boundaries constitute an area full of structural defects where the diffusion will always be important, but the appearance of continuous precipitation reaction stops the discontinuous reaction happening there by reducing the migration of solute atoms from the matrix to the grain boundary [11, 12]. On the other hand reciprocal effect, that is, any influence of the discontinuous decomposition reaction on the continuous precipitation, has not hitherto been observed. We know pertinently that this cannot take place for two reasons that we think are important:

- Discontinuous precipitation starts only at grain boundaries and therefore cannot prevent the appearance of a continuous precipitate nucleation within the grain on any defect (dislocation for instance).
- Outside the cell containing the precipitates lamellae, the matrix remains still supersaturated during the discontinuous precipitation and therefore "does not know" that the latter is happening.

In the Cu-13 wt. % Sn alloy used as the matrix of super-conducting Nb/Cu-Sn composites, intensive discontinuous decomposition was discovered after 10% cold deformation followed by prolonged ageing at 553K [13]. The decomposition of  $\text{Cu}_3\text{Sn}$  from a supersaturated solid solution of tin in copper during ageing is initiated by discontinuous precipitation and followed by continuous precipitation. The cell growth rate decreases with ageing time after linear growth rate of the cells. This was attributed to the influence of continuous precipitation on the cell growth. The mass transport of tin during the linear cell growth occurs by grain boundary diffusion of tin in a copper-tin solid solution and prior cold work increases the rate of continuous precipitation but has no effect on discontinuous precipitation [11].

The basic sequence of decomposition in Al-Ag alloys has been found to be as follows [14]:

$\alpha(\text{fcc})$  phase  $\rightarrow$  spherical GP zones  $\rightarrow$  metastable  $\gamma'$ -phase (hcp)  $\rightarrow$  equilibrium  $\gamma$ - phase (hcp). The interfacial structure and growth kinetics of  $\gamma'$  and  $\gamma$  ( $\text{Ag}_2\text{Al}$ ) precipitate plates in Al-Ag alloys have been studied by conventional and in-situ transmission electron microscopy (TEM) technique because these precipitates represent one of the simplest diffusion transformations involving a distinct change in crystal structure, i.e. from fcc to hcp [15].

In a sample of Al-4.5 at. % Ag alloy aged at temperatures up to 498K where coarser GP zones exist, reversion into a plate-like metastable  $\gamma'$ -precipitates takes place [16]. The study of the growth effect of GP zones near the surface and grain boundaries as vacancy sites of the stress-strain parameters of Al-Ag alloys has been carried out [17].

A study of ageing in cold-worked Al-Ag alloys during the first stage of precipitation was performed, by means of small-angle x-ray scattering. The deformation of precipitated particles by cold-work is a new and powerful means of investigating the mechanism of plastic deformation inside the material [18].

## 2. *Experimental methods*

These materials were prepared in our laboratory by fusion in a device at a high vacuum ( $10^{-5}$  Torr) using pure materials. After the melting the ingots have undergone plastic deformation by cold rolling before the homogenization treatment in order to accelerate the structure homogenization kinetics. The homogenization temperature and ageing were chosen from the equilibrium diagrams [13].

After mechanical polishing with diamond paste, the samples are attacked in the following chemical baths after cleaning with alcohol and ultrasounds: concentrated nitric acid (53%) for Cu-13 wt. % Sn alloy during one second and Keller's reagent for the Al – 20 wt. % Ag alloy at room temperature for (1-20) s. The microstructure evolution has been followed mainly by optical microscopy and X-ray diffraction. The X-ray diffraction analysis is performed by a "PAN Alytical X"

Pert PRO" diffractometer using  $\text{CuK}\alpha$  radiation; to prevent oxidation of the samples during different analysis a protective atmosphere of nitrogen was used. The Vickers microhardness was measured with an AFFRI hardness testing machine.

The chemical analysis of the Al-20 wt. % Ag and Cu- 13 wt. % Sn alloys is presented in Table 1:

Element	Al	Zn	Fe	Cu	Si	Mg
wt. %	79.92	19.95	0.05	0.02	0.05	0.01
Element	Cu	Sn	Al	Ni	Si	Mg
wt. %	86.95	12.89	0.07	0.03	0.04	0.02

Table 1: Chemical composition of Al-20 wt. % Ag and Cu- 13 wt. % Sn alloys

### 3. Results and discussions

#### 3.1. Cu – 13 wt. % Sn alloy

A 40 minutes homogenization performed after plastic deformation is normally insufficient to trigger the recrystallization reaction. If it is followed by quenching and ageing at lower temperature, it must therefore have an influence on the precipitation phenomenon, because of structural defects it introduces into the matrix.

Thus, we took three samples which were subjected to deformation by cold rolling 20, 40 and 60 % respectively, followed by homogenization annealing 40 minutes at 873K, quenching in water and ageing at 553K. For the first sample ( $\epsilon = 20\%$ ) the precipitation takes place only on the grain boundaries (in a form of cells which tend to stretch and become rods of well defined direction with regards to the position of grain boundary) (Fig. 1a, b). We note that the precipitation kinetics is very slow and it is the phase  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ ) that is observed according to equilibrium diagram and literature data [9-11].

For the second sample ( $\epsilon = 40\%$ ), we observed two types of precipitation: inter-granular and intra-granular (Fig. 2). The latter is stimulated by the presence of sliding lines and shows to be more abundant after a long ageing (Fig. 2a). In some areas of the grain it forms a structure similar to that of Widmanstätten (Fig. 2b). In all cases it is always the  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ ) that arises.

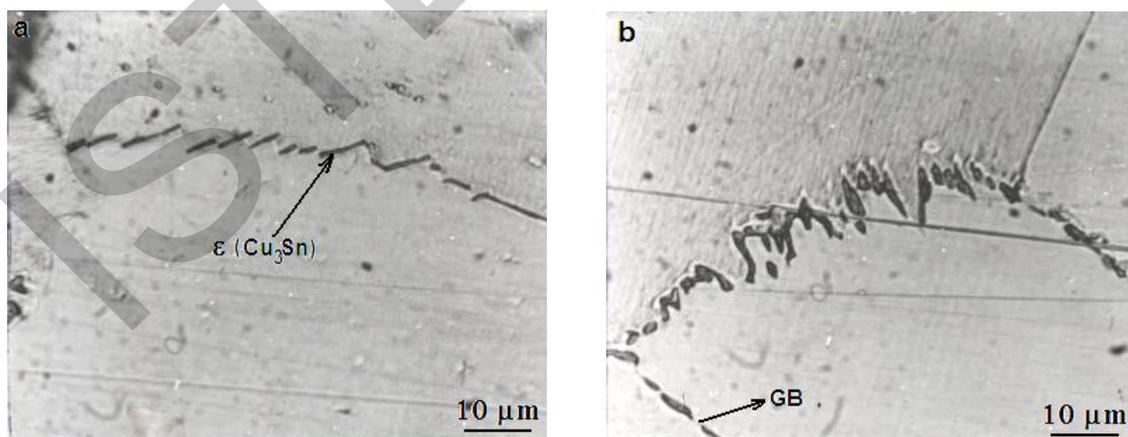


Fig.1. Cu-13 wt. % Sn alloy deformed of 20 %, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 350 hours (a) and 1700 hours (b), (GB-grain boundary).

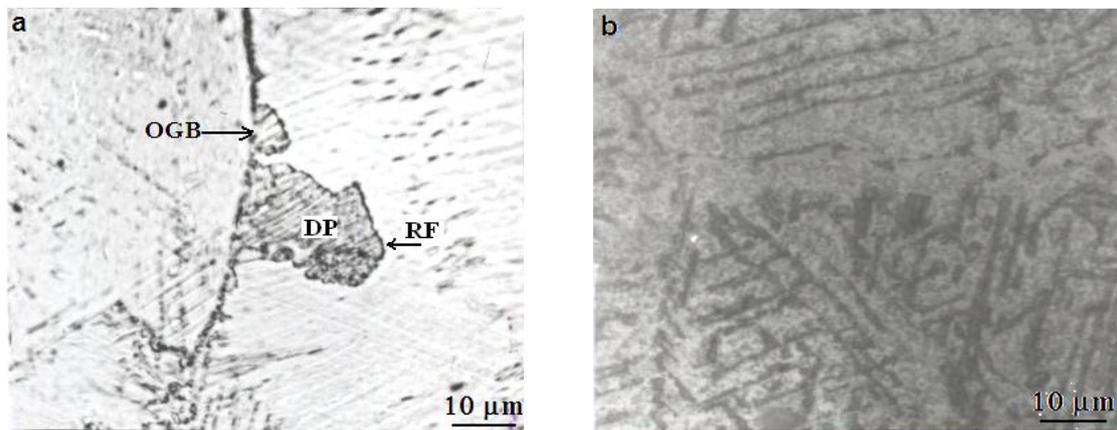


Fig.2. Cu-13 wt. % Sn alloy, deformed of 40%, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 400 hours (a, b). **OGB**-location original grain boundary, **RF**-reaction front of DP.

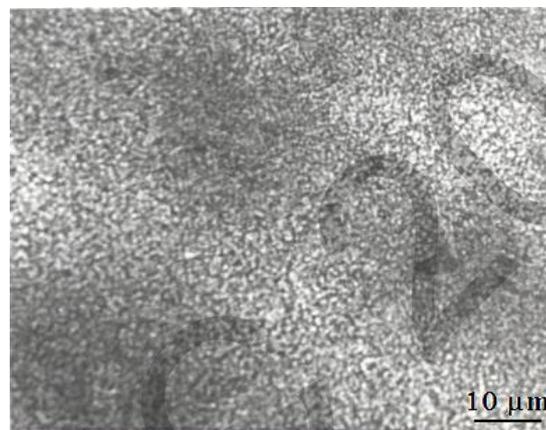


Fig.3. Cu-13 wt. % Sn alloy deformed of 60 %, homogenized at 873K for 40 min, quenched in iced water and ageing at 553K for 1400 hours.

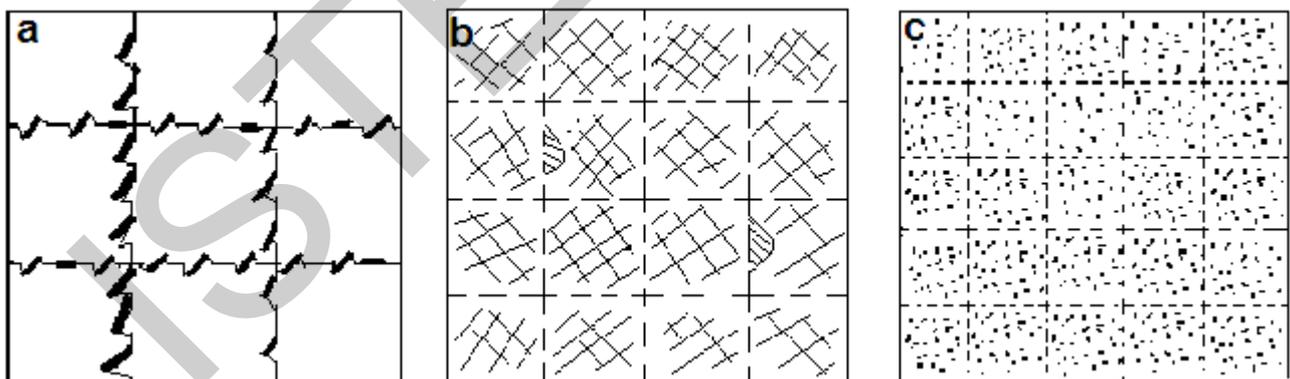


Fig.4. Types of precipitation observed for a Cu-13 wt. % Sn alloy, deformed  $\epsilon = 20\%$  (a),  $40\%$  (b) and  $60\%$  (c), homogenized for 40 mn at 873K quenched and aged at 553K.

For the third sample ( $\epsilon = 60\%$ ), the precipitation is more homogeneous and takes place within the grains; it is comparable to a continuous precipitation of  $\epsilon$  phase (Fig. 3). Figure 4 sums up the results of this study and shows clearly that the precipitation is stimulated by a prior deformation of the sample (it does not practically appear for these same

maintaining times at 553K) if the sample was not submitted to a prior deformation (case of an alloy studied by Sudareva et al [12]).

The microhardness variation curves of Cu-13 wt. % Sn alloy during ageing at 553K are presented in Fig. 5. The alloy becomes soft with ageing time extension and its mechanical properties are reduced by the appearance of equilibrium precipitate  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ ). As expected, it has been found that when discontinuous precipitation leads to the formation of lamellae, the coarsening did not lead to a globalization but only to an increase in the lamellae spacing. It is then always possible to distinguish between continuous and discontinuous precipitation [19].

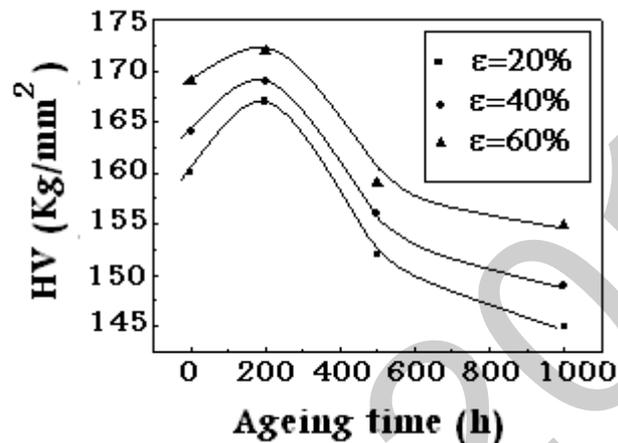


Fig. 5: Vickers microhardness variation HV for Cu-13 wt. % Sn alloy, homogenized for 40 mn at 873K quenched and aged at 553K.

### 3.2. Al – 20 wt. % Ag alloy

In the Al-Ag system, optical metallographic is therefore a straightforward method to study the precipitation morphology. Typical microstructures of aged specimen at higher temperature (623K) are shown in Fig. 6. Contrary to most alloys that exhibit discontinuous precipitation, the aspect of precipitate particles at grain boundaries is quite different.

The third sample has been aged at 623K. Two types of precipitation were observed:

1. Discontinuous precipitation at grain boundaries (Fig. 6 a-c).
2. Intergranular continuous precipitation which occurs in a form of needles inside the grain, comparable to the Widmanstätten structure (Fig. 6d).

It should be noted that despite a long extension of the ageing time, the lamellar cells do not progress well within the grain because of the occurrence of continuous precipitation in the form of Widmanstätten structure, which hinders the development of the cells.

The spectrum of X diffraction shown in Figure 7 confirms obviously the discontinuity of reaction; during the ageing a halving of the peak of diffraction is observed. We also note a displacement of the diffraction lines in the continuous precipitation and any peak of the phases  $\gamma'$  and  $\gamma$ . To better appreciate this halving of the lines we have still recourse to the diffraction of the X-rays by using a Debye-Scherrer back plan Fig. 8. For the not deformed samples, the obtained movies presenting spots of diffraction are characteristic of a structure with big grains the nature of which it is difficult to estimate [19]. For the deformed sample 30 %, after 1 hour of ageing in 553K, we observe rings of diffraction, characteristics of a structure with fine grains.

The precipitate grows as a faulted structure, but after long ageing times the faults are removed and the lattice becomes ordered. The transformation occurs by discontinuous precipitation involving a grain growth mechanism.

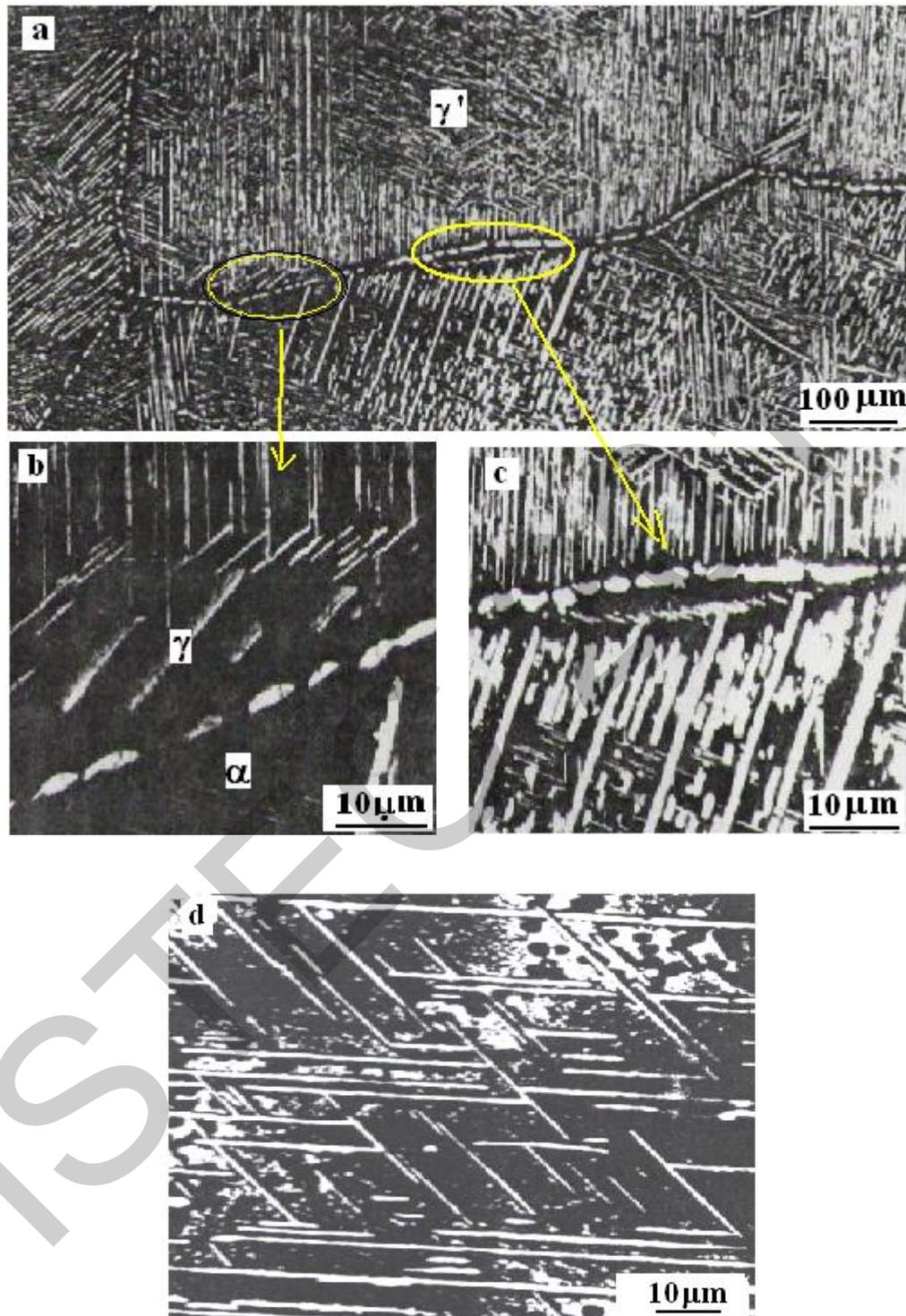


Fig. 6: Microstructures of Al – 20 wt. % Ag alloy homogenized 16 hours at 823K, quenched in iced water and aged at 623K during 115 hours (a-c) and 190 hours (d).

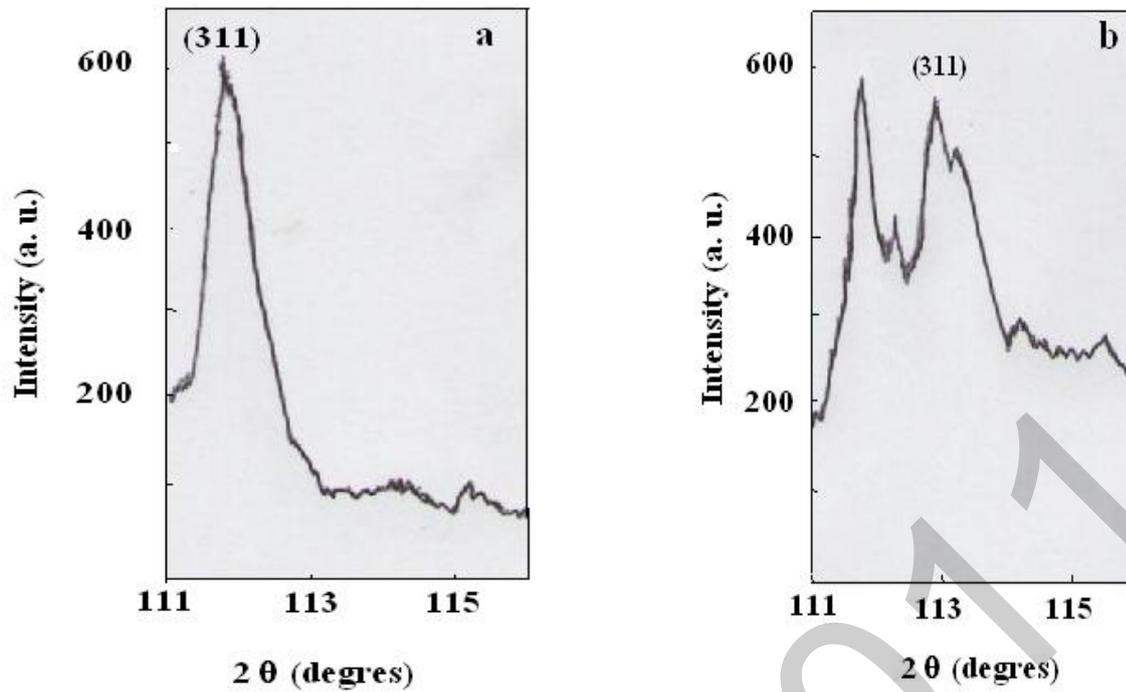


Fig. 7: X-ray diffraction peak of Al-20 wt. % Ag alloy, homogenized at 823K for 5 h quenched (a) aged at 553K for 5 h (b). CuK $\alpha$  radiation (10 mA, 30 kV)

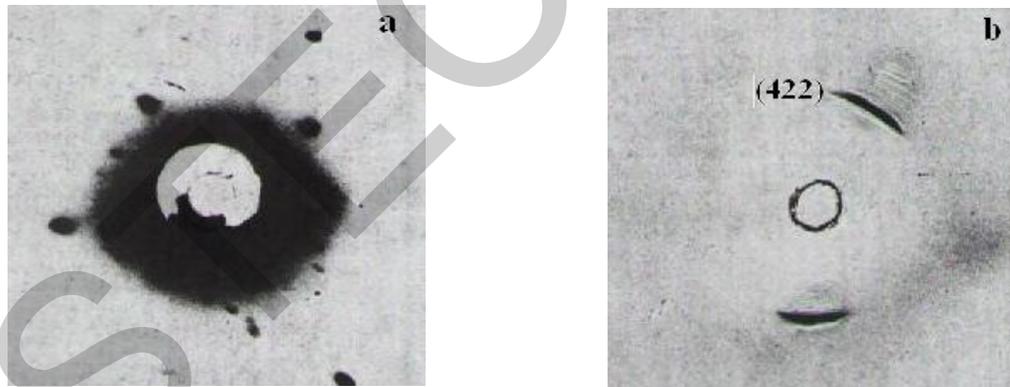


Fig. 8: Debye-Scherrer back plane films of Al-20 wt. % Ag alloy, homogenized at 823K for 5 h quenched (a), deformed 30% and aged at 553K for 1 h (b). CuK $\alpha$  radiation (10 mA, 30 kV)

#### 4. Conclusion

The study of both Cu-Sn and Al-Ag alloys has enabled us to confirm the multiplicity and complexity of precipitation phenomena and to better appreciate the interaction and mutual influence of two types of precipitation in an alloy.

By means of very simple experimental methods but quite rigorous, we show that:

- \* The precipitation reaction is very slow in the Cu-13 wt. % Sn alloy and only a preliminary plastic deformation can stimulate appreciably.
- \* The plastic deformation is important (10 and 30 %), moreover, the grain obtained after homogenization and quenching is fine.
- \* Two types of precipitation occur in Cu-13 wt. % Sn alloy. However, the intermittent precipitation is limited to a deformation of the grains boundaries in an attempt of development stopped by plentiful one haste continues intergranular (in the form of structure of Widmanstatten).
- \* In Al-20 wt. % Ag, the formation of cells with lamellae is observed inside grains as well as on the boundaries.
- \* Both types of precipitation are observed in both alloys: discontinuous with lamellar form and continuous inside the grains that stop the growth of these blades by depriving them of solute atoms flow towards the reaction front.

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# PREDICTION OF SLOPE STABILITY USING STATISTICAL METHOD AND FUZZY LOGIC

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## ABSTRACT

The main goal of this research is to predict the stability of slope using fuzzy logic, Adaptive Neuro Fuzzy Inference System (ANFIS), and statistical method, Multiple Linear Regression (MLR). Four limit equilibrium methods (LEM) i.e. Morgenstern-Price, Janbu, Bishop and Ordinary were used to calculate the safety factors for various designs of slope. For prediction, five parameters were used as the inputs i.e. height of slope, unit weight of slope material, angle of slope, coefficient of cohesion, and internal angle of friction, while the output parameters are factors of safety. MLR obtained regression square ( $R^2$ ) of 0.470 for Bishop, 0.459 for Janbu, 0.470 for Morgenstern-Price, and 0.468 for Ordinary Method, while ANFIS obtained regression square ( $R^2$ ) of 0.9996 for Bishop, 0.9994 for Janbu, 0.9995 for Morgenstern-Price, and 0.9997 for Ordinary Method. The result showed that ANFIS could predict the safety factors with high accuracy compare with MLR.

## INTRODUCTION

Slopes either occur naturally or engineered by humans. Slope stability problems have been faced throughout history when men and women or nature has disrupted the delicate balance of natural soil slopes, so the slope failure become a common natural disaster which takes place around the world. In addition, the increasing demand for engineering cut and fill slopes on construction has only increase the need to understand analytical methods, investigative tools, and stabilization methods to solve slope stability problems. Slope stabilization methods involve specialty construction techniques that must be understood and modeled in realistic ways. An understanding of geology, hydrology, and soil properties is central to applying slope stability principles properly. Investigations of failures of soil masses are subjects touching both geology and engineering. These investigations call the joint efforts of engineering geologists and geotechnical engineers. Slope stability problem has been an important issue in geotechnical engineering. The evolution of slope stability analyses in geotechnical engineering has followed closely the developments in soil. Geotechnical engineers have to pay particular attention to geology, ground water, and shear strength of soils in assessing slope stability. Analyses must be based upon a model that accurately represents site subsurface conditions, ground behavior, and applied loads. Judgments regarding acceptable risk or safety factor must be made to assess the results of analyses. Therefore, slope investigation and classification are important for the community (Lee et al. 2002; Choobbasti et al. 2009; Ping et al. 2009; Vector 2008).

The limit equilibrium methods (LEMs) (i.e. linear methods: infinite slope analysis, wedge analysis, circular arc methods; non-linear methods: Bishop's routine method, Janbu's simplified method, Spencer's method, Morgenstern and Price's method, Janbu's rigorous analysis) are widely used for the analysis of slopes (Nash 1987). Historically, these methods were developed before the advent of computers; computationally more complex methods followed later. These computational methods have varying degrees of accuracy, depending on the suitability of the simplifying assumptions for the situation being analyzed. A useful concept in the application of limit equilibrium methods for slope stability analysis and design is the idea of mobilized shear strengths and mobilized shear strength parameters (Bromhead 1999; Sakellariou & Ferentinou 2005).

The power of Artificial Intelligent (AI) becomes more authoritative when the system is programmed to cater the need of complex applications. Adaptive Neuro-fuzzy Inference System (ANFIS) Model using neuro adaptive learning techniques which are similar to those of neural networks was originally presented by Jang. Given an input/output data sets, ANFIS constructs fuzzy Inference System (FIS) whose membership function (MF) parameters are adjusted using back propagation algorithm or other similar optimization techniques. Hence, the advantages of a fuzzy system can be combined with a learning algorithm (Sivarao et al. 2009; Merikoski et al. 2001; Jang 1996; MathWorks 2009 and Sakellariou & Ferentinou 2005).

Regression is most often used by scientists and engineers to visualize and plot the curve that best describes the shape and behavior of their data. As with most statistical analyses, the goal of regression is to summarize observed data as simply, usefully, and elegantly as possible. Researchers are often interested in the relationships between one variable and several other variables. Regression procedures find an association between independent and dependent variables that, when graphed on a Cartesian coordinate system, produces a straight line, plane or curve. The general purpose of Multiple Linear Regression (MLR) is to seek for the linear relationship between a dependent variable and several independent variables. (SigmaPlot 9 2004; SigmaPlot 11 2008; Sanford 2005; Xin & Xiaogang 2009).

The main objectives of this research are; calculate safety factors of various slopes using limit equilibrium methods (LEM), predict the result using Adaptive Neuro-fuzzy Inference System model and Multiple Linear Regression and develop a computer program to present the stability of slopes using Graphical User Interface (GUI).

## METHOD

In this research 210 different designs of slope which created by software that applied limit equilibrium methods were used. The range for the input parameters for those designs are: height of slope,  $H$  (1–6 m), unit weight of slope material,  $\gamma$  (15–22 kN/m<sup>3</sup>), angle of slope,  $\theta$  (11.31°–78.69°), coefficient of cohesion,  $c$  (0–50 kN/m<sup>2</sup>) and internal angle of friction,  $\phi$  (20°–40°) and the output is factors of safety. The comprehensive formulation of the software made it possible to easily analyze both simple and complex slope stability problems using a variety of methods to calculate the safety factors (Geo-Slope 2004). After carrying out the stability analyses, ANFIS model were used to predict the result for over all safety factors for all LEMs. The prediction constructed the rule statements based on the descriptions of the input and output variables defined with the fuzzy inference system. Another prediction method using Multiple Linear Regression applied for the same over all safety factors for all LEMs. From predicted data, Graphical User Interface program was generated to present the stability of slopes for all LEMs.

## RESULTS AND DISCUSSION

Five inputs, height of slope, unit weight of slope material, angle of slope, coefficient of cohesion, and internal angle of friction, and one output, factor of safety, were used as membership functions to build the fuzzy inference system with 243 rules and three epochs. On the other hand, the five input parameters and the over all output safety factors were used also for Multiple Linear Regression prediction.

The regression square ( $R^2$ ) which obtained by Adaptive Neuro-fuzzy Inference System prediction are 0.9996 for Bishop, 0.9994 for Janbu, 0.9995 for Morgenstern-Price, and 0.9997 for Ordinary Method, while the regression square ( $R^2$ ) which obtained by Multiple Linear Regression prediction are 0.470 for Bishop, 0.459 for Janbu, 0.470 for Morgenstern-Price, and 0.468 for Ordinary Method. Figure 1 until 4 for Bishop, Janbu, Morgenstern-Price, and Ordinary, respectively, showed the calculated values using SLOPE/W and the predicted values using Adaptive Neuro Fuzzy Inference System. The result showed that Adaptive Neuro Fuzzy Inference System could predict the safety factor with high accuracy and close to the target data. In addition, figure 5 until 8 for all LEMs, showed the calculated values using SLOPE/W and the predicted values using Multiple Linear Regression. The result showed that Multiple Linear Regression could predict the safety factor with low accuracy compared with Adaptive Neuro Fuzzy Inference System. Figure 9 until 12 showed the comparison between ANFIS and MLR prediction and the calculated data for all LEMs.

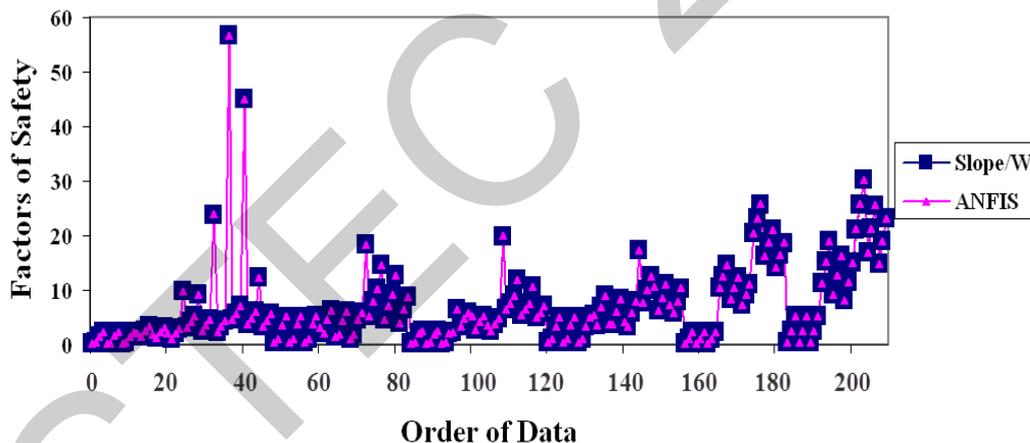


Figure 1 Comparison of calculated factor of safety using Bishop and predicted using ANFIS

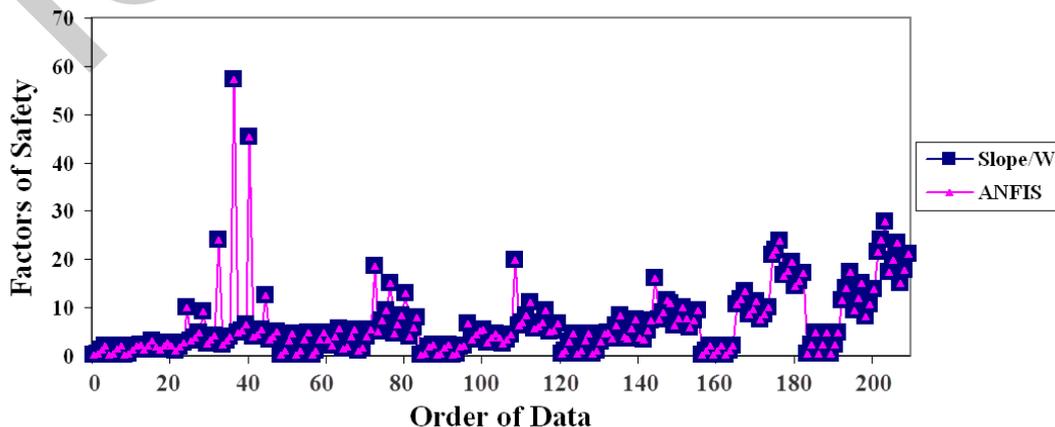


Figure 2 Comparison of calculated factor of safety using Janbu and predicted using ANFIS

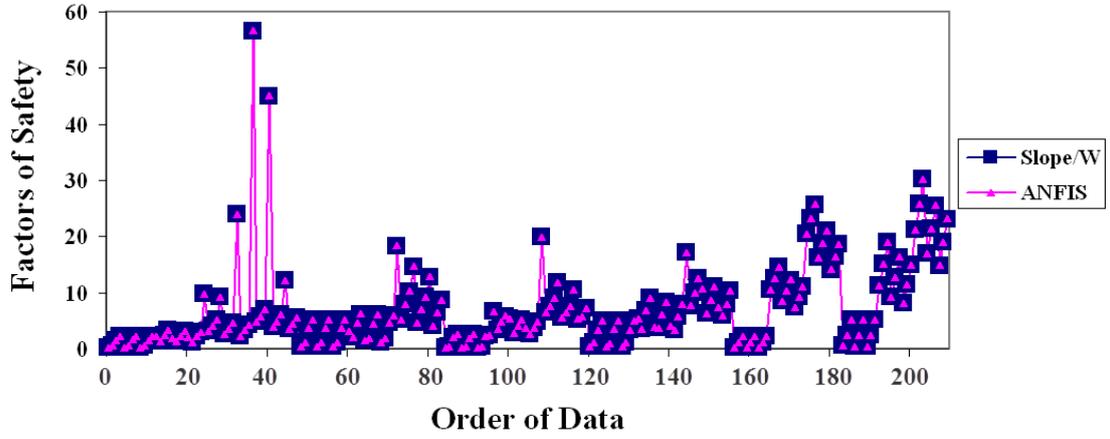


Figure 3 Comparison of calculated factor of safety using Morgenstern-Price and predicted using ANFIS

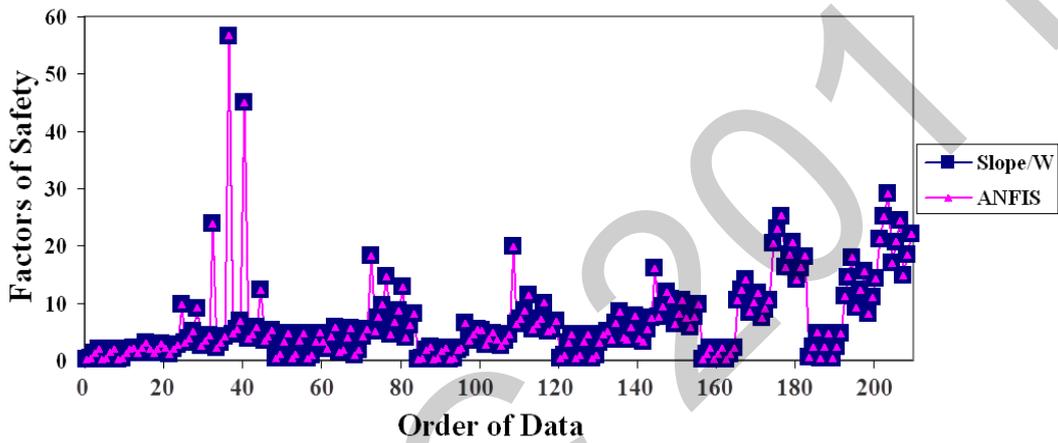


Figure 4 Comparison of calculated factor of safety using Ordinary and predicted using ANFIS

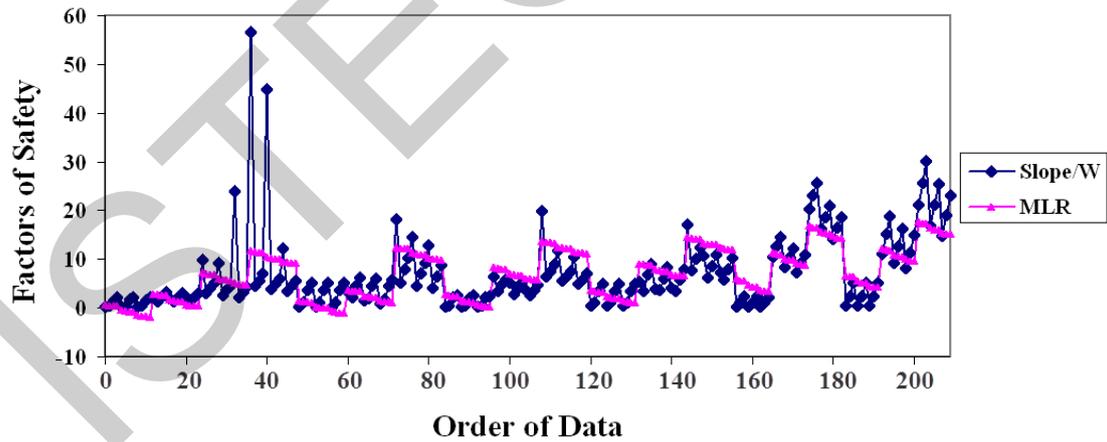


Figure 5 Comparison of calculated factor of safety using Bishop and predicted using MLR

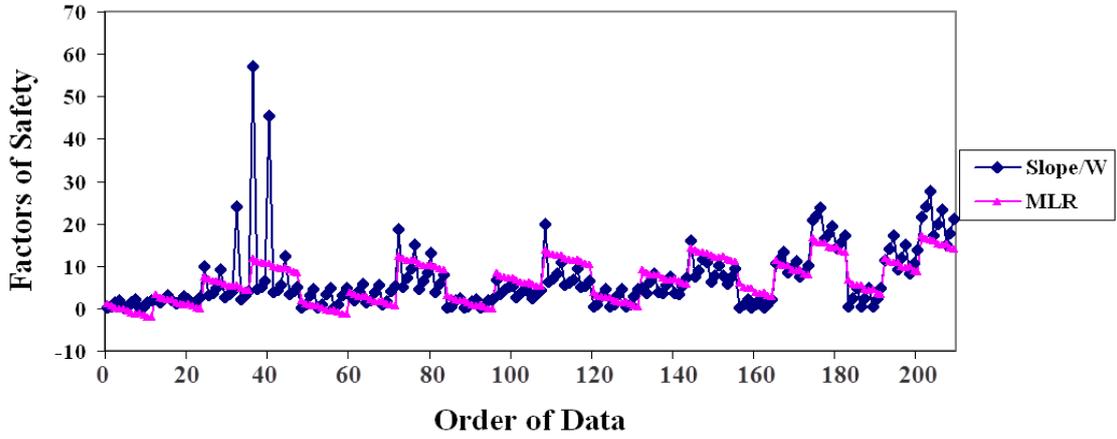


Figure 6 Comparison of calculated factor of safety using Janbu and predicted using MLR

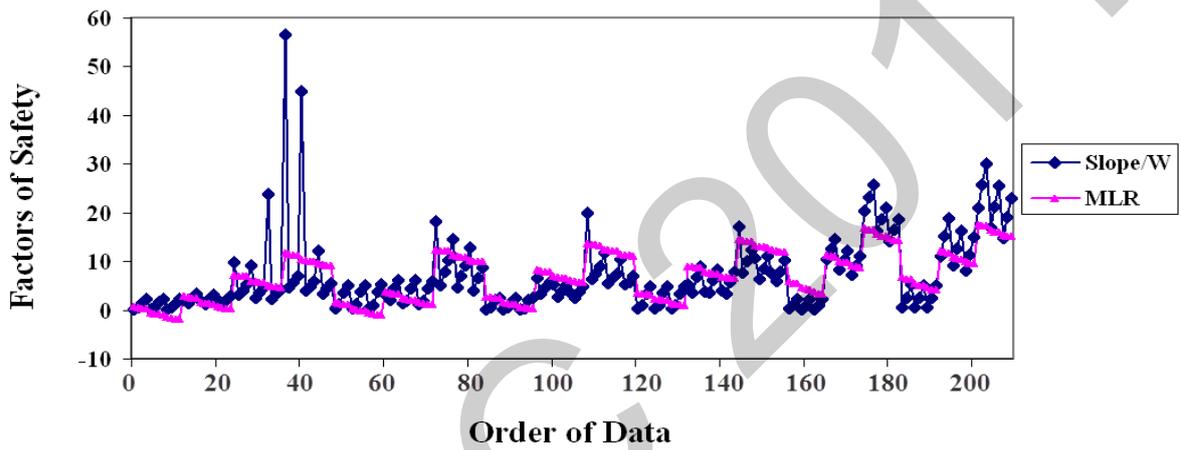


Figure 7 Comparison of calculated factor of safety using Morgenstern-Price and predicted using MLR

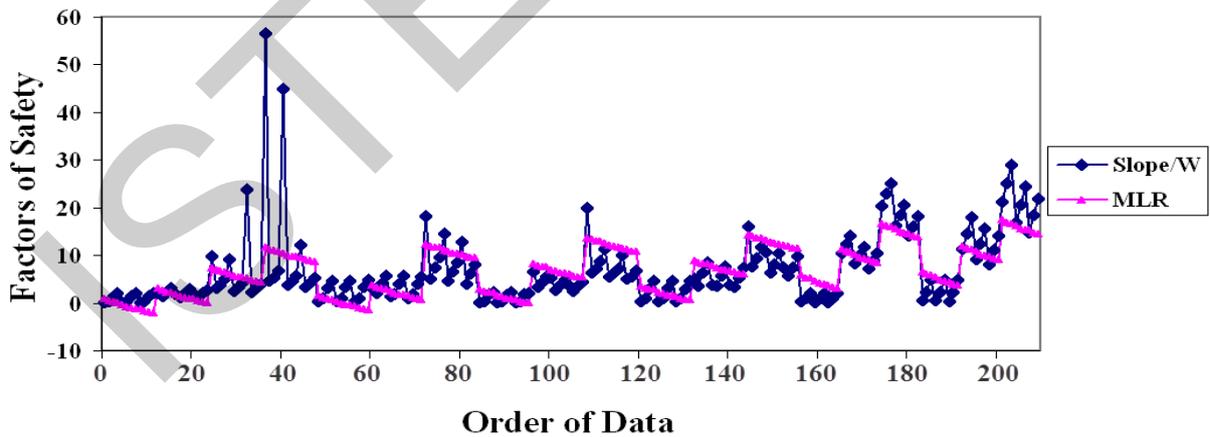


Figure 8 Comparison of calculated factor of safety using Ordinary and predicted using MLR

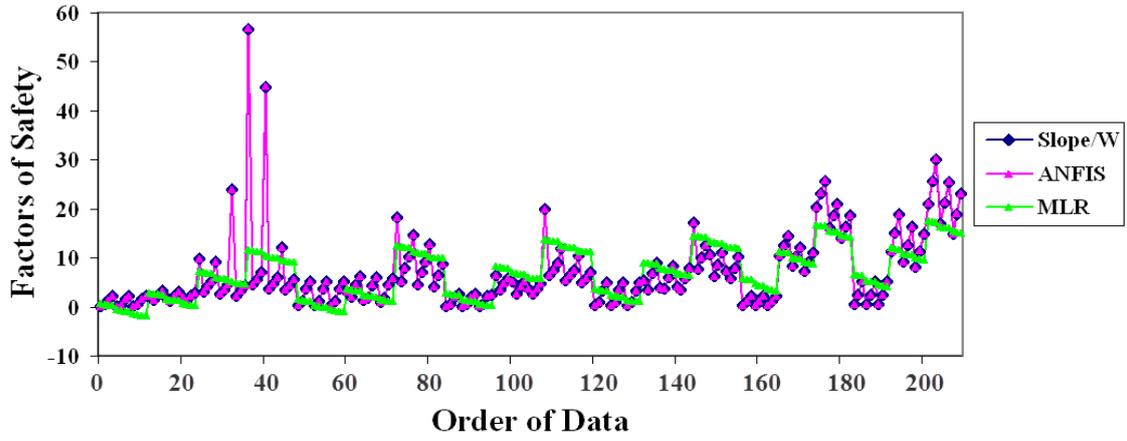


Figure 9 Comparison of ANFIS and MLR for Bishop

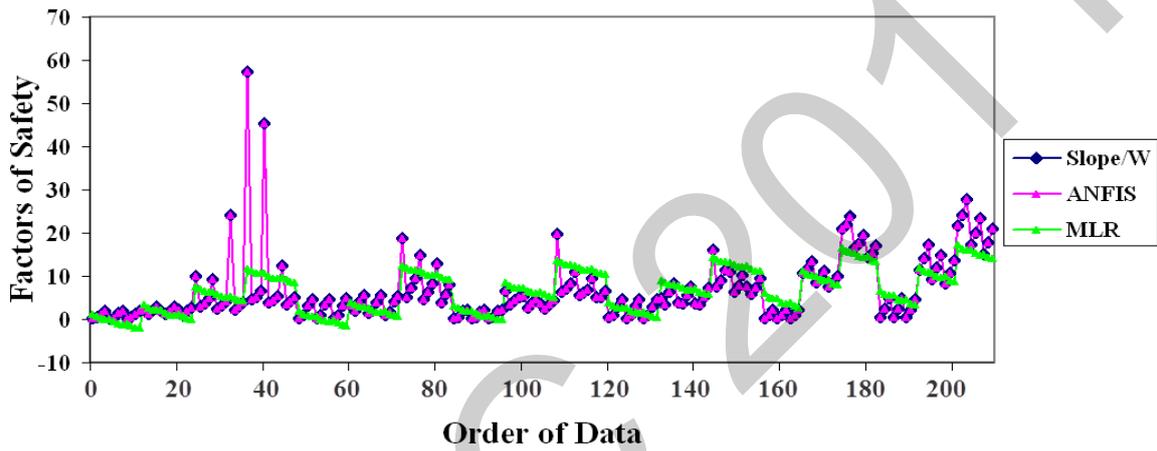


Figure 10 Comparison of ANFIS and MLR for Janbu

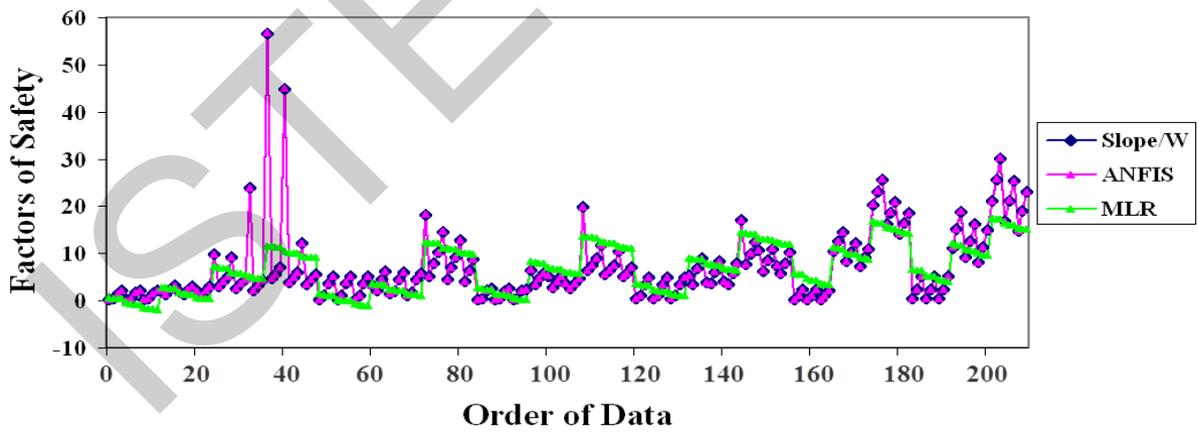


Figure 11 Comparison of ANFIS and MLR for Morgenstern-Price

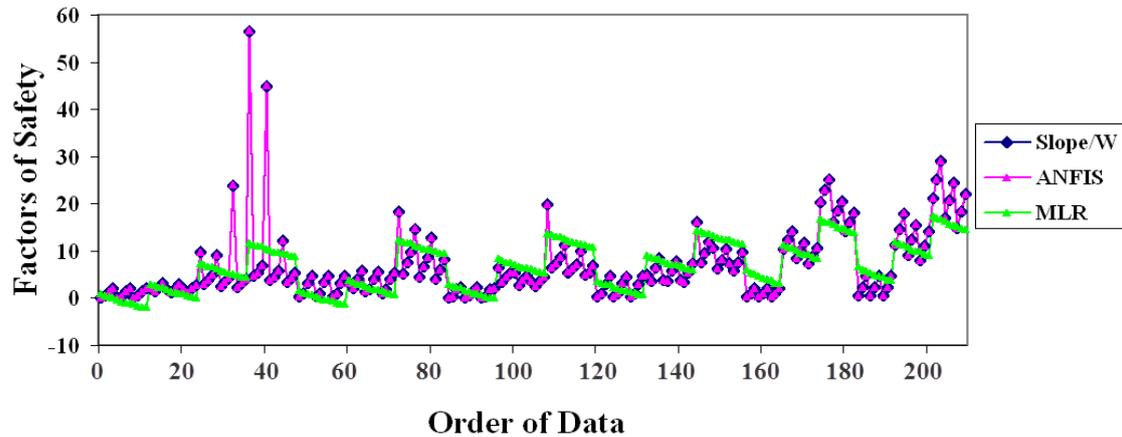


Figure 12 Comparison of ANFIS and MLR for Ordinary

## CONCLUSION

Limit equilibrium methods were used to calculate safety factors for 210 different designs with five input parameters: height of slope, unit weight of slope material, angle of slope, coefficient of cohesion, and internal angle of friction. Adaptive Neuro Fuzzy Inference System model and Multiple Linear Regression were used to predict the five input parameters and the overall output safety factors. From predicted data, Graphical User Interface program was generated to present the stability of slopes. The result seemed that Adaptive Neuro Fuzzy Inference System model could predict the safety factors with high accuracy compared with Multiple Linear Regression model.

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# PRESSURE DISTRIBUTION ON HYDRODYNAMIC THRUST BEARING SHOE, SOLVING REYNOLDS EQUATION

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## Abstract

In this article pressure distribution on the shoe of thrust bearing of a centrifugal pump has been calculated, using two dimensional Reynolds equations with help of MATLAB software. The thrust bearing has been analyzed in steady and unsteady states individually and compared logically. API 610 and ISO 13709 standards are governing at the same time. The result of this investigation is exact location of critical point on shoe area, pressure distribution over the shoe and maximum pressure amount on the critical point. The aim of finding this pressure is to discover the reason of pad deformation and metal to metal contact in result of thin oil film thickness.

## Introduction

Studying hydrodynamic lubrication started in 19th century [3]. Raimond and Boyd [5] and Cole and Hughes [1] by theoretical and experimental studies proved curved boundaries for lubricant layer load-bearing. Sassenfeld and Walter [7] published that these boundary conditions were unstable moving in nature. The accurate analysis and solution of the Reynolds equation does not happen in many conditions. Logically the numerical methods [2,4] are needed to solve Reynolds equation [6]. By assuming thin-film lubrication approximation, the pressure is described, understanding Reynolds equation. Integrating the continuity equation and joining with the Navier-Stokes equation gives us a partial differential equation of elliptical type that is numerically solved by use of software. To obtain more exact results, recent improvements in computing technology have been used. The aim of this research is to present a pressure distribution valid in boundary conditions. Eventually, the important parameters are clearly compared to demonstrate the final result.

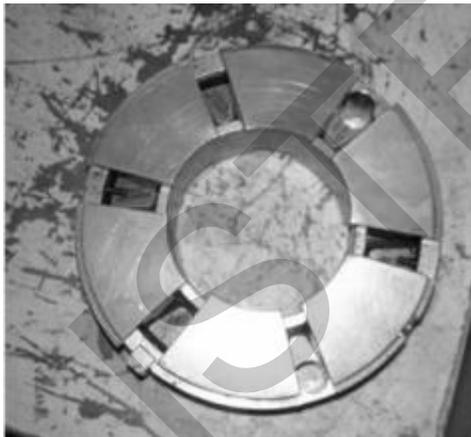


Fig1: Thrust bearing up-view



Fig2: Thrust bearing side view

## Governing equations

The studying of the behavior of hydrodynamic bearings needs the understanding of the fluid film between two solid surfaces in relative motion and the differential equation that governs the movement of this fluid. In hydrodynamic thrust bearing applying in a centrifugal pump, after a not very long time operating the pad area has metal to metal contact and loses the smooth surface, which happens in cause of abrasion between collar and shoe surface. Present study goals to find the critical point contact happens and measures the amount of pressure at this point. The solving process occurs under standard conditions and highest speed. The accuracy of this solution of Reynolds equation depends on how close the real conditions are to be. In general the developments use different combinations of short and long bearing solutions. An incompressible and isothermal Newtonian fluid is considered this approximation distributed a simple pressure distribution. The Reynolds equation is given joining the mass and momentum balances

and integrating the mass balance within the thickness of the film considering non-slip boundary conditions over the walls for all velocity components. The Continuity Equation and The Equilibrium Equation are called respectively as:

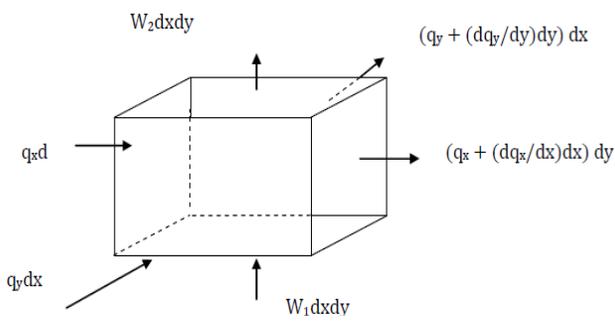


Fig3: Continuity equation element

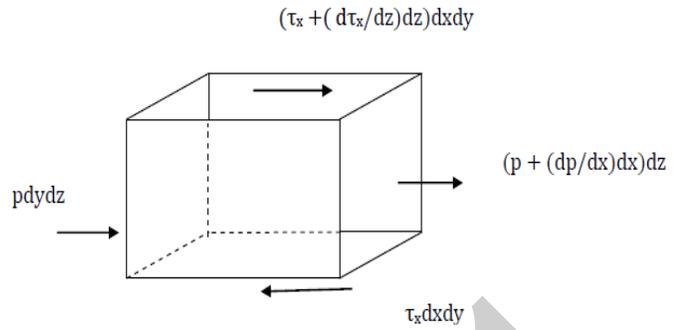


Fig4: Equilibrium Equation element

$$q_x dy + q_y dx + w_1 dx dy = \left( q_x + \frac{\partial q_x}{\partial x} dx \right) dy + \left( q_y + \frac{\partial q_y}{\partial y} dy \right) dx + w_2 dx dy$$

$$p dy dz + \left( \tau_x + \frac{\partial \tau_x}{\partial z} dz \right) dx dy = \left( p + \frac{\partial p}{\partial x} dx \right) dy dz + \tau_x dx dy$$

By substituting the continuity equation in to equilibrium equation regarding to boundary condition as below, we have the so called Reynolds equation.

$$\frac{\partial}{\partial x} \left( \frac{ph^3}{12\eta} \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{ph^3}{12\eta} \frac{\partial p}{\partial y} \right) = \frac{\partial}{\partial x} \left( p \frac{u_1 + u_2}{2} h \right) + \frac{\partial}{\partial y} \left( p \frac{v_1 + v_2}{2} h \right) + \frac{\partial}{\partial t} (ph)$$

We cannot solve this equation accurately unless we simplify that with:

- 1-  $v_1=v_2=0$  and  $u_1$  and  $u_2$  are independent of  $x$ .
- 2- Assuming incompressible fluid.
- 3- Having no changes of  $\eta$  with  $y$  or  $x$ .

For steady state we'll have:

$$\frac{\partial}{\partial x} \left( h^3 \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( h^3 \frac{\partial p}{\partial y} \right) = 12\eta u \frac{\partial h}{\partial x}$$

And for unsteady the equation we'll be as:

$$\frac{\partial}{\partial x} \left( h^3 \frac{\partial p}{\partial x} \right) + \frac{\partial}{\partial y} \left( h^3 \frac{\partial p}{\partial y} \right) = 12\eta \left[ u \frac{\partial h}{\partial x} + \frac{\partial h}{\partial t} \right]$$

Regarding to pump characteristics and shoe drawing:

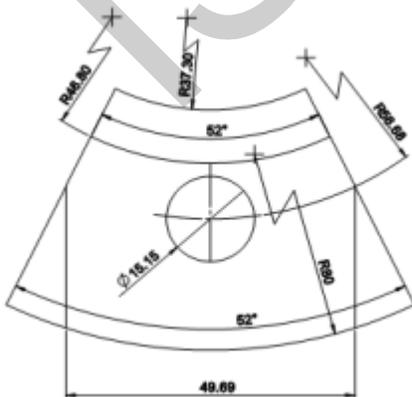


Fig5: shoe pad drawing

Company: Nuovo Pignone PVS – BARI

Type: 4x12 DDHF

Plant Location: Bandar Imam, IRAN

Service: HHP Boiler feed water pump

Speed: 4000 RPM

Drive: ELECTRIC MOTOR (Type: CT 500 Y2)

The properties below are given:

$$A = \int_0^{\theta} \int_{R_i}^{R_o} r dr d\theta = \int_0^{52^\circ} \int_{37.3}^{76} r dr d\theta = \theta \left[ \frac{r^2}{2} \right]_0^{52 \times \frac{\pi}{180}} \Big|_{37.3}^{76} = 1.989 \times 10^{-3} \text{ m}^2$$

$$T_{\text{eff}} = T_i + 0.8\Delta T = 50 + 0.8 \times 80 = 114^\circ\text{C}$$

ISO grade 46 oil viscosity regards to standard is:

$$\eta = 8.48 \times 10^{-7} \text{ Reyn} = 0.00585 \text{ Pa} \cdot \text{s}$$

$$R_m = 56.65 \text{ mm}$$

$$u = r\omega = 56.65 \times 10^{-3} \times 4000 \times \frac{2\pi}{60} = 23.7 \text{ m/s}$$

Respecting to API 610 the solution should satisfy two conditions:

- 1- Minimum film thickness should be greater than 8  $\mu\text{m}$ .
- 2- Maximum load divided by area should be smaller than 3500 kPa.

So by axial load formulation [ ] we have:

$$P_z = \bar{P}_z \times \frac{6\mu u b l^2}{h_0^2},$$

$$\mu = 0.00585 \text{ Pa} \cdot \text{s}, \quad u = 23.7 \frac{\text{m}}{\text{s}}, \quad b = 38.7 \text{ mm}, \quad l = 54.3 \text{ mm}, \quad \bar{P}_z = 0.1602,$$

$$\Rightarrow 3500 \times 10^3 = 0.1602 \times \frac{0.00585 \times 23.7 \times 38.7 \times 10^{-3} \times (54.3^2) \times 10^{-6}}{h_0^2}$$

$$\Rightarrow h_0 = 19.08 \mu\text{m} \rightarrow 19.08 \mu\text{m} > 8 \mu\text{m}$$

By these facts the model is acceptable. Now we calculate the gradient of shoe pad under operation:

$$h(x) = h_i - (h_i - h_0) \frac{x}{l}$$

$$\bar{h}_i = \frac{h_i}{h_0} = 2.18, \quad h_0 = 19.02 \mu\text{m} \rightarrow h_i = 41.59 \mu\text{m} \quad (\text{Design point for maximum load capacity})$$

$$h(x) = 41.59 \times 10^{-6} - 4.15 \times 10^{-4} x$$

For defining steady state, it should be said, in this state the distribution of pressure does not change respect to time and it is constant, so the  $dh/dt$  term in Reynolds equation is omitted.

$$\frac{\partial}{\partial x} \left( h^3 \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial y} \left( h^3 \frac{\partial P}{\partial y} \right) = 12\mu u \frac{\partial h}{\partial x}$$

In this state, the pump has been started for at least 30 seconds and has reached the final speed. In unsteady state term  $dh/dt$  in Reynolds equation appears and its effect on pressure distribution is apparently observed.

$$\frac{\partial}{\partial x} \left( h^3 \frac{\partial P}{\partial x} \right) + \frac{\partial}{\partial y} \left( h^3 \frac{\partial P}{\partial y} \right) = 12\mu u \frac{\partial h}{\partial x} + 12\mu \frac{\partial h}{\partial t}$$

Now regarding to pump datasheet it should be considered that operating of pump is fully loaded at starting time. Change of load while operating respect to time is equal to zero so:

$$\frac{\partial h}{\partial t} = \left( \frac{\partial h}{\partial t} \right)_u + \left( \frac{\partial h}{\partial t} \right)_p = \frac{\partial h}{\partial p} \times \frac{\partial p}{\partial t} + \frac{\partial h}{\partial u} \times \frac{\partial u}{\partial t} = \frac{\partial h}{\partial u} \times \frac{\partial u}{\partial t}$$

The function below is approximately estimated for electric motor running in startup time 3 seconds. This speed function is fitted to the start up diagram of electric motor in Datasheets.

$$t = 3s \longrightarrow u = 0.38t^3 - 0.95t^2 + 7.4t - 0.057$$

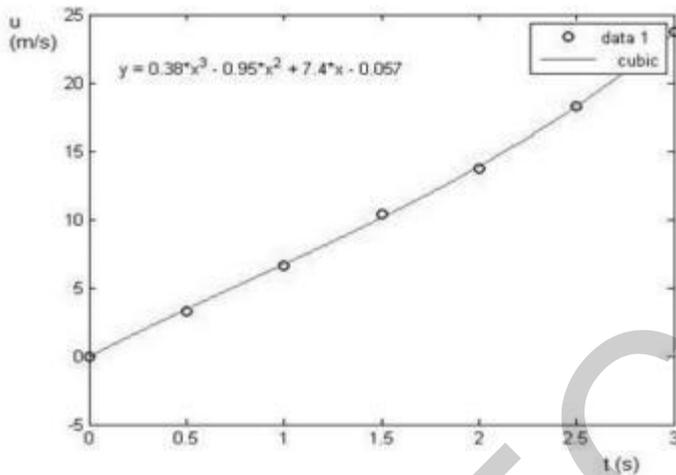


Fig 6: Speed fitted function and graph

By differentiating this function the maximum of the gradient is obtained.

$$t = 3s, \quad \frac{\partial u}{\partial t} = 3 \times 0.38 t^2 - 2 \times 0.95 t + 7.4$$

$$\frac{\partial^2 u}{\partial t^2} = 2 \times 3 \times 0.38 t - 2 \times 0.95 = 0 \longrightarrow t = 0.83$$

$$\longrightarrow \left( \frac{\partial u}{\partial t} \right)_{\max} = 6.608$$

It is obtained by this calculation that critical moment happens in  $t = 0.83$  approximately.

**Results**

All the results refer to a bearing is considered in standard situations and minimum errors. By now, numerically solution of Reynolds equation is clearly done and presented. The effect of gradient of shoe pad respect to time is completely shown in figure. Next level, in 2D domain pressure distribution on both states on x axis and y axis referring the electric motor startup function is clearly presented in figure and. Right here it is obvious that the maximum pressure occurs in unsteady state under 3 seconds and while the electric motors is reaching final speed so this state is much more critical than steady state. The critical point is to be found at  $x = 0.03455$  and  $y = -0.0001209$  on shoe pad surface and maximum pressure is  $4.033 \times 10^6$  kPa. It is also clear that in y axis comparison the graph is clearly symmetric with maximum volume in the middle, but in x axis analysis the graph is obviously unsymmetrical and with a peak towards the outer line of shoe area.

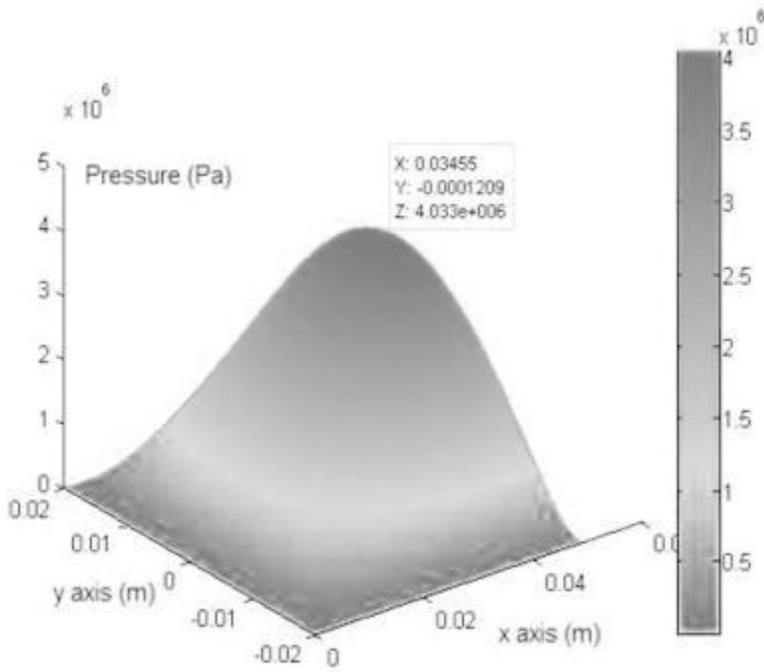


Fig7: Numerical solution of Reynolds equation in 3D

The difference between 2D steady state solution and 2D unsteady state solution is same in both axis, but the increase in pressure in unsteady state is 5.76% meaning 213 kPa proportion to steady state. With no doubt, it should be mentioned that in startup time the 2D Reynolds equation must be solved because ignoring one of the dimensions cause a enormous error in results.

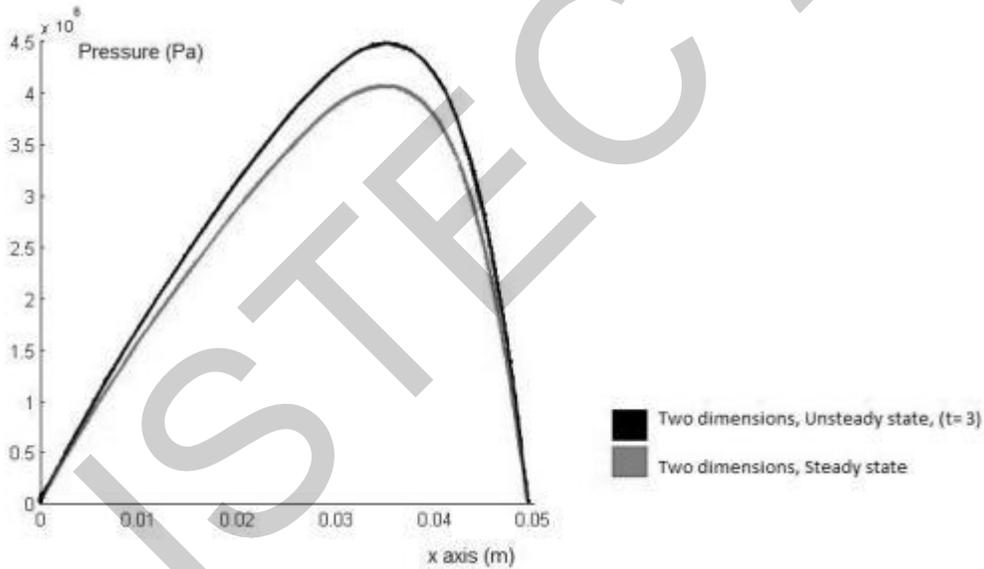


Fig8: steady and unsteady comparison in x axis

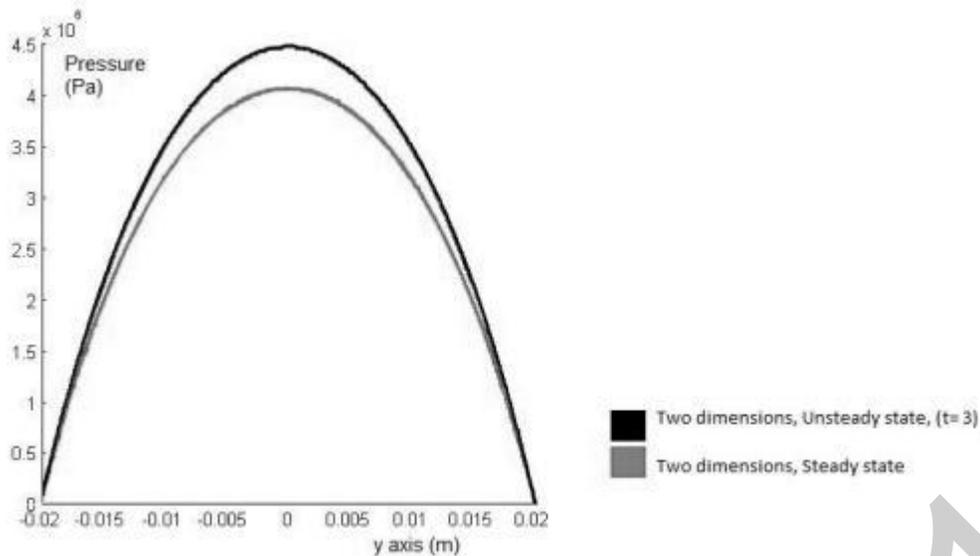


Fig9: steady and unsteady comparison in y axis

## Conclusion

In observation on shoe pads of hydrodynamic thrust bearing, there are several unwanted scratches and lines on pad surface and surface machining is no longer finished. In this paper, the location of critical point causing these lines and the time of this metal to metal contact are found and the maximum pressure in this critical moment on oil film has been predicted. This pressure has an important role in finding the answer. It is absolutely clear that dynamic forces analysis makes the results more accurate.

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## PRINCIPAL COMPONENTS ANALYSIS OF SOME F<sub>1</sub> SUNFLOWER HYBRIDS AT GERMINATION AND EARLY SEEDLING GROWTH STAGE

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### ABSTRACT

Genetic diversity estimation of breeding materials based on morphological, physiological and biochemical data and selection of superior hybrids are essential in sunflower breeding programs. Principal components analysis is one of the multivariate statistical methods that can be utilized for genetic diversity estimation and grouping of genotypes through biplot diagrams. In order to study the principal components analysis of some F<sub>1</sub> sunflower hybrids at germination and early seedling growth stage, a randomized complete block design has been conducted in three replications. Plant materials were 18 single cross sunflower hybrids set of six male restorer lines crossed with 18 female (CMS) lines in North Carolina Design I scheme. Two components have been extracted that were accounted for 80.93 % of the variability in the original data. Seed vigor index (SVI) has a highest weight in first component while second component was more associated with the shoot/root ratio (SHRR). Based on biplot diagram, three distinct groups were formed by components. The results of this study indicated that there is a great genetic diversity at germination and early seedling growth stage of sunflower F<sub>1</sub> hybrids. This diversity can be explained by two components and show on a biplot diagram.

**Key words:** genetic diversity, hybrid, principal components analysis, sunflower

# PROBIOTIC POTENTIAL OF LACTIC ACID BACTERIA ISOLATED FROM HUMAN GUT

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## ABSTRACT

The aim of this study was to characterize human gut lactic acid bacteria group strains on the basis of their phenotypic profiles. In addition, their *in vitro* potential probiotic properties were evaluated with a view to identifying potential interesting application. Fifteen strains of lactic acid bacteria were isolated and identified. Among the strains, both biochemical and physiological characteristics differed noticeably and also showed a remarkable heterogeneity. The strains were grouped into the species *Lactobacillus gasseri*, *Lb.casei* ssp *casei*, *Lb. delbrueckii* ssp *lactis*, *Lb. fermentum* and *Lb. delbrueckii* ssp *bulgaricus*. These strains have an inhibitory activity against enterobacteria including *Escherichia coli* and *Salmonella* sp. A major part of these strains survived at pH 2.5 and in 0.3% bile salts. Additionally they produced no haemolysis, were resistant to kanamycin and adhered to epithelial cells.

The results showed that the strains *Lb. gasseri* HG8 and *Lb. fermentum* HG3 have the best potential probiotic properties.

**Keywords:** Human gut, Lactic acid bacteria, Probiotic.

## INTRODUCTION

Intestinal microflora is a complex ecosystem formed by a number of bacterial populations, which are crucially important for the host. Most of the bacteria (>400 species) colonizing the intestine are strict anaerobes (*Bacteroides* sp., bifidobacteria, eubacteria, propionibacteria, clostridia) while aerobes (enterobacteria, especially *E. coli*, enterococci) and facultative anaerobes form a minor part (2–5 %) (Fanaro et al., 2003).

The large intestine in the human body is where the highest numbers of microbes are housed. It is believed that the general well-being of humans depends on the number and type of microbes associated with the gastrointestinal (GI) tract, especially those colonizing the large intestine (Mitsuoka, 1992).

Among colon biota, lactobacilli have drawn considerable attention among researchers in last four to five decades. Since their lactobacilli have attracted the attention of researchers because of their probiotic and therapeutic advantages (Mayur et al., 2002). The contemporary definition of a probiotic is “a microorganism which, when administered in adequate amounts, confers a health benefit on the host” (FAO/WHO 2002).

To exert a beneficial effect, it is generally considered essential that probiotic cells remain viable during transit of the gastrointestinal tract (GIT) in sufficiently high numbers to either establish residence (i.e. to colonise) or to benefit the host (Sheehan et al., 2007).

However, the ability of lactobacilli to survive in the GIT varies considerably between different species and strains. For probiotic cells to accumulate in the GIT, they must adhere to mucus or tissue cells and then survive exposure to the relatively harsh conditions imposed by gastric acids, bile and digestive enzymes and by the highly diverse and competitive commensal microbiota of the GIT (Saulnier et al., 2008).

Adhesion to the intestinal mucosa is considered an essential trait of probiotic bacteria and is thought to be a possible mechanism where by probiotics provide protection against pathogens through competition for binding sites and by localised production of antimicrobial substances (Coconnier et al., 1993).

The objective of the current study was to isolate identify and characterize a number of lactic acid bacteria (LAB) isolated from adults faeces. The strains were further characterized by tolerance to low pH and bile, and adhesion to intestinal mucous of poultry. The competitiveness of selected strains with Gram negative strains was also evaluated.

## MATERIAL AND METHODS

### Samples:

Fresh faecal samples were obtained from five healthy adults' person (region of Chekfa, Taher and Texana, Algeria). Samples were transported to the laboratory at 4°C.

### Isolation and identification of lactobacilli strains:

From each sample aliquots, five 10-fold dilutions were prepared and these were inoculated on plates of MRS agar (Pasteur institute, Algeria), acidified with glacial acetic acid to pH5.7 and incubated anaerobically for 48h at 37°C.

The identification of isolates was performed according to the criteria of Bergey's Manual of Determinative Bacteriology and using the methods and criteria of Sharpe (1979).

The ability of the isolated strains to produce acid from different carbohydrates was determined by API 50 CHL test kits (Bio Merieux, S.A., France). The API test strips were prepared as recommended by the kit supplier and scored after incubation for 24 and 48 hours at 37°C. The results were loaded on the API system software, which used the phenotypic data to predict a species identity (%) for each isolate.

#### Sensitivity of isolates to several parameters:

**Bile salt tolerance:** The overnight cultures of LAB cells were inoculated into MRS broth with or without 0.3% bile salt (Pasteur institute; Alger's, Algeria).

Initial bacterial cell in the culture broth was measured by reading the optical density (OD) at 620nm and numeration using the Thomas Cell. After 4 h incubation at 37 °C, the same parameters were determined. The percentage of bile tolerance was calculated by comparison of the OD values of the bacteria cultures in MRS broth with bile salt to those in MRS broth without bile salt (Lin et al., 2007).

**Acid tolerance:** To determine the acid sensitivity or resistance of lactobacilli isolates, MRS broth was prepared in accordance with the manufacturer's instructions. pH were adjusted to pH2, pH3 and pH4 with glacial acetic acid, the media were autoclaved. The overnight cultures of LAB cells were inoculated into MRS broth and incubated for 3h at 37°C.

Viable bacterial counts were determined by plating serial dilutions (in PBS, pH 7.2) on MRS agar followed by incubation at 37 °C for 48 h (Lin et al., 2007).

**Antibacterial activity:** The inhibitory activity was screened by the agar spot agar (Schillinger and Lucke, 1989) in MRS agar at 37°C. The indicator strains used were of human gut origin (*Escherichia coli*, *Klebsiella* sp, *Enterobacter* sp, *Salmonella* sp and *Citrobacter* sp). A well diffusion assay with the inhibitory strain was performed.

The neutral supernatant culture fluid was tested. The plates were incubated overnight at 37°C. The diameters of the inhibition zones were measured.

**Adherence of LAB to the epithelial cell:** The method described by Annika et al. (1983) was used for the preparation of epithelial cells. Segment of poultry ileum was washed with sterilized phosphate-buffer saline (PBS, pH 7.2). It was held at 4°C for 30 min and then washed three times with PBS. The epithelial cell concentration was adjusted to approximately  $5.10^4$  cells/ml.

Briefly, cell pellet from overnight culture of LAB was resuspended to approximately  $1.10^8$  cells/ml in PBS (pH 7.2). One ml of such bacteria suspension was mixed with 1 ml of the cell suspension of epithelial cells. The mixture was incubated at 37°C for 30 min. The adhesion was observed using phase contrast microscopy (magnification fold, 200) after stained with 0.5% crystal violet for 5 min.

## RESULTS AND DISCUSSION

#### Isolation and identification of LAB:

Forty isolates, primarily lactobacilli were recovered from faecal samples of healthy adults' person (figure1). Only fifteen isolates were identified. From this collection, five of the identified *Lb.* strains was *Lb. gasseri*, which accounted for 33.33 % of the total isolated strains. The species *Lb.delbrueckii* ssp *bulgaricus*, *Lb.casei* ssp *casei*, *Lb.delbrueckii* ssp *lactis* and *Lb.fermentum* represent respectively 26.66%, 20%, 13.33% and 6.66% of the total isolated strains.

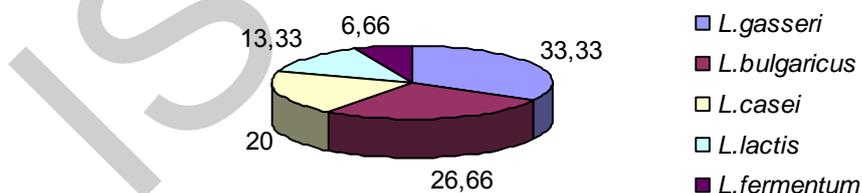


Figure1. Repartition of the identified isolates of lactic acid bacteria

#### Bile salt Tolerance:

The bile in intestine is an important factor which affects the viability of LAB cells. Although the composition of human bile juice is not exactly the same as that of the 0.3% oxgall solution, most studies used oxgall as one substitute for human bile because of their similarity (Lin et al., 2006)

The best results were obtained, only with 6 out of 15 strains tested. From the results (table1), *Lb. fermentum* HG3 exhibited the highest bile acid tolerance (98.83%) followed by *Lb.gasseri* HG 8 (85.59%). The lowest bile acid tolerances were observed by *Lb. delbrueckii* subsp. *lactis* (21.25%). The results of this study were in accordance with those found by some authors. In similar study, Garriga et al. (1998) found that the selected LAB strains were resistant to 4% of bile salts. Gilliland et al. (1984)

observed a great variability among *Lb.acidophilus* strains isolated from calf intestinal contents in their ability to grow in vitro in the presence of bile salts

**Table1.** Effects of bile salt on the growth of some lactobacilli strains

Strains	OD <sub>620nm</sub>		Percentage of tolerance
	Without bile salt (BS)	With 0.3 % BS	
<i>Lb.fermentum</i> HG3	0.942	0.931	98.83
<i>Lb.bulgaricus</i> HG2	0.793	0.505	63.68
<i>Lb.casei</i> ssp <i>casei</i> HG3	0.797	0.495	62.11
<i>Lb. delbrueckii</i> ssp <i>lactis</i> HG4	0.480	0.102	21.25
<i>Lb.gasseri</i> HG8	0.951	0.814	85.59

**Tolerance to Low pH:**

The effect of acidity on the viability of the isolates was assessed by adjusting the growth medium to different pH values. At pH 2, the strains' viability was affected, where this pH value was considered as the lethal for all cultures (data not shown).

The results showed (table 2) that the five isolates were able to grow on the MRS broth with different pH. The viable bacterial counts for these LAB strains changed after incubation in the pH 2. After 3 h incubation in the pH 2 or pH 3, the viable LAB counts decreased about 1–2 log value for a few strains.

In comparison to the acid tolerance of the *Lactobacillus* species which we isolated from the gastrointestinal tracts of human, strains of *Lb. fermentum*, *Lb.gasseri* and *Lb.delbrueckii* ssp *bulgaricus* seem to have better acid tolerance. These results were in accordance with previous study. The results of study conducted by Idoui et al. (2007) showed that *Lb.plantarum* BJ0021 was resistant to pH3 and this strain shows a good resistance to rabbit gastric juice.

**Table2.** Survival of some lactobacilli strains at different pH values

Strains	Number of cell / ml			Percentage of reduction (%)
	pH2	pH3	pH4	
<i>Lb.fermentum</i> HG3	5.48× 10 <sup>5</sup>	2.00× 10 <sup>6</sup>	1.92× 10 <sup>7</sup>	97.14
<i>Lb.bulgaricus</i> HG2	7.40× 10 <sup>5</sup>	2.80× 10 <sup>6</sup>	2.32× 10 <sup>7</sup>	97.18
<i>Lb.casei</i> ssp <i>casei</i> HG3	6.76× 10 <sup>5</sup>	6.40× 10 <sup>6</sup>	2.72× 10 <sup>7</sup>	96.51
<i>Lb. delbrueckii</i> ssp <i>lactis</i> HG4	3.32× 10 <sup>5</sup>	3.20× 10 <sup>6</sup>	2.40× 10 <sup>7</sup>	92.81
<i>Lb.gasseri</i> HG8	3.60× 10 <sup>5</sup>	5.80× 10 <sup>6</sup>	2.28× 10 <sup>7</sup>	98.42

**Antibacterial activity evaluation of the isolated strains:**

One of the major probiotic properties for probiotic LAB is its inhibitory effect on the growth of pathogenic bacteria. In our study, the bacteria used as indicator is a Gram negative bacteria, such as *E. coli*, *Salmonella* spp., *Klebsiella* spp., *Enterobacter* spp and *Citrobacter* spp from human origine.

Table shows that LAB exhibited an inhibitory activity to the indicator bacteria, although inhibitory extents are variable and we observed that *Klebsiella* spp strain seem to be more tolerant to LAB inhibition when compared to the other bacteria, such as *E. coli*. In the other hand, the antagonistic effect of the isolate was more pronounced on *E. coli* (table 3).

In study conducted by Garriga et al. (1998), 77 lactobacilli strains showing inhibition against one or more enteric indicator strains (*E.coli*, *Salmonella.enteritidis*). In addition, Xanthopoulos et al. (2000) indicated that *Lb.paracasei* subsp.*paracasei* and *Lb.acidophilus* strains isolated from infant feces had weak antibacterial activity on *E.coli* and *Yersinia enterocolitica*

**Table3.** Growth inhibition zones of enterobacteria caused by some lactobacilli strains.

Inhibition zone (mm)	<i>Lb.fermentum</i> HG3	<i>Lb.bulgaricus</i> HG2	<i>Lb.casei</i> ssp <i>casei</i> HG3	<i>Lb.delbrueckii</i> ssp <i>lactis</i> HG4	<i>Lb.gasseri</i> HG8
<i>E.coli</i>	3	3	3	2	3
<i>Enterobacter</i> spp	3	3	2	2	2
<i>Salmonella</i> spp	3	3	2	0	2
<i>Klebsiella</i> spp	2	3	1	1	2
<i>Citrobacter</i> spp	3	2	3	1	1

diameter of inhibition zone: 3 >10mm; 10 mm >2 > 5 mm; 1 < 5 mm; 0 < 0 mm

In our study, supernatant broths were neutralized to pH6.5; the inhibition activity to enterobacteria isolates became lower. The result obtained with neutral supernatant, showed that the inhibition was not related to lactic acid but might be due to other antimicrobial substances.

The results indicate that neutral supernatant inhibited the tested indicator strains (table4). Excepted the strain *Lb.casei*, *In vitro* inhibitory capability of neutral supernatant of the other strains against indicator bacteria seems to be a good probiotic property. Daeschel, (1989) has reported that the antimicrobial effect exerted by LAB is due to the production of lactic acid and reduction of pH, acetic acid, diacetyl, hydrogen peroxide, fatty acids, aldehydes and other compounds.

**Table4.** Growth inhibition zones of enterobacteria caused by neutral supernatants of some lactobacilli strains

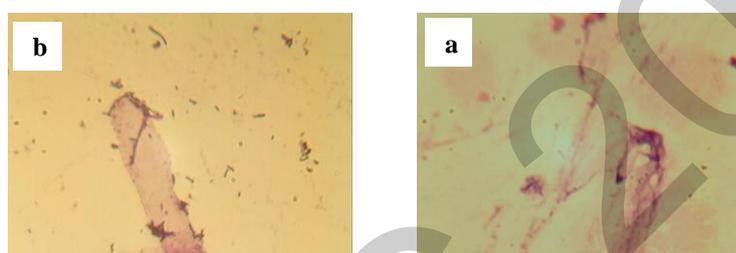
Inhibition zone (mm)	<i>Lb.fermentum</i> HG3	<i>Lb.bulgaricus</i> HG2	<i>Lb.casei</i> ssp <i>casei</i> HG3	<i>Lb.delbrueckii</i> ssp <i>lactis</i> HG4	<i>Lb.gasseri</i> HG8
<i>E.coli</i>	2	2	1	1	2
<i>Enterobacter</i> spp	2	2	1	0	2
<i>Salmonella</i> spp	2	2	1	0	2
<i>Klebsiella</i> spp	2	1	1	0	1
<i>Citrobacter</i> spp	1	1	0	0	1

diameter of inhibition zone: 3 >10mm; 10 mm >2 > 5 mm; 1 < 5 mm; 0 < 0 mm

#### Assay of the adherence capability for LAB isolates:

The ability to adhere to host intestinal mucosa is considered as an important selection criterion for LAB strains intended for probiotic use. It should be reminded that for LAB strain, only more than 15 LAB cells adhered on one epithelial cell, it could be considered as "positive" adherent strain.

In our case, we found that solely *Lb. fermentum* HG3 and *Lb.gasseri* HG8, showed the adherence specificity to the chicken intestinal epithelium (fig.2). We don't know if they are able to adhere to the human intestinal epithelium.



**Fig. 2.** Adherence of isolated *Lactobacillus gasseri* on the epithelium cells: (a) negative adhesion (control) (b) positive adhesion of *Lb. gasseri* HG8

#### CONCLUSION

From the results of the study reported here, potential lactobacilli strains isolated from human gut able to be used as probiotics may be found. Strains *Lb.fermentum* HG3 and *Lb.gasseri* HG8 were able to adhere to the intestinal epithelium from poultry. In addition, they were resistant to acid and were also bile tolerant. As the antagonistic effects of strains against enterobacteria, the isolates HG3 and HG8 might be the most preferential strain of choice.

Therefore, this study provides the information that human digestive tract offer a potential source for the isolation of probiotic LAB strains suitable for use as feed supplements.

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# PROCESS SUPPORT OF CRISIS STAFF: CASE STUDY ABOUT ACCIDENTS INVOLVING DANGEROUS SUBSTANCES

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## ABSTRACT

Large-scale emergencies are solved by Crisis Staff in the Czech Republic. Accidents involving dangerous substances are a representative example. The disaster has a direct impact not only on the property and the environment but also on the lives and health of human beings. These emergency situations are managed with the help of contingency plans in textual representation, or ad-hoc. The main aim of this paper is to support decision-making process of the Crisis Staff. Therefore it is necessary to identify, model, and then automatize the processes involved in disaster management. Selected procedures are described from the methodological perspective but also from the perspective of software architecture, which allows processes automation. The paper emphasizes the use of standards and best practices in the field of process management. The result represents a comprehensive information support for the Crisis Staff. This solution can be used in practice during dealing with crisis situations or for training and educational purposes, which are obligatory once in a year. Finally, it is necessary to stress that accidents involving dangerous substances are only one example of many crisis situations arising from the risk analysis in the Czech Republic.

**Keywords:** Process Management, Crisis Staff, Accident, Dangerous Substances, Process Diagrams, Software Architecture.

## 1. INTRODUCTION

Crisis management (disaster management) is defined in the Czech Republic as a summary of management activities of the competent authorities aimed to analyse and evaluate security risks, planning, organizing, implementing and controlling the activities performed in connection with the solution of crisis situations [3]. An extraordinary event can lead to a crisis situation, which is characterized as harmful impact of forces and phenomena caused by human activities, natural causes, and accidents that threaten life, health, property or the environment and need necessary rescue and relief work. For the purpose of coping with emergencies, Integrated Rescue System was built in the Czech Republic, which consists of basic components such as the *Fire Brigade, Police or Medical Rescue Service*. A crisis situation is defined as an extraordinary event where the state of emergency was declared.

Crisis management bodies, and thus the Crisis Staff, are legally obliged to use information systems for crisis management during planning emergency measures and solving crisis situations [3]. Currently, information systems used in crisis management are the primary data-oriented in order to provide the user with all the necessary information to address the situation. Actual options of Information Technology allow, besides the data perspective, to support the on-going processes of the Crisis Staff. For this purpose it is appropriate to use process management.

Process Management is a field of combining management and technology focused on aligning organizations with the wants and needs of clients [12]. It is a complex management approach that promotes effectiveness and efficiency while striving for innovation, flexibility, and integration with technology. Process management attempts to improve processes continuously. It could therefore be described as an optimization process.

The main objective of the paper is to apply process management approach to crisis management on the level of Crisis Staff. Integration of crisis and process management is not unique and similar manners are used to achieve information support of crisis management by many other experts or research projects [5] [10]. The solving of crisis situations is quite difficult problem and so the proposed paper is describing a case study that focuses on accidents solutions involving dangerous substances.

## 2. PROBLEM DOMAIN DEFINITION

Large-scale accident caused by selected hazardous chemical substances and chemical products (see the Seveso II Directive, The amendment of Act no. 59/2006 Coll.) is extraordinary event manifested by uncontrolled flows of energy (fire, explosion), and leaks of toxic substances.

These are partially or totally uncontrollable, time-and space-bounded event (with maximum territorial extent. To 20 km) which was created or whose inception is imminent in connection with the use of the building or facility where the hazardous substance is manufactured, processed, used, transported or stored, and that leads to immediate or delayed serious damage or

threat to life and health of people, livestock, environment (harmful substances in the environment may persist for several years) or for damage to property [9].

Predicting of emergency situation is generally very difficult because suddenly arise mainly depending on the physic-chemical parameters of the substance, processes and environments. However, in some cases can be used monitoring devices or historical analysis of chemical accidents in the area to estimate the potential threads such as using the following criteria:

- Types of industrial facilities and stored producing hazardous chemicals.
- Types of storage facilities of hazardous chemicals (military, agricultural, business centres).
- Types of storage of chemical substances intended for destruction or permanent storage (dump, excavated pits, finished mining).
- Heavy trafficked roads with an increased frequency of accidents.
- Places with increased accumulation of the population, property, cultural monuments and other areas threatened by terrorist attacks.

Desired state is the stabilization activities in the chemical facility and decontamination of equipment in the immediate vicinity of the accident. The ultimate aim is the stabilization of public service authorities.

Solving large-scale accidents as well as other emergency situation takes place at three levels. The levels are *local*, *regional* and *state* [6]. Proceed according to the corresponding contingency plans, which are processed for each level separately. Emergency Plan is a set of documents containing a description and analysis of threats and a summary of emergency measures and procedures that are proceed by Ministry, other administrative authorities and local and regional authorities to arrange preparedness to crisis situations. Contingency plans also contain attachments where *model action plans* or *operational plans* belong. *Modell action plans* represent different types of crisis situation and recommended practices, principles and measures for their solution. In contrast, *operational plans* are basically elaborate types of plans and other documents for the administrative office area, component or object.

To solve large-scale emergency, it is appropriate to use the corresponding Modell action plan called “large-scale accidents caused by selected hazardous chemical substances and chemical products” processed by Ministry of Interior of the Czech Republic, which addresses issues across the board-wide Czech Republic. Another information source is operational plans at regional level. These specifically include individual emergency plans, which are subdivided into:

- *Regional Emergency Plan* (Regional Emergency Response Plan) – Fire fighter processes in cooperation with the region, all the possible places where accidents can occur mainly anthropogenic action, see Act. 239/2000 Coll. and Decree no. 328/2001 Coll.
- *Internal Emergency Plan* (particular facilities or subject) – processes the body meeting the requirement of the Act no. 18/1997 Coll. or no. 59/2006 Coll.
- *External Emergency Plan* (particular facilities or subject) – Fire fighter processes – Internal Emergency Plan continues to see this legislation Decree. 328/2001 Coll.

Main source of information is the regional emergency plan and an external emergency plan. Both documents have a consistent structure that documents divided into three parts: information part, operative part and plans for specification [4]:

- *Information Part* – contains the basic characteristics about the region or municipality, but also actually results in the analysis of a possible incident.
- *Operative Part* – discusses the forces and means that it is possible to deploy during crisis situation.
- *Plans for Specific Actions* – the most detailed processed part, which contains concrete plans to deal with a combination of intrusion crisis.

### 3. PROCESS METHODOLOGY

The aim of this chapter is to describe the procedures of processes deployment at the Crisis Staff. Generally, while creating information system, it is appropriate to follow the established methodology. For this purpose, a process-oriented methodology was selected [8]. The methodology progressively describes the phase of the process deployment, namely the *identification*, *modelling*, *configuration*, *implementation/monitoring* and *optimization*. These are complex issues, and therefore the paper emphasizes primarily the phase of processes identification and modelling.

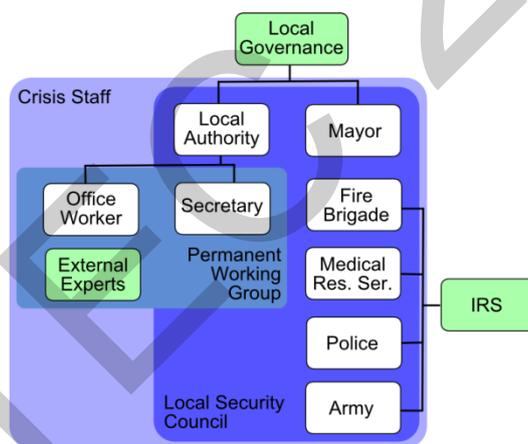
The phase of processes identification consists primarily of identifying of users roles and primary and support processes at the Crisis Staff. The aim is to link these insights and to define the clear responsibility of users' roles for identified processes. An integral part is also the creation of terminological vocabulary that would enable to make the communication between professionals oriented to crisis management and specialists in information technology more effective. For this purpose, it is possible to use the vocabulary defined by the Ministry of Interior, which is focused on the issue of crisis management. The vocabulary describing the processes and information technology issue had to be defined. The result of these activities is the creation of requirements for the functioning of the Crisis Staff, which comprehensively covers the situation and provides the basic view needed for the subsequent modelling, optimization and process automation at the Crisis Staff.

The first step of the process automation is to identify the users' roles. It is necessary to follow the regulation of the Ministry of Interior that regulates uniform rules of Crisis Staff organizational structure of regions and communities, putting it into standby,

keeping records and some other details. The basic component of the Crisis Staff is a standing working group. Managers of the permanent Working Group are the Secretary of the Crisis Staff, the Head of the Permanent Working Group and the Head of expert groups. According to the model action plan of the Ministry of Interior describing an accident with a leakage of hazardous substances it is appropriate to determine following expert groups and their responsibilities [9]:

- *The Expert Group of Interaction and Communication* – the cooperation and collaboration with operational centres of basic IRS, notifying of public authorities and the IRS about the situation, actions taken and the current changes.
- *The Expert Group of Military Logistics* – to standardize the requirements for the supply of deployed IRS, especially external, for all the necessary material and technical support, including food security, accommodation, health services.
- *The Expert Group of situation analysis and planning* – analysis of specific incident and prognosis of further development, evaluation of efficiency of crisis and emergency plans, the creation, management and use of maps and graphical illustration of the incident.
- *The Expert Group of Deploying forces and resources* – centralizing information on interventions by commanders of intervention through the operational centres, evaluation of the effectiveness of interventions, conducting of surveys for the deployment of the Integrated Rescue System and other forces and resources.
- *The Civil Protection Expert Group* – public warning and information support, providing shelter, organizing of decontamination and identification of hazardous areas, medical support, registration of missing persons, identification and burial of the dead persons, the protection of farm animals, protection of water resources, protection of cultural monuments and other protective measures.

Crisis Staff is working body of a county governor or mayor (head of Crisis Staff) who convenes it and uses for the crisis resolution and mitigation of consequences, including the tasks of crisis management in situations of national emergency declared in connection to securing the defence of the Czech Republic and during the state of war or while coordinating rescue and relief work by the county governor or mayor with extended powers in solving crisis. The convention of a Crisis Staff is made under the direction of the Crisis Staff, which also determine the time and place of the initial joint meeting of the Crisis Staff. A part of the Crisis Staff is already listed the permanent working group, the village mayor or governor, including representatives of different components of the IRS. These representatives are primarily from the Police, Fire and Rescue Service, ambulance services or the Army of the Czech Republic. The basic structure of the Crisis Staff is described by Figure 1.



**Fig. 1.** Organization Structure of Crisis Staff

Other important users roles include the operator KOPIS (Operational Centre) and the Head of intervention. The operator KOPIS receives a direct information about an occurred crisis. The operator of Fire Registration Office or the command centre receives a report on the event with calmness and deliberation. The operator has to find out the maximum of information from the caller, namely: the address of event, type of incident (fire, natural disaster or other extraordinary event), details of events required for the unit (e.g., danger to persons, their number and character of the building in which the event occurred, what other risks are there), name of the person reporting on the event, its phone number and address (place) where it is called. Then the operator informs IZS and if the situation is of larger extent, he informs the mayor. Another key role is the Head of the intervention. The Head of intervention manages activities of the intervention units and other entities whose cooperation demands on the intervention site. He determines the management structure on intervention site. By a complex intervention, requiring the coordination of rescue and relief work with other components of the IRS site and outside intervention, the Head of intervention can request convening of local Crisis Staff through operational and information centre IZS and to ask for the coordination of emergency relief work.

The next step for successful information support of the Crisis Staff is to identify processes and procedures executed to manage the release of a hazardous substance. This information is processed in the county emergency plan, or the external emergency plan of the organization with the potential risk of leakage of hazardous substances. The aim of these documents is to propose a procedure for dealing with the following [4]:

*Notification plan* – the ways of informing the parts of IRS about occurred accident, notification schemes including contact information, list of the notification system, which is provided by an operator and patterns of primary information about an accident.

*The plan of warning the population* – the ways to alert the population, including a description of the desired behaviour of the population after the warning, the ways of the information about the desired behaviour of citizens in case of an accident and the end of the accident, the responsibility for the warning.

*Plans of sheltering, evacuation and individual protection of the population* – for practical reasons, these plans were merged into the Plan for the person that solves all three closely related areas; a priority in case of an accident is an improvised shelter and protection of the population.

*IRS action plan* – provides a means of coordination intervening parts of IRS, defines the location of probable deployment of components, including the determination of access roads, technical and protective equipment.

*Plans for the decontamination* – decontamination of persons specifies the ways, means and immediate surroundings of affected by an accident, the resources needed for decontamination and methods for the protection.

*Monitoring plan* – describes the methods of monitoring and communication of the measured variables (weather, concentration), it defines responsibilities and measures.

*Traumatology plan* – it informs about dangerous effects on the human body and diagnosis of body contact with a hazardous substance; plans medical procedures, policies and procedures for implementation of medical assistance and ways of securing medical assistance of evacuated and hidden population.

*Veterinary emergency plan* – describes the status and location of livestock in the emergency planning zone. It sets out measures for their survival, methods of treatment and classification of the affected health of farm animals, action against intoxicated animals including the disposal of dead animals.

*Plan for prevention of distribution and use of food, feed and water contaminated with dangerous substances* – provides a means of control of contaminated food, feed and water, giving instructions how to prevent their distribution, methods of disposal of contaminated and to ensure safe distribution of food, water and feed.

*Plan for preventive measures to prevent or restrict domino effect* – it contains a list of resources that may be vulnerable in an accident to domino effect, including measures that may prevent the domino effect or limit.

*Plan treatment of deceased persons in the affected area* – provides a means of deceased persons search and identification methods of the handling and establish methods of burial.

*Action plans to prevent or limit the impact of the accident on the components of the environment* – an overview of the effects and consequences of the impact of hazardous substances on the environmental review measures to prevent or mitigate the impacts of the accident on the environment, including accountability for these measures.

*Arrangements for ensuring public order and security control and plan the movement of people and traffic* – defines a solid guard to prevent access to contaminated areas, mobile patrols intended for informing the population about the potential danger, creating of escort groups, filter points, information centre, defines driveways for intervening components, diversion of access road to a secure area, power and resources, tasks, operations centre and plan to merge.

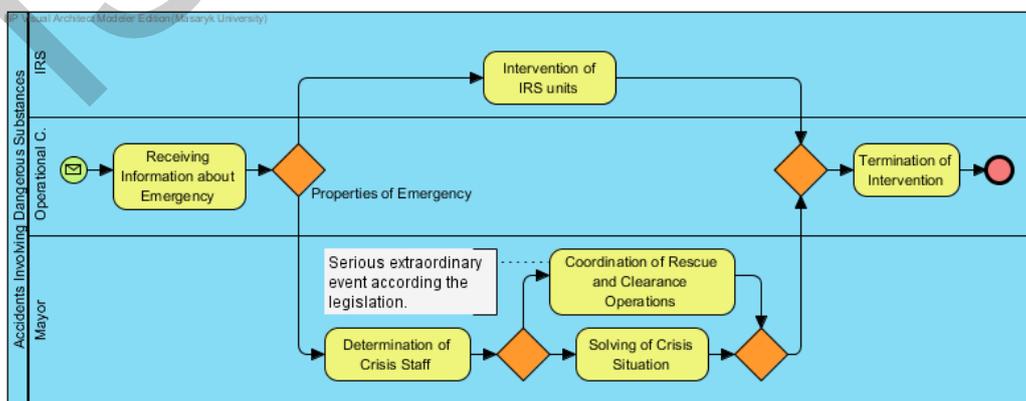


Fig. 2. Notification Plan of Crisis Staff (Business Process Modelling Notation [11])

Before the crisis management of an accident with the of leakage dangerous substances it is necessary for intervening components to have available all necessary information [4]. This information can be divided primarily into two groups. First, the information that is relevant to the area. For example: Population density, population of the municipalities (parts), significant buildings (offices, schools, theatres, and galleries), sources of threat (establishments with dangerous substances, stadiums, power components, and nuclear radiation), areas which are of particular importance and objects of critical infrastructure. This information is often part of general knowledge of participants of the Crisis Staff but it is also a part of the contingency plan of the region and also part of the emergency plan of a county or municipality.

Additional necessary information is the information about available resources and means to solve the crisis. These are primarily human resources (enough firemen, police officers etc.) but also the necessary material in the form of equipment such as specialized suits to allow movement in a dangerous zone, or other specific equipment. When all these resources are available it is possible to address the crisis situation. It is therefore necessary to ask for help more units, facilities to cope with these specific crisis situations.

#### 4. SOFTWARE ARCHITECTURE

The practical usage of introduced architecture is illustrated by Business Process Management Suite named Bonita Open Solution (BOS) [2]. The BOS represents the open source solution for process automation and support. Unlike other commercial BPMS, the BOS has some advantages and disadvantages typical for smaller software solutions based on open source technologies. The Processes Reporting an Emergency Incident and Alarm for Fire Protection Unit have been chosen for the specific use of the defined architecture. This architecture helps automation of emergency operational processes in the Czech Republic.

The Bonita Open Platform Solution is primarily based on the three integrated tools built on the Java language. It is Bonita Studio, Bonita Workflow Engine and Bonita User Experience. There are also extensive opportunities for integration with other tools using predefined connectors.

The Bonita Studio is a modelling tool that allows process design through the BPMN. In addition, besides a simple drawing, tool is also able to design almost a complete implementation process. For this reason, the tool contains the Form Designer and Connectors. The Connectors are software classes written in Java and they implement the interface. They are intended for partial or full automation of processes in the Bonita Open Solution.

The Bonita Workflow Engine (Bonita Runtime) is a generic and extensible workflow engine which performs proposed process. To achieve the deployment of the entire process on the production server the Bonita Studio Export of applications is necessary. Therefore, a ZIP archive with a complete application is generated and it can be deployed on the Java EE application server.

The Bonita User Experience (XP User) is a Web-based user interface that is similar to web email clients (Gmail) and serves to the entire administration and running processes from both the user and the administrator perspective. The User Experience Bonita accesses workflow engine through client Java API. In the same way, other remote applications can also access.

The implementation of novel architecture cannot be considered as complete unless the Bonita Open Solution is integrated with the instruments for cartographic support for emergency management. Particularly, it is contextual cartographic visualization which allows to visualize map elements by a different way for different users in different emergency situations [6]. The outcome imaging device is also very important. It is necessary to display the map on a large screen display and also on a PDA (Personal Digital Assistant) display with a relatively small screen.

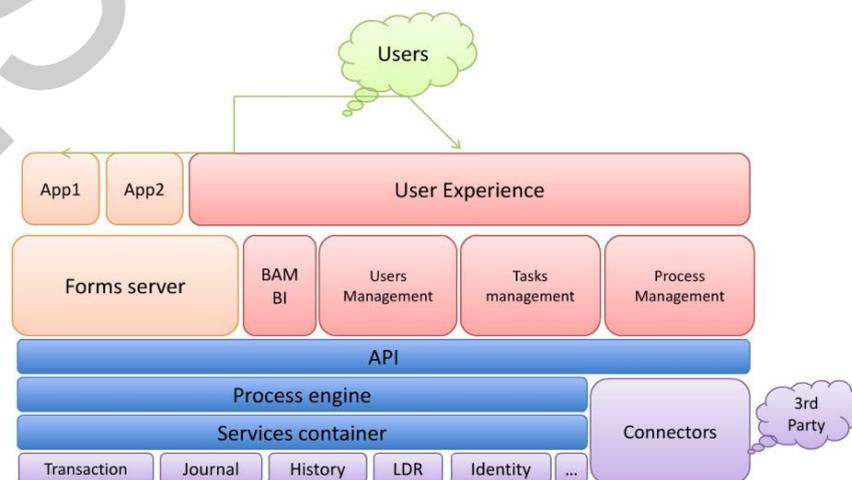


Fig. 3. Software Architecture Defined by Bonita Open Solution [1]

## 5. CONCLUSIONS

The main aim of this paper is to support decision-making process of the Crisis Staff. Therefore it is necessary to identify, model, and then automatize the processes involved in disaster management. Selected procedures are described from the methodological perspective but also from the perspective of software architecture, which allows processes automation. The paper emphasizes the use of standards and best practices in the field of process management. The result represents a comprehensive information support for the Crisis Staff.

For an overall understanding of the described issue it is also appropriate to familiarize with the Process Framework for Emergency Management [7]. This contribution emphasizes the importance of the two perspectives in the deployment process of emergency management. It should be noted that the architecture itself is not sufficient for the automation of emergency management processes. It should be supplemented by a methodology that defines how to proceed with process automation and deployment. Such methodology has been already published by authors in the article entitled Process Methodology for Emergency Management [8]. This methodology has been used during the automation of selected emergency management scenarios described in this paper.

Finally, it should be noted that the proposed architecture is suitable not only for the automation and deployment of emergency scenarios in the Czech Republic, but also for educational purposes. Thus the defined process oriented architecture allows reflecting any changes in emergency scenarios quickly and also creating scenarios for educational purposes. Students understand emergency planning issues and emergency management more easily when illustrated on real examples. The resulting architecture allows students to model emergency scenarios using process maps, optionally supplemented with additional process data which can enable simulation or deployment on a process engine to test their effectiveness in the model situation in practice.

## ACKNOWLEDGMENT

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# PRODUCTION AND CHARACTERIZATION OF BACTERIOCIN OF *Lactobacillus plantarum* F12 WITH INHIBITORY ACTIVITY AGAINST *Listeria monocytogenes*

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## ABSTRACT

Thirty five lactic acid bacterial isolates from different origins (fermented Milk, chicken, olive oil, butter and newborn feces) were tested for their ability to produce bacteriocins against 12 indicator strains. These isolates presented a broad inhibitory spectrum against many indicator strains such as Methicilin resistant *Staphyococcus aureus*, *Escherichia coli*, *Salmonella* sp., *Listeria monocytogenes*... Only six isolates produced antimicrobial activity in the neutralized cell-free supernatant treated with catalase against indicator strains. The bacteriocin produced by *Lactobacillus plantarum* F12 was characterized and showed sensitivity to proteolytic hydrolysis (trypsin, chymotrypsin and pronase) and resistance to  $\alpha$ -amylase and lipase. The activity of bacteriocin remained constant after heating at 100°C for 30 min and no change in activity was recorded after 4 h at pH 6.0. Bacteriocin production is dependent on biomass concentration; it's started at the beginning of the log phase of the bacterial growth till reached its maximum level at the stationary phase at 37°C as the optimum temperature of production. Due to the inhibitory effect of this bacteriocin on *L. monocytogenes*, it can be used to prevent food spoilage by this pathogen.

**Keywords:** antimicrobial activity, bacteriocin, Lactic acid bacteria, *Lactobacillus plantarum*, *Listeria monocytogenes*

## INTRODUCTION

Lactic acid bacteria (LAB) are microorganisms widely used in food industry in a variety of fermentations such as the development of meat products, vegetables and many dairy products including fermented milk, cheese, yogurt and butter (Dortu & Thonart, 2009; Makhoulouf, 2006). LAB produce organic acids such as lactic, acetic acid and hydrogen peroxide which possess antimicrobial activity against several pathogenic and spoilage microorganisms (Benabbou, 2009). LAB represent a major class which produces bacteriocins that become a current subject for several researches. These bacteriocins are now being explored for their potential utility in human and animal health applications, food biopreservation and agricultural uses (Parada *et al.*, 2007; Todorov *et al.*, 2011b).

Bacteriocins differ from most therapeutic antibiotics in being proteinaceous agents that are rapidly digested by proteases in the human digestive tract. They are ribosomally synthesized peptides, and this fact creates the possibility of improving their characteristics to enhance their activity and spectra of action (Parada *et al.*, 2007). In additions, it has been shown that some strains of LAB possess interesting health-promoting properties; one of the characteristics of these properties is the potential to combat gastrointestinal pathogenic bacteria such as *Helicobacter pylori*, *Escherichia coli* and *Salmonella*. The antimicrobial spectrum frequently includes spoilage organisms and food-borne pathogens such as *Listeria monocytogenes* and *Staphylococcus*. The activity against Gram-negative bacteria such as *E. coli* and *Salmonella* has been shown, but usually only when the integrity of the outer membrane has been compromised, for example after osmotic shock or low pH treatment, in the presence of a detergent or a chelating agent, or after pulsed an electric field or high-pressure treatment. An experimental focus on bacteriocin production by probiotics LAB strains has indicated that this potential might play a considerable role during in vivo interactions occurring in the human gastrointestinal tract, for instance towards *H. pylori* (De Vuyst & Leroy, 2007; Osmanagaoclu & Beyatli, 2002;).

Several authors have recommended the use of bacteriocins combined with other preservation methods to create a series of hurdles during the manufacturing process to reduce food spoilage by microorganisms. In fact, it has been proven that application of chemical preservatives, physical treatments (heat), or new mild non-thermal physical methods (pulsed electric field, HHP, vacuum, or modified atmosphere packaging), which increase the permeability of cell membranes, positively affects the activity of many bacteriocins. Notably, combined treatments of bacteriocins with selected hurdles affecting outer-membrane permeability increase the effectiveness of some LAB bacteriocins against Gram-negative cells, which are generally resistant (Ananou *et al.*, 2007; Galvez *et al.*, 2007; Dortu & Thonart, 2009).

The main purpose of our work was to select bacteriocinogenic strains from a group of LAB with antimicrobial activity isolated from different origins, to characterize the produced bacteriocin and to determine the antimicrobial spectrum of this bacteriocin produced by the selected isolate.

## MATERIALS AND METHODS

### Bacterial strains and culture conditions

Lactic acid bacterial isolates used in this study were previously isolated and identified from different origins (Raibe " traditional fermented milk", chicken, olive oil, butter and newborn feces) (Table 1). Isolates were grown at 37°C in Man Rogosa Sharpe (MRS) broth (Biokar Diagnostics, France) (g/l: 10g glucose, 10g beef extract, 5g yeast extract, 0.5g sodium acetate, 2g Bipotassic phosphate, 2g ammonium citrate, 0.2g magnesium sulfate, 0.05g manganese sulfate, 1ml Tween 80, pH 6.5). To confirm the purity of the isolates each strain was individually streaked on MRS agar plates (MRS broth + 15g agar) and single colonies were isolated and tested for antimicrobial activity. Indicator strains used for determining antimicrobial activity were grown on nutrient agar. The antimicrobial activity and bacteriocin assay were realized on Muller-Hinton agar.

**Table 1:** The total number of LAB used in this study and their origin

Test strains	origin
<i>Lb. brevis</i> H27 ThT	Traditionally extracted olive oil
<i>P. acidilacticii</i>	Commercial strain
<i>Lb. plantarum</i>	Olive oil
<i>Lb. bifementans</i> , <i>Lb. plantarum</i> R17, <i>Lc. lactis sp lactis</i> R4, <i>Lb. delbrueckii sp lactis</i> R4, <i>Lb. curvatus</i> R12	Raibe "traditional fermented Milk"
<i>Lc. lactis sp pac</i> B7, <i>Lb. Curvatus</i> BJ, <i>Lb. delbrueckii sp bulgaricus</i> B8,	Traditional butter
<i>Lb. delbrueckii sp delbrueckii</i> , <i>Lb. bifementans</i> , <i>St. thermophilus</i> , <i>Lc. Lactis sp cremoris</i> B13, <i>Lb. delbrueckii sp delbrueckii</i> , <i>Lb. plantarum</i> , <i>Lb. delbrueckii sp delbrueckii</i> , <i>Lc. Reffinolactis</i> , <i>Lc helveticus</i> , <i>Lb. curvatus</i> , <i>Lc. lactis sp cremoris</i> , <i>St. salivaricus sp thermophilus</i> , <i>Lc. Cremoris</i> , <i>Lc. lactis sp diacetylactis</i>	Butter
<i>Lb. cremoris</i> NNN105	Goat butter
<i>Lb. fermentum</i> G8, <i>Lb. fermentum</i> G12, <i>Lb. plantarum</i> G13	Chicken gizzard
<i>Lb. plantarum</i> F12, <i>Lb. curvatus</i> G6, <i>Lb. casei ssp tolerans</i> G4, <i>Lactobacillus sp.</i> B5, <i>Lb. gasseri</i> , <i>Lb. plantarum</i>	Newborn feces

### Antimicrobial activity assay

The isolated strains were grown in MRS broth (pH 6.5) inoculated with 1% of an overnight culture and incubated at 37°C for 18-24 h. After incubation, cells were removed from the growth medium by centrifugation (6000×g for 20 min, 4°C). The cell-free supernatant was sterilized by filtering through a 0.22 µm Millipore filter. The antimicrobial spectrum of the bacteriocin from LAB was determined using the well diffusion method (WDM) (Tagg and Mc-Given, 1971). The indicator bacteria were cultured on nutrient agar for 24 h at 37°C, and used to prepare cell suspensions in 9 ml normal saline. Twenty ml of Muller Hinton agar cooled to 45°C was mixed with 110µl of the indicator strain suspension, pooled in a Petri dish and incubated aerobically for 2 to 4h at 37°C. Six mm wells were made and filled with 100 µl of the supernatants. Plates were incubated at 37°C for 24h. Inhibition zones were determined by measuring the diameter of the clear zones around the well.

### Screening for bacteriocin producing strains

The cultures of LAB that showed antimicrobial activity against indicator bacteria based on the well diffusion assay were tested for their potential to produce bacteriocins. The assay of bacteriocin was carried out as follow; the cell-free supernatants of LAB were adjusted to pH 6.0-6.5 using NaOH 5N to exclude the antimicrobial effect of organic acids. Inhibitory activity of hydrogen peroxide was eliminated by the addition of catalase at a final concentration of 1mg/ml. The catalase-treated samples were incubated for 2h at 37°C, after incubation the treated and neutralized cell-free supernatants were then tested for antagonistic activity against indicator bacteria by the WDM as described above (Ghalfi et al., 2006). Bacteriocin activity was expressed in arbitrary units (AU/ml). One AU was defined as the reciprocal of the highest level of dilution resulting in a clear zone of growth inhibition (Rajaram et al., 2010). Zone of 1 mm and above was considered as inhibition.

### Characterization of bacteriocin

The bacteriocin samples were characterized with respect to thermal and pH stability, and susceptibility to denaturation by enzymes. The effect of temperature on the bacteriocin was tested by heating the cell-free supernatants to 40, 60, 80 and 100°C during 60 min. Aliquots of each treatment were taken after: 0, 15, 30 and 60 min. 100µl of each heat-treated sample were used for the well diffusion method, the residual activity was determined using methicillin-resistant *Staphylococcus aureus* (MRSA) as indicator organism. The effect of pH on the bacteriocin was determined by adjusting the cell-free supernatant between pH 2.0 and 12.0 with sterile 1N HCl or 5N NaOH. The adjusted supernatants were incubated for 4 h at room temperature, 100µl of each sample were tested by the WDM using MRSA as indicator organism and the residual activity was determined.

The supernatants were treated with the following enzymes at a final concentration of 1mg/ml: lipase (Sigma), trypsin (Sigma), α-chymotrypsin (Merck), pronase E (Merck), α- amylase (Fluka). 5µl of the enzyme solution were added to 100µl of the cell-free supernatant. Controls consisted of only cell-free supernatant and tris-HCl buffer. Both the samples and the controls were incubated at 37°C for 2 hours and heated in boiling water for 5 min to inactivate the enzymes. The remaining bacteriocin activity was determined by the WDM described above using the MRSA as indicator organism. All enzymes were used at a final concentration of 1mg/ml and maintained in tris-hydrochloric buffer (pH 8.0).

### Monitoring of bacteriocin production

One ml of an 18h-old culture was used to inoculate 100 ml of MRS broth and incubated at 37°C for 48 hours. Samples were taken after time interval and examined for bacterial growth (OD 660nm), changes in culture pH, and antimicrobial activity against MRSA. The WDM was used and the activity expressed as AU/ml as described previously.

### Effect of temperature on bacteriocin production

To determine the optimum temperature for bacteriocin production, we used 100ml Erlenmeyer flask. In each flask, 50ml of MRS broth was inoculated with 0.5ml of an overnight culture. The Erlenmeyer flasks were incubated at different temperatures: 30, 37 and 40°C. Samples were collected after 24h and examined for bacteriocin production as described earlier.

## RESULTS AND DISCUSSION

### Screening for bacteriocin producing isolates

Thirty five LAB isolated from different origins were examined for displaying bacteriocin activity against a set of 12 indicator strains. These strains presented a broad inhibitory spectrum since they were able to inhibit many of the indicator strains tested such as *E. coli* ATCC29522, *K. oxytoca*, *K. pneumoniae*, *Proteus mirabilis*, *Salmonella* sp. *S. aureus* ATCC29523, *P. aeruginosa*, *E. coli* ATCC25922, MRSA, *B. subtilis*, *E. coli* ATCC28484, *L. monocytogenes* and the pathogenic *Klebsiella* 111. The inhibitory effect, which was observed by the formation of clear and distinct zones around the wells, may be due to the production of several antimicrobial compounds like organic acids, hydrogen peroxide or bacteriocins (Labioui *et al.*, 2005).

The activity of the inhibitory agent was tested under conditions which eliminate the possible effect of organic acids by adjusting the pH of the cells-free supernatant to 6.0 and of hydrogen peroxide by catalase treatment. Six of 35 strains (*Lb. plantarum* F12, *Lb. curvatus* G6, *Lb. gasseri*, *Lb. plantarum*, *Lb. casei* ssp *tolerans* G4, and *Lactobacillus* sp. B5) produced antimicrobial activity in the neutralized cell-free supernatant against four indicator strains (MRSA, *Bacillus subtilis*, *L. monocytogenes* and pathogenic *Klebsiella* 111). When the cell-free supernatant was treated with catalase (1mg/ml) the six strains confirmed their activity only against three indicator strains (MRSA, *L. monocytogenes* and *B. subtilis*). The diameters of inhibition zones of the indicator strains by the cell-free supernatant neutralized and treated with catalase are ranging from 14 to 20 mm. The highest diameter (20mm) was obtained with the cell-free supernatant of *Lb. plantarum* F12 and *Lb. curvatus* on *B. subtilis*, whereas the lowest diameter was obtained with the cell free supernatant of *Lactobacillus* sp. B5 against MRSA.

The fact that, the cell-free supernatants (neutralized and treated with catalase) inhibited the growth of the indicator strains gives evidence that the antimicrobial activity is due to the production of bacteriocins (Tatsadjieu *et al.*, 2009). Gram-positive indicator bacteria are much more sensitive to bacteriocin of our LAB strain than Gram-negative indicator bacteria. These results indicated that our LAB had an inhibitory spectrum towards closely related Gram-positive bacteria. The resistance of Gram-negative bacteria is attributed to the particular nature of their cell membrane; the mechanism of action described for bacteriocin involved a phenomenon of adsorption. Ivanova *et al.* (2000) found that, the bacteriocin produced by *Lactococcus lactis* subsp. *lactis* B14 inhibited only wide range of strains from the group of closely related LAB. The known bacteriocins does not still act on the sorts taxonomic close, for example, nisin has an inhibitory effect against a wide variety of Gram-positive food-borne pathogens and spoilage microorganisms and can also act on several Gram-negative bacteria when the integrity of their outer membranes is disrupted (Savadogo *et al.*, 2004). The isolate *Lb. plantarum* F12 was selected for further studies. *L. monocytogenes* has become one of the most significant food borne pathogens. In food industry, the control of this pathogen remains a challenge because of its widespread occurrence and its ability to survive and persist even in hostile environment (Hartmann *et al.*, 2011). For this reason we tested the ability of bacteriocins produced by *Lb. plantarum* F12 to inhibit this bacterium. Hartman *et al.* (2011) observed that the cell-free supernatant produced by eight antagonistic bacteria strains were able to inhibit *L. monocytogenes* in different food matrices. In another study, Singh and Prakash, (2009) found that, several LAB strains isolated from cottage cheese are capable of inhibiting pathogenic microorganisms in the food environment and display crucial antimicrobial properties with respect to food preservation and safety. They can also be used more specifically to inhibit certain high-risk bacteria like *L. monocytogenes* in food. Application of bacteriocins may help reduce the use of chemical preservatives and /or the intensity of heat and other physical treatments, satisfying the demands of consumers for foods that are fresh tasting, ready to eat, and lightly preserved.

### Characterization of bacteriocin

The effect of heating, pH and enzymes were studied in this work by using MRSA as indicator strain. Based on the results showed in Fig. 1, the inhibitory compounds produced by the tested isolate were considered to be heat stable. The activity of bacteriocin produced by *Lb. plantarum* F12 remained constant after heating at 100°C for 30 min followed by subsequent decline after 60 min. Similar results were recorded for a number of bacteriocins produced by *Lactobacillus* spp. and *Lactococcus* spp.. In addition, lacticin NK24 produced by *Lc. lactis* NK24, lost only 87.5% of its activity after 30 min at 100°C and was completely inactivated after 15min at 121°C (Todorov *et al.*, 2011b). On the other hand, Sarika *et al.* (2010) observed that, the bacteriocin GP1 produced by *Lb. rhamnosus* had a remarkable stability over heat treatment even at the autoclaving temperature for 20 min. Heat stability of *Lb. plantarum* F12 at 100°C is important if the bacteriocin is used as a food preservative, because many procedures of food preparation involve a heating step.

As shown in Fig. 2, the antimicrobial activity of *Lb. plantarum* F12 is significantly influenced by pH. In this respect, it was observed that the residual activities were significantly higher in the range of pH 6.0 to pH 10.0 than those at pH 2.0, 4.0 and 12.0; with a maximum activity at pH 6.0, suggesting that compounds other than acids inhibited growth of MRSA. These observations are in agreement with those reported by Ogunbanwo *et al.* (2003) who showed that *Lc. brevis* excreted other compounds such as bacteriocins that inhibited the growth of pathogens. According to these results, we can say that the antimicrobial activity of *Lb. plantarum* F12 presents stability in the range of pH from 2.0 to 12.0. This property has been considered highly useful for their application as food preservative.

The effect of various enzymes on the inhibitory agent was studied. Complete inactivation or significant reduction in activity was observed after treatment of the cell-free supernatant with chymotrypsine, trypsin and pronase which confirmed the proteinaceous nature of the active agent. The other enzymes tested in our study (amylase and lipase) did not cause inactivation. This confirmed that carbohydrate and lipid moieties if existing were not required for the inhibitory activity. Similar results were recorded by Todorov *et al.* (2004) for bacteriocins produced by *Lc. plantarum* ST13BR whereas Ivanova *et al.* (2000) observed that trypsin, chymotrypsin and rennin had no effect on bacteriocin produced by *Lc. lactis* subsp. *lactis* b14 isolated from boza Bulgarian Traditional cereal beverage.

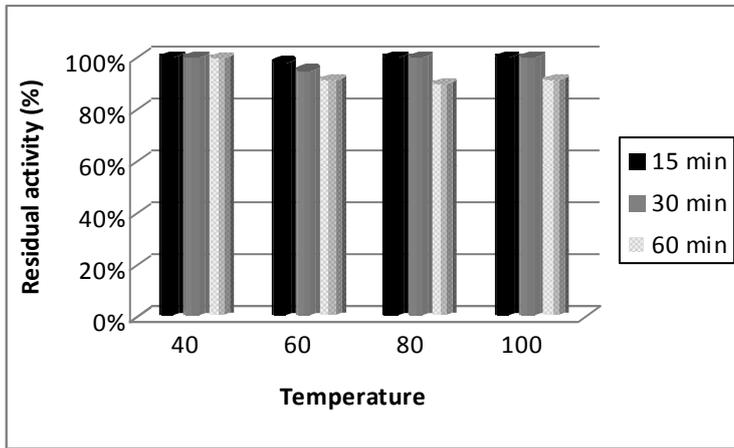


Fig. 1: Effect of temperature on bacteriocin activity produced *Lb. plantarum* F12.

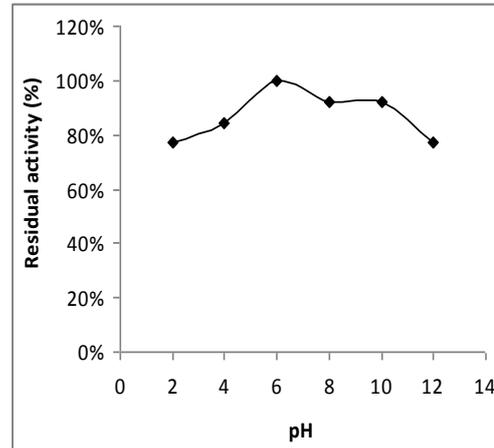


Fig. 2: Effect of pH on bacteriocin activity produced by *Lb. plantarum* F12.

**Monitoring of bacteriocin production**

Bacteriocin production was monitored during 48 hours of growth in MRS broth. Fig. 3 illustrates the growth, pH and the level of *Lb. plantarum* F12 bacteriocin production through 48 hours of incubation. Data showed that bacteriocin production started at the beginning of the log phase of the bacterial growth (after 4 h), and increased gradually with bacterial growth till it reached its maximal level (2416 AU/ml) after 30 hours of incubation (in stationary phase). After 32 h of incubation a decrease in bacteriocin production was observed (2166 UA/ml). During the same period of growth the pH of the medium decreased from 6.5 to 4.5. The growth of *Lb. plantarum* F12 increased gradually and reached its optimum after 32 h and remained more or less constant during the following 16 hours. Several studies have shown that bacteriocin production is dependent on biomass concentration. Todorov and Dicks, (2005) reported that optimal levels of plantaricin ST194BZ, produced by *Lb. plantarum* ST194BZ, were obtained in growth media that supported high biomass production, such as MRS. A similar bacteriocin production profile was reported for bacteriocin ST311LD produced by *E. faecium* ST311LD isolated from fermented olives, in which maximal bacteriocin production was reported after 20 hours growth in MRS broth, followed by a decrease in activity in the following 5 hours. The decrease in activity of bacteriocins produced by *Lb. plantarum* F12 at the end of the monitored period could be explained by the degradation of the bacteriocin by extracellular proteolysis enzymes, similar decreases have also been observed for bacteriocins produced by *Enterococcus faecium* ST311LD (Todorov & Dicks, 2005), *Enterococcus mundtii* ST4SA and *Pediococcus acidilacticii* NRRL B5627 (Todorov *et al.*, 2011a).

**Effect of temperature on bacteriocin production**

The effect of temperature on bacteriocin production by *Lb. plantarum* F12 was tested in Erlenmeyer flasks cultures containing sterile MRS and maintained at different temperatures (30, 37 and 40°C). Fig. 4 shows the effect of temperature on bacteriocin production. The optimum temperature for the production of bacteriocin was 37°C, thus the bacteriocin activity at this temperature was higher than that observed at 30 and 40°C. According to these results we can say that, the optimum temperature for production and the one for growth are correlated, as observed elsewhere for lactocin A, enterocin 1146, lactocin S and nisin Z (Todorov *et al.*, 2004). So, growth temperature seems to play an important role on bacteriocin production. Different results were recorded by Mataragas *et al.* (2003), as they found that the optimum temperature for the production of bacteriocins produced by *Leuconostoc mesenteroides* L124 and *Lb. curvatus* L442 was 25°C and was lower than that of growth (30°C).

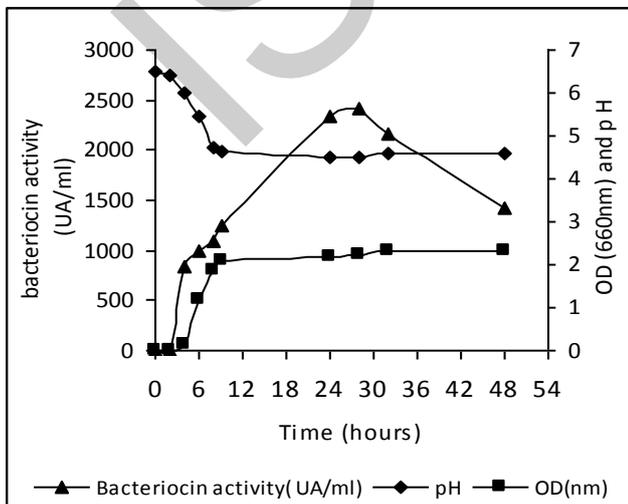


Fig. 3: Monitoring of bacteriocin production from *Lb. plantarum* (F12) in MRS medium at 37°C during 48 h.

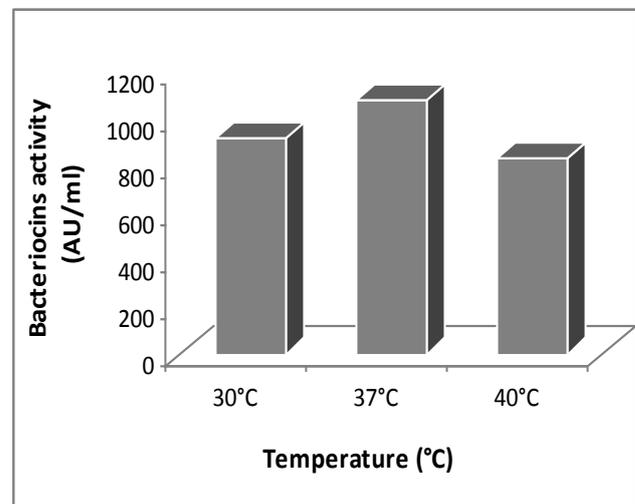


Fig. 4: Effect of temperature on bacteriocin production from *Lb. plantarum* F12 in MRS medium at 37°C.

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# PRODUCTION OF ARTIFICIAL RICE BASED ON CASSAVA FLOUR AND WATER YAM

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## ABSTRACT

Rice is the primary food source in Indonesia. In the last few years, the food security has been decreasing because of some factors such as the increasing population, natural disaster and decreasing land productivity. One alternative to reduce rice consumption is introducing artificial primary food based on cassava and water yam. Aim of the research was to find out the best treatment in producing artificial primary food. The result showed that mentioned best treatment was proportion of cassava : water yam flour, 80:20 by adding 3% porang flour. The product was characterized by water content 8.62%, fat 3.17%, protein 2.4%, ash 1.56%, starch 71.95%, carbohydrate total 84.25%, rehydration 172 %, lightness 48.10, texture 1.37 N and the organoleptic characteristic in the range of quite like the taste 3.20, aroma 2.90, color 3.05 and texture 3.15.

Keywords : artificial rice, flour proportion, porang flour concentration, physical, chemical and organoleptic parameter

## INTRODUCTION

Artificial primary food is a kind of primarily food diversification that processed from raw material based on carbohydrate with addition of the certain substance to reform the quality of main food. The ideas about the equipping availability of artificial primarily food could be realistic as non rice food which be similar to rice, in spite of technically and economically could be done, in spite of taste and aesthetics aspect should be needed advanced examination (Samad, 2003). As far as now, rarely found the presence of primarily food that be similar to rice which made from non rice materials. However, kind of familiar granule form product on society, such as pearl sago palm and oyek (cassava rice). Artificial staple food (artificial rice) could be made from sweet potato (Antarlina and Utomo, 1999) or soybean powder with extruction method (Kohei and Chiharu, 2007). Whereas, the meaning of enriched artificial rice is grain or seed that made by heating process of the batter flour proportion which added with 20-50% of water at the temperature of 90-120°C for 45 ± 1 minute or till whole the essence has been semi-gelatinization. Essence and gluten were added as the tied material till the granulated butter could be curved like rice seed, then these enriched artificial rice was dried off and protected by water resistant material (Katsuya *et al*, 2003). The several previous researches that made artificial primarily food might be found in Table 1.

Tabel 1. Hasil Penelitian PPT Perlakuan Terbaik

Komposisi	Erliyanti (2008)	Miranda (2009)	Fakhriyah (2009)	Kinanthi (2009)
KH (%)	82,43	82,25	-	-
Pati (%)	-	-	20,68	69,23
Kadar Air (%)	9,93	9,49	7,82	5,73
Protein (%)	4,81	7,08	2,71	6,76
Serat kasar (%)	5,16	2,49	-	3,85
Daya Rehidrasi (%)	276,94	-	216,70	275,16
L*	44,98	39,13	58,13	56,52

Artificial rice making refers to the nutrient values that balanced with rice (Haryadi, 2006), in other side, to get the quality that almost treat the same as the rice, must be support by several parameters, namely include the ratio of amilosa-amilopektin, protein content, gelatinization temperature, volume expanding, water absorbtion, gel viscosity, and essence gel consistency (Astawan, 2004). Cassava flour is a kind of flour that made from fresh cassava pass through the flouring step. The steps of cassava flour processing consist of: peeling, washing, cutting, drying, pounding, and sieving (Anonymous, 2000).

Cassava flour has content of carbohydrate about 32,4 gr, 567 of calories energy per 100 gram of cassava (Aminah, 1999) and sold with the price about 40-60% lower than the price of rice or wheat flour, thus the cassava flour could be marketed at country as well as in the city as the source of good calories to substitute the rice. According to Aminah (1999), cassava flour is not too communicable yet in Indonesia. The developing of cassava flour agroindustry in Indonesia is a kind of diversification alternative type of cassava flour products. It potentially could raise the farmer income, expand the market, support food diversification and have a role of developing any food industries (Indraswari, 2011).

Kurachi (1995), explained that the process of making enriched artificial rice, in a point of manner, divided into 4 steps, namely mixing, molding, steaming, molding to curve the granule rice and drying. Fellows (1990), explained that mixing is an operation unit where got the uniform size from one or more components, by spreading a component into another components. Generally, mixing has important effects on sensoric quality, until increase the consumer revenue and food material uniformly, which will be needed advanced processing.

Molding process is done by using *roll-type granulator*. Its aim is to make the size and form of artificial rice uniformly. In this step, the artificial rice still on long form like noodles, because the textures of molding result was still on soft and brittle, so then could not do the molding process with rice size (Miranda, 2009).

Steaming is step of the process that cause the essence gelatinization happened. According to the patent of making enriched artificial rice (cooked), steaming's aim is to make the essence partly gelatinized, curve the viscos butter, so it make essence easier to mold (Teruo *et al*, 2004). Grain modling is done manually by using scissor. The half ripe long butter is slicing to curve the size of it be similar to rice grain with no more 1 cm of length and 0,25 cm of width (Miranda, 2009).

Drying is the manner to remove or decrease water partly of the material by vaporized manner. These process is done with the heat energy and usually the water content is decreased untill the microorganism's limit and the enzymatic activities could not cause the significant damaged (Susanto and Saneto, 1994). According to the patent of making enriched artificial rice, drying is done on the temperature of under 80°C untill the water degree reaches out 5-15% (Teruo *et al*, 2004). There are several factors that has influences toward the characteristics of artificial rice, namely (Indraswari, 2011):

1. Essence Glatinization
2. Content of Amilosa dan Amilopektin
3. Content of Glukomanan

## METHODS AND PROCEDURES

### Materials

The materials that used in these research, consist of white cassava, rice flour, and pure porang flour. Whereas, the chemical materials that used on it, consist of chemical materials with pureness of pro analyze, namely: 80% of alcohol, Nelson reagent, arsenomolibdat reagent, standard glucose solution, 45% of NaOH, strong H<sub>2</sub>SO<sub>4</sub>, 3% of H<sub>3</sub>BO<sub>3</sub>, strong HCl, Petroleum eter (PE), Kjeldahl tablet, 10% of K<sub>2</sub>SO<sub>4</sub>, 0,01 N of I<sub>2</sub>, anhidrat of Na<sub>2</sub>SO<sub>4</sub>, pp indicator, amilum indicator. The analyze materials with technical pureness namely aquades and filter paper.

### Methods and Procedures

The research was carried on using Factorial Randomized Block Design contain 2 factor, that each factor consists of 3 levels and each procedure was repeated 3 times.

The first factor was the proportion of cassava and water yam flour:

- C1 = 90 : 10
- C2 = 80 : 20
- C3 = 70 : 30

The second factor was the porang concentration:

- P1 = 2%
- P2 = 3%
- P3 = 4%

### Research Implementation

#### *Making Cassava Flour*

Within Rostini (1990), the process of making these flour was begun from sorting of fresh cassava and weighing for 15 kg. Then, the cassava was sliced by knife and washed by water to minimalize the manure that adhere on it, all at once threw away the bad parts of the cassava, so that could not influence the flour production. The next step was, did the blinding process to decrease the cassava size, with aim to expand the wide surface, so then the drying process of these cassava could being running faster and spread evenly. After the size was decreased, did the drying process by using lamp dryer with the temperature of  $55 \pm 5^{\circ}\text{C}$  for 12 hours. Then, the last step was, refining the dry cassava by using the dry blender and sift by 80 Mesh sifter.

#### *Making Hulled Rice Flour*

Within Tarwiyah (2001), the process of making these flour was begun from winnowing the rice to clean the manures such as gravels, husk, and unhulled paddy, then weighed for 1 kg and did washing process as well as submerged inside the water to make rice texture soft with proportion of 1 : 3 for 60 minutes. Before doing roll to decrease the rice size by using roller, the rice was leak through to separate the rice from the water submerged. Then, the rice was dried with cabinet dryer with the temperature of  $55 \pm 5^{\circ}\text{C}$  for 5 hours, with the aim of decreasing the water degree till under 14%. The last step was, sieve the dry flour by using 80 Mesh sifter.

#### *Making Coarse Konjac Flour*

Within Thomas (1997), the process of making coarse porang flour was begun from sorting of porang tuber for the weight and the age of porang tuber uniformly. Then, the washing was done for disappearing the soil that adhere on porang tuber, and then did the weighing. After clean, the porang tuber was sliced with the thickness of 1-2 mm to decrease the size and make it easier to the drying process by using cabinet dryer with the temperature of  $55 \pm 5^{\circ}\text{C}$  for 18 hours till got the dry porang chip. Then, these porang chip was weighed for 1,5 kg and pounded with the pounder load of 7 kg, with the speed of 64 pound per minute for 16 hours to get the result of porang chip. And the last step was sieving the porang chip by using 30 Mesh sifter to separate the uncomplete pounded ones, and continued to 80 Mesh sifter that aim to separate between coarse konjac flour and oxalate.

### **Making Artificial Rice (Hulled)**

Within Erlianti (2008), the process of making artificial rice (hulled) was begun from the weighing of cassava flour and water yam with the proportion of 90 : 10, 80 : 20, and 70 : 30, and the weighing of porang flour with proportion of 2%, 3%, and 4%. The aims of these proportion were to get the best proportion and show the real differences in the characteristic parameters test of physic, chemistry, and organoleptic. After weighing, the next step was added 110% of clean water (v/b) and then mixed till the homogen butter became dull (unsticky). After the butter was dull, so it was mold by cookies molder, then steamed with the temperature of  $80 \pm 5^{\circ}\text{C}$  for 15 minutes so that the butter rice was not broken when the cutting was done. The last step was drying off the grain of artificial rice with using cabinet dryer for 3 hours with the temperature of  $55 \pm 5^{\circ}\text{C}$ .

### **Making Artificial Rice (Cooked)**

Making artificial rice (cooked) was done by the artificial rice (hulled) rehydration by hot water at the temperature of  $90 \pm 5^{\circ}\text{C}$  and let for 3 minutes, and then leak through. The next step was steaming for 15 minutes with the temperature of  $80 \pm 5^{\circ}\text{C}$ .

### **Data Analysis**

The chemical and physic observation data was analyzed using ANOVA and continued using 5% BNT (Beda Nyata Terkecil) or DMRT (*Duncan Multiple Range Test*) test. The best treatment is selected using the method of effectiveness index (De Garmo *et al*, 1984).

## **RESULTS**

### **Characteristics of Raw Materials**

The results cassava flour analysis showed water content 6,5% and equal with Susilawati and Medikasari (2008). Cassava flour starch content 68,09% insufficient than starch content in hulled rice (Samad, 2007). That is influenced by cassava because have many varieties (Antarlina dan Utomo, 1999), among those difference shape, size, storage capacity, chemical composition, processing characteristic and harvest period. Moreover, the important compound after carbohydrate in staple food is protein. Protein content to milled rice is 6% (Thai Food Composition Tables, 1999 dalam Arbiyanti dkk., 2007) so that artificial rice from water yam flour have sufficient protein similar with hulled rice.

### **Chemical Properties of Artificial Rice**

#### **1. Water Content**

Results of analysis showed that the factor proportions of various cassava flour, water yam flour and concentration factor konjac flour have real influence ( $\alpha = 0.05$ ) on artificial water content of rice. The interaction between these two factors do not give real effect. The higher the proportion of cassava flour, the starch content of rice products artificially higher, so the more water-binding agent and result in increased water content of artificial rice. Amylose and amylopectin in cassava flour tends to increase the absorption of water (Mc Williams, 2001) because the starch has the ability to absorb water very large (Winarno, 2002).

#### **2. Starch Content**

Starch content of artificial rice growing niche tend to increased with increasing proportions of cassava flour. Susanto and Saneto (1994) argues that the dried food will cause the loss of water content and concentration of the remaining ingredients such as carbohydrates and protein so that it will present in greater numbers per unit dry weight. Additional factors influence the concentration of flour porang no significantly to starch content. This is because the starch, protein and starch porang there is no synergy in the binding process water.

#### **3. Protein Content**

Protein content in artificial rice had downward trend with decreasing proportion of cassava flour and starch porang addition of increasing concentration. The highest protein content of cassava flour in the proportion of treatment: uwi flour is 60: 40. Artificial rice protein levels that do not tend to decrease sharply as the addition of flour concentration porang allegedly affected by the water content in the material (Susanto and Saneto, 1994).

### **Physical Properties of Artificial Rice**

#### **1. Color**

Brightness level of artificial rice tends to decrease with increasing proportions of cassava flour and konjac flour additions. The addition of treatment the proportion of cassava flour : water yam flour, have a real influence artificial brightness of dry rice. Addition of increasing proportions of cassava result in diminishing the value of artificial brightness which causes the color of brown rice. Artificial brightness level of mature rice tends to decrease with increasing proportions of cassava flour and increasing brightness as the addition of flour porang concentration. Level yellow (+ b) artificially dried rice due to differences in the proportion of cassava flour : water yam flour and the addition of konjac flour concentrations ranged from 14.15 to 15.78. While the level of artificial yellow rice cooked with a variety of treatments ranging from 11.88 to 14.48.

#### **2. Texture**

The texture of cooked artificial rice according to observations of various treatments ranged from 1.07 to 1.83%. Starch is added to the food has a function to improve the texture and density (Whistler, 1997). Kovacs and Matuz (1996a, 1996b) in Gallagher et al (2004) stated that the hydrocolloid as a binding agent in the formulation of gluten-free breads based on corn starch resulted in increased volume and texture are significant.

### 3. Rehydration Capacity

Rehydration capacity of artificial rice with various treatments range from 152.03 to 202.46%. Rehydration capacity of artificial rice increase as cassava flour and adding konjac flour concentration increase. Wu and Fang (2003) stated glucomannan have some special physical properties such as absorption of water is very high and the development of up to 138-200% takes place very rapidly in the water.

## Organoleptic Properties of Artificial Staple Food

### 1. Taste

The mean level of preference for artificial flavor rice ranged from 2.95 to 3.35 (do not like to neutral). Favorite flavor lowest percentage rate obtained from the treatment the proportion of cassava flour and water yam flour (70:30) with the addition of a concentration variation (2%), whereas the highest level of taste preference on the proportion of cassava flour treatment and water yam flour (60:40 and 70 : 30) with a variation of the addition of konjac flour concentration of 3% and 4%. Starch will raise sweet taste perceive, however if there is in high amount will causing mask flavor (Zayas, 1997 dalam Miranda, 2009).

### 2. Color

The mean level of preference for artificial rice ranged from 2.55 to 3.25 (do not like to neutral). The lowest percentage rate favorite color is obtained from the treatment the proportion of cassava flour : water yam flour (80:20) with the addition of a concentration variation porang flour (4%), whereas the highest level of preference in the treatment of cassava flour: water yam (70:30) with the addition of variations konjac flour concentration of 3%.

### 3. Flavor

The mean level of preference for artificial rice ranged from 3.05 to 3.35 (do not like to neutral). Percentage favorite aroma lowest level obtained from the treatment the proportion of cassava flour: water yam flour (60:40) with the addition of a concentration variation konjac flour 3%, while the highest level of preference in the treatment of cassava flour: water yam (80:20) with a variation of the addition of konjac flour concentration of 4%.

### 4. Texture

Panelists tend to be neutral with respect to the proportion of texture to the treatment of cassava flour: water yam (80:20) with the addition of konjac flour 2%, but from each treatment showed no significant difference. This is due to the high proportion of cassava flour contributes to a high starch content in artificial rice (Whit, 2002).

## Best Treatment

Determination of best treatment artificial rice based on effectivity index (De Garmo) method. Assesment parameter include physical, chemical and organoleptic parameter. Calculation from overall parameter showed there are no interaction among each treatment. Calculation for best treatment categorized based on composite flour and konjac flour usage. The best treatment of artificial rice obtained at proportion cassava flour : water yam flour = 80 : 20, and best treatment for konjac flour usage was 3%

## CONCLUSION

Organoleptic test usage proportion of cassava flour and water yam flour with adding konjac flour as binding agent did not showed significant influence. The physical and chemical parameter value of best treatment artificial rice had no significant effect than control, so to speak that this best treatment artificial rice have potential as substitute food of hulled rice.

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# RADIATION PATTERN OPTIMIZATION BY API APPROACH FOR SMART ARRAY ANTENNAS SYSTEMS

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## ABSTRACT:

In modern mobile communications systems, both desired and interfering signals change their directions continuously. Therefore, a fast tracking system is needed to constantly track the users and then adapt the radiation pattern of the antenna to direct multiple narrow beams to desired users and nulls interfering sources. This paper proposes a smart array antenna system, which can improve performance by spatial filtering. Smart array antennas backed by strong signal processing algorithms are able to automatically change the beam pattern in accordance with the changing signal environment. The adaptation is achieved by multiplying the incoming signals with complex weights and then summing them together to obtain the desired radiation pattern. Adaptive array optimization is an NP-hard problem. In this paper, a technique based on the API (Pachycondyla Apicalis algorithm) is presented to solve this problem. Several illustrative examples of patterns with imposed single and multiple null directions are given to show the versatility of the present method.

**Key words:** Smart arrays antenna, Beamforming, Optimization, Metaheuristic, API (Pachycondyla Apicalis).

## 1. INTRODUCTION

In recent years a substantial increase in development of broadband wireless access technologies for evolving wireless internet services and improved cellular system has been observed because of them there is traffic that demands on both the manufacturer and operators to provide sufficient capacity in the networks. This becomes major challenging problems for service provider to solve since there exist certain negative factors in the radiation environment contributing to limit the capacity. As the growing demand for mobile communications is constantly increasing, the need for better coverage, improved capacity, and higher transmission quality rises. Thus, a more efficient use of the radio spectrum is required.

Smart antenna systems [1] are capable of efficiently utilizing the radio spectrum and are a promise for an effective solution to the present wireless systems problems while achieving reliable and robust high-speed, high-data-rate transmission.

The increasing pollution of the electromagnetic environment has prompted the study of array pattern nulling techniques. These adaptive techniques are very important for minimising degradation in signal-to-noise ratio performance due to undesired interferences. The adaptation is achieved by multiplying the incoming signals with complex weights and then summing them together to obtain the desired radiation pattern. Adaptive array optimization is an NP-hard problem [2-9].

The techniques of placing nulls in the antenna patterns to suppress interference and maximizing their gain in the direction of desired signal have received considerable attention in the past and are still of great interest using evolutionary algorithms such as genetic algorithms (GA) [10, 11] or the sequential quadratic programming (SQP) algorithm [12].

In this work we present an optimization metaheuristic method based on a model of the foraging behavior of a population of primitive ants (Pachycondyla Apicalis) to determine the optimal radiation pattern for an adaptive linear array antenna. These ants are characterized by a relatively simple but efficient strategy for prey search in which individuals hunt alone and try to cover a given area around their nest [13].

The remainder of this paper is organized as follows. Section 2 briefly exposes the metaheuristic method (API) principle. Section 3 presents the strategy of array antennas optimization by API and analyzes the simulation results. Section 4, as a conclusion, summarizes our principal observations.

## 2. API ALGORITHM

In this paper, we are interested in a model of the foraging strategy of the Pachycondyla apicalis ponerinants [13, 14] and in its application to adaptive array antennas optimization problems. These ants use relatively simple principles to search their preys, both from global and local view-points. Starting from their nest, they globally cover a given surface by partitioning it into many hunting sites. Each ant performs a local random exploration of its hunting sites and its site choice is sensitive to the

success previously met on the sites. These principles can be used to implement a new strategy for the search of a global minimum of a function  $f$  in a search space  $S$ .

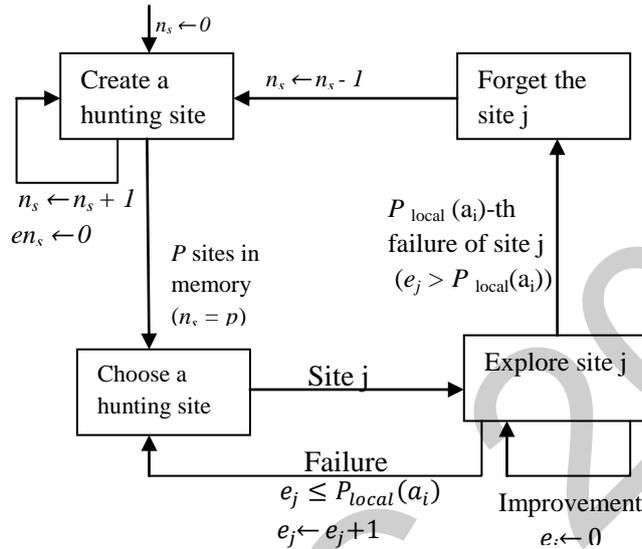
The stepwise procedures of the API algorithm are described as following [14]:

- 1) Initialization: set the algorithm parameters.
- 2) Generation of new nest (exploration)
- 3) Exploitation

**3.1) Intensification search:**

- For each ant  $a_i$ , if it has less than hunting sites in its memory, then create a new site in the neighborhood of and exploit this new site;
- Else If the previous site exploitation is successful, then exploit the same site again;
- Else exploit a probabilistically selected site (among its sites in memory).

The following diagram illustrates the principle of intensified research by each ant.



**Fig 1: The behavior model of a Pachycondyla apicalis ant  $a_i$  [14]**

$n_s \leq p$  represents the number of sites memorized by the ant.  $e_j$  represents the number of unsuccessful explorations successively performed by the ant on site  $j$ .

**3.2)Information sharing:**

Probabilistically replace a site in the memory of the ant by the best one searched so far in this cycle.

**3.3)Nest movement:**

If the condition for nest movements is satisfied, go to (4); otherwise, go to (3.1).

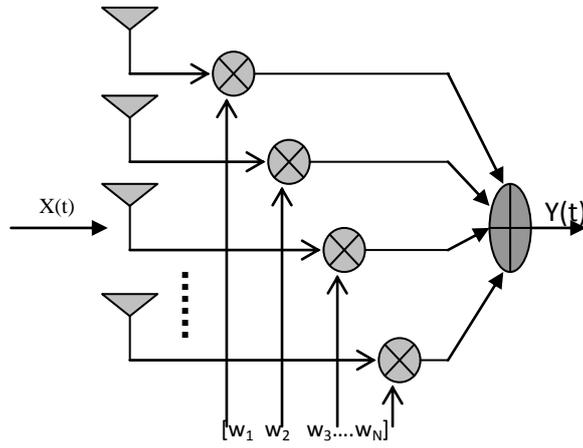
**4) Termination test:**

If the test is passed, stop; otherwise, empty the memories of all ants and then go to (2).

**3. API ALGORITHM FOR ADAPTIVE ARRAY ANTENNAS OPTIMIZATION**

**3.1 Adaptive array antennas problem formulation**

For some applications single element antennas are unable to meet the gain or radiation pattern requirements. Combining several single antenna elements in an array can be a solution. The goal of array antennas is to combine received signals in such a way that the ratio of desirable to undesirable content in the array output is maximized. There are several methods for combining the received signals in a multi-antenna array, but the simplest conceptually is to multiply the signal vector by the complex array weight vector and then to sum over the  $N$  antenna elements in the array [7-8]. The receiving beamformer is shown in Figure 2. In this receiving beamformer, each signal  $x$  is multiplied by a complex weight  $w$  and summed to form the output of the array denoted by  $Y$ .



**Fig.2: Narrow band array antennas with a complex weighting.**

The output of beamformer at time t is given by:

$$y(t) = \sum_{n=1}^N w_n^* x_n(t) = w^H x \tag{1}$$

Where \* denotes the complex conjugate and (.) denotes hermitian (complex conjugate) transpose operation. The vectors w and x, referred to as array weight vector and the array signal vector, respectively, are:

$$w = [w_1 \ w_2, \dots, \ w_N]^T \tag{2}$$

$$x = [x_1(t) \ x_2(t), \dots, \ x_N(t)]^T \tag{3}$$

Where T denotes the transpose operation. The array signal vector x can also be written as:

$$x(t) = s_d(t)a(\theta_d) + \sum_{i=1}^L s_i(t)a(\theta_i) + N(t) \tag{4}$$

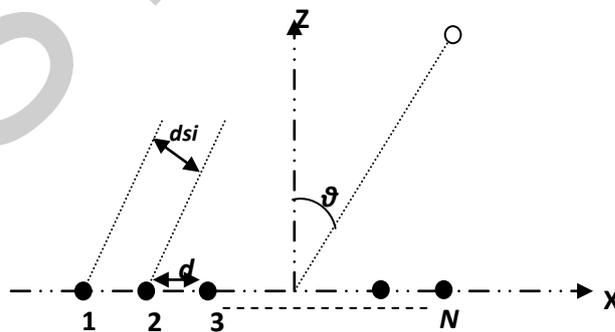
where  $s_d$  and  $s_i$  are the desired and interfering signals arriving at the array at an angle  $\theta_d$  and  $\theta_i$ , respectively, L is the number of interfering signals, and N is the gaussian noise at the array elements.  $a(\theta_d)$  and  $a(\theta_i)$  are the steering vectors for the desired and interfering signals, respectively.  $a(\theta)$  is given by :

$$a(\theta) = [1, \ e^{-j\frac{2\pi}{\lambda}d\sin(\theta)}, \dots, \dots, \ e^{-j\frac{2\pi}{\lambda}d(N-1)\sin(\theta)}]^T \tag{5}$$

Where  $\lambda$  is the wavelength.

The weights selection process is carried out by adaptive algorithms which build reference signals by a preestablished knowledge of the communication signals structure or a portion of the data transmitted [4-8].

Consider a uniformly spaced linear array with M omnidirectional antenna elements shown in Figure 3 . Interelement spacing is d and the plane wave front is impinging upon the array at an angle of  $\theta$  with respect to the array normal.



**Fig 3: Uniformly spaced linear array antennas**

We admit there does not exist coupling between the sources, and that each source, in presence of the others, rayon the same field  $f(\theta)$  . The total field radiated by the linear array antennas, will be the sum of the various contributions of the fields radiated by each source weighted by a excitation coefficient.

$$F(\theta) = f(\theta) \sum_{i=0}^{N-1} a_i \exp(jk_0 id \sin \theta \cos \varphi + b_i) \tag{6}$$

Where  $\theta$  et  $\varphi$  : observation angles ,  $a_i$  : amplitude of the element  $i$  excitation ,  $b_i$  : phase of the element  $i$  excitation,  $d$  : interelement spacing,  $f(\theta)$  : radiation pattern of an element of the array antennas and  $k_0$  : wave number.

By varying the phase  $b_i$  and amplitude  $a_i$  of the feeding currents to the elements, the overall array pattern can be steered in the desired user's direction and minimizing the radiation levels in the interferences directions without physically moving any of the individual elements. For reducing the complexity and the obstruction of the array antennas feeding system, the approach used here is to fix the amplitude of weighting and to seek only the law of optimal phase only by hybrid API . The objectif fonction is :

$$\text{fitness} = 20 \log_{10} \left( \sum_{i=1}^{M+1} s_i f(\theta_i) \sum_{n=1}^N a_n \exp(jk_0 n d \sin \theta_n \cos \varphi_n + b_n) \right) \quad (7)$$

Where  $M$  : number of interferences, and  $s_i$  : space vector of sources.

### 3.2 API adaptation

The strategy adopted here, consists in overall modifying population of initial solutions repeatedly to lead to a satisfactory final solution in a reasonable time. For this purpose, the API method uses movements to pass from a solution to another inside a research space. It is divided into two essential iterative phases: a diversification phase for the promising solution detection by applying *Orand* stochastic operator, followed by an intensification phase to intensify research in the zone of this solution by applying *Oexplo* stochastic operator, for finding the best phase vector.

The algorithm starts with a random generation of  $F$  solutions. Each solution corresponds (hunting site: point in research space) to a vector phase  $X(x_1, x_2, \dots, x_h, \dots, x_n)$ ,  $N$  represents the number of antennas and  $F$  the number of ants. The solutions generated initially are well dispersed in the research space  $[-\pi, \pi]$ .

Each ant begins its research with the disturbance of the corresponding solution, by applying a stochastic transformation presented by:

$$X_k(j+1) = X_k(j) + O_{rand}(X_k(j)) \quad \text{In diversification phase} \quad (8)$$

$$X_k(j+1) = X_k(j) + O_{explo}(X_k(j)) \quad \text{In intensification phase} \quad (9)$$

Where  $k$  is index of ant,  $j$  represents the algorithm iteration and  $O_{rand}(X_k(j))$ ,  $O_{explo}(X_k(j))$  transformers determined by the experiment.

The solutions evaluation (phase vectors) is done according to the minimization criterion of the cost function (equation 7). It is also necessary to store the last solutions visited in a dynamic vector *tabk* which contains the list of the solutions visited by the ant  $k$ .

During the algorithm execution, we will retain the absolute optimum among the minima generated during all the algorithm unfolding. The stop criterion is fixed according to a certain iteration number chosen initially. The following algorithm presents the essential phases of the adaptation by API algorithm:

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" - (1) Initialization of the parameters of: API ( N, Plocal , T, stopping criterion ) , array antennas, useful signal and interferences.
" - (2) Choose randomly the initial nest location S /* best phase vector (initially)
" - (3) Random generation of the N ants /* N phase vectors
" - (4) for each ant ai(phase vector) , i ∈ [1 ... N]:
"   If ai has less than p hunting sites in memory (dynamic vector tabk) then Create a new site in the neighborhood of S and Explore
"   this created site. /* application of Orand operator to generate and memorize a whole of favorite /*phase vectors.
"   Else
"     If the previous site exploration was successful then Explore again the same site. /* application of Oexplo operator for finding
"     the best phase vector /*in this zone
"     Else Explore a randomly selected site (among the p sites in memory).
" - (5) Remove from the ants memories all sites (the favorite phase vectors) which have been explored unsuccessfully more
"     than Plocal(ai) consecutives times.
" - (6) Perform recruitment (best phase vector copying between two randomly selected ants)
" - (7) If more than T iterations have been performed then Change the nest location ( best solution S' ) and Reset the memories of
"     all ants.
" - (8) Go to (4) or stop if a stopping criterion is satisfied.
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$P$ : hunting sites (favorite phase vectors) in the neighborhood of  $S$

$P_{local}(a_i)$ : times without catching any prey (not solution improvement in the zone of the favorite phase vector)

$T$ : movement of the  $N$  ants.

### 4. SIMULATION RESULTS

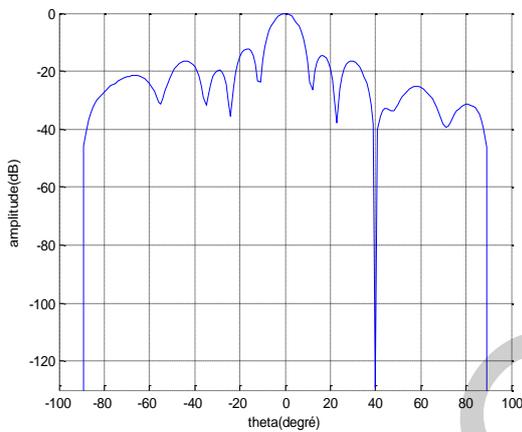
In this section, we present simulation results performed on Matlab 7.0 illustrating the performance properties of the proposed method. In API there are a number of parameters that need to be set. After several tests and benchmarks, we set the following values: the number of ants was set to  $n = 10$ , the number of hunting sites for each ant was set to  $P = 10$  and the number of explorations performed by each ant between two nest moves was set to  $T = 100$ . Finally, we set the parameters  $P_{local}$  to 100. In this way, ants will forget a site only when the nest is moved. Moreover, recruitment is used unless indicated otherwise.

A linear array is considered with a half-wavelength spacing where the element pattern is omnidirectional. The input Signal consisting of user signal at 0 degree, Gaussian Interferers and White Gaussian Noise at each element with SNR of 10 dB is added. The beam pattern is obtained by first calculating an Array factor for the array from  $-90^\circ$  to  $90^\circ$  degrees and then multiplying the weights with it. Amplitude response is obtained by taking  $20\log_{10}$  of the values obtained during beam pattern.

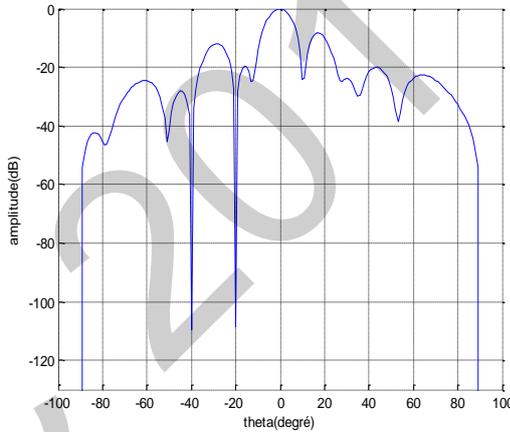
Various situations and examples were simulated. The goal is to examine the efficiency of API algorithm in his ability to:

- (1) To preserve the signal coming from the desired direction, and
- (2) To place a nulls in the directions of interfering signals.

Figure 4 shows a simulation of a 10 element linear array antenna pattern after API weights have been applied. An interfering signal is impinging on the array from  $40^\circ$  at an SNR of 10 dB.



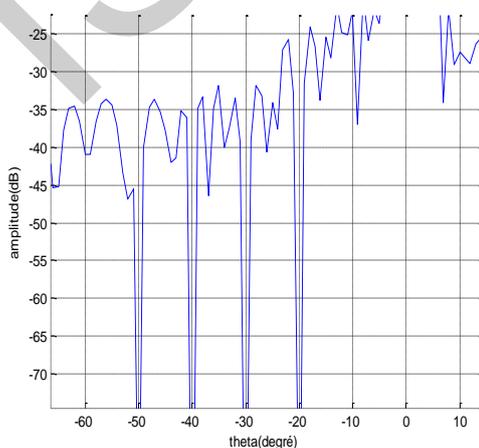
**Fig4: Beam pattern of API algorithm and interference rejection at - 40°**



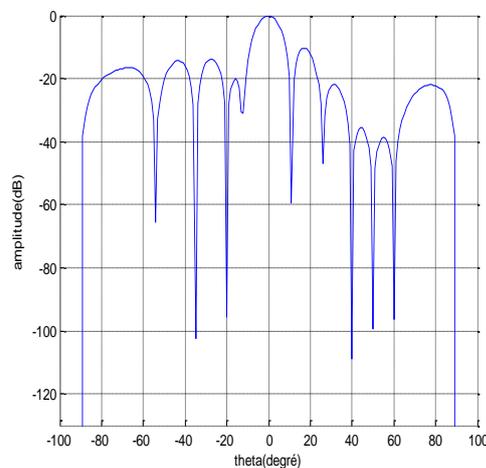
**Fig5: Beam pattern of API algorithm and interference rejection at - 40° and -20°.**

Figure 5 shows a plot of an  $M = 10$  element array antenna pattern. Two interfering signals are impinging on the array from  $-20^\circ$  and  $-40^\circ$  at an SNR of 10 dB. According to these figures,, we note that the rejection is done systematically in the interference direction and the null depth level is remarkably very low ( $< -100$  dB). The array pattern does not undergo any degradation in the useful signal direction. The main beam peak at  $0^\circ$ .

In the following part of simulation, we will study the behavior of the API process in the presence of several interferences simultaneously. We use the same linear array antennas with the same input API parameters used the first case but while varying the number of elements array antennas. In the first example, we assumed a 50 element array antenna and the interferers are located at  $(-50^\circ, -40^\circ, -30^\circ, 20^\circ)$ . The resultant pattern is shown in Figure 6. In the second example, we assumed a 10 element array antenna and seven interferers located at  $40^\circ, 50^\circ, 60^\circ, 10^\circ, -20^\circ, -35^\circ,$  and  $-50^\circ$ . The resultant pattern is shown in Figure 7.



**Fig.6: Partial Beam pattern of API algorithm and interference rejection at -50°, - 40°, -30°and -20°.**



**Fig.7: Beam pattern of API algorithm and interference rejection at 40°, 50°, 60°, 10°, -20°, -35°, and -50°**

It is clear from the Figure 6 and 7, that the achieved null depths for API algorithm have very good performance (about -100dB). The interference rejection capability increases as well. We can be seen that main lobe is formed towards user at angle 0 and interfering signals are being rejected as nulls are placed towards them.

## 5. CONCLUSION

The results in this paper show that the technique of using API to control radiation pattern of array antennas, though an optimum set of array excitations to achieve a specified pattern. This technique is very effective and simple in creating nulls in the direction of the interference signals. Let us note that these interferences rejections were obtained, by optimizing one parameter of the array antennas excitation, namely the phase and by preserving fixed amplitude. These causes direct to reduce the cost of array antennas realization and its obstruction. The results obtained with this technique encourage using it in another array configuration: phased array; arbitrary spatial position; and others.

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# RADICAL SCAVENGING AND ION CHELATING ACTIVITIES OF AQUEOUS AND METHANOLIC EXTRACTS OF *SANTOLINA CHAMAECYPARISSUS*

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## ABSTRACT

The search for antioxidants from natural sources has been receiving much attention and efforts have been put into identify compounds that can act as suitable antioxidants to replace synthetic ones. This study aims to evaluate the antioxidant potential of aqueous and methanolic extracts of the aerial part of *Santolina chamaecyparissus* by using DPPH free radical scavenging assay and the ferrous ion chelating method. Methanolic and aqueous extracts exerted a high scavenging activity toward DPPH with IC<sub>50</sub> of  $16.65 \pm 3.18 \mu\text{g/ml}$  and  $22.64 \pm 0.82 \mu\text{g/ml}$ , respectively. These values are higher than that obtained with BHT (IC<sub>50</sub> =  $71.96 \pm 1.23 \mu\text{g/ml}$ ) which used as a standard antioxidant. On the other hand, both methanolic and aqueous extracts have even though good but lower chelating activity than EDTA. Results indicated that the extracts from *Santolina chamaecyparissus* may be valuable natural antioxidant sources and potentially applicable in both medicine and food industry.

**Key words:** medicinal plants, antioxidants, *Santolina chamaecyparissus*, free radicals, chelating activity

## INTRODUCTION

The imbalance between production of reactive oxygen species (ROS) and the capacity of the normal detoxification system in favor of the oxidants lead to oxidative stress, which itself lead to cellular damage caused by the interaction of ROS with cellular constituents. Oxidative damage to cellular components is believed to be implicated in the pathology inflammatory joint disease, cardiovascular diseases, and cataract and could play a role in neurodegenerative diseases and ageing processes (Steer, Millgard, Sarabi, Wessby, & Kahan, 2002; Pham-Huy, He, & Pham-Huyc, 2008). Medicinal plants are considered to be an important source of antioxidant compounds and the therapeutic benefit of many medicinal plants is often attributed to their antioxidant properties. The preservative effect of many plant species and herbs suggests the presence of antioxidants such as flavonoids, phenolic acids, and phenolic diterpenes (Dutra, Leite, & Barbosa, 2008). *Santolina chamaecyparissus* (*S. chamaecyparissus*), plant from the Asteraceae family is a hardy aromatic, dwarf evergreen shrub native to the West and Central Mediterranean area. This plant is widely used in Mediterranean folk medicine for their analgesic, anti-inflammatory, antiseptic, antispasmodic, bactericidal, fungicidal, digestive and vulnerary properties (Buolos, 1983; Da Silva, 2004; Akerreta, Cavero, López, & Calvo, 2007). The essential oil of *S. chamaecyparissus* has anti-candidadal properties (Suresh, Srirama, Dhanaraja, Elangoa & Chinnaswamy, 1997). Several species of this taxon have been investigated chemically yielding a number of secondary metabolites such as flavonoids, essential oils, coumarins and polyacetilenic compounds (Sacchetti, Romagnoli, Ballero, Tosi, & Poli, 1997). A literature survey did not reveal any reference to any previous work comparing the antioxidant activities of this specie. The aim of the present study was to examine the *in vitro* antioxidant activities of the aqueous and the methanolic extracts from the aerial parts of *S. chamaecyparissus*. Therefore, we think that the results presented here will provide new information on this plant.

## MATERIALS AND METHODS

### Chemicals

All of the chemicals used in this work were purchased from Sigma (Germany), in exception of FeCl<sub>2</sub>, linoleic acid and butylated hydroxytoluene (BHT) were from Fluka (France). The chemicals were analytical grade.

### Plant Material

Aerial flowering parts of *S. chamaecyparissus* were collected in June, 2010 from Hammam Essoukhna, Sétif, region in eastern of Algeria. The plant was authenticated and the voucher specimens have been deposited at the Herbarium of Botany, University of Sétif. Aerial flowering parts of the plant were air-dried at room temperature and then reduced to powder.

### Preparation of *Santolina chamaecyparissus* Extracts

Aqueous extract was prepared by boiling 30g of powdered plant material in 300 ml of distilled water for 20 min. After filtration, the filtrate was lyophilized to give a yellow powder (yield: 10% w/w). Methanol extract was prepared by maceration of 30 g of powdered plant material with 80% methanol at room temperature for 24 h with frequent agitation. After filtration, the filtrate was concentrated under reduced pressure at 40°C. The residue was lyophilized to give a brown powder. The yield obtained was 12%. The dried extracts obtained from each plant material was stored in -32°C until further use.

### DPPH Radical-Scavenging Assay

The potential antioxidant activity of *S. chamaecyparissus* extracts was assessed using the stable 1,1-diphenyl-2-picryl-hydrazyl (DPPH) radical according to the method of Que, Mao, and Pan (2006) with slight modifications. Two milliliters of DPPH (0.1mM) was mixed with different concentrations of extracts or the standard antioxidant BHT. The mixture was shaken vigorously and incubated for 30 min in the dark at room temperature and the decreases in the absorbance values were measured at 517 nm. The decrease in absorbance is a measure of the scavenging of the DPPH radical by extracts. All experiments were performed at least in triplicate. The percentage of DPPH scavenging activity was calculated using the following equation:

$$\% \text{ of DPPH scavenging activity} = [(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}] \times 100$$

where  $A_{\text{control}}$  is the absorbance of the control reaction mixture without the test compounds, and  $A_{\text{sample}}$  is the absorbance of the test compounds. IC<sub>50</sub> values, which represent the concentration of the extract that caused 50% neutralization of DPPH radicals, were calculated from the plot of inhibition percentages against concentration.

### Ferrous Ion Chelating Activity

Ferrous ion chelating activity was measured by inhibition of formation of the iron(II)–ferrozine complex after the treatment of test material with  $\text{Fe}^{2+}$  according to the method of Le, Chiu, and Ng (2007) with slight modifications. The reaction mixture contained 500  $\mu\text{l}$  of different concentrations of *S. chamaecyparissus* extracts or the standard chelator EDTA, 100  $\mu\text{l}$   $\text{FeCl}_2$  (0.6 mM) and 900  $\mu\text{l}$  methanol. The control contained all the reaction reagents except the extracts and EDTA. The mixture was thoroughly shaken and allowed to react at room temperature for 5 min. One hundred microlitres of ferrozine (5 mM) was then added, the mixture shaken again, followed by further reaction at room temperature for 10 min to complex the residual  $\text{Fe}^{2+}$  ion. The absorbance of the  $\text{Fe}^{2+}$ -ferrozine complex was measured at 562 nm. All experiments were performed at least in triplicate. The chelating effect was calculated as a percentage using the following equation:

$$\% \text{ of the chelating activity} = [(A_{\text{control}} - A_{\text{sample}}) / A_{\text{control}}] \times 100$$

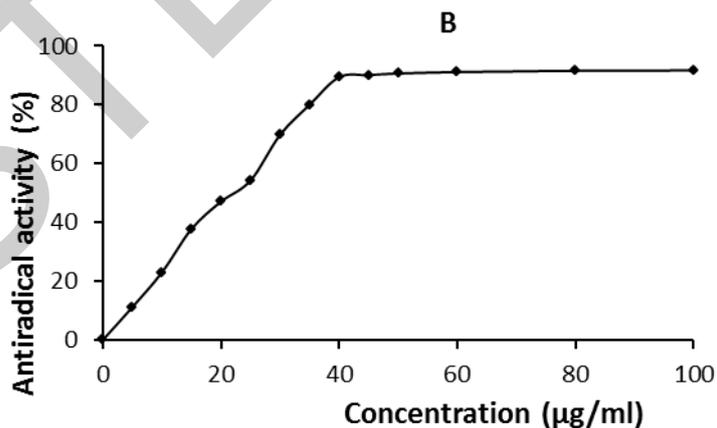
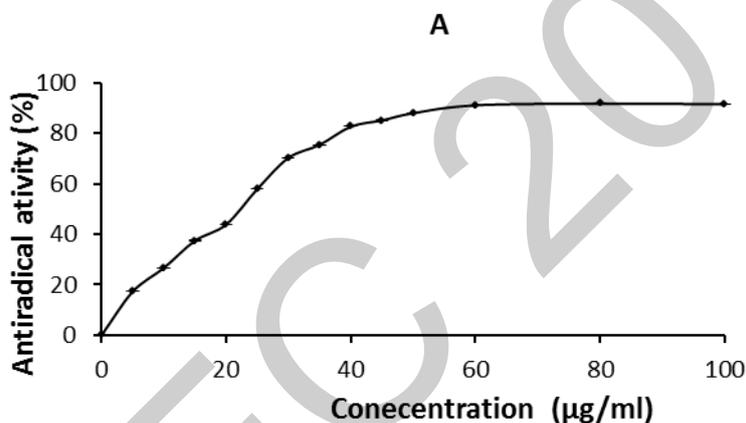
where  $A_{\text{control}}$  is the absorbance of the control reaction mixture without the test compounds, and  $A_{\text{sample}}$  is the absorbance of the test compounds.  $\text{IC}_{50}$  values, which represent the concentration of the extract that caused 50% of  $\text{Fe}^{2+}$  ion chelation, were calculated from the plot of chelating percentage against concentration.

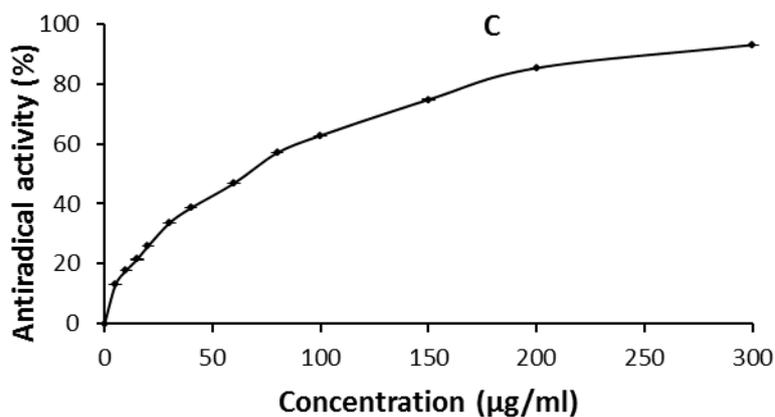
### Statistical analysis

Data obtained are expressed as mean  $\pm$  S.D. A probability of  $P < 0.05$  was considered significant.

## RESULTS

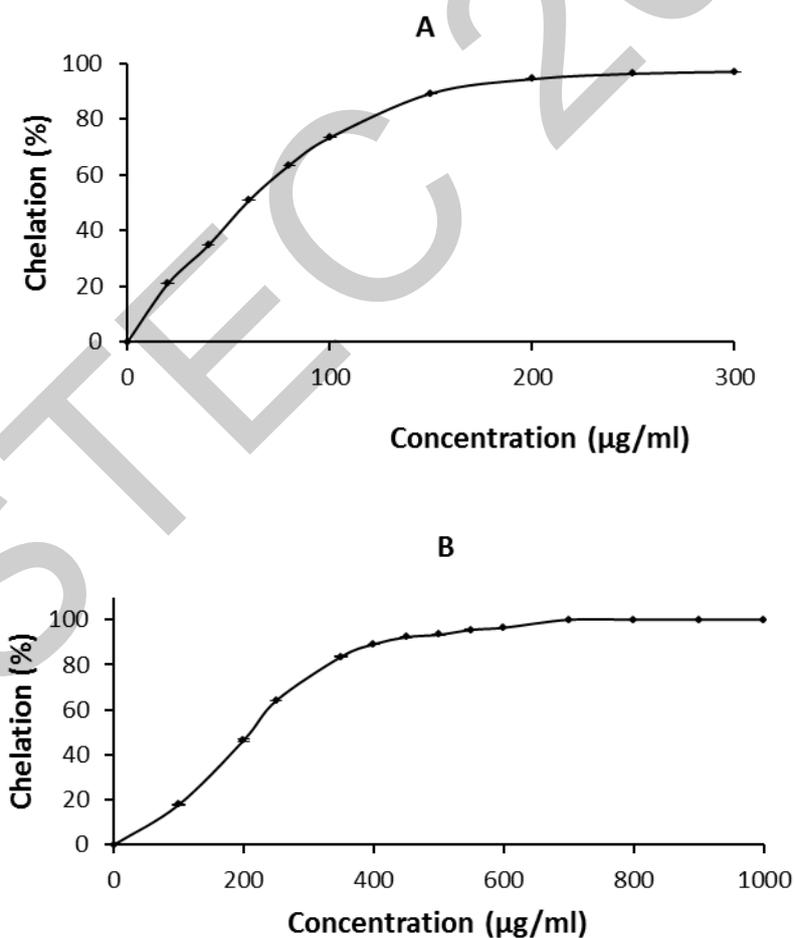
Aqueous and methanol extracts of aerial parts of *S. chamaecyparissus* exhibited a strong scavenging activity against the DPPH radical in a concentration-dependent manner. A maximal effect of 91% was exerted by 60  $\mu\text{g}/\text{ml}$  of aqueous or methanolic extracts. At 300  $\mu\text{g}/\text{ml}$ , the BHT used as a standard antioxidant, showed a maximal effect of 93% against the radical DPPH (Figure 1). The values of  $\text{IC}_{50}$  were  $22.64 \pm 0.82$   $\mu\text{g}/\text{ml}$  and  $16.65 \pm 3.18$   $\mu\text{g}/\text{ml}$  for aqueous and methanol extracts, respectively.

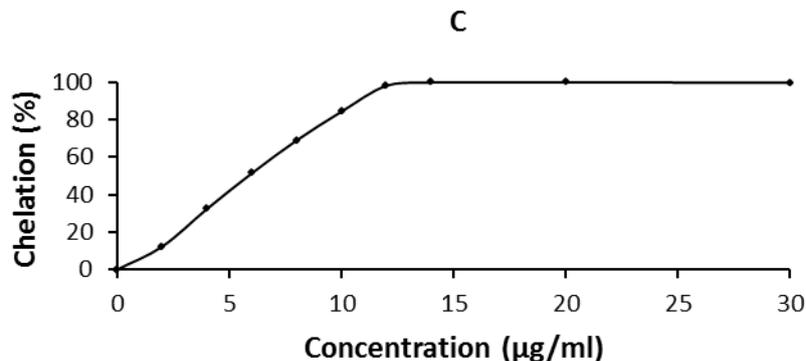




**Figure 1.** Antiradical Activity of Aqueous Extract (A), Methanolic Extract (B) from the Aerial Parts of *S. chamaecyparissus* and the Standard Antioxidant BHT (C). Values are Expressed as Means  $\pm$  S.D. (n = 3).

Moreover, the results showed that both extracts of aerial parts of *S. chamaecyparissus* were able to chelate ferrous ions in a concentration-dependent manner. Nevertheless, the methanolic extract showed a lower chelating activity than aqueous extract. In fact, maximal values of inhibition of 94% and 92% were obtained by 200  $\mu\text{g/ml}$  and 450  $\mu\text{g/ml}$  of aqueous and methanolic extract, respectively. The  $\text{IC}_{50}$  values were  $61.47 \pm 3.93 \mu\text{g/ml}$  and  $197.88 \pm 33.47 \mu\text{g/ml}$  for aqueous and methanolic extracts, respectively. However, chelating activity of both extracts were lower than that of the standard chelator EDTA (Figure 2).





**Figure 2.** Chelating Activity of Aqueous Extract (A), Methanol Extract (B) from the Aerial Parts of *S. chamaecyparissus* and the Standard Chelator EDTA (C). Values are Expressed as Means  $\pm$  S.D. (n = 3).

### DISCUSSION

Synthetic antioxidants such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), commonly used, are very effective, but they might be mutagenic (Namiki, 1990) carcinogenic (Whysner, Wang, Zang, Iatropoulos, & Williams, 1994) and even toxic (Moure et al., 2001). Therefore, there is an increasing interest in natural antioxidants, and many of them have already been isolated from different parts of many plants. Recently, a great interest has been recently focused on the natural foods, medicinal plants and phytoconstituents due to their antioxidant power. Various phytochemical components, especially polyphenols (such as flavonoids, phenyl propanoids, phenolic acids, tannins, etc) are known to be responsible for the free radical scavenging, chelating transition metals and antioxidant activities of plants. The therapeutic effect of many plants and herbs is caused by the presence of antioxidant constituents such as flavonoids (Rice-Evans, Miller, & Paganga, 2004), phenolic acids, and phenolic diterpenes (Shahidi, Janitha, & Wanasundara, 1992). Our data suggest that the aqueous and the methanolic extracts of the aerial parts of *S. chamaecyparissus* contained constituents that are good radical scavengers. Flavonoids, and essential oils have been isolated from *S. chamaecyparissus* (Becchi & Carrier, 1980; Demirci, Özek & Baser, 2000). Moreover, oxidative damage depends also on the availability of free metal ions and the mechanism of antioxidant action includes chelating trace elements involved in free-radical production. Our results suggest that the aqueous and the methanolic extracts of the aerial parts of *S. chamaecyparissus* contained considerable amount of water-soluble compounds that efficiently compete with ferrozine for chelation of ferrous ions. Iron chelators mobilize tissue iron by forming soluble, stable complexes that are then excreted in the feces and/or urine (Shinar & Rachmilewitz, 1990). Chelation therapy reduces iron-related inflammatory diseases such as arteriosclerosis (Lamar, 1964) and Alzheimer (Reznichenko et al., 2006).

### CONCLUSION

The ability of *Santolina chamaecyparissus* extracts to scavenge free radicals and chelate ions may be a mechanism underlying the antioxidant activity of this plant. The health beneficial effect of *Santolina chamaecyparissus* extracts is likely caused by several substances contained in both methanol and aqueous extracts. Further experiments are necessary to verify the relation between chemical composition and these activities.

### ACKNOWLEDGEMENT

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# REINFORCEMENT LEARNING AS A TOOL FOR ADAPTIVE CONTROL STRATEGY DESIGN

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## ABSTRACT

The number of control techniques implemented as a part of Intelligent Transportation Systems (ITS) in signal control, ramp metering, driver information via VMS, surveillance, incident detection is huge during the last decade. But, still there are challenges for the researchers to optimize traffic operations. The aim of this paper is to prove the ability of artificial intelligence control technique known as reinforcement learning to respond to real-time traffic conditions and adapt while controlling freeway entry access. Reinforcement learning agents are implemented as controllers in order to provide optimal performance on the freeway corridor. The algorithm used was Q learning algorithm. The effectiveness of the agents and implemented algorithm was measured by few measures: total travel time spend in the network, delay of the all vehicles in the network, stop time. The results are promising, proving that the Q learning algorithm is capable for optimal coordinated control of entrance freeway ramps.

**Keywords** : Artificial intelligence, Intelligent Transportation System (ITS), Ramp metering, optimal adaptive real-time freeway entry ramp control, reinforcement learning, multi agent systems

## 1. INTRODUCTION

Freeway management systems are used in order to manage traffic flow and make better use of the existing freeway infrastructure. Freeway management systems use control strategies, and operational activities to keep congestion from occurring in the first place, and shorten the duration and extent of congestion when it does occur. Ramp control on the freeway is the application of control devices for the purpose of achieving some operational objective. Devices could be traffic signals, signing and gates and they are used to regulate the number of vehicles entering or leaving the freeway. Typically, the objective is to balance both demand and capacity of the freeway in order to maintain optimum freeway operation and prevent congestion. The main objective in the process of controlling entrance ramps is to regulate the number of vehicles entering the freeway so that traffic density is kept lower than the critical density which corresponds to capacity of the freeway. Installation of entrance-ramp control signals may appear when it results in a reduction of the total expected delay to the traffic in the freeway corridor, including freeway ramps and local streets, and at least one of the following conditions exist (Carvel, 1997; Homburger, 1996): there is recurring congestion on the freeway, or there is recurring congestion or a severe accident hazard at the freeway entrance because of an inadequate ramp merging area, the signals are needed locally for the freeway traffic operation, the signals are needed to reduce (predictable) sporadic congestion on isolated sections of freeway caused by short-period peak traffic loads from special events or from severe peak loads of recreational traffic.

Examples of freeway access control systems are numerous (Kotsialos, et al, 2002) (Hasan, et al., 2002) (Wang, 2009). ALINEA is the first control strategy on a local level that is based on direct implementation of classical control theory with feedback (Papageorgiou, 1991) (Papageorgiou, 1995) (Papageorgiou, and others, 1998). Other efforts include genetic fuzzy approach (Bogenberger, El-Araby and Keller, 2000), artificial neural networks (Zhang and Ritchie, 1997) and two level freeway ramp metering approach (Alessandri, and others, 1995).

Most of the existing algorithms for freeway ramp metering, although traffic responsive, are not truly adaptive to traffic parameter changes. Most of them are of local regulator type (Wang, 2010) and not truly adaptive. Adaptive in this context is opposite of the common misunderstanding in the literature. It means more than giving an answer to the traffic in real time. The meaning is that the control policy changes itself as an answer to the inherent systems characteristics. In other words, in order to be adaptive, the system should be capable of continuous learning.

In order to provide proper metering rate signal timing has to be tuned in accordance with specific geometry of the site, grades, driver characteristics, vehicle mix, and other factors. There are two types of traffic lights settings: one car per green with control via red phase duration and traffic cycles. Several criteria have to be fulfilled to adjust signal timing. All control strategies calculate suitable ramp volumes.

## 2. CONTROL STRATEGY

There are two possibilities to design a control strategy, to imitate the behavior of a human operator known as expert system approach, and to attempt to understand the process behavior and then to apply systematic methods that lead to an adequate control strategy, known as automatic control approach (Papageorgiou, 1998) (Papageorgiou, 1990).

There are several types of control measures that can be implemented: regulator or optimal control, open or closed loop control strategy, local or corridor control. The type of the algorithm used in this research allows optimal control to be performed.

Control strategy implemented in this research is traffic responsive adaptive and optimal coordinated control strategy. It is traffic responsive because of self-corrective feedback provided with measurements of the system states downstream the ramp on the freeway. It is adaptive because the technique implemented to determine the metering rates is capable of continuous learning. It means that the control policy itself is continuously changing in response to temporal changes in inherent systems characteristics. Optimal control can be performed as the control agents learn to maximize system performance and not rely on a pre-set value.

### 3. ARTIFICIAL INTELLIGENCE TECHNIQUES IN TRAFFIC

Information technology (IT) has a huge impact on modern life. In traffic control we are witnessing a transition towards digital communication based on open international standards.

AI techniques could help adjusting traffic signal timings automatically in response to traffic situations and can detect changes in traffic conditions and incidents quickly and accurately.

Roosmond and Veer (1999) in their paper of usability of intelligent agents systems in traffic control have concluded that the most developed and the most usable AI techniques in traffic engineering and control are Expert Systems (ES), Neural Networks (NN), Genetic Algorithms (GA) and fuzzy logic (FL). Agent technology is not yet developed into a good usable commercially available technique but seemingly very promising and other AI techniques can be incorporated into an agent. The emerging AI techniques usable in traffic control are learning from experience or reinforcement learning (RL) and multi agent control (Katwijk, 2005) as part of Distributed Artificial Intelligence (DAI).

#### 3.1. Learning

One of the defining features of intelligence is ability to learn. Thus, machine learning is central to the field of artificial intelligence and neural computation. Learning is a very general term denoting the way in which people and computers increase their knowledge and improve their skills. But, increasing knowledge has its own meaning. Learning denotes 'changes in the system that are adaptive in the sense that they enable the system to do the same task or tasks drawn from the same population more efficiently and more effectively the next time' (Shi, 1992).

Learning is usually formulated as a search conducted in an abstractly defined space and a large collection of mathematical concepts can be brought to bear on the problems of understanding and designing procedures or algorithms, or enabling a program to improve its performance over time. This process is far from being computationally trivial, 'its strongest ties are to the mathematical theories and computational procedures that are exceedingly useful in practice and surprisingly complex' (Barto, Sutton, 1998) (Watkins, 1990).

#### 3.2. Reinforcement Learning

Behaviorism is one of the learning strategies, traced back to Aristotle, but also used as a model in artificial intelligence to define one of the most interesting techniques in machine learning reinforcement learning. The school of Behaviorism, where learning is a complex process of responses to several kinds of distinct stimuli defines it as a three-term system comprised of a discriminative stimuli, a response, and a reinforcing stimulus.

Reinforcement learning is a machine learning technique, which can work without supervision. It is goal-directed learning from interaction with an environment, technique that will learn what to do - how to map situations to actions, in order to maximize a numerical reward signal. Technique used for our control strategy is performed by intelligent agents. How these agents work? As a result of taking action  $a$  in state  $s$ , the agent receives a reward or reinforcement  $r(s,a)$ , which depends on the effect of this action on the environment. The combination of state  $s$ , action  $a$ , and reward  $r(s,a)$  is used to recursively update the previous estimate (as of time  $n-1$ ) of the Q-value:

$$\hat{Q}_n(s,a) \leftarrow (1-\alpha_n)\hat{Q}_{n-1}(s,a) + \alpha_n[r + \max_{a'} \hat{Q}_{n-1}(s',a')] \quad (\text{Eq. 1})$$

Where  $s$  and  $a$  are the state and action updated during the  $n$ -th iteration,  $r$  is the reward received for taking action  $a$  while in state  $s$ ,  $\hat{Q}_{n-1}$  is the previous estimate of the Q-value of taking action  $a$  while in state  $s$ ,  $\max(\hat{Q}_{n-1}(s',a'))$  is the previously estimated Q-value of following the optimum policy starting in state  $s'$ .

Training rate taking values between 0 and 1 is:

$$\alpha_n = \frac{1}{1 + \text{visits}_n(s,a)} \quad (\text{Eq. 2})$$

Where  $visits_n(s,a)$  is the total number of times this state-action pair has been visited up to and including the n-th iteration. When  $\alpha_n$  is 1, this rule is suitable for deterministic case. By reducing  $\alpha_n$  at an appropriate rate during training, convergence of the Q values can be achieved. Also, a discount factor is taken for future rewards, which reflects the higher value of short-term future rewards relative to those in the longer term. The updated estimate of Q-value is stored in look-up table (Veljanovska, 2008).

#### 4. STRATEGY TESTING

Scientific research is conducted with VISSIM microsimulator, with direct programming of the functions in the simulator in order to implement the technique of reinforcement learning with multi agents.

A simple network was created in Vissim version 4.10. The simple network consists of one segment of a freeway with three lanes and three ramps with one on-ramp lane. Detectors are located upstream the on-ramp entrance, on the freeway downstream of the ramp and before the end of the freeway segment, at the destination zone. System state data was gathered directly by simulator. The timing plans of the ramp signal controllers were updated at the end of the fixed intervals.

In order to test the control strategy, a few scenarios were divided into two test phases in accordance with the traffic parameters:

- First test phase - coordinated control and parameters' measurements taken at the freeway exit, with known traffic demand on the main line
- Second test phase - coordinated control and measurements taken downstream at each freeway entry, with unknown traffic demand on the main line. During this test phase two types of scenarios were developed: testing when there is no traffic congestion and testing when there is traffic congestion on the corridor.

In order to estimate the feasibility of the suggested strategy for optimal adaptive coordinated control of the freeway entry ramp, the results from the agents that learn were compared to the results from the case with no control strategy and to those from the case with ALINEA control - the widely implemented control strategy used as a regulator.

The results gained from the simulations with no control strategy were taken as the base case and the rest of the results that were compared to it were estimated. Testing was conducted after sufficient number of iterations with different numbers of states and after Q-values convergence.

#### 5. DISCUSSION OF THE RESULTS

Within the *first test phase* (coordinated freeway access control, measurements at the exit of the corridor, traffic demand known), improvements were as follows: savings in travel time (up to 14.50%), decreased delay (26%), decreased average stop time per vehicle (37%), decreased average number of stops per vehicle (35%) and increased number of vehicles exiting the network (14%).

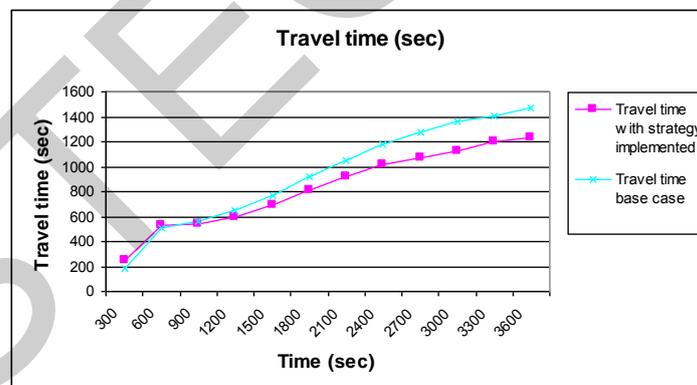


Figure 1. Travel time comparison between the time spent in the network with ramp metering strategy implemented and without control strategy

However, it was evident that this type of control strategy implementation needs longer phase of learning for the agents, which makes the strategy not enough efficient.

Therefore, localized freeway entry access was implemented, where traffic parameters are measured on the mainline downstream of the each ramp (**second phase of the testing**). During this phase two types of testing are performed: 1. Testing when no traffic congestion, 2. Testing when traffic congestion on the corridor. Traffic demand is unknown.

After the testing with data when no traffic congestion, it was noticeable that:

- There are significant improvements regarding delay (lowered for 30%), average stop time per vehicle (lowered for 78%) and average number of stops per vehicle (lowered for 80%), which shows that traffic flow is smooth.
- After longer traveling, travel time and delay decrease is evident, and there is a significant difference after one hour of travel.
- But, travel time (lowered for 3.29%), number of vehicles exiting the corridor (increased for 3%) and speed (increased for 0.33%) have very little improvement.

- It is noticeable that the strategy follows traffic parameters changes in real time, especially during the transition from the state of congestion to the normal state.

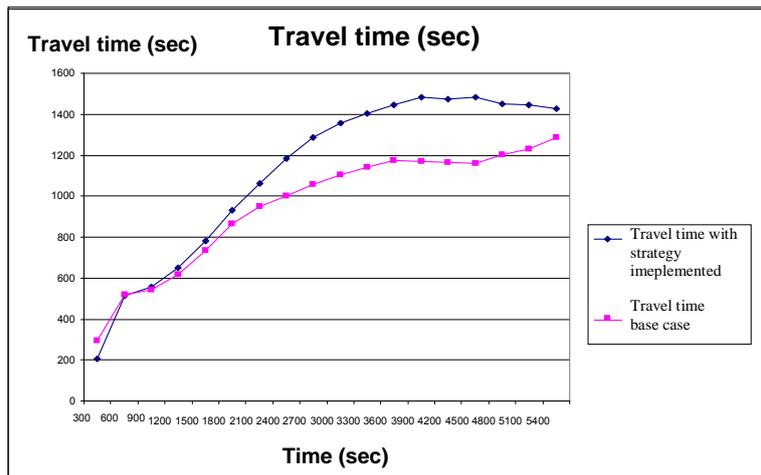


Figure 2. Travel time comparison between the time spent in the network with ramp metering strategy implemented and without control strategy (second phase, testing when traffic congestion on the corridor)

The results from implementation of ALINEA for the same effectiveness measures are similar to the corresponding results gained with the suggested control strategy. That could be explained with the fact that there is no recurrent congestion on the corridor, which makes the strategy inferior compared to ALINEA.

Regarding travel time saving, increasing the speed and number of vehicles exiting the corridor the results gained with ALINEA are not very promising (important because for the ALINEA strategy there are some parameters calibrations that need to be made for the particular freeway and the corresponding traffic demand, while for the suggested strategy for coordinated control, testing is performed on unknown traffic demand). Therefore, in the case where there is no traffic congestion, suggested strategy could be implemented with learning performed with similar traffic demand prior to the implementation.

During the second test phase (no traffic congestion on the corridor), the strategy that uses Q-learning shows extraordinary good results after relatively small number of iterations (about 1500) with unknown traffic demand:

- Savings in travel time (15%), delay (26%), average stop time per vehicle (38%), average number of stops per vehicle (35%), increase in number of vehicles exiting the network (10%), speed (9.85%). Improvements are almost doubled compared to the results with ALINEA implementation with the same measures of effectiveness (8.41%, 13%, 20%, 19%, 6.22%, 3.55% respectively).

The strategy adjusts itself with the traffic conditions, i.e. it is adaptive and responds to the traffic demand in real time.

The best improvement is in the case of implementation of the control with non-congested data (for the average stop time per vehicle and average number of stops per vehicle).

Regarding all the measures of effectiveness, the best results with control strategy implementation on unknown traffic demand, which causes congestion, are gained. That shows that suggested strategy is feasible for coordinated freeway ramp metering that is optimal, adaptive and traffic responsive.

After the testing with data where there is traffic congestion on the corridor, the strategy that uses Q-learning shows extraordinary good results after relatively small number of iterations with unknown traffic demand. Thus, its feasibility and efficacy is being shown.

Suggested strategy for coordinated control is better than ALINEA related to the average stop time per vehicle and average number of stops per vehicle during the rush hour, which shows the smoothness of the traffic flow with no interruptions in terms of "stop-and-go". This leads to reduced fuel consumption per vehicle, reduced air pollution, and reduced surroundings pollution as well.

## 6. CONCLUSIONS

Taking the results of the model testing in mind, it can be concluded that optimal adaptive coordinated freeway ramp metering control is feasible for performing coordinated freeway ramp metering control.

This research opens broad possibilities for reinforcement learning technique implementation in traffic control. Some of the next steps in scientific research would be

- coordinated control for non-recurrent traffic congestions,
- implementing optimization of the Q-learning algorithm in terms of faster learning and
- inspection of the model efficacy after implementation.

We can conclude that this type of adaptive control and reinforcement learning technique are promising as: the strategy is very simple, there is no need to model the environment while creating the strategy, the strategy is truly adaptive, the supervision is not necessary and there is no need for traffic parameters' prediction.

Taking all these into account, it could be concluded that this approach could be improved in further research as adaptive coordinated traffic corridor control that is capable of self-learning from the stimuli taken from the interaction with an environment.

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# REMOVAL OF CR(III) IONS FROM TANNERY WASTEWATER THROUGH FUNGI

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## ABSTRACT

Cr(III) removal potential of a wood-rotting fungus viz., *Ganoderma lucidum* (Curt. Fr.) P. Karst was studied from tannery wastewater. Preliminary laboratory assays indicate an optimum pH, 4.5, stirring intensity 150 rpm with increase in removal rate on increasing initial metal ion concentration (4-20 mg L<sup>-1</sup>) in the medium. The maximum biosorption capacity of fungus biomass was 2.16 mg g<sup>-1</sup> with suitability of Langmuir and Freundlich models on acquired experimental data. In tannery wastewater, fungus showed a maximum of 1.6 mg g<sup>-1</sup> biosorption capacity and 43% efficiency. To make this technique practically applicable and economically feasible, the study was further extended by mass cultivated this fungus on agro-wastes followed by assessment of its biosorption potency for Cr(III) ions. Rice straw colonized with *G. lucidum* mycelia could be utilized as an excellent biosorbent thus exhibited 73-76% efficiency for Cr(III) adsorption from tannery wastewater at low concentration of the metal (4-20 mg L<sup>-1</sup>).

## INTRODUCTION

Biosorption, metal removal ability of the certain biomass e.g. algae, fungi and bacteria is well-recognized, attractive and cost effective biotechnology for treatment of metal-loaded water. Fungi have been well known for metal removal ability from aqueous phase. Gadd (2001) stated filamentous network of hyphae help them to grow and survive in variety of ecosystems thus provides additional metal binding potential from the contaminated environment. The multilaminar and microfibrillar structure of fungal cell wall along with distinctive aspects of high percentage of cell wall material attributes excellent metal-binding properties. Generally on the basis of sizes, fungi are recognized as micromycetes and macromycetes. So far, numbers of micromycetes like species of *Aspergillus*, *Rhizopus*, *Penicillium*, *Mucor* and *Absidia* have been studied for their metal sorption capability (Dursun *et al.*, 2006; Congeevaram *et al.*, 2007; Subudhi and Kar, 2008). The role of wood rotting fungi or macromycetes in removing heavy metals from the metal-loaded medium could not be negated. Number of macromycetes like *Pleurotus ostreatus*, *Ganoderma lucidum*, *Schizophyllum commune*, *Phanerocheate chrysogenum*, *Coriolus versicolor*, *Agaricus bisporus* and *Pycnoporus cinnabarinus* has been investigated for their metal uptake capability with very promising results (Arica *et al.*, 2003, 2004; Javaid *et al.*, 2008, 2010, 2011).

Macromycetes are commonly famous as mushrooms are found in world humid environment. Mushrooms are a appetizing and nutritious food group of fungi. Resihi mushroom or *Ganoderma lucidum* is well-known oldest medicinal mushroom and is very important economically. Its fruit bodies typically grow in a fanlike or hoof like form on the trunks of living or dead trees. Spores have double-walled, truncate with yellow to brown ornamented inner layers. *G. lucidum* produces a group of triterpenes, called ganoderic acids, having similarity in molecular structure to steroid hormones. Other common compounds of this mushroom are variety of polysaccharides (beta-glucan, coumarin, mannitol) and alkaloids (Paterson, 2006). The potential of both fruiting body and mycelium of *G. lucidum* in bioremediation of heavy metal is well known.

The most compelling reasons for using biosorption technology are utilization of renewable or waste raw materials in economic way. The application of biosorption technology could become more effective keeping economic feasibility through utilization some cheap source for mycelial production of fungi. By doing this practice we not only get economic substrate for mycelial mass cultivation but there would be addition adsorbent having plant cell wall properties. The plant by products e.g. wheat straw and husk, rice straw and husk and cotton waste etc are easily available substrates for raising fungal mycelium in bulk. However, the biosorption potential of macromycetes preparation on agro-waste especially for industrial heavy metal ions removal has not been extensively attempted.

The aim of current research work was to explore the role of *G. lucidum* in removing Cr(III) from tannery wastewater. For large scale industrial application mycelium of *G. lucidum* was mass cultivated on rice straw and colonized straw was used for removal of Cr(III) from tannery water

## METHODOLOGY

Fungal biomass was prepared in liquid phase in 250 ml Erlenmeyer flasks filled with 100 mL of a culture medium i.e. 2% Malt Extract (ME) composed of 20 g L<sup>-1</sup> ME powder (DIFCO). The prepared fungal mat after 10 days of incubation was collected, washed with generous amounts of distilled water as long as the pH of the washing solution was in the near-neutral range (7.0-7.2). Dried at 60 ± 1 °C was utilized in metal sorption assays.

Batch experiments were performed by taking 0.2 g of oven dried biomass of test fungus in 250 mL flask containing 100 mL of 14.35 mg L<sup>-1</sup> (particular concentration chosen on the basis of quantitative measurement of Cr(III) present in tannery water) of Cr(III) solution at 150 rpm and 25 °C for 3 hours. To select the optimum pH, this parameter was varied over the range of 2-6. The rotation speed was monitored at low (50 rpm), medium (100 rpm) and high (150 and 200 rpm) taking non-agitated system as the control. Effect of initial metal ion concentration was investigated by changing the initial concentration of Cr(III) ions

within the range of 4-20 mg L<sup>-1</sup> at constant pH and temperature. At the end of experiment, remaining Cr(III) in the supernatant was measured on Atomic absorption spectrophotometer (Model, Varian AA 1275 series).

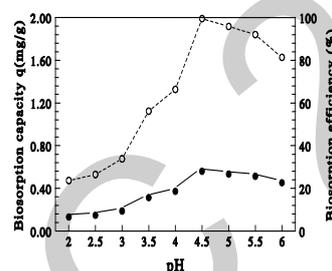
Cr(III) removal ability of fungus was checked with water of tannery by repeating batch biosorption experiment in same way mentioned above. Acid digestion of the samples was carried out with aquaregia for measurement of residual metal ion concentrations.

Rice straw was used for mycelial cultivation *G. lucidum*. The pre autoclaved inoculated plastic bags (20 x 30 cm) were kept in an incubator at 25°C for 12-15 days. The prepared straw colonized with fungus mycelia was dried in oven and sun. Oven drying was carried out at 60°C for 24 hours and for sun drying prepared material was exposed directly to sun light (40-42°C) for 12-14 hours at 40-50 °C. The biosorption experiments were performed with tannery water under pre optimized biosorption conditions as mentioned in section batch biosorption experiments.

## RESULTS AND DISCUSSION

### Effect of pH

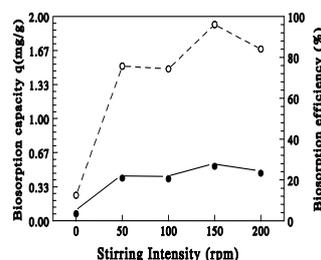
The biosorption capacity/efficiency of the candidate fungus for Cr(III) was recorded to increase significantly at appreciable amount on increasing pH from 4.5 (2.0 mg g<sup>-1</sup>/28%) to 5.5 (2.0 mg g<sup>-1</sup>/27%) with slight reduction at pH 6.0 (1.63 mg g<sup>-1</sup>/23%). However, at high acidic pH range i.e., 2.0-4.0 the test fungus exhibited only up to 7-18% efficiency. Consequently, predilection of pH by the test fungus for the highest adsorption of metal ion exhibited following sequence 4.5 > 5.0 ≥ 5.5 > 6.0 > 4.0 > 3.5 (Fig.1). Similar to present records, pH range 4.5-6.0 has been reported as optimal for biosorption of Cr(III), Cu(II), Ni(II) and Zn(II) ions both by micro and macro fungi in several previous studies (El-Syed and El-Morsey, 2004; Javaid et al., 2010; Javaid et al., 2011). These authors attribute that low pH (4.0 and below) limits the biosorption metal ions on to fungal biomass surfaces, probably due to the ion exchange between metallic species and competition effects with oxonium (hydronium) ion to some extent in the biosorption mechanism.



**Figure 1:** Effect of pH on biosorption potential of the *G. lucidum* for Cr(III) ions. Initial concentration of Cr(III) ion in the reaction mixture: 14.35 mg L<sup>-1</sup>. Biosorption conditions: biosorbent concentration, 0.2 g 100 mL<sup>-1</sup>; pH range (2.0-6.0); 150 rpm and 25°C for 5 hours.

### Effect of Stirring Intensity

The effect of the agitation of the sorbent/sorbate system indicated that all agitation speeds exerted a remarkable increase in biosorption efficiency of 21-27% over the non-agitated system that holds only 3.48% efficiency. Therefore, metal removal capacity reached its maximum level at 150 rpm (1.92 mg g<sup>-1</sup>) and then decreased slightly at 200 rpm (1.68 mg g<sup>-1</sup>) followed by 50 and 100 rpm (1.50 mg g<sup>-1</sup>) in comparison to control (0.25 mg g<sup>-1</sup>) (Fig. 2). Agitation facilitates proper contact between the metal ion in solution and the biomass binding sites and thereby, promotes effective transfer of sorbate ion to the sorbent sites (Chergui *et al.*, 2007).



**Figure 2:** Effect of stirring intensity on sorption potential of *G. lucidum* for Cr(III) ions. Initial concentration of Cr(III) ion in the reaction mixture: 14.35 mg L<sup>-1</sup>. Biosorption conditions: biosorbent concentration, 0.2 g 100 mL<sup>-1</sup>; pH, 5.0 at 25°C for 5 hours.

### Effect of Initial Concentration of Metal ions

The fungus subjected to varied concentrations of Cr(III) from 4-20 mg L<sup>-1</sup>, exhibited an increase in sorption capacity of 1.02-2.40 mg g<sup>-1</sup> on increasing metal ion concentrations and maximum uptake was evident at the highest applied concentration (Fig. 3). There is evidence that at high metal ion concentration the number of ions sorbed is more than at low metal concentration, where more binding sites were free for interaction (Cossich *et al.*, 2002; Loukidou *et al.*, 2004).

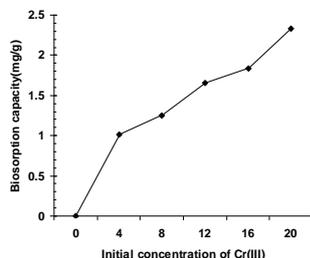


Figure 3: Biosorption capacity of *G. lucidum* for Cr(III) ions at various initial concentrations.

**Isotherm Assessment**

Through the scatter diagram the analysis of Langmuir (1906) and Freundlich (1916) isotherm models were obtained for the test fungal biomass (Table 2, Fig. 4 A, B). The distribution of  $q_{eq}$  point calculated by the model in function of the experimental values of  $q_{eq}$  shows a linear tendency among the observed and predicted values. This indicated that the experimental data were very well adjusted to the two models.

Table 2: Isotherm parameters for the biosorption of Cr(III) ion onto fungal biomass.

Test fungus	$q_{exp}$ (mg g <sup>-1</sup> )	Langmuir			Freundlich		
		$q_m$ (mg g <sup>-1</sup> )	$b$ (mg L <sup>-1</sup> )	$R^2$	$K_F$	$n$	$R^2$
<i>G. lucidum</i>	1.92	2.16	0.42	0.91	1.37	2.59	0.96

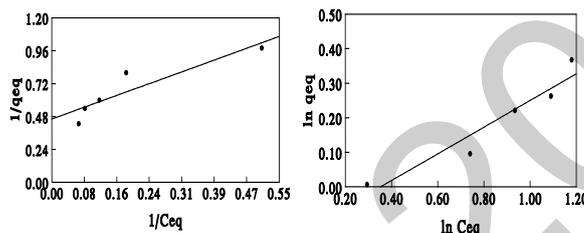


Figure 4 A & B: The linearized Langmuir (A) and Freundlich (B) adsorption isotherm for Cr(III) ion biosorption by *G. lucidum*.

**Physicochemical Analyses of Tannery Wastewater**

The results obtained on physicochemical analyses of the tannery wastewater are shown in Table 1. All analytical techniques employed were item standard methods (APHA, 1995) and chemicals used in the experiment were of analytical grade (MERCK).

Table 1: Physico-Chemical Characterization of Tannery Treatment Plant.

Parameters	Tannery Treatment Plant, Current status	NEQS Acceptable limits	WHO Acceptable limits
Copper (II), mg L <sup>-1</sup>	1.21	1.00	0.20
Chromium (III), mg L <sup>-1</sup>	14.35	1.00	0.10
Nickel (II), mg L <sup>-1</sup>	0.05	1.00	0.20
Zinc (II), mg L <sup>-1</sup>	0.54	5.00	2.00
pH Value (acidity/basicity)	8.5-9.5	6.0-10	No guideline
Temperature (°C)	27-29	40	No guideline
Biochemical Oxygen Demand (BOD) at 20°C, mg L <sup>-1</sup>	500	80	No guideline
Chemical Oxygen Demand (COD), mg L <sup>-1</sup>	4000	150	No guideline
Total Dissolved Solids (TDS), mg L <sup>-1</sup>	1510	3500	No guideline

National Environmental Quality Standards (NEQS) for liquid Industrial Effluents (2001); World Health organization Standards (WHO) for drinking water (2006).

**Biosorption Assays with Tannery Water**

The optimized conditions determined from preliminary biosorption assays were used to conduct biosorption experiment with tannery water. For comparison parallel batch experiment was conducted with synthetic solution. Results acquired indicate only 1% reduction in biosorption efficiency of the biosorbent in tannery wastewater in comparison to control (synthetic solution) (Table 3). Similar findings were recorded by Matheickal and Yu (1999) while investigating the effect of light metal ions Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> on the biosorption of Pb(II) by *Durvillaea potatorum* and *Ecklonia radiata*. They found that biosorbents had much higher relative affinity for heavy metals than for light metals.

Table 3: Comparison of biosorption capacity and efficiency of the test fungus for Cr(III) ions in synthetic solution and Tannery Treatment Plant Water. Initial concentrations of Cr(III) ion in both systems: 14.35 mg L<sup>-1</sup>. Biosorption conditions: pH 4.5, 150 rpm for 3 hours.

Treatments	Rice straw (OD)	Rice straw (SD)
Control (uncolonized agro-waste)	67.73c	69.82b
Colonized agro-waste with mycelia of <i>G. lucidum</i>	73.98ab	75.84a

Values with the different letters showed significant difference among treatments at p < 0.01 according to Duncan's multiple comparison tests.

**Biosorption Assays with Colonized and Uncolonized Agro-waste**

Both uncolonized and colonized straw with *G. lucidum* mycelia exhibited significantly greater metal removal potential from tannery water (Table 4). However, colonized agro-wastes exhibited greater biosorption potential (70-76%) as compared to un-

colonized (60-70%). Enhancement in adsorption ability of colonized rice straw could be owing to fungal lignin and cellulose degradation of agro-wastes. As results of this degradation, the polymer core of straw turn into soluble form and more binding sites on straw are available for metal binding in addition to fungal cell wall molecular binding sites on mucelium (Lee and Rowel, 2004). Results showed that sun dried rice straw exhibited significantly greater adsorption capacity/efficiency (1.36 mg g<sup>-1</sup>/75.84%) in comparison to oven dried straw (1.33 mg g<sup>-1</sup>/73.98%). There might be possibility that oven drying cause denaturtaion of some important chemical groups on the cell wall of biosorbents which remain intact in case of natural drying under sun (Huang and Hunag, 1996).

**Table 4:** Comparison of biosorbents biosorption efficiency (%) for uptake of Cr(III) ions from Tannery wastewater

Parameters	Synthetic solution of Cr(III)	Actual wastewater of Tannery treatment plant
Biosorption capacity (mg/g)	1.57	1.51
Biosorption efficiency (%)	43.87	42.51

## CONCLUSION

Due to low cost involved and simplicity of the technique, rice straw colonized with *G. lucidum* mycelia could be utilized as an excellent biosorbent exhibited efficiency of 73-76% for removal of Cr(III) ions from tannery water containing diluted concentration of the metal (4-20 mg L<sup>-1</sup>).

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# RESEARCH CONCERNING THE PRECISION OF THE THIN WALL PRODUCTS MANUFACTURED THROUGH INVESTMENT CASTING

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**Abstract:** In this paper the authors investigate the precision of the metallic parts made through investment casting. The main objective is to find out the influence of the contractions upon the accuracy of the products thin walls. There were considered all the stages of the manufacturing process for accuracy determination. First, the wax model is studied and the obtained accuracy, considering the fabrication process, is presented. Second, the contractions that appear after the investment casting of the metallic parts are taking into account. Three dimensions for the wall thickness were considered and the influence upon the contractions both for wax models and after casting, are presented. The results can be used for dimensional deviations offset due to contractions, by a proper design of the thin-wall parts even from the CAD modeling phase.

**Keywords:** wax patterns, silicon rubbers, investment casting, dimensional accuracy

## 1. Introduction

The metallic parts with thin walls are difficult to obtain considering both their shape and the manufacturing technology. An essential condition is to find a manufacturing technology through which an adequate accuracy and a lower costs price will be achieved. Usually, when a high accuracy is needed, the injection moulding technology is used.

The Investment Casting is a technology used in order to obtain complex metallic parts with high accuracy, high quality surface and low cost price [1]. The main working phases of this technology are [2]:

1. Part design;
2. Manufacturing of a wax model which is a copy of the designed part;
3. Manufacturing of a ceramic form onto the wax model;
4. Preheated the ceramic form followed by the melting of the wax model, so into the ceramic form it will result the negative of the part;
5. The melting of the metal into the ceramic form;
6. After the molten metal has cooled, the ceramic form can be broken and the casting model removed;
7. Finishing operations onto the part and the technical control of it.

From the phases presented above it results that in the beginning a wax model is realised and the metallic part is the counterpart of this model. This means that the accuracy of the wax model has a direct influence on the accuracy of the metallic part. The wax models are fabricated through different manufacturing technologies depending on the amount of the required models. If there is a need to fabricate an average production, the injection moulding technology in metallic moulds is used. This gives good results but the cost price is high. If there is a need for small-lot production or sole exemplars, a Rapid Prototyping technology will be used. These technologies realise the wax model quick and cheap, shortening very much the execution time of the metallic parts. Two of them are mostly used [3] [4]:

- a) 3D Printing technology – in this case the wax model is realised directly;
- b) Using the silicone rubber moulds – in this case, on the first phase a master model, which is used to fabricate the rubber mould, is realised. The rubber mould is used for making the wax model through pouring the melting wax in it.

No matter the technology used for fabricating the wax model it will appear a certain deviation from the dimensions of designed part and this will influence directly the accuracy of the metallic part.

This dimensional deviation is influenced by several factors such as [5]:

- Casting temperature;
- Injection temperature;
- Injection pressure;
- Wax contractions;
- Thermo-mechanical and thermo-physic characteristics of the wax.

The metallic part is a counterpart of the wax model so any imperfections of the model are transmitted onto the part. The accuracy of the metallic part is influenced not only by the manufacturing but also by the thermo-physic characteristics, and also by the processing parameters (casting temperature, casting pressure, working conditions). All dimensional and also shape deviations which occur during the technological process will appear onto the metallic part. Considering all the factors which

influence the accuracy of the part, the most important is the thermal contractions. These contractions appear during wax solidification and during solidification of the metal after casting it in the ceramic form.

From the data presented above it is revealed that it is important to know how the dimensional accuracy is influenced by the contractions that appear during the manufacturing and if they have a uniform influence on the entire part or not.

Knowing the values of the contractions and the way in which they are displayed is useful because even from the designing stage it can be established the proper dimensions of the wax model in order to compensate the contractions, as the final metallic part must have the imposed dimensional accuracy.

Although the contractions influence the parts accuracy, it is a complex phenomena and difficult to analyze and the problems which occurs can be studied independently.

## 2. Experiment design

In this case study there is presented how the wall thickness is influenced by the dimensional shrinkage that occurs during casting. This contractions occur in the transition from molten to solid state of the materials. The following aspects are investigated:

- the way in which the dimensional contractions manifests on wax patterns;
- the way in which the dimensional contractions manifests on metal parts;
- position and shape errors transmission during manufacturing process;
- the influence the thin-wall parts onto the dimensional and positional accuracy of the bores;

Because it is difficult to follow and to quantify all the aspects on a real part, in the experiment implementation we started from a simplified one (figure 1). The simplification of a real part was made starting from the dezideratum that any complex shape can be decomposed into simple surfaces. In this study we designed a simplified part that consists only of flat and cylindrical surfaces. These types of surfaces have the advantage of beeing easy to measure. On the simplified piece, thin walls are present between  $\text{Ø}10$  mm halls. It is noted that the walls have thickness of 1 mm, 2 mm and 3 mm. The other holes with different diameters are used to control the results because in this case does not matter thickness, shape and position deviations occur only due to shrinkage.

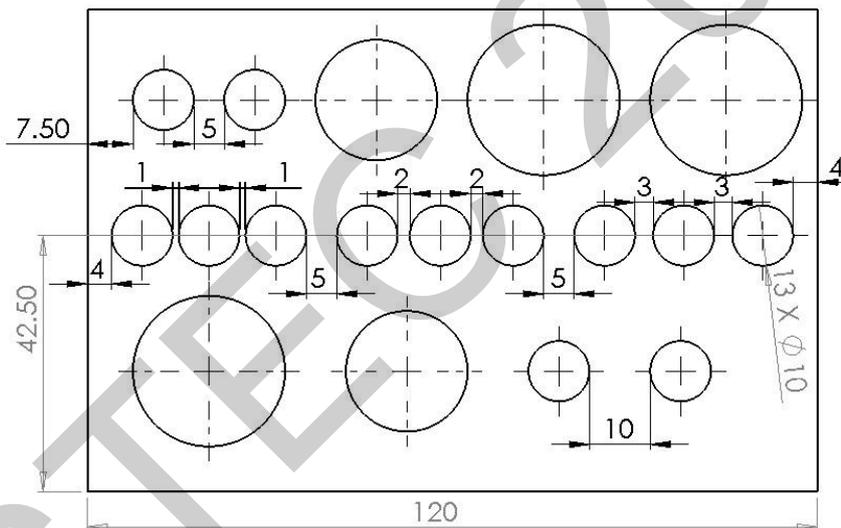


Figure1 Drawing of the simplified part

The phases of the experiment are shown schematically in figure 2, following the manufacturing phases of metal parts through Investment Casting process.

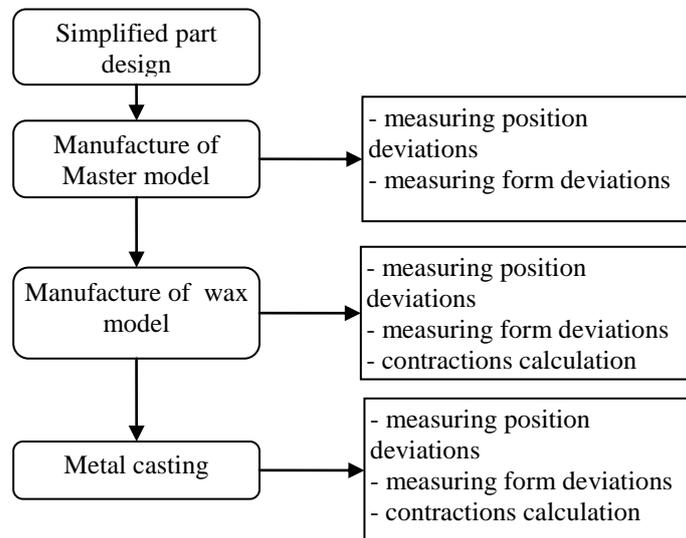


Figure 2 Experiments phases

The experiment was performed starting from the simplified part design, shown in figure 1, and manufacturing resulting Master model. This Master model is the metal part that we want to obtain. In this experiment, the Master model was achieved by milling. Using this Master model a silicone rubber mould which includes the model, is made. After extracting the pattern from the mold, it resulted the negative of the Master model. In the mould the wax is poured and after cooling, the wax model results. The wax model was measured considering the issues presented in figure 3. With the wax pattern, the ceramic form has been made. The obtained ceramic shape was placed in an oven where, by heating, the wax was evacuated from the form. Heating the form has a double purpose: the wax removal and preheating the form for metal casting. In the last phase, the ceramic form containing the negative wax pattern was put into Indutherm 1000D vacuum casting machine and was cast an aluminium alloy, resulting, in ceramic form, the metal part. This was extracted from ceramic form and measured for achieving the proposed objectives.

### 3. Analysis and interpretation of the obtained data

After the realisation of the Master pattern, wax models and metal parts they have to be measured. The measurements were performed using Werth coordinate measuring machine - Video Check IP 250. It aimed to establish bores dimensional and positional deviations.

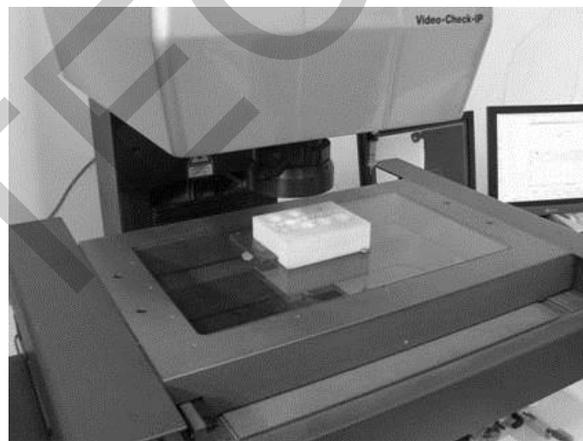


Figure 3. Equipment for bores measurement

From the measurements, the hole diameter value for each phase of manufacturing are obtained, starting from the Master model and ending with obtaining cast metal parts. There were also determined the coordinates  $x$ ,  $y$  of each bore, individually for each stage of manufacture.

After measuring the diameters of the holes on the master model, on the wax model and on the metal part, the graphics presented in figure 4 can be realized:

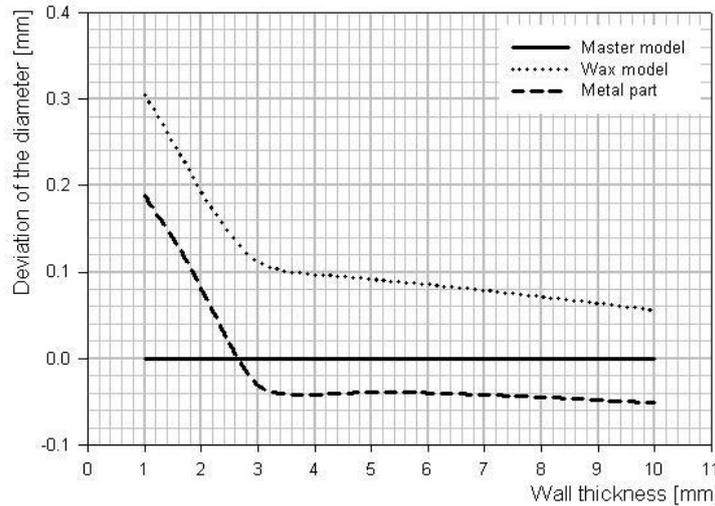


Figure 4. Deviation of the holes size depending on the wall thickness

From the graph it can be seen that the diameter deviation  $T_{\phi D}$  on thin-walled parts manifests differently depending on wall thickness after equation (1):

$$T_{\phi D} = f(g_p) \tag{1}$$

In the case of thin-wall parts, with thicknesses ranging from 1 to 2.5 mm, diameter deviation is strongly influenced by contractions that occur during piece cooling. These contractions are less manifested to the parts that are thicker than 2.5 mm. In figure 5 there are overlapped represented the holes obtained on the Master model, wax model and metal part. It is to be observed that the wax model has changed position of the holes center, resulting in a position deviation due to contractions that occurred during the wax cooling. This position deviation is amplified during casting the metallic material. Position deviations of holes centers have a direct influence on the precision of manufacturing and part wall thickness.

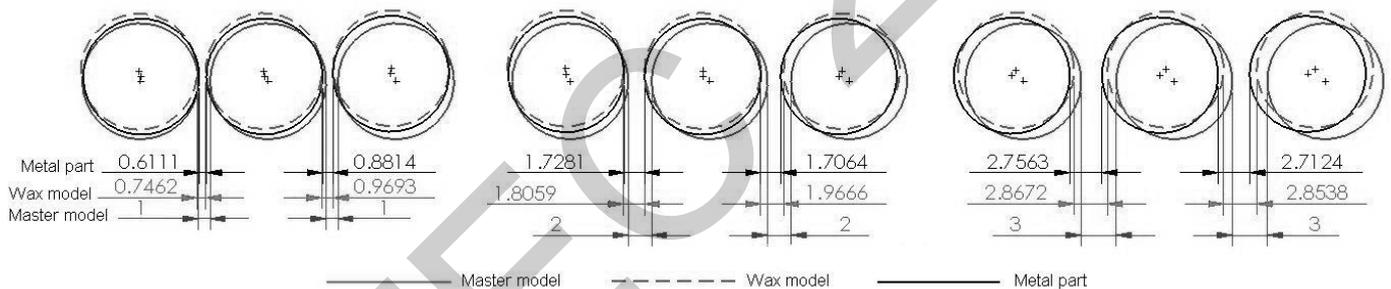


Figure 5. Variation of the wall thickness

It is observed from figure 5 that only in the case of one millimeter walls thickness there is a significant variation of their dimensional deviation. So, on the first wall of 1 mm we have a result thickness of 0.6111 mm for metal piece, and on the second wall of 2 mm we have a small change in resulted wall thickness. In the case of 3 mm wall thickness there is also a small change in the wall thickness resulting in the final part.

In figure 6 is presented the percentage variation histogram of dimensional deviations of the thin walls from the designed value to the values obtained in the process of making wax models and final metal parts.

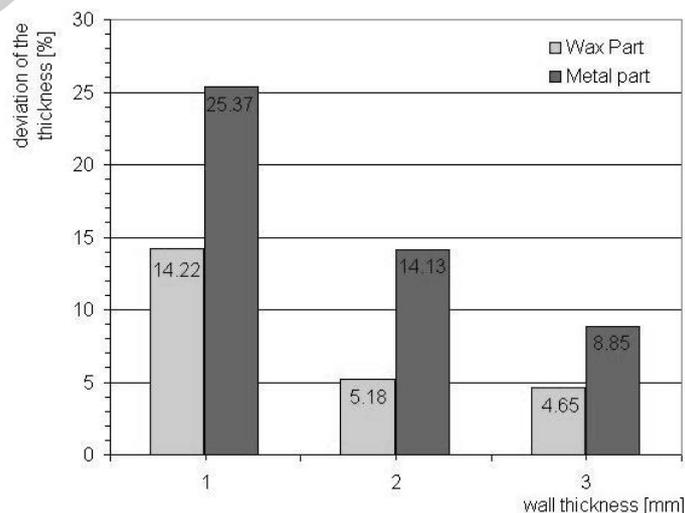


Figure 6 The percentage variation of dimensional deviation of the thin walls

From figure 6 it is observed that there is a high percentage variation of dimensional deviation of wall thickness for 1 mm wall thickness. For other wall thicknesses, percentage variation is smaller. On 2 mm walls thickness we have a deviation of 14.13% for wax model and 5.18% for metal parts. For the wall thickness of 3 mm, there is a small difference between the deviation of the wall thickness of the wax model and of the metal piece.

#### 4. Conclusions

In this article there was analysed how the manufacturing precision of the complex metal parts with thin walls is influenced by the dimensional changes that occur during the manufacture of the wax patterns and the metal parts. This dimensional change is a normal physical phenomenon that occurs in transition of material from one state of aggregation to another. In the analyzed case, melted materials pass from liquid to solid state, which lead to contractions. Theoretically, these contractions are manifested by outer size decreasing and diameter increasing of the holes.

From measurements made on wax models and metal parts that have been obtained by Investment casting we reached the following conclusions:

- the contractions of the used materials (wax, metal alloy) influence the manufacturing precision of pieces with thin walls.
- the bore diameter on the parts with thin walls (mm) are influenced by contractions that appear by increasing the diameter by about 0.1 to 0.2 mm;
- the bore diameter on the pieces with thin walls ( $2.5 < g_p < 10$  mm) are less influenced by contractions that occur, the parts diameter shrinks with 0.05mm;
- the position deviation of the bores center is higher for thin-walled parts that have the thickness value less than 1.5 mm;
- wall thickness of the thin-walled parts is influenced by the contractions in an almost uniform manner, but a dimensional deviation of 0.2 mm from the designed wall thickness appeared;

Although these contractions can not be avoided, however they can be provided in the design of the part. From this study on thin-walled parts, some conclusions that are useful in the design phase are presented. Using the obtained data, the designer can determine Master model dimensions so that the final metal part will have the wanted dimensional and positional precision.

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# SAC METAL ŞEKİLENDİRME PROSESİNDE ELEKTROMİKNATIS DESTEKLİ BASKI PLAKASI İLE ELDE EDİLEN FRENLEME KUVVETİNİN İNCELENMESİ VE KESTİRİMİ

## IN SHEET METAL FORMING PROCESS INVESTIGATION AND PREDICTION OF RESTRAINING FORCE THROUGH THE ELECTROMAGNET AIDED BLANKHOLDER

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### ÖZET

Kırışma, yırtılma ve geri esneme sac şekillendirme prosesinde ortaya çıkan kusurların en önemlilerinden birkaçıdır. Bu kusurlar baskı plakası kuvveti gibi kontrol edilebilir cihazlar ile ortadan kaldırılabılır. Bu çalışmada sac şekillendirme prosesi değişkenlerinden sac kalınlığı (1, 1.2 ve 1.5mm) ve elektromıknatısa uygulanan gerilimin (0-21V), elektromıknatıs destekli baskı plakasının oluşturduğu frenleme kuvvetine etkisi deneysel olarak incelenmiştir. Elde edilen veriler kullanılarak, frenleme kuvvetinin kestirimi için regresyon model oluşturulmuştur. Model sonuçları ile deneysel veriler karşılaştırıldığında regresyon modelin her bir parametre değişiminde elde edilecek frenleme kuvvetinin bulunmasında kullanılabileceğini görülmüştür.

**Anahtar Kelimeler:** Elektromıknatıs, Sac Şekillendirme, Frenleme Kuvveti, Kestirim

### ABSTRACT

Wrinkling, tearing and springback are a few of the most popular deleterious defects arising in sheet metal forming processes. These defects may be eliminated by using a controllable device for which the blank holder force (BHF) is adjustable. In this paper, effect of the variables of sheet metal forming process such as blank thickness (1, 1.2, 1.5mm) and the current of the electromagnet (0-21V) to the electromagnetic blank restrainer (EMBR) force are investigated experimentally. Regression model for the prediction of the EMBR force was developed using experimental data. The predictions of regression model are compared with the experimental data. The comparison results demonstrated that the regression model can be used to determine the EMBR force for each case.

**Keyword:** Elektromagnet, Sheet Metal Forming, Magnet Force, Prediction

### GİRİŞ

Günümüzde sac metal şekillendirme prosesi başta otomotiv sektörü olmak üzere birçok sektörde kullanılmaktadır. Şekillendirme prosesinde kalıp tasarımı, malzeme seçimi, parça geometrisi, baskı kuvveti, yağlayıcı ve şekillendirme hızı gibi faktörler kalıp boşluğuna akan sac miktarını değiştirerek ürün kalitesini etkilemektedir (Koyama ve ark., 2004). Malzeme seçimi ve parça geometrisine göre kalıp tasarımı yapıldıktan sonra sac akışını düzenleyerek ürün kalitesine etki eden kontrol edilebilir proses parametreleri; baskı plakası kuvveti, yağlayıcı ve şekillendirme hızıdır. Şekillendirme hızı genel olarak ürün kalitesinden çok şekillendirilen ürün adedini artırmak amacıyla değiştirilmektedir. Yağlayıcı kullanımından ise şekillendirme sonrası arındırma gibi işlemlerden kurtulmak ve atık miktarını azaltmak amacıyla kaçınılmaktadır. Bu etmenler göz önüne alındığında şekillendirme prosesi için en uygun kontrol edilebilir parametre baskı plakası kuvvetidir (Cao ve ark., 2001).

Literatürde baskı plakası kuvvetinin belirlenmesi ve kontrolü ile ilgili farklı yaklaşımlarda bulunulmuştur. Demirci ve arkadaşları (Demirci ve ark 2008), derin çekme prosesinde, baskı plakası kuvvetinin sac malzemenin et kalınlığı ve üründeki kırışma üzerindeki etkisini deneysel ve sonlu elemanlar yöntemlerini (SEY) kullanarak incelemişlerdir. Böylece şekillendirme için optimal baskı plakası kuvvetini elde etmişlerdir. Ujihara ve arkadaşları (Ujihara ve ark., 1992), otomotiv saclarındaki ürün kalitesini ve şekillendirilebilirliği artırmak için değişken baskı plakası kuvveti kullanmışlardır. Traversin ve Kergen (Traversin ve Kergen 1995), çeşitli sac şekillendirme prosesi değişkenlerine göre baskı plakası kuvvetini değiştiren kapalı çevrim kontrol sisteminin, şekillendirmeye etkisini ve avantajlarını araştırmışlardır. Siegert ve Ziegler (Siegert ve Ziegler 1997), derin çekme prosesinde baskı plakası kuvvetini dalga formunda değiştirerek, malzemenin şekillendirilebilirliğini ve dolayısıyla prosesdeki çekme derinliğinin artırılabilceğini göstermişlerdir.

Li ve Qianzhu (Li ve Qianzhu, 2008), derin çekme prosesinde zeki sistem ile elde edilen optimal baskı plakası kuvveti sayesinde şekillendirme prosesinin gerçek zamanlı kontrolünü yapmışlardır. Hsu ve arkadaşları (Hsu ve ark., 2000), sac metal

şekillendirme prosesine ait kontrolör tasarımı için gerekli olan proses modelini oluşturdukları çalışmada baskı plakası kuvveti ile zımba kuvveti arasındaki matematiksel ilişkiyi tanımlamışlar ve deneysel olarak doğrulamışlardır. Wu-rong ve arkadaşları (Wu-rong ve ark, 2010) sac şekillendirme prosesinde değişken baskı plakası kuvvetini farklı yapıdaki baskı plakası tasarımları üzerinde SEY kullanarak denemiş ve elde ettikleri verileri deneysel veriler ile karşılaştırmışlardır. Değişken baskı plakası kuvveti ile kritik bölgelerde sac malzemenin et kalınlığında iyileşmelerin olduğu görülmüştür. Seo (Seo, 2008) ise sac metal şekillendirme prosesinde sacın hareketinin kontrolü için demir içerikli malzemelerin manyetik çekim gücüne dayanan (EMBR-Elektromagnetic Blank Restrainer, Elektromanyetik Baskı Plakası) yeni bir teknoloji geliştirmiştir. EMBR kalıp içine yerleştirmiş ve şekillendirme sırasında aktif olarak kontrol etmiştir. EMBR kullanılarak şekillendirilmiş sac incelendiğinde şekillendirme kalitesinin arttığı görülmüştür.

Bu çalışmada, baskı plakası kuvvetinin kontrolünü daha basit, modüler ve hassas hale getirmek için proseste pot çemberinin elektromıknatis ile desteklenmesi önerilmiş ve gerilim ve sac kalınlığı değişimine bağlı olarak elde edilecek frenleme kuvveti deneysel olarak incelenerek matematiksel bir model oluşturulmuştur.

## DENEYSEL ÇALIŞMA

Proseste kullanılan sac malzemenin kalınlığı ve genişliği ile elektromıknatisa uygulanan gerilimin değişimiyle elde edilen frenleme kuvvetini ölçmek için bilgisayar kontrollü bir çekme düzeneği hazırlanmıştır (Şekil 1). Bu düzenekte 100 tonluk bir hidrolik pres üzerine konum ölçer ve yük hücresi yerleştirilmiş ve algılayıcılardan gelen veriler veri toplama yazılımı yardımıyla kaydedilmiştir.



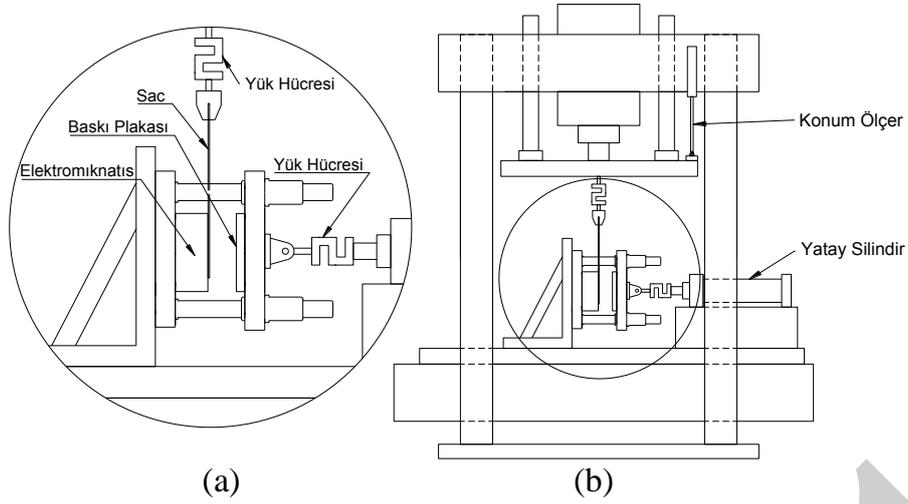
Şekil 1. Bilgisayar kontrollü çekme düzeneği

Deneylerde Tablo 1'de mekanik özellikleri verilen 100 mm genişliğinde, 1, 1.2 ve 1.5 mm kalınlıklarında soğuk haddelenmiş sac malzeme kullanılmıştır.

Tablo 1. Soğuk haddelenmiş çelik sacın mekanik özellikleri (Erdemir)

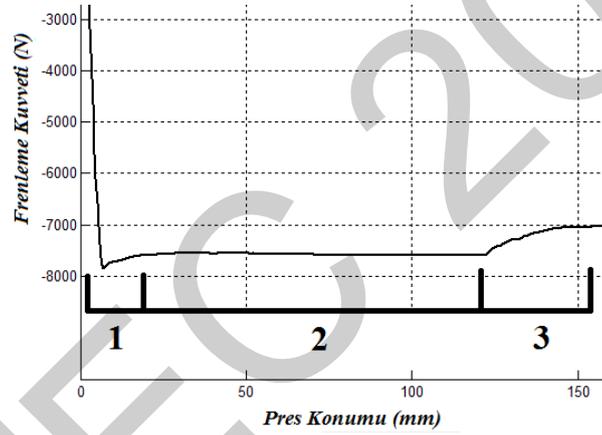
Standart	Kalite	$\sigma_y$ (N/mm <sup>2</sup> )	$\sigma_u$ (N/mm <sup>2</sup> )	$\epsilon_{min}$ (%)	$r_{90}^0$ min	$n_{90}^0$ min
DIN EN 10130	DC 04	210	270-350	38	1.6	0.18

Sac malzeme üzerinde oluşan frenleme kuvvetini ölçebilmek için elektromıknatisın boyutlarına uygun baskı plakasını da içeren bir kalıp seti tasarlanmıştır (Şekil 2-a). Bu kalıp seti pres alt tablasına dikey pozisyonda yerleştirilerek üzerine yük hücresi monte edilmiş yatay bir silindir yardımıyla kalıp setinin açılıp kapanması sağlanmıştır. Silindirde bulunan yük hücresi sayesinde elektromıknatisın karşısında bulunan baskı plakasına uygulanan kuvvet hassas bir şekilde ayarlanabilmektedir. Kalıbın kapanmasıyla birlikte elektromıknatis ile baskı plakası arasındaki sürtünmeden dolayı oluşan frenleme kuvvetini ölçmek için pres üst tablasına sac tutma çeneleriyle beraber yük hücresi monte edilmiştir. Ayrıca frenleme kuvvetini pres üst tablasının konumuna bağlı olarak ölçebilmek için tablaya bir de konum ölçer bağlanmıştır. Tasarlanan bu sistem Şekil 2-b'de gösterilmiştir.



Şekil 2. a. Kalıp seti ve ölçüm cihazları b. Kalıp setinin pres içine montajı

Deney sonuçları kullanılarak sacın konumuna bağlı olarak değişen frenleme kuvvetinin görülebildiği konum kuvvet grafiğinde malzemenin statik sürtünme katsayısını yendiği ve sacın tamamının mıknatıs ile baskı plakası arasında bulunduğu Şekil 3'de gösterilen 2. bölgedeki kuvvet değerlerinin ortalaması, uygulanan gerilime karşı elde edilen frenleme kuvveti olarak kabul edilmiştir.



Şekil 3. Matlab GUI ortamında tasarlanan grafik çizdirme yazılımı

Bu deneyler, baskı plakasına uygulanan 10000N luk kuvvet ve elektromıknatısa uygulanan 0-21 V arasındaki farklı gerilim değerleri için tekrarlandığında frenleme kuvveti değerleri elde edilmiştir. Gerilim değeri 0 iken mıknatıstan kaynaklanan herhangi bir kuvvet elde edilmemekte, sadece baskı plakasına uygulanan kuvvet nedeniyle oluşan sürtünmeden dolayı frenleme kuvveti elde edilmektedir. Tablo 2'de 10000N'luk baskı plakası kuvvetine karşılık elde edilen frenleme kuvveti yardımıyla hesaplanan sürtünme katsayıları gösterilmiştir. Sürtünme katsayı değerleri birbirine çok yakın olduğundan malzemelerin yüzey özelliklerinin aynı olduğu kabul edilmiştir. Elektromıknatıs tarafından üretilen frenleme kuvvetinin bulunabilmesi için baskı plakası frenleme kuvveti deney sonucunda ölçülen frenleme kuvveti değerlerinden çıkarılmıştır. Elde edilen bu değerler elektromıknatıs frenleme kuvvetinin matematik modellenmesinde kullanılmıştır.

Tablo 2. Sürtünme katsayıları ve baskı plakası frenleme kuvveti

Sürtünme Katsayıları			Ortalama Sürtünme Katsayısı	Baskı Plakası Frenleme Kuvveti (10000 N)
		Sac Genişliği (mm)		
		100		
Sac Kalınlığı (mm)	1	0,346	0,347	3470
	1,2	0,345		
	1,5	0,349		

## MATEMATİK MODEL

Gerçekleştirilen deneylerden elde edilen veriler kullanılarak elektromıknatısa uygulanan farklı gerilim değerleri ve sac kalınlığına bağlı frenleme kuvvetinin hesaplanabildiği matematiksel bir bağıntı elde edilmiştir. Matematik model için değişik regresyon model tipleri denenmiş ve optimum sonucu veren ikinci dereceden etkileşimli regresyon model sistemin matematik modeli olarak kabul edilmiştir.

Bağımsız değişken sac kalınlığı (K) ve elektromıknatısa uygulanan gerilim (V) ile bağımlı değişken elektromıknatıs frenleme kuvvetine (EMFK) ait deneysel veriler kullanılarak katsayılar hesaplanmış ve aşağıdaki gibi bir ikinci dereceden etkileşimli regresyon model elde edilmiştir. Şekil 4’de deneysel veriler ile regresyon model sonuçları karşılaştırılmıştır.

$$EMFK = 2494.98 + 288.42 * V - 1504.65 * K + 19.12 * V * K - 8.46 * V^2 + 452.41 * K^2$$

Deneysel veriler ile regresyon modelden elde edilen sonuçlar arasındaki hata,

$$Hata = Deneysel Veri - Regresyon Model$$

şeklinde hesaplanmıştır. Ayrıca regresyon modelin performansı hakkında bilgi veren Korelasyon Katsayısı  $R^2$  ve Hataların Karelerinin Ortalamasının Karekökü (RMSE) hesaplanmıştır.

Korelasyon katsayısı,

$$R^2 = \frac{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (2)$$

Hataların karelerinin ortalamasının karekökü,

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (3)$$

olarak ifade edilir. Burada,

$y$  : Gerçek çıkış değeri,

$\hat{y}$  : Modelden kestirilen çıkış değeri,

$\bar{y}$  : Çıkış değerlerinin ortalaması ve

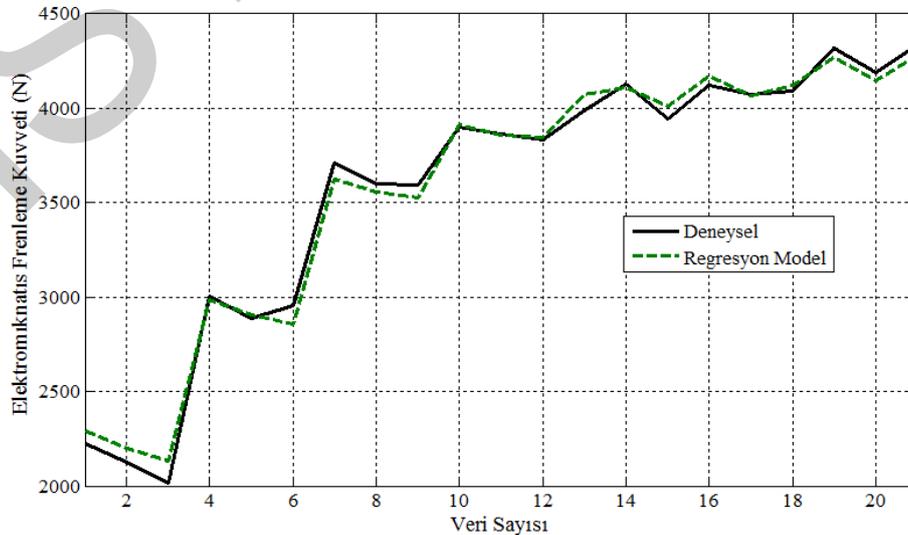
$n$ : Örnek sayısını gösterir.

İkinci dereceden etkileşimli regresyon modelin performansını belirleyen ölçütler;

Korelasyon katsayısı,  $R^2 = 0,992$

Hataların karelerinin ortalamasının karekökü,  $RMSE = 134,35$

olarak hesaplanmıştır.



Şekil 4. Deneysel veriler ile model sonuçlarının karşılaştırılması

## SONUÇLAR

Bu çalışmada baskı plakası ile elektromıknatis arasından geçen çelik sacda oluşan frenleme kuvvetinin mıknatısa uygulanan gerilime ve sac kalınlığına göre değişimi incelenmiştir. Elde edilen kuvvet değerleri incelendiğinde gerilim değeri arttıkça frenleme kuvvetinin de arttığı gözlenmiş olup 9 V'a kadar kuvvet değerlerindeki değişimin fazla, bu değerden sonraki değişim miktarının azaldığı görülmektedir. Ancak sac kalınlığı incelendiğinde ise malzemenin kalınlığı arttıkça elektromıknatis frenleme kuvveti azalmaktadır. Çalışmanın ikinci aşamasında, elektromıknatisin oluşturduğu frenleme kuvvetini kestirmek için regresyon yöntemi kullanılarak gerilim değeri ve malzeme kalınlığının değişimine bağlı ikinci dereceden etkileşimli regresyon model elde edilmiştir. Geliştirilen matematiksel model incelendiğinde deneysel sonuçlar ile oldukça uyumlu olduğu ve modelin performansı hakkında bilgi sahibi olduğumuz korelasyon katsayısının ( $R^2$ ) 0,992 olduğu görülmüştür. Güvenirlik katsayısı da denen bu değer 1'e oldukça yakın olması hesaplanan polinom modelin başarılı sonuç verdiğini ve modelin kullanılabilirliğini göstermektedir. Bu matematik model sayesinde çalışmada kullanılan sac malzeme için sac kalınlığı ve mıknatisin gerilim değerine karşılık elde edilecek frenleme kuvveti miktarı kolaylıkla hesaplanabilmektedir. Diğer taraftan, farklı boyut ve özelliklerde imal edilen mıknatisin kontrolünün kolay olması ve kalıp içinde istenilen konuma yerleştirilebilmesi gibi özelliklerinden dolayı elektromıknatisin sac şekillendirmede kullanılması, şekillendirilebilirliği ve dolayısıyla ürün kalitesini artıracakları öngörülmektedir.

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# SAVING THE NILE DELTA BY AN OVER- FLOW TO THE QATTARA DEPRESSION

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## ABSTRACT

No one can deny the importance of the Nile Delta to the Mediterranean basin. Not only it is unique in its formation but also the Nile Delta is of historical, economic and social importance to Egypt.

According to all scientific investigations during the last 30 years on the climate changes and the global warming; this part of Egypt is considered as one of the most vulnerable parts in the world .It could become endangered within few years.

Arctic sea ice is melting so fast most of it could be gone in 3 decades . A new analysis of changing conditions in the region, using complex computer models of weather and climate, says conditions that had been forecast by the end of the century could occur much sooner. That makes, SAVING THE NILE DELTA IS NOT AN OPTION , IT IS A MUST, and now not tomorrow.

Many scenarios had been proposed, in order to minimize the effects on the Mediterranean coasts. All are good scientific ideas, but they all designed on earlier calculations.

We suggest returning to an old project goes back to the 20<sup>th</sup> century. We think that a connection between the Mediterranean and the Qattara Depression by a canal could solve a great part of the problem.

Eventually the past proposed passages is not feasible for many reasons because of the continual development of the coastal area in this part of Egypt .A new but longer passage is proposed for the time being. This could be confirmed by geological and engineering investigations later on .

Moreover we have a proposed action plan for this International and National urgent project to accelerate the action against the forecast of the fast and acute climate changes within the near future.

A good preparation and well organization could make the dream a reality within 10 years.

### Key words:

Nile Delta , Mediterranean , global warming , Qattara Depression , climate changes , coastal lakes , Lake Mariout Egypt , Mediterranean Coast of Egypt, Vulnerable regions .

## INTRODUCTION

Many environmental research ideas come from living a problem or having a target to get for the well being of humanity on Earth.

As Marine Biologist, the coastal Environments and Biodiversity conservation, was among the most important subjects in my works through the last 3 decades. During 10 years I am living in the western coasts on the Egyptian Mediterranean. Attracting by the climate changes consequences and the possible sea level rise and reviewing the Global Warming consequences, I recalled some ideas proposed to save the Nile Delta. Good ideas are those having rational. Joining the Qattara Depression by the Mediterranean was proposed in the beginning of the last century and remained hot tell eighties. This was the most suitable choice I could reach after my preliminary investigations and testing the other hypothesis in order to save the Nile Delta against the forecast of the acute climate changes .

### Global Warming could lead to Earth worming

Arctic sea ice is melting so fast most of it could be gone in 30 years. The new report by Muyin Wang of the Joint Institute for the Study of Atmosphere and Ocean and James E. Overland of the National Oceanic and Atmospheric Administration's Pacific Marine Environmental Laboratory appeared in the Geophysical Research Letters the 3<sup>rd</sup> of April 2009. . A new analysis of changing conditions in the region, using complex computer models of weather and climate, says conditions that had been forecast by the end of the century could occur much sooner. They expect the area covered by summer sea ice to decline from about 2.8 million square miles normally to 620,000 square miles within 30 years.

"Due to the recent loss of sea ice, the 2005-2008 autumn central Arctic surface air temperatures were greater than 5 degrees Celsius (9 degrees Fahrenheit) above" what would be expected. That amount of temperature increase had been expected by the year 2070. While the precise rate of sea level rise is uncertain, current models indicate that climate change will cause the rate to increase.

Based on the trend of sea level rise from 1961 through 2003, sea level would rise by almost 6-inches by the end of this century in the absence of any effects of climate change. Taking climate change into account, sea level is projected to rise between 7 and 21 inches by 2100. This increase would result in the threat of more sustained extreme storm surges, increased coastal erosion, escalating inundation of coastal wetlands and saline intrusion. These catastrophic events could alter the natural features of the shoreline, such as beaches, dunes, and wetlands, and threaten people and property. Moreover, in Egypt, construction of new residential development, reconstruction of existing residential development, continue on the Mediterranean coastal areas add to the problem. With anticipated accelerating sea level rise and increasing vulnerability to the risks of coastal hazards will be exacerbated and the costs of damages and losses resulting from the events will increase. These expected catastrophic events require anticipatory preparations for the inevitability of an event, the capacity for rapid response to an imminent threat of an event, and preparation for addressing the aftermath of an event.

### THE NILE DELTA

"Egypt is the gift of the Nile," wrote the Greek historian Herodotus in the fifth century B.C. No other country owes its very existence to a single lifeline. The annual cycle in which the Nile flood deposits layers of silt at the rate of several centimeters per century built the highly fertile Nile Delta in the north of Egypt and the Nile Valley in the south. El-Sayed and van Dijken 1994.

Egyptian Mediterranean coast can be differentiated into 3 sub-regions:

**Western Coast:** Which has higher rain precipitation, higher altitude, witnesses higher but rare snowfalls and it is colder than the other 2 portions. It also has more vegetation and Fig and Olive terrains, with a long part of the original Mariout lake .

**Nile Delta Coast:** Which is settled by larger populations and hosts larger cities. It has the Delta features. Sometime frost and frozen ground during winter nights destroy the crops and agriculture plants. The ewt lands are very important there . Three of Egypt's Northern Lakes are located there; Lake Manzala , Burullus Lake and Lake Edku , in addition to the Eastern small part of Mariout Lake .

**Sinai Coast:** It has the least precipitation. It is colder on its eastern part than its other part. 2 Northern lakes of Egypt are found in this sub-region as well; The remainders of Lake Manzala cut by the Suez Canal ( El Tina Planes ) and hyper saline Lake Bardawil.

### THE PROBLEM VISION

No one can deny that the Nile Delta is one of the 3 most vulnerable points in the world. It could be washed by the sea level rise.

"All deltas undergo alternating construction to destruction phases due to fundamental changes in the relative influence of sediment input from rivers and redistribution by marine coastal processes. During the past 7000 years world deltas, including the Nile, have been in an overall construction phase." Daniel Jean Stanley and Andrew G. Warne 1998.

Nile Delta is about 25,000 km<sup>2</sup> with about 34 million inhabitants (Cairo is not included). It is among the most densely populated agricultural areas in the world, with 1,360 inhabitants per km<sup>2</sup>. About half of the area is used for agriculture. The fish productivity is more than 185000 Tons/year from the northern lakes (Mariout, Manzala, Edku and Burullus). About 40% of all Egyptian industry located in Nile Delta. Most of the investments and economic activities apparently go the delta region.

The Sect. Gen. UN declared 17th Mai 2009; that Egypt could be one of 3 countries most touched by catastrophic consequences of the sea level rise .

Washington Report on Middle East Affairs, January-February 2009, pages 32-33 ; While it may be too early to predict the extent of climate change in Egypt, the facts on the ground appear to hint toward a calamitous situation that could see much of the northern part of the country awash with water. The question appears to be not if Egypt will face devastation, but when.

Environmental News Network, via Associated Press: Friday, August 24, 2007 "Sea level rise threatens the Nile Delta ; Millions of Egyptians could be forced permanently from their homes, the country's ability to feed itself devastated. That's what likely awaits this already impoverished and overpopulated nation by the end of the century, if predictions about climate change hold true. The World Bank describes Egypt as particularly vulnerable to the effects of global warming, saying it faces potentially "catastrophic" consequences."

Generally, it is expected that the following impacts will be happened:

- Direct inundation and loss of beaches and archaeological sites with associated loss of tourism.
- Loss of arable and agricultural land and fishing grounds and a decrease of fish catch in some areas and an increase in other areas.
- Increase in the rate of salt water intrusion, soil salinity, water logging, desertification and a loss of land productivity.
- A change in the coastal water circulation pattern, with associated changes in fish catch and navigation.
- A decrease of life spans of coastal buildings and archaeological sites due to increase of saltwater intrusion.
- Contamination of fresh water aquifer, with associated agricultural losses.
- A decrease of the River Nile budget and flow rate (as predicted by some models), would result in an increase of the rate of erosion and salt water intrusion at the Northern Delta coast.
- Impacts on the harbors designs due to changes in sea level and frequencies of storm surges. This may cause severe economic losses.
- About 15% of the arable delta land will possibly be subject to inundation over the next century with extension as far as 20 km inland from already existing coasts.
- Land productivity will also suffer due to salt water intrusion effects up to the belt of 2 m contour which is 30 to 60 km wide.
- This belt includes important cities such as Alexandria, Port Said, , Rosetta, Demietta.
- In one scenario, it was assumed that aquaculture development in northern lakes will have a large effect on fish production potential.

We cannot stand watching, blaming, and waiting .Now it is a must.

Efforts had been started by many environmental organizations ,but still not sufficient facing the slow Tsunami coming from the Atlantic soon.

### **DIFFERENT HYPOTHESIS**

All hypothesis were motivated by the need to face and anticipate coastal changes caused by accelerating sea-level rise, as well as lake-level changes caused by climate change, over the next century. The goal of all assessments was to provide information that can be used to make long-term (decade to century) management decisions. Analyzing the results of coastal vulnerability assessments for several coastal parts of Egypt in comparison with others indicate that physical changes may occur , based on analysis of the following variables: tidal range, ice cover, wave height, coastal slope, historical shoreline change rate, geomorphology, and historical rate of relative sea- or lake-level change. This approach seeks to combine a coastal system's susceptibility to change with its natural ability to adapt to changing environmental conditions, and it provides a measure of the system's potential vulnerability to the effects of sea- or lake-level change.

Beach nourishment and groins:

- Beach nourishment strategies include depositing sand onto the open beach.
- Beach scraping or building artificial dunes as storm beach sand reservoirs buffers.
- Laying pipes underneath the beach to suck in the water.
- Groins trap sand, which cover the beach.

Breakwaters:

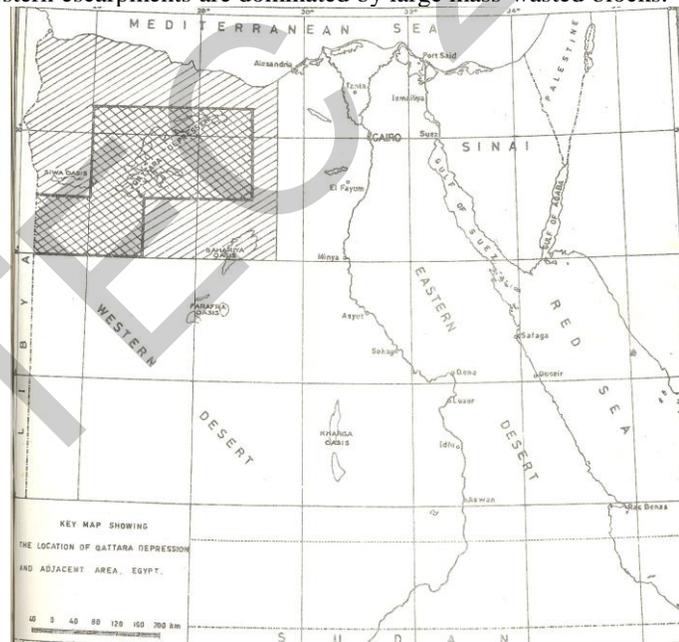
- Break-waters are hard structures used to reduce the wave energy reaching the shoreline.
- The net benefit of this strategy is only along the coastline.
- It is the best available tool for the lowland areas protection.

We had tested all hypotheses and Scenarios which aim to prevent vulnerability and protect the Nile Delta . A connection between the Mediterranean and the Qattara Depression by a canal could solve a great part of the problem. We concluded that the only environmental , economic as well as social idea is to use a sink and to create a lake using the flow of water coming to the Egyptian coasts .

In order to evaluate its feasibility we had to discern various types of errors, including bias ,identify confounding factors ,select and use appropriate measurement tools ,prepare for data management and set a work plan. A new but longer passage is proposed for the time being. This could be confirmed by geological and engineering investigations later on .

### QATTARA DEPRESSION

The Qattara Depression is a desert basin north-western Egypt ,contains the second lowest point in Africa and considered as the biggest sink hole .The Depression forms one of the most significant geomorphological features of the West desert of Egypt. It is a closed inland basin bounded from the north and west by steep escarpments, with an average elevation of 200 masl (above sea level) . Towards the south and east the floor of the Depression rises gradually from 60 mbsl to the general desert level of 200 masl again. The Depression has an area of some 18,130 to 19,500 sq. km and an average depth of 60 m below sea level (bsl); the lowest point, lat the SW part, being 134 m bsl. The Depression is estimated to have an excavated volume of 3200 cu. Km. Within the Depression, cones, towers, rocky masses, and plateau-like hills, ranging in height from 5 to 30 m, are common, especially near the western scarp. Sinkholes and caves are also common in the northern Diffa Plateau, separating the Depression from the Mediterranean frontal plain. The northern and western escarpments are dominated by large mass-wasted blocks.



The Qattara Depression in the northern part of the Western Desert is the largest natural closed depression of the Eastern Sahara. It is a region where salt weathering appears to be particularly effective. In spite of earlier research in the 1940's and 1950's, the origin of this Depression is still a geological puzzle. A common origin by wind deflation to a base level controlled by the ground water table, is the generally accepted explanation. Other explanations include solution, mass-wasting followed by wind deflation, or that the depression was originally excavated as a stream valley, to be subsequently modified. It has also been suggested that the Depression is of structural control origin.

Qattara Depression had been discovered in the beginning of the last century .Prof. penk;1912 a Berlin Geography specialist suggested for the first time the utilization of Qattara Depression for generating



## CONCLUSION

SAVING THE NILE DELTA IS NOT AN OPTION IT IS A MUST, now.

Discharging over 70% of the sea water coming to the Mediterranean to the biggest sink hole in the world has International and National benefits. Not only the idea presents a solution to save the Nile Delta, but also it is highly beneficial to Mediterranean region.

Although targets are so far to reach but have to be the first to consider the project could have the positive advantages and add to the Environmental , Social , and Economic development of the region by;

Generating electricity.

Developing industries.

Distillation of sea water could develop land reclamation in the region.

Facilitating oil mining or prospect ion.

Developing tourism facilities.

Creating fisheries industry.

Creating new settlements for youth.

Creating new jobs.

Improving climate in the western part of Egypt.

The management plan operates with other instruments to deliver the objects of the Act:

+Provide for the protection, conservation, rehabilitation and management of the Lake Mariout, including its resources and biological diversity.

+Have regard to the goal, core objectives and guiding principles of the National Strategy for Ecologically Sustainable Development in the use of Qattara Depression ,

+Provide, in conjunction with other legislation, a coordinated and integrated management and administrative framework for the ecologically sustainable development of the Egyptian coastal zone on the Mediterranean. This could encourage the enhancement of knowledge of natural resources and the effect of human activities on the Qattara Lake zone.

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# SEMANTIC ADAPTATION APPROACH FOR ADAPTIVE WEB-BASED SYSTEMS

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## ABSTRACT

The principles of the WWW used today rely solely on links and on content presented through simple HTML tags. The drawback of the above mentioned modus operandi is that it is purely syntactic with no clear emphasis on meaning about data. The Semantic Web approach tries to bridge that gap by providing additional information, mainly conceptual to the data at hand. In this paper we are focusing on extension of the adaptation methods with semantic adaptation dedicated to Adaptive Web-Based Systems. The approach is consisted of five steps based on querying RDF resources through SPARQL every time the user is visiting a particular resource. It is worth mentioning that the retrieved resources represent similar resources relevant to the currently visited resource which guides the user towards the desired information while browsing.

## 1. INTRODUCTION

The expansion of the web in the latest years consecutively with the increase of new applications and social web phenomena has made it a place where information is not simply posted, searched, browsed and read, but also has made it a place where it can be adapted in various ways for a single purpose of action, which is meeting user's needs. The second part of the above mentioned clause is being conducted through the use of *Adaptive Web-Based Systems*. Adaptive Web-Based Systems represent systems that tend to arrange its internal link structure, content or both based on user access patterns.

In (Raufi & Georgieva, 2008), a layered framework is introduced that concentrates on the issue of complexity in adaptive web-based systems. The proposed framework guarantees:

- **Flexibility:** that offers quicker discovery of new knowledge and the reuse of the existing.
- **Expressiveness:** this allows extensive usage of semantic web technologies in the sense of good manipulation and reasoning with the knowledge at hand.
- **Interoperability:** offers sharing and accessing of data from other resources for performing adaptation (closed or open corpus adaptation).
- **Modularity:** that allows a certain degree of independence between layers.

The proposed layered framework is consisted of five layers as illustrated in (Raufi & Georgieva, 2008):

- **Data Layer** where all the data and the site's internal link structure resides. Also this is the layer where the atomic information is located with the precedence and next links as well as their particular information weights.
- **Concept Layer** represents the knowledge representation layer of the system, consisted of concepts and concept relationship. This layer represents the semantic layer of the proposed framework
- **User Layer** where user preferences like access patterns and user behaviour are collected and used for performing the adaptation process.
- **Adaptation Layer** which performs the adaptation based on knowledge gained from concept layer and user layer.
- Finally the **Presentation Layer** is what the user sees at the end as a final product of adaptation. In this stage, a rearrangement of atomic pieces of information or whole pages is done so the adaptation goal posed in adaptation layer can be met.

In (Raufi & Georgieva, 2010) we have introduced the work done in each layer of the above proposed framework. In this paper we are focusing on semantic adaptation aspects for the framework and approaches proposed in (Raufi, Georgieva, Luma, Ismaili & Zenuni, 2010) and (Raufi, Georgieva, Luma, Ismaili & Zenuni, 2010). The rest of the paper is structured as follows: In section 2, a semantic web technology available for adaptation is introduced. Section 3 outlines an approach towards adaptation which utilizes the Semantic Web, whilst section 4 illustrates an example of semantic adaptation with an included case study and finally section 5 concludes this paper with some future direction towards semantic adaptation approaches.

## 2. SEMANTIC WEB TECHNOLOGIES AND ADAPTATION

The advent of *World Wide Web (WWW)* has substantially altered the understanding on how people communicate with each other. This change transformed the world and smoothly pushes the web toward knowledge based society. The above mentioned transform also changes the way how people understand computers. While, at the beginning, the computers were used for performing solely numerical calculations, today their main goal is given to data processing even though the latter is not intended to be human understandable. Data mining is a typical example for this. However, most of the web content today is used for human consumption, disregarding the aspect of what the data conceptually represents in its essence. This disadvantage makes the content usable only for browsing, online ordering, filling forms or searching.

The reason of using Semantic Web techniques for Adaptive Web-Based System can be outlined as follows:

- 1) Semantic web can be used to describe every document in adaptive web-based system's repository (documents and any other smaller units) according to a certain vocabulary.
- 2) After their description, these documents can become machine processable and conceptually describable.
- 3) Numbers of these described documents are scaling optimally with no particular increase in processing power. Such examples have been detected in OpenLink Virtuoso, BigOWLIM, Garlik 4store and many more (W3C Media Wiki - Large Triple Store., 2010)
- 4) These described documents can be queried through a particular endpoint and presented to the user.

Knowledge representation through semantic web uses many underlying methods and technologies starting from those used for describing resources on the web (like RDF and RDF Schema), representing knowledge and knowledge flow (like OWL) up to use of rules (like Rule markup languages). All the above mentioned technologies are meant to make the web more machine-processable, which is also a requirement for building adaptive web-based systems.

One promising way of making content for Adaptive Web-Based Systems more machine-processable as well as human readable is the use of method for describing resources on the web with utilization of RDF (Resource Description Framework) (Becket & McBride, 2004) which is more like a data model rather than a language and is based on *object-attribute-value* (also referred to as *resource-property-value*) triples called *statements*.

- **Resource:** Represents every object or thing that is describable. Every resource has its own URI (Unified Resource Identifier) that uses the underlying web's standard URL naming to gain access to the resource itself. Even though RDF does not require a strict accessible resource, however the Linked Open Data Initiative (Heath, 2010) that deals with linking web resources highly recommends such an action. Our approach in Semantic Adaptation follows the Linked Open Data recommendation.
- **Property:** Represents also a special kind of resources that describe relations among resources (objects). For example, *writtenBy*, *age*, *visited* etc. are typical properties. The same as objects, properties are also represented by URI's
- **Value:** Is the actual value of the object itself, such as page name given in the above statement. It is worth mentioning that property value can also be another resource or a simple literal.

In (Raufi, 2011) we propose an architectural model for addressing the complexity of Adaptive Web-Based systems by dividing it into two logical modes: the *offline* and *online* mode.

The *offline mode* orchestrates computer exhaustive tasks such as data mining within web site's repository (clustering and association rule mining), navigation pattern mining and session reconstruction within web server's log files. The reason for performing such tasks offline is the intensive calculation nature of the above mentioned functions considering that dealing with online web application with many requests and clicks during user visits would render the system inefficient. Therefore the offline mode utilizes the above mentioned techniques on the background, issued by the webmaster which performs the overhead tasks, analyzes them and the extracted knowledge is incorporated in the overall adaptation process. The incorporation involves putting additional information on the adaptive presentation panel besides the information retrieved by adaptation algorithm. Based on the above mentioned claim, the offline mode does not obstruct the overall functioning and performance of the system because it is being conducted on the background as a separated task from that of the adaptive web application.

*Online* mode on the other hand considers the adaptation "on-the-fly" presented through the adaptation algorithm elaborated extensively in (Raufi, Georgieva, Luma, Ismaili & Zenuni, 2010). The online mode traces the user visits through the links it clicks and presents adaptive content based on the visited information units (documents or atomic units). The characteristic of the online mode is that it offers two types of adaptive content. The first one is adaptive content delivery through the adaptation algorithm which was based on web site's link structure and document similarity measures and the second one is adaptive content delivery by querying the knowledge repository as presented in figure 1 which in fact is the concept layer of our framework. Querying is conducted on the generated RDF triples from Relational database, represented through RDF Repository. For this purpose SPARQL (Prud'hommeaux & Seaborne, 2008) query language was utilized for querying the knowledge base. The results of SPARQL queries can be presented as result sets, RDF graphs or as RDF triples presented for human consumption through web pages (Adida & Birbeck, 2008), (Prud'hommeaux & Seaborne, 2008).

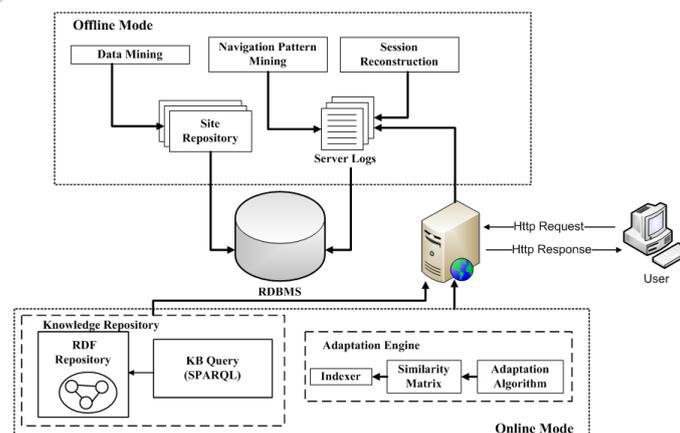


Figure 1 Architectural Model for Adaptive Web-Based Systems

Main goal of this paper is to explore the possibilities of utilizing the *Knowledge repository* as given in figure 1, consisted of *RDF Repository* and *Knowledgebase Query (KB)*, for performing RDF-Resource adaptation for users. The mechanism for querying the RDF triples mentioned in the above architecture will be elaborated in section 3.

### 3. SEMANTIC ADAPTATION APPROACH FOR ADAPTIVE WEB-BASED SYSTEMS

Many systems regarding adaptation for semantic web have emerged the recent years like (Mikroyannidis & Theodoulidis, 2007) and (Partarakis, Doulgeraki, Leonidis, Antona & Stephanidis, 2009). However, the approach mentioned on the systems above focus mostly on case of web usage and text mining methodologies for semi-automatic construction and evolution of Web ontologies characteristic mostly for the former and on user interface adaptation which is characteristic mainly for the latter approach.

Developing particular applications for adaptive content presentation on Semantic Web requires a set of particular skills that need to be mastered. The first skill that needs to be considered is the aspect of data representation as recommended from Open Linked Data (Heath, 2010) initiative, which is consisted of four basic rules which are (Berners-Lee, 2006):

1. Use URIs as names for things
2. Use HTTP URIs so that people can look up those names.
3. When someone looks up a URI, provide useful information, using the standards (RDF, SPARQL)
4. Include links to other URI's so that they can discover more things.

The second important skill, which is logically derived from rule 3 and 4 given above, is extracting useful information from the visited links and recommending to the users as sources for discovering new resources represented through URI's. This can be achieved in two methods:

- The first method is by simply following the typed links that Semantic Web offers, i.e. each of these links have a clearly defined semantics which allows us to precisely know which links to present to users. For example, `rdfs:seeAlso` and `owl:sameAs` clearly defined semantics and by simply using *Depth-First* or *Breadth-First* search strategies to determine which links should be offered.
- The second method, which will be followed in our approach, is by using a query language SPARQL (Prud'hommeaux & Seaborne, 2008) for querying closed or open corpus repositories in relation to link (resource) that user have already visited.

A typical SPARQL query that can retrieve everything about a particular concept can be written as:

```
SELECT ?propertyValue ?propertyName
WHERE {
  <Resource>
  ?propertyName ?propertyValue.
}
```

Where `<resource>` represent a particular dereferencable URI. Having all these aspects in mind, the proposed semantic adaptation algorithm is consisted of steps given as:

- Step 1:** user visits (clicks) a particular resource while browsing.
- Step 2:** execute a SPARQL query for every resource the user is visiting.
- Step 3:** present similar resources to the one that user have currently visited.
- Step 4:** present the resources to the user in user friendly way
- Step 5:** repeat steps 2-4 every time the user is visiting a resource

The whole semantic adaptation process goes by visiting and providing resources by querying RDF internal or external repositories. It is worth mentioning that resources can be described by generally accepted vocabularies like SKOS (Miles & Bechhofer, 2008), FOAF (Miller & Brickley, 2010) or more general adaptive web-based system ontology (Raufi, Ismaili & Zenuni, 2009). The above mentioned five step algorithm is going to be illustrated with a simple case study outlined in the following section.

### 4. SEMANTIC ADAPTATION: A CASE STUDY

Let us suppose that a particular RDF resource is being requested over the semantic web application and we are requesting some information about person from DBpedia `<http://dbpedia.org/resource/Tim_Berners-Lee>`. Executing SPARQL query that will achieve the above mentioned steps between 2 and 4 can be done by utilizing properties from OWL language. One of the properties is the `owl:sameAs` property. The overall query will look like:

```
SELECT ?aliasURI WHERE {
  {
    <http://dbpedia.org/resource/ Tim_Berners-Lee>
    <http://www.w3.org/2002/07/owl#sameAs> ?aliasURI.
  }
  union
```

```

    {
      ?aliasURI <http://www.w3.org/2002/07/owl#sameAs>
      <http://dbpedia.org/resource/Tim_Berners-Lee>.
    }
  }

```

After the execution of the query, the retrieved resources will be outlined as follows:

```

<http://www4.wiwiss.fu-berlin.de/flickrwrappr/photos/Tim_Berners-Lee>
<http://mpii.de/yago/resource/Tim_Berners-Lee>
<http://www4.wiwiss.fu-berlin.de/dblp/resource/person/100007>
<http://rdf.freebase.com/ns/m/07d5b>

```

It is worth mentioning that every time the user is visiting a particular resource, similar resources will be presented to the user as part of the above mentioned algorithm. The sole aspect that needs to be considered is the large number of retrieved resources which often can be enormous; therefore a proper filtering of such resources may be required.

## 5. CONCLUSION AND FUTURE WORK

In this paper we have introduced a semantic approach towards adapting the content in the conceptual aspect by utilizing semantic web. We have introduced an approach towards adaptation through querying the RDF resources from internal or external repositories. The proposed semantic adaptation approach delivers similar and relevant resources every time the user clicks an RDF resource. With this algorithm, constant and up to date information is being presented to the user.

The future work on presenting adaptive on semantic level would involve:

- Limiting and filtering the number of resource according to their relevance and
- Presenting the content of resources in a more user friendly manner. Fortunately, there is a promising W3C standard technology called RDFa which is designed to present such resources in a manner which is more “human-consumable” (Adida & Birbeck, 2008).

The above presented future guidelines would ensure minimum robustness to the system considering that resources presented will be limited and filtered based on some criteria as well as it will provide readability of resources by presenting them in user friendly trait.

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# SEMI-ACTIVE FUZZY CONTROLLER DESIGN FOR SEISMICALLY EXCITED STRUCTURES WITH BASE ISOLATION

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**Abstract:** In this paper, a fuzzy controller is designed to augment a passive base isolated structure to mitigate seismic vibrations. Actuator is placed on top of structure and velocity feedback is used. A three -storey structure is modeled and used to demonstrate the feasibility of proposed controller. Simulations indicate a reasonable vibration suppression compared with passive base isolation.

## 1. Introduction

Base isolation of civil structures and components is used worldwide to protect structures such as hospitals, power plants, storage tanks, and data & communication centers against forces generated by seismic excitation (Naeim & Kelly, 1999). It aims at reducing the transmission of vibration energy from the shaking ground to a resilient connection between structure and source of vibration. Hence, instead of relying entirely on the inelastic deformation of the structure to dissipate the earthquake energy, several approaches have gradually been introduced to mitigate undesired vibrations in earthquake excited structures (Gould & Abu-Sitta, 1980; Al-Hussaini, Zayas & Constantinou, 1994). These approaches are broadly divided into passive, active, and semi-active control (Balas, 1997; Symans & Constantinou, 1999).

In this work, semi-active base isolation is considered where a passive base isolation system is complemented with an active control device. This hybrid control strategy has been investigated by many researchers and has a great appeal due to its reliability, effectiveness, and natural appeal to civil engineers. The addition of an active element should improve the performance of the base isolation system with less cost than other structural control systems (Naeim & Kelly, 1999). Several techniques for semi active base isolation have been investigated including semi-active fluid damping (Johnson, Ramallo, Spencer & Sain, 1998; Madden, Wongpraser & Symans, 2003), nonlinear dynamic analysis and optimal control (Dai, 2002). Fewer results have been reported using fuzzy control (Ayyub & Hassan, 1990; Symans & Kelly, 1999).

It should be emphasized that fuzzy logic controllers have been successfully implemented in the control of linear and nonlinear systems (Lin & Lee, 1996). Unlike conventional controllers, fuzzy logic controllers do not require exact mathematical modeling and they can easily deal to a certain extent with nonlinearities and uncertainties of controlled systems (Nie & Linkens, 1995).

## 2. Modeling of a Flexible Multi-storey Building

The building considered in this paper is a three story flexible structure with ground floor isolated from shaking ground as shown in Figure 1. However, the model can be easily extended in a direct way to  $n$  storey structures.

Now, consider damping provided by structure walls and use a free body diagram to depict the various forces acting on the each floor rigid slab as shown in Figure 2 below. Then, the equations of motion in the lateral direction for this structure can be written as:

$$M \ddot{\mathbf{x}} + C \dot{\mathbf{x}} + K \mathbf{x} = \mathbf{u} \quad (1)$$

$$\text{where } K = \begin{bmatrix} k_0 + k_1 & -k_1 & 0 & 0 \\ -k_1 & k_1 + k_2 & -k_2 & 0 \\ 0 & -k_2 & k_2 + k_3 & -k_3 \\ 0 & 0 & -k_3 & k_3 \end{bmatrix} \in \mathfrak{R}^{4 \times 4}, C = \begin{bmatrix} c_0 + c_1 & -c_1 & 0 & 0 \\ -c_1 & c_1 + c_2 & -c_2 & 0 \\ 0 & -c_2 & c_2 + c_3 & -c_3 \\ 0 & 0 & -c_3 & c_3 \end{bmatrix} \in \mathfrak{R}^{4 \times 4},$$

$$M = \text{diag}\{m_0, m_1, m_2, m_3\}, \text{ and } u = [F_{\text{ext}}, 0, 0, 0]^T \in \mathfrak{R}^4,$$

represent the stiffness matrix, and damping matrix, mass matrix, and forcing function vector, respectively.

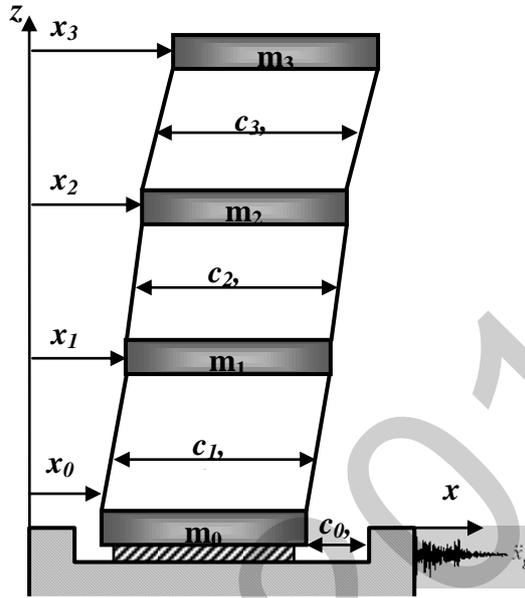


Figure 1: Model of a 3 storey structure with base isolation.

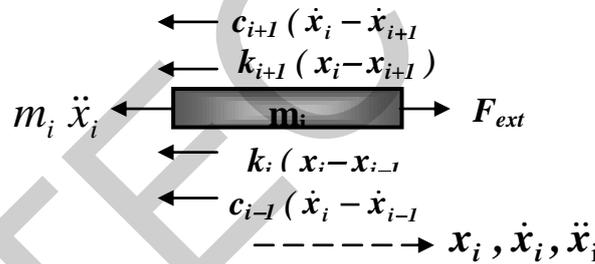


Figure 2: Various forces acting on floor slabs.

The modal analysis of this system can be not possible in general. However, modal analysis can be applied directly if the damping matrix  $C$  can be written as a linear combination of the mass and stiffness matrices, i.e.  $C = \alpha M + \beta K$ , where  $\alpha$  and  $\beta$  are proportionality constants. This type of damping is called proportional damping (Inman, 1996).

Equation (1) can also be written in state space model  $S(A,B,C)$ :

$$\dot{z} = \begin{bmatrix} 0 & I \\ -M^{-1}K & -M^{-1}C \end{bmatrix} z + \begin{bmatrix} 0 \\ M^{-1} \end{bmatrix} u \tag{2}$$

$$y = [0 \quad I] z + [0] u$$

where  $z = [\dot{x} \quad x]^T \in \mathfrak{R}^8$  represents state vector.

SimuLink is used to simulate this system along with proposed fuzzy controller. Structure parameters are shown in Table 1 below (Wang, Roschke & Yeh, 2002) and are used for Matlab simulations. Structure response to seismic excitation (Kobe data) is shown in Figure 3.

Table 1: Model parameters

$m = 1.05 \times 10^6 \text{ kg}$	$k = 350 \times 10^6 \text{ N/m}$	$c = 1.575 \times 10^6 \text{ N-s/m}$
$m_0 = m_1 = 2m$	$k_0 = k_1 = 2k$	$c_i = c$
$m_2 = m_3 = m$	$k_2 = k_3 = k$	

For these parameters, the structure has the following eigenvalues:

$$\lambda_1 = -1.8385 \pm j32.2058, \lambda_2 = -1.3352 \pm j 28.3095, \lambda_3 = -0.4953 \pm j 16.3156, \text{ and } \lambda_4 = -0.0811 \pm j 7.4452$$

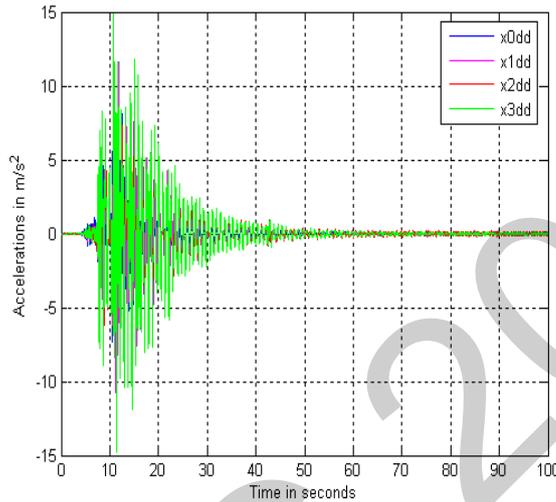


Figure 3: Absolute acceleration response for structure (Kobe data).

### 3. Fuzzy Logic Controller Design

The main objective of the fuzzy controller is to resolve the inherent conflict between effectively supporting the integrity of the structure and properly isolating it from the undesired vibrations produced by the seismic acceleration. The block diagram of this controller is shown in Figure 4.

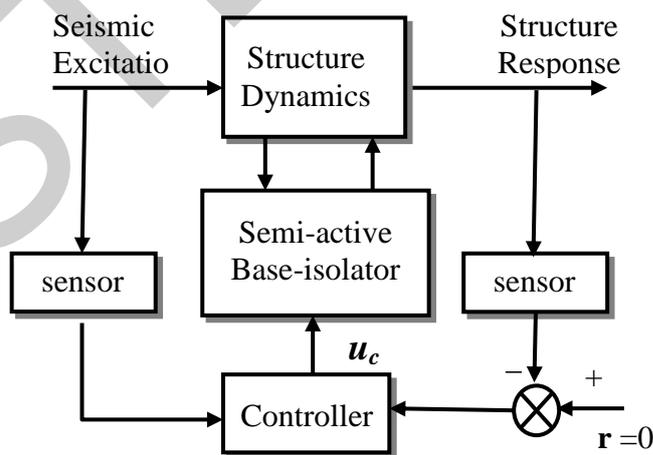


Figure 4: Block diagram of semi-active isolation feedback system.

The active actuator is placed at the top of the structure (3rd storey) to produce actuating force to compensate for forces mitigated into the structure. This is actually an elastic inverted pendulum with moving base and control action is applied at its tip. Displacement is extremely difficult to measure and is of no practical value in

structural control. Acceleration on the other hand can be measured more reliably and it is common to use acceleration for feedback control. However, velocity can also be used and is relatively easy to measure.

The Mamdani fuzzy inference system (FIS) is used to edit and visualize rules and membership functions. Velocity of the 3rd storey is used for feedback and the rule-base for such controller is shown in Table 2 below. Figure 5 shows the graphs of input and output membership functions (MFs) used in the design of the FLC as well as a 3d surface view of used rule-base.

Table 2: Fuzzy controller rule-base.

		x3dot							
Fc		NL	NM	NS	ZE	PS	PM	PL	
x3dd	NL	PL	PL	PL	PS				
	NM	PL	PL	PS					
	NS	PS	PS	NS	NS	NS			
	ZE	NS				NS			
	PS				NS	NL	NS	NS	
	PM				NL	NL	NL	NL	
	PL						NL	NL	

It is clear that the rules for this FLC are simple and related to the physics of the model. The controller gains used to obtain simulations are  $G_{xd} = 0.6$ ,  $G_{xdd} = 0.7$ , and  $G_c = 0.3$ . Measurement noise of SNR=40 dB has been used to make simulation results more realistic. System response with this controller is shown in Figure 6 where we note an improved displacement and acceleration responses for the controlled structure. The Simulink model of the structure with fuzzy controller implemented is shown in Figure 7.

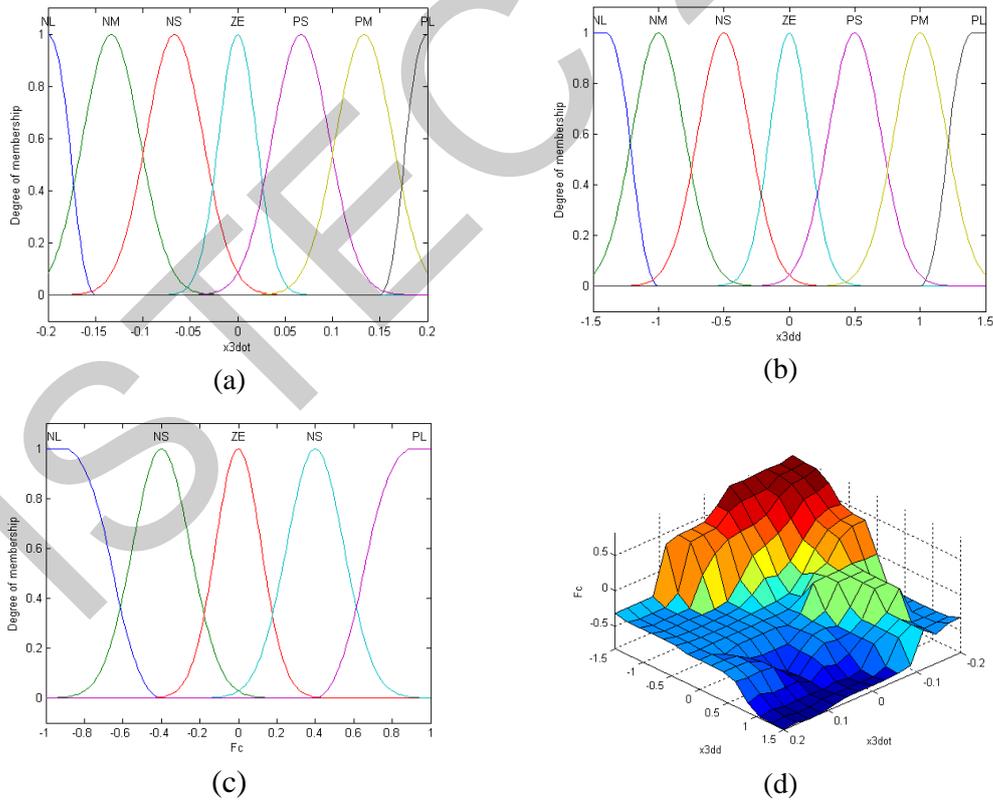


Figure 5: (a) & (b) Membership functions for input signals. (c) Membership functions for output signal. (d) Rule surface view for designed FLC.

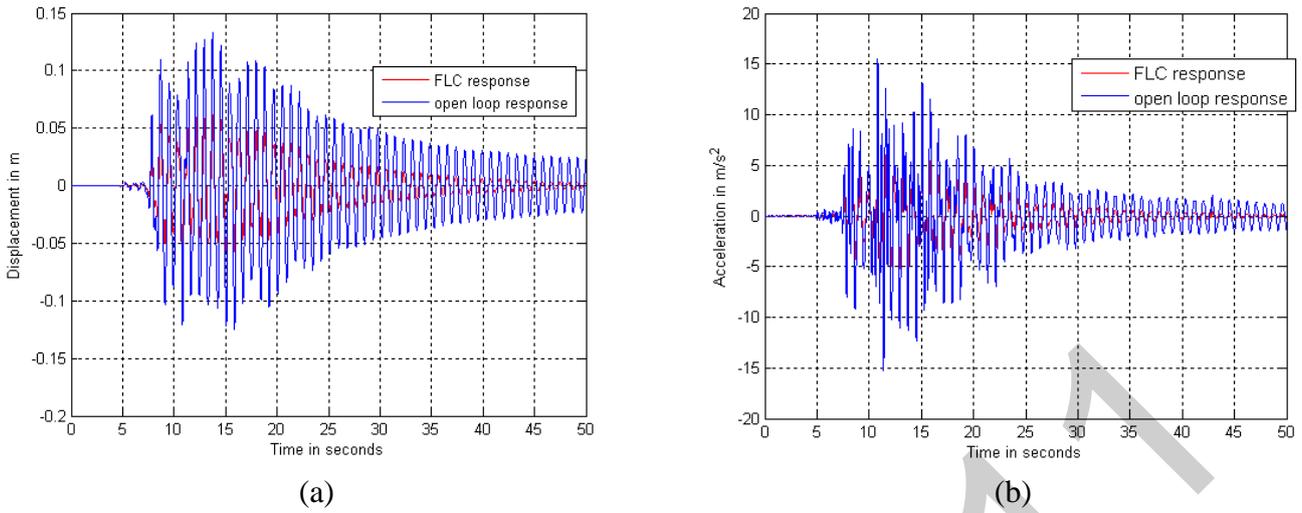


Figure 6: (a) Displacement response for controlled structure.  
(b) Acceleration response for controlled structure.

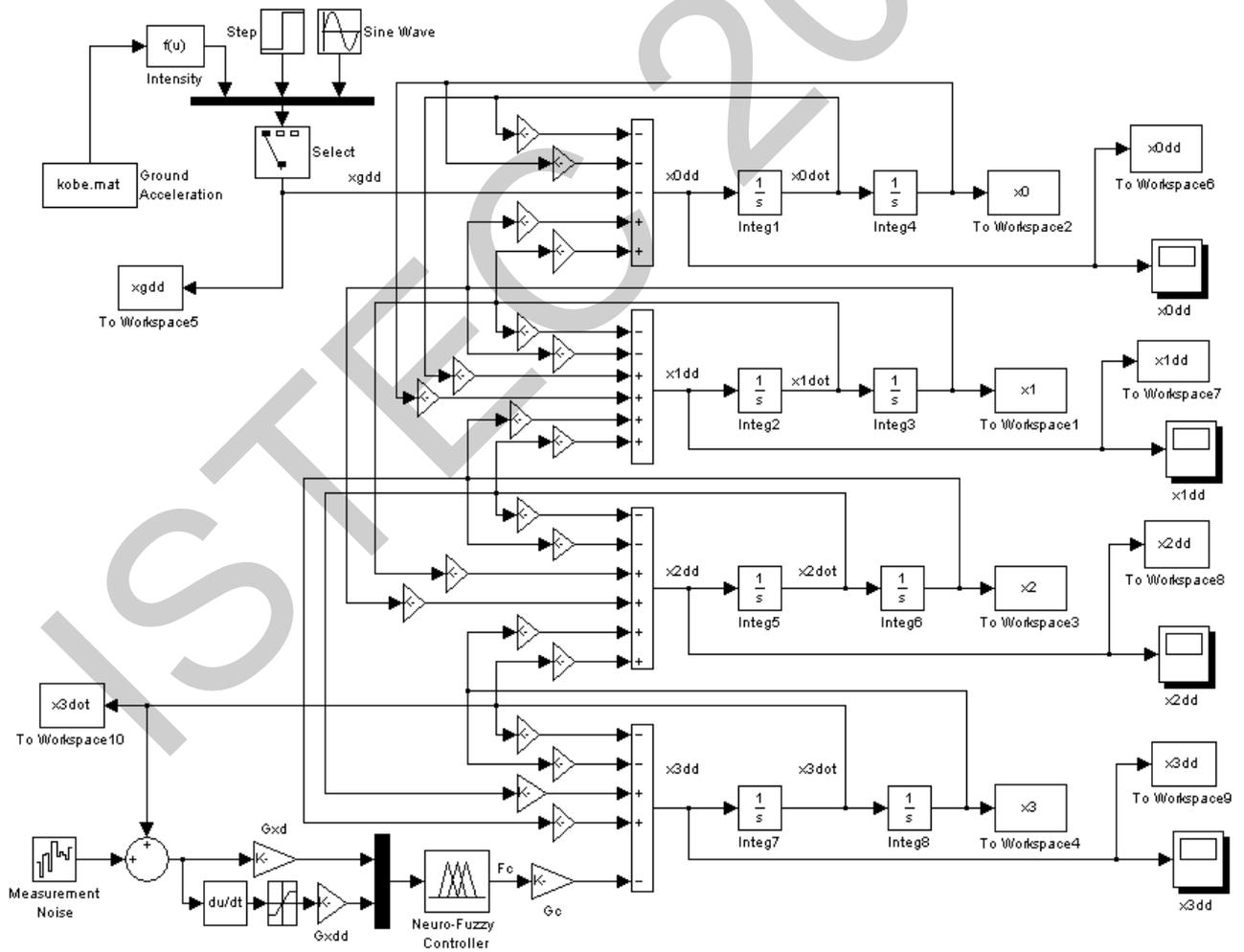


Figure 7: Simulink model of fuzzy controller augmented with structure model.

#### 4. Conclusion

A fuzzy controller is designed for a semi-active controller for a multi-storey structure with base isolation. The designed controller enhanced the vibration isolation performance of the structure. The designed controller structure is intuitive and appeals for the physics of the structure. Real-time implementation issues need further investigation.

#### Acknowledgement

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# SİLİS DUMANI VE FİLLER MALZEMENİN BETON ÖZELLİKLERİNE VE Klorür GEÇİRİMLİLİĞİNE ETKİSİNİN İNCELENMESİ

## THE EFFECT OF THE USE OF SILICA FUME AND FILLER MATERIAL ON THE CHLORIDE ION PERMEABILITY AND CONCRETE PROPERTIES

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### ÖZET

Bu çalışmada silis dumanı ve filler olarak kalker tozu kullanımının beton özelliklerine etkisi araştırılmıştır. Bu kapsamda çimento ile %5, %10 ve %15 oranlarında silis dumanı ve filler ikameli karışımlar üzerinde 7, 28, 56 ve 90 günlük basınç dayanımı ve elastisite modülü deneyleri yapılmıştır. Ayrıca 90 günlük numuneler üzerinde hızlı klorür geçirgenliği deneyi yapılarak silis dumanı ve filler malzemenin betonda boşluk doldurma etkisi incelenmiş ve şahit beton olarak isimlendirilen ve herhangi bir mineral katkı içermeyen betonla kıyaslanmıştır. Deney sonuçları göz önüne alındığında silis dumanının filler malzemeye göre beton özellikleri üzerinde daha olumlu etkisinin olduğu görülmüştür.

**Anahtar Kelimeler:** Beton, Silis dumanı, Filler malzeme, Basınç dayanımı, Hızlı klorür geçirgenliği.

### ABSTRACT

In this study, it was investigated that the use of silica fume and filler additive in various replacement rates with cement as mineral additives on the compressive strength, elastic modulus and rapid chloride ion permeability. For this reason, binder content was determined as 400 kg/m<sup>3</sup> and cement was replaced at three proportions (5 %, 10 %, 15 %) with fly ash and filler additive. Totally 7 series of mix proportions, of which one of them was control mixture, six mixtures were containing mineral additives were tested in different combinations. Before rapid chloride ion permeability test, compressive strength and elastic modulus were performed at 7, 28, 56 and 90 days. Starting from the 90th day, the rapid chloride ion permeability experiment was conducted on cylinder specimens. The test results indicated that the incorporating of silica fume performed better than filler additive for compressive strength, elastic modulus and rapid chloride ion permeability tests.

**Keywords:** Concrete, Silica fume, Filler additive, Compressive strength, Rapid chloride ion permeability.

## 1. GİRİŞ

Beton, günümüzde en yaygın kullanılan yapı malzemelerinden birisidir. Servis ömrü boyunca yapılar çeşitli çevresel etkilere maruz kalmaktadır. Yapıya etki edecek çevresel hususlar iyi bilinmeli ve tasarımda dikkate alınmalıdır. Belirlenen çevresel etki altında yapı işlevini yerine getirmeye devam edebilmeli, yapıda kullanılan malzemelerin kalıcılık özellikleri yeterli olmalı ve böylece yapının performansı belirli bir düzeyin altında kalmamalıdır (Şengül 2003). Doğal kaynakların daha az tüketilmesi, çevre kirliliğinin daha aza indirilmesi ve enerji maliyetlerinin azaltılması amacıyla endüstriyel atık kullanımı gün geçtikçe daha fazla ilgi çeken bir konu olmaktadır.

Silis dumanı, silisyum veya demir silisyum alaşımlarının ergime yöntemi ile üretimi sırasında elde edilen, ana bileşeni 1 µm' den küçük, küresel, amorf, camsı silis (SiO<sub>2</sub>) partiküllerinden oluşan, yüksek düzeyde puzolanik aktiviteye sahip bir yan üründür (Koca 1996). Silikon metalinin veya silikonlu metal alaşımların üretimi esnasında ortaya çıkan gazın hızlı soğutulması sonucunda elde edilen ve % 85 - % 98 arasında silis içeren amorf yapıya sahip çok ince katı parçacıklardan oluşan malzemeye "silis dumanı" adı verilmektedir. Silis dumanı, amorf yapıda ve çok ince taneli malzeme olmasından ötürü ve yüksek miktarda SiO<sub>2</sub> içermesi sebebiyle, mükemmel bir puzolanik malzemedir (Erdoğan 2003).

Silis dumanının betona ilavesi basınç dayanımını oldukça arttırmaktadır. Silis dumanının betondaki boşlukları doldurma ve puzolanik etki olmak üzere iki işlevi bulunmaktadır. Silis dumanının tanecik yapısının çok ince olması, çimento tanecikleri arasına girerek boşlukları doldurmasına ve agrega-çimento hamuru ara yüzeyini geliştirmesine neden olmaktadır (Toutanji vd. 2004). Silis dumanının beton basınç dayanımına olumlu etkisi erken yaşlarda daha belirgindir. Betonun 28 günlük dayanımını arttırmayı amaçlayan çalışmalarda silis dumanının genellikle çimentonun %10-20'si oranında betona katıldığı görülmektedir (Yeğinobalı 1993). Silis dumanının beton içindeki davranışı fizikokimyasaldır. Bu davranışın fiziksel kısmı çimento hamuru matrisindeki, özellikle de agrega-çimento arayüzeyindeki, boşluk sisteminin boyutunun küçültülmesidir. Kimyasal kısım ise zayıf kalsiyum- hidroksit kristallerini kalsiyum-silikat hidrateye dönüştüren puzolanik reaksiyondan oluşmaktadır (Özturan 1993; Tautanji and Bayasi 1999). Bu davranış sonucunda silis dumanı beton basınç ve çekme dayanımını artırmanın yanısıra kalıcılık ve geçirimsizlikte de oldukça önemli iyileşmeler sağlar (Tautanji ve Bayasi 1999). Silis dumanının beton içinde

kullanılması, betonun durabilitesini artırmakta, boşluk oranını ve geçirimsizliğini azaltmaktadır (Aköz, vd., 1995; Turker vd., 1997; Aköz vd.,1999; Erdoğan, 2003).

Betonda filler malzeme kullanımı, beton karışımlarının katı iskeletini zenginleştirmekte, betonu daha kompakt hale getirmekte ve harcın agregaları daha iyi sarmasını sağlamaktadır. Filler malzemeler olarak en yaygın kullanım alanı bulan malzeme ise kalker tozudur (Petersson vd. 1996; Domone vd. 1997). Kalker tozunun beton karışımı dahil edilmesi, çimento hidratasyon oranını ve dayanım gelişimini ve taze haldeki betonun stabilitesi ile hareket kabiliyetini artırmaktadır (Pera vd. 1991; Ghezal 2002). Kalker tozunun beton karışımı ilave edilmesiyle belirli oranlarda basınç dayanımında artışlar meydana gelmektedir. Bu artış, kalker tozunun bünyesinde bulunan  $\text{CaCO}_3$ 'ün çimento ile kimyasal reaksiyona girmesi ile seyreltme ve heterojen çekirdeklenme etkisi sayesinde gerçekleşmektedir (Lawrence vd. 2003; Cyr vd. 2005). Kalker tozunun çimento özelliklerine etkileri üzerine birçok araştırma yapılmıştır. Yapılan birçok çalışmada, kalker fillerinin %5-%6 oranında beton bileşimine dahil edilmesinin beton basınç dayanımına negatif bir etki meydana getirmediği görülmüştür (Topcu vd. 2003). Betonda kalker tozu kullanımının etkileri üzerine yapılan benzer bir çalışmada ise karışımdaki ince agreganın %7-10'unun kalker tozuyla yer değiştirilmesi ile betonun basınç dayanımı ve diğer özelliklerinin olumlu yönde geliştiği görülmüştür (Çelik 1996).

Betonda kalıcılık bir yapının içinde bulunduğu ya da bulunacağı çevresel etkiler altında, servis ömrü boyunca, dayanım ve diğer işlevlerini koruyabilmesi özelliğidir (Öner 2005). Beton dayanıklılığı çevresel koşullar ve bünyesinde bulunan kimyasallar ile ilgili bir konudur. Bununla birlikte ortamda su ve nemin varlığı beton içine zararlı maddeleri taşıyacağından dayanıklılıkta önemli bir faktördür. Betonun içerisine sızan su, karbondioksit, oksijen, sülfat, asit ve klor gibi maddeler, betonda değişik türlerdeki kimyasal olayların oluşmasına neden olmaktadır. Betonda yer alan kimyasal ve fiziksel olaylar sonucunda, beton daha boşluklu bir malzeme durumuna gelebilmekte, içerisindeki demir donatılar paslanabilmekte, aşınabilmekte ve iç bünyede çok büyük gerilmeler oluşabilmektedir (Massazza 1997). Bütün bu kimyasal ve fiziksel olaylar betonun hasar görmesine ve beklenen hizmeti veremez duruma gelmesine yol açmaktadır (Karakurt 2008). Klorür geçirgenliği betonun en önemli kalıcılık kriterlerinden biridir. Betonarme yapılara klorür iyonları nüfuz ettiğinde özellikle deniz yapılarında donatı korozyonunu hızlandırır ve betonun bünyesinde de bir takım mekanizmalar oluşturarak betonda bozulmalar meydana getirir.

Bu çalışmada; silis dumanı ve filler kullanımının betonun basınç dayanımı, elastisite modülü ve hızlı klorür geçirgenliği özellikleri üzerindeki etkisi deneysel olarak incelenmiştir. Bu amaçla, çimento ile %5, %10 ve %15 oranlarında silis dumanı ve filler ikameli karışımlar kullanılarak betonlar üretilmiş ve bu betonlar üzerinde 7, 28, 56 ve 90 günlük basınç dayanımı ve elastisite modülü deneyleri gerçekleştirilmiştir. Hızlı klorür geçirgenliği deneyleri 90 günlük numuneler üzerinde yapılmış, böylelikle; silis dumanı ve filler malzemenin betonda meydana getirdiği puzolanik etki ile boşluk doldurma etkisinin bu betonların bazı mekanik ve kalıcılık özelliklerine etkisi belirlenmiştir.

## 2. DENEYSEL ÇALIŞMALAR

Çalışmada agrega olarak Sakarya-Geyve yöresinden tedarik edilen ve maksimum tane çapı 16 mm olan kalker agregası, çimento olarak TS EN 197-1 standardına uygun olarak üretilen CEM I 42.5 çimentosu kullanılmıştır. Mineral katkı maddesi olarak kullanılan silis dumanı, İSTON tarafından tedarik edilmiştir. Filler malzeme ise agrega ocaklarında farklı tane boyutlarında üretilmek üzere agregaların kırılması sonucu öğütülmüş hale gelen tozların filtreleme sayesinde tutulması sonucu elde edilmiştir. CEM I 42.5 çimentosu ve mineral katkılara ait kimyasal, ve fiziksel özellikler Tablo 1'de gösterilmiştir.

Numunelerin hazırlanmasında çimento miktarı  $400 \text{ kg/m}^3$  olarak belirlenmiş ve basınç dayanımı deneyi için kullanılan numuneler 10 cm ebatında küp olarak üretilmiştir. Deneylerde üretilen tüm numunelere katılan su miktarı, 150-160 mm arasında çökme değerini sağlayacak şekilde ayarlanmıştır. Üretilen numuneler kalıptan alındıktan sonra  $20 \pm 2 \text{ }^\circ\text{C}$ 'de kirece doymun su içerisinde deney zamanına kadar bekletilmiştir. Beton numuneleri üzerinde 7, 28, 56 ve 90 gün sonunda basınç dayanım deneyleri yapılarak, silis dumanı ve filler ikameli betonların basınç dayanımı değerleri şahit betonla karşılaştırılmıştır. Toplam 7 seri beton üretimi gerçekleştirilmiş, her iki mineral katkı da % 5, % 10 ve % 15 oranlarında çimento ile ikame edilerek kullanılmıştır. Üretilen betonların karışım oranları Tablo 2'de verilmiştir.

Tablo 1. Çimento ve mineral katkılara ait kimyasal ve fiziksel özellikler

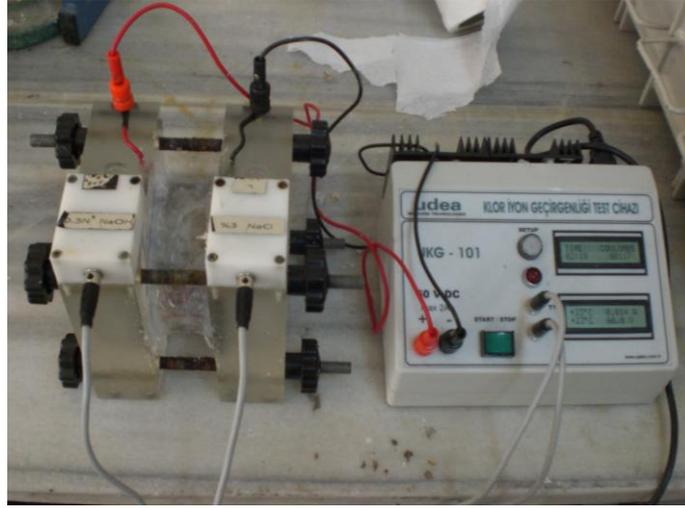
Kimyasal Bileşim (%)			
Bileşen Adı	Çimento	Silis Dumanı	Filler
SiO <sub>2</sub> Çözünen	22.06	89.72	4.93
Çözünmez kalıntı	0.12	2.19	-
Al <sub>2</sub> O <sub>3</sub>	4.25	0.15	0.82
Fe <sub>2</sub> O <sub>3</sub>	0.20	0.12	0.58
CaO	65.39	1.09	51.97
MgO	1.13	0.85	0.58
SO <sub>3</sub>	2.98	4.65	-
Kızdırma Kaybı	2.53	1.79	40.40
Tayin Edilemeyen	1.90	1.27	-
Serbest CaO	1.56	-	-
Na <sub>2</sub> O	0.54	0.21	-
K <sub>2</sub> O	0.55	4.96	-
Fiziksel Özellikler			
Özgül ağırlık	3.11	2.24	2.79
Özgül Yüzey (cm <sup>2</sup> /g)	4400	-	2500
Priz Başlangıcı (dak.)	135	-	-
Priz Sonu (dak.)	160	-	-

Tablo 2. Her seri için beton karışımlarına dahil olan malzeme miktarları

Beton no	Beton kodu	Çimento (kg/m <sup>3</sup> )	Silis dumanı (kg/m <sup>3</sup> )	Filler mal. (kg/m <sup>3</sup> )	Su (kg/m <sup>3</sup> )	s/ç	su / toz mal.	Doğal kum (kg/m <sup>3</sup> )	Kırmataş I (kg/m <sup>3</sup> )	Kırmataş II (kg/m <sup>3</sup> )	Çökme (mm)
1	ŞAHİT	400	-	-	205	0.51	0.51	877	513	341	156
2	SD5	380	20	-	208	0.55	0.52	875	511	342	157
3	SD10	360	40	-	218	0.60	0.54	872	512	340	154
4	SD15	340	60	-	216	0.64	0.54	879	511	345	159
5	F5	380	-	20	211	0.55	0.52	875	513	344	156
6	F10	360	-	40	214	0.59	0.53	876	515	343	158
7	F15	340	-	60	213	0.62	0.53	875	510	342	156

Elastisite modülü deneyleri 15 cm çapında ve 30 cm yüksekliğindeki silindir numuneler üzerinde gerçekleştirilmiştir. Bu deney için hazırlanan silindir numuneler 7, 28, 56 ve 90 gün boyunca su içerisinde kür edilmiş ve her seri için 3 adet numune üzerinde bu deneyler yapılmış ve elde edilen sonuçların ortalamaları alınarak elastisite modülü değerleri belirlenmiştir. Statik elastisite modülü için deney numuneleri basınç dayanım deneyine tabi tutulmadan önce % 70 kükürt ve % 30 grafit tozundan oluşan karışım ile başlanmış ve başlanmış. Daha sonra TS 3502 (1981) ve ASTM C 469 (1994)'a göre başlangıç ve sınır yükleri bulunarak numune sınır yüküne kadar yüklenip deformasyon çerçevesinin üzerindeki "birim kısalma ölçer" göstergesinin hareket edip etmediği gözlemlenmiştir. Başlangıç ve sınır yükleri 10 parçaya bölünerek başlangıç yükünden sınır yüküne kadar her parçadaki kısalma değerleri okunmuştur. Bu çalışmada başlangıç yükü 5000 kg, sınır yükü numunelerin basınç dayanımının % 40'ı olarak alınmıştır. Elde edilen sonuçlar ilgili standartlara göre değerlendirilerek numunelerin statik elastisite modülü değerleri belirlenmiştir.

Silis dumanı ve filler ikameli numunelerin dayanıklılık özelliklerinden birisi olarak klorür geçirgenlik özellikleri ASTM C 1202-97 (1997) standardı referans alınarak gerçekleştirilmiştir. Bu amaçla 10 cm çapında ve 20 cm yüksekliğinde üretilen silindirik numuneler 28 gün boyunca su içerisinde kür edildikten sonra 90. güne kadar açık havada bırakılmış ve 90. günde uçlarından kesilerek ortada kalan 5 cm kalınlığındaki dilim deney için kullanılmıştır. Bu dilim, hızlı klorür geçirgenliği deney aletine yerleştirilmeden önce bazı işlemlerden geçirilmiştir. Deneye başlanmadan önce deney numunelerinin yan yüzleri silikonla kaplanıp kurumaya bırakılmıştır. Daha sonra numuneler desikatöre yerleştirilerek 3 saat boyunca vakumlanmıştır. Ardından vakum haznesine su doldurularak numunelere vakum etkisinde 1 saat su emdirilmiştir. Deney numuneleri, ayrıca su içerisinde 18 saat bekletildikten sonra deney hazır hale getirilmiştir.



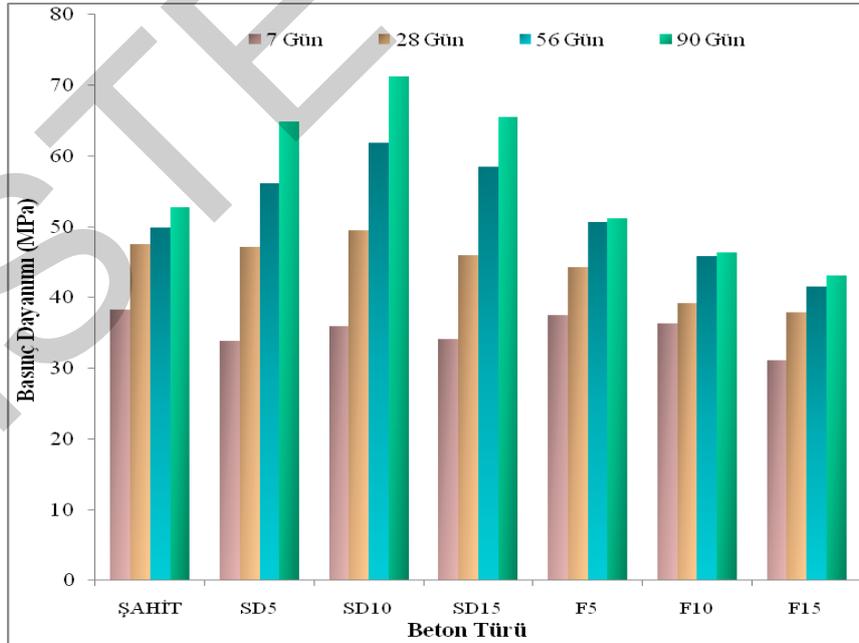
Şekil 1. Hızlı klor iyon geçirgenliği test cihazı

Hızlı klor iyon geçirgenliği test cihazı Şekil 1’de görüldüğü üzere elektronik ölçüm ve değerlendirme ünitesi ile pleksiglastan üretilmiş iki adet hücreden oluşmaktadır. 100 mm çapında ve 51 mm boyundaki deney numuneleri deney hücrelerine hücre ile arasında metal elek ve conta olmak üzere düzgün bir şekilde yerleştirilmiş ve test hücresi üzerindeki vidalar iyice sıkıştırılmıştır. Sızıntıları engellemek amacıyla beton ile test hücrelerinin birleştiği bölge silikonla kaplanmıştır. Mevcut iki test hücresinin birine % 3’lük kütleli olarak saf su ile hazırlanmış NaCl solüsyonu, diğerine ise 0,3 N (yine saf su ile) NaOH solüsyonu doldurularak deneye başlanmıştır. Hızlı klor geçirgenliği deneyi, betonun elektriksel iletkenliği esasına dayanmaktadır. Deney numunelerine 60 V sabit potansiyel farkı uygulanarak beton diskten geçen elektrik akım şiddeti miktarı belirli aralıklarla kaydedilmiştir. 6 saat boyunca her yarım saatte numunelerden geçen akım şiddeti ölçüldükten sonra akım şiddeti-zaman grafiği çizilerek grafik altındaki alan yardımıyla bu sürede iletilen elektrik akımı miktarı Coulomb cinsinden hesaplanmıştır.

### 3. DENEYSEL BULGULAR VE TARTIŞMA

#### 3.1. Basınç dayanımı

Silis dumanı ve fillerin çimento ile farklı ikame oranlarında kullanılmasıyla üretilen betonlar üzerinde yapılan 7, 28, 56 ve 90 günlük basınç dayanımı sonuçları Şekil 2’de verilmiştir.



Şekil 2. Üretilen betonların 7, 28, 56 ve 90 günlük basınç dayanımı sonuçları

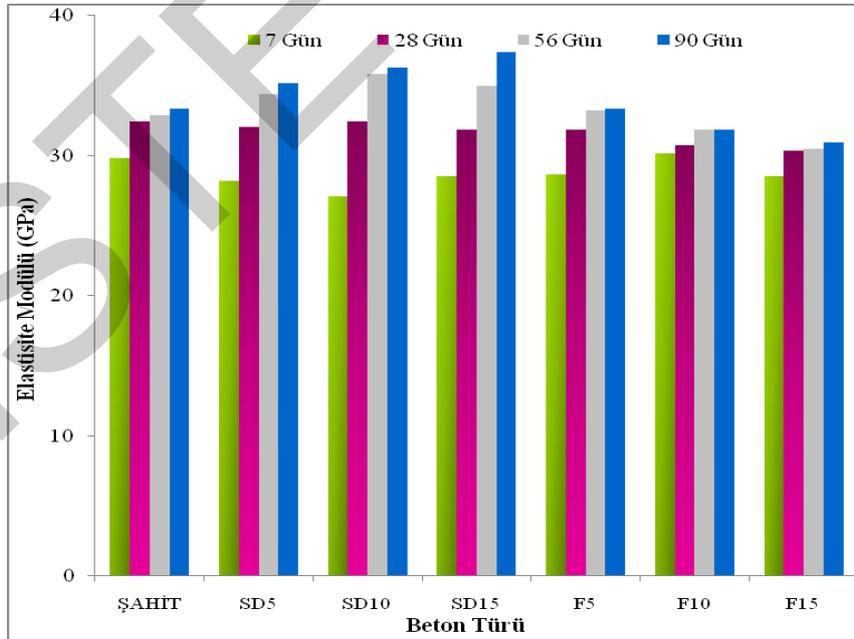
Beton numuneleri içerisinde 7 günlük en yüksek dayanım değerini şahit beton vermiş 28 günlük betonlar içerisinde ise silis dumanının çimento ile %10 ikame oranında kullanılmasıyla üretilen karışım vermiştir. Bu karışım şahit betona göre % 3.97 daha yüksek basınç dayanımı değeri vermiştir. Silis dumanının çimento ile %10 ikame oranında kullanılmasıyla üretilen karışımın 56. günde en yüksek basınç dayanımı değeri elde edilmiş iken bu karışım şahit betona kıyasla % 19.47 daha yüksek

basınç dayanımı değeri vermiştir. 90 günlük numuneler içerisinde en yüksek basınç dayanımı silis dumanının çimento ile % 10 oranında ikame edilmesiyle üretilen karışımdan elde edilmiştir. Bu karışım şahit betona kıyasla %25 daha fazla dayanım değeri vermiştir. Şahit beton karışımının 7 günlük erken dayanım özelliklerinin silis dumanı ve filler içeren karışımlara göre daha iyi olması, erken yaşlarda puzolanik reaksiyonların yavaş olması nedeniyle puzolanik etkinin dayanıma olumlu bir katkı yapamamasına bağlanabilir. Silis dumanı içeren karışımların ileri yaş dayanımlarının şahit betona göre yüksek olmasının nedeni olarak silis dumanının puzolanik özellik gösteren bir mineral katkı maddesi olmasından ötürü zaman içerisinde puzolanik reaksiyonlar sayesinde çimentonun bünyesinde bulunan serbest kireci bağlayarak yani kalsiyum hidroksitle reaksiyona girerek yeni kalsiyum-silikat-hidrate bağlayıcı jellerini oluşturması, bu durumun da çimento-agrega ara yüzey bölgesini kuvvetlendirmesi gösterilebilir. Dolayısıyla, silis dumanı içeriği nedeniyle arayüzey bölgesi kuvvetlenen betonların basınç dayanımları şahit betona göre daha yüksek olmaktadır.

Filler malzemenin puzolanik etki göstermemesine ve çimento ile ikame edilmeleri sonucu toplam bağlayıcı madde miktarını azaltmasına rağmen %10 ikame oranına kadar kullanılması durumunda şahit betona yakın basınç dayanımı değerleri vermesi bu malzemenin, boşluk doldurma etkisine ve ayrıca inert katkı ve ultra ince taneli malzeme olarak hidrasyon için uygun çekirdeklenme meydana getirmesine ve bu sayede hidrasyona katalizör etkisi sağlamasından kaynaklanmaktadır. Diğer bir ifadeyle, filler malzemenin düşük ikame oranlarında kullanılması sonucu basınç dayanımını artırmaları, filler malzeme tanelerinin CH kristallerinin çekirdeklenme bölgeleri olarak davranmasına bağlanabilir (Kelham 1998;Erdogdu 2002). Bir başka faktör de filler malzemenin bir kısmının hidrasyonun silika fazı esnasında C-S-H jeliyle birleşmesi neticesinde karbone hidrat kalsiyum silikat bileşimlerini oluşturarak dayanıma olumlu katkı sağlamasıdır (Rahhal vd. 2005; Felekoglu vd. 2003). Filler malzemeler içerisinde kalker tozu, çimentonun C<sub>3</sub>A fazı ile reaksiyona girerek monokarboalüminat formasyonu oluşturmaktadır. Böylece, kısmen etrenjit rolü üstlenerek erken dayanım artışı sağlamaktadır (Turker 2004).

### 3.2. Elastisite modülü

Silis dumanı ve filler ikameli numuneler üzerinde yapılan elastisite modülü deneyi sonucunda elde edilen değerler Şekil 3'te görülmektedir. Deney sonuçları değerlendirildiğinde 7 günlük numuneler içinde en yüksek elastisite modülü değerini filler malzemenin çimento ile %10 oranında ikame edilmesiyle üretilen karışım, en düşük elastisite modülü değerini ise silis dumanının çimento ile % 10 oranında ikame edilmesiyle üretilen karışım vermiştir. Silis dumanının çimento ile % 10 oranında ikame edilmesiyle üretilen karışımdan 28. ve 56. günde en yüksek elastisite modülü değerleri elde edilmiş iken filler malzemenin çimento ile % 15 oranında ikame edilmesiyle üretilen karışımdan ise 28. ve 56. günde en düşük elastisite modülü değerleri elde edilmiştir. 90 günlük numuneler içinde silis dumanının çimento ile % 15 oranında ikame edilmesiyle üretilen karışım en yüksek elastisite modülü değerini vermiş iken, filler malzemenin çimento ile % 15 oranında ikame edilmesiyle üretilen karışım ise en düşük elastisite modülü değeri vermiştir. Bu sonuçlar ışığında silis dumanı ve filler malzemenin çimento ile ikame oranının artması elastisite modülü değerlerinde kısmi düşümlere neden olmuştur. Silis dumanı içeren karışımların 28, 56 ve 90 günlük elastisite modülü değerlerinin şahit betona göre daha yüksek olmasının nedeni olarak silis dumanının puzolanik etkisi nedeniyle artan basınç dayanımının elastisite modülünü de artırmasına bağlanabilir.



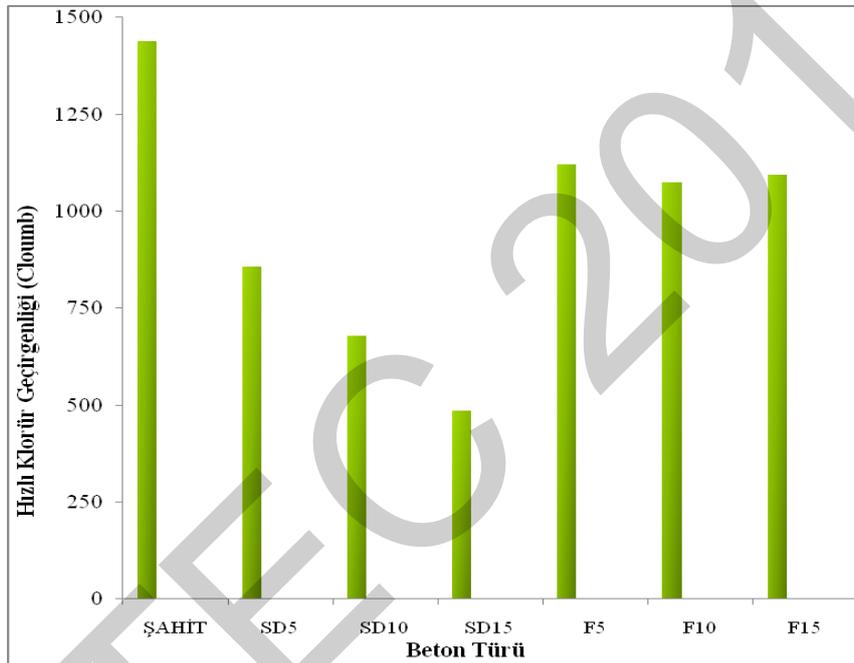
Şekil 3. Üretilen betonların 7, 28, 56 ve 90 günlük elastisite modülü deney sonuçları

### 3.3. Hızlı klorür geçirgenliği deneyi

Farklı karışımlarda hazırlanan silis dumanı ve filler malzeme ikameli deney numuneleri üzerinde 90. günde ASTM C1202 standardı referans alınarak yapılan hızlı klorür geçirgenliği deneyleri sonucunda beton üretiminde mineral katkı kullanımının betonun klorür geçirgenliği değerlerini düşürdüğü görülmüştür. Tüm karışımlar içerisinde en düşük klorür geçirgenliği

değerini silis dumanının çimento ile % 15 oranında ikame edilmesiyle elde edilen karışım vermiştir ve bu değer ASTM C1202 (1997) standardına göre çok düşük boyutlardadır. Bu karışım aynı zamanda şahit betona göre % 66.18 daha az klorür geçirgenliği değeri vermiştir. Silis dumanı ikame edilerek üretilen karışımlar şahit betonla kıyaslandığında daha düşük klorür geçirgenlik değerleri vermiştir. Yine aynı şekilde, silis dumanının çimento ile ikame oranı arttıkça Şekil 4'te görüleceği üzere klorür geçirgenliği değerlerinde azalma görülmüştür. Karışımlar içerisinde filler malzemeler kullanılarak üretilen betonlar şahit betona kıyasla daha düşük klorür geçirgenliği değerleri vermiştir. Tüm karışımlar içerisinde en yüksek klorür geçirgenliği değerini ise şahit beton karışımı vermiştir.

Betonda klorür geçirgenliği öncelikle betonun bünyesinde bulunan boşluk sistemi ile ilgilidir. Daha az boşluk içeren, mikroyapısı daha sıkı olan ve boşlukları birbiriyle sürekli olmayan beton daha az iyon yükü ileterek daha düşük klorür geçirgenliği değeri vermektedir. Bu yaklaşımla silis dumanı ikameli betonların gerek mikro yapılarının oldukça sıkı olması ve gerekse bünyelerinde çok az boşluk içerip bu boşlukların sürekli olmaması nedeniyle klorür geçirgenliği değerlerinin düşük olduğu aşikardır. Özellikle silis dumanı betonda puzolanik etki meydana getirerek ve betonun bünyesindeki boşlukları doldurarak çok düşük klorür geçirgenliği değerlerinin elde edilmesine olanak tanımıştır. Karışımlar içerisinde şahit beton, diğer karışımlara göre daha fazla bağlayıcı içermesine rağmen, klorür geçirgenliği deneyinde filler ve puzolanik etkinin daha fazla önem taşıması nedeniyle, daha yüksek klorür geçirgenliği değeri verdiği görülmüştür. Filler malzemeler içeren karışımlar ise çok daha az bağlayıcı içermelerine rağmen betonun bünyesindeki boşlukları doldurarak şahit betona kıyasla daha düşük klorür geçirgenliği değeri verdiği anlaşılmıştır.



Şekil 4. Üretilen betonların hızlı klorür geçirgenliği deney sonuçları

#### 4. SONUÇLAR

Yapılan deneysel çalışmadan elde edilen sonuçlar aşağıdaki gibi özetlenebilir;

- Basınç dayanımı sonuçları değerlendirildiğinde silis dumanının çimento ile ikame oranı arttıkça her yaş grubunda basınç dayanımında artışlar meydana gelmiştir. Ayrıca, filler malzemenin puzolanik etki göstermemesine ve çimento ile ikame edilmesi sonucu toplam bağlayıcı madde miktarını azaltmasına rağmen %10 ikame oranına kadar kullanılması durumunda şahit betona yakın basınç dayanımı değerleri vermiştir.
- Silis dumanı ve filler malzemenin çimento ile ikame oranının artması elastisite modülü değerlerinde kısmi düşüslere neden olmuştur. Silis dumanı içeren karışımların 28, 56 ve 90 günlük elastisite modülü değerlerinin şahit betona göre daha yüksek olmasının nedeni olarak silis dumanının puzolanik etkisi nedeniyle artan basınç dayanımının elastisite modülünü de artırmaya bağlanabilir.
- Silis dumanı ve filler malzeme ikameli deney numuneleri üzerinde 90. günde ASTM C1202 standardı referans alınarak yapılan hızlı klorür geçirgenliği deneyleri sonucunda beton üretiminde mineral katkı kullanımının betonun klorür geçirgenliği değerlerini düşürdüğü görülmüştür. Ayrıca, silis dumanının çimento ile ikame oranı arttıkça klorür geçirgenliği değerlerinde azalma görülmüştür. Ancak, filler malzemenin çimento ile ikame oranı arttıkça klorür geçirgenliği değerleri düşmekle beraber bu durum hissedilir boyutlarda değildir.

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# SIMULATION AND OPTIMIZATION OF ETHYL ACETATE REACTIVE PACKED DISTILLATION PROCESS USING ASPEN HYSYS

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## ABSTRACT

The simulations and optimizations of a reactive packed distillation process for the production of ethyl acetate, water being the by-product, from the esterification reaction between acetic acid and ethanol has been carried out in this work using Aspen HYSYS 3.2 process simulator. The main column, apart from the condenser and the reboiler, was divided into five sections: rectification, acetic acid feed, reaction, ethanol feed and stripping sections. In the simulations, Non-Random Two-Liquid model was used as the fluid package and the reaction occurring in the reaction section of the column was modeled as an equilibrium one. In order to validate the results of the simulator, experiments were carried out in a reactive packed distillation pilot plant. The data input and output of the experiments were done with the aid of MATLAB/Simulink via electronic modules. The results of Aspen HYSYS simulations were compared with those obtained from the experimental studies.

**Keywords:** Reactive packed distillation; Esterification reaction; Aspen HYSYS; Simulation; MATLAB/Simulink.

## INTRODUCTION

In recent years, integrated reactive separation processes have attracted considerable attentions in academic research and industrial applications, (Völker, Sonntag, and Engell 2007). One of these processes which is known as “reactive distillation” is potentially attractive whenever conversion is limited by reaction equilibrium (Balasubramhanya and Doyle III, 2000).

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It has a lot of advantages for those reactions occurring at temperatures and pressures suitable for the distillation of the resulting components. Its main advantages are derived from the elimination of equipment and the constant removal of products (Sneesby, Tade, Datta, and Smith 1997). It is known that increased overall conversion can be achieved in equilibrium reactions if the products are continuously removed from the reaction zones. Its other advantages include reduced investment and operating costs, environmental impacts (Pérez-Correa, González, and Alvarez 2008), higher conversion, improved selectivity, lower energy consumption, scope for difficult separations and avoidance of azeotropes (Jana and Adari, 2009).

However, due to the occurrence of both reaction and separation in a single unit, reactive distillation exhibits complex behaviors (Khaledi and Young, 2005) such as steady state multiplicity, process gain sign changes (bidirectionality) and strong interactions between process variables (Jana and Adari 2009). These complexities have made the modeling of the process extremely difficult especially when the column type is a packed one and/or the reaction is solid-catalyzed. Thus, the representation of this process in the form of a model is still a challenge to chemical engineers because the reactive distillation process, especially one involving continuous flows of feeds, is never truly at steady state. Feed and environmental disturbances, reboiler fouling and catalytic degradation continuously upset the conditions of the smooth running of the process. One approach discovered for the representation of a process with these kinds of behaviors is the use of Aspen HYSYS process simulator.

Aspen HYSYS is a process simulation environment designed to serve many processing industries. It is an interactive, intuitive, open and extensible program. It also has many add-on options to extend its capabilities into specific industries. With this program, rigorous steady state and dynamic models for plant design can be created. Apart from this, monitoring, troubleshooting, operational improvement, business planning and asset management can be performed with the process simulator. Through the completely interactive HYSYS interface, process variables and unit operation topology can be easily manipulated (Aspen, 2003).

Therefore, this paper is aimed to develop, simulate, optimize and validate, using experimental studies, an esterification process for the production of ethyl acetate using reactive packed distillation column with the aid of Aspen HYSYS.

## PROCEDURES

### Experimental Procedure

The experimental pilot plant in which the experiments were carried out was a reactive packed distillation column (RPDC) set up as shown in Figures 1a and b. The column had, excluding the condenser and the reboiler, a height of 1.5 m and a diameter of 0.05 m. The column consisted of a cylindrical condenser of diameter and height of 5 and 22.5 cm respectively. The main column section of the plant was divided into three subsections of 0.5 m each. The upper, middle and lower sections were the rectifying, the reaction and the stripping sections respectively. The rectifying and the stripping sections were packed with Raschig rings while the reaction section was filled with Amberlyst 15 solid catalyst (the catalyst had a surface area of 5300 m<sup>2</sup>/kg, a total pore volume of 0.4 cc/g and a density of 610 kg/m<sup>3</sup>). The reboiler was spherical in shape and had a volume of 3

Litre. The column was fed with acetic acid at the top (between the rectifying and the reaction sections) while ethanol was fed at the bottom (between the reaction and the stripping sections) with the aid of peristaltic pumps which were operated with the aid of a computer via MATLAB/Simulink program. All the signal inputs (reflux ratio (R), feed ratio (F) and reboiler duty (Q)) to the column and the measured outputs (top segment temperature ( $T_{top}$ ), reaction segment temperature ( $T_{rxn}$ ) and bottom segment temperature ( $T_{bot}$ )) from the column were sent and recorded respectively on-line with the aid of MATLAB/Simulink computer program and electronic input-output (I/O) modules that were connected to the equipment and the computer system. At each case of the experimental studies, the operating parameters were fixed based on the conditions being studied. The esterification reaction taking place in the column is given as:

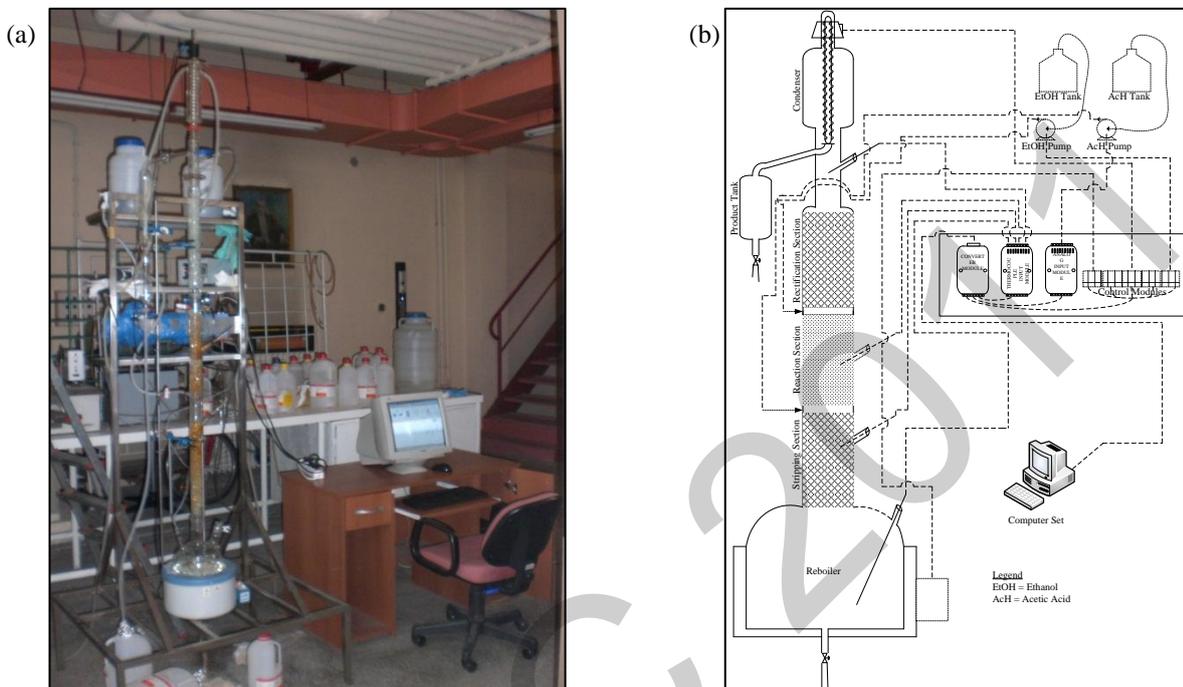
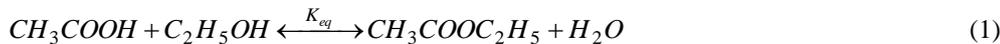


Figure 1 Reactive packed distillation pilot plant: (a) Pictorial view; (b) Sketch view

**HYSYS Modeling Procedure**

Figure 2 below shows the flowsheet of a reactive packed distillation column built and modeled in HYSYS 3.2 environment. The column consisted of a condenser, a rectifying section, an acetic acid feed section, a reaction section, an ethanol feed section, a stripping section and a reboiler. The operating parameters used for the HYSYS model formulation and steady state simulation are as shown in Table 1.

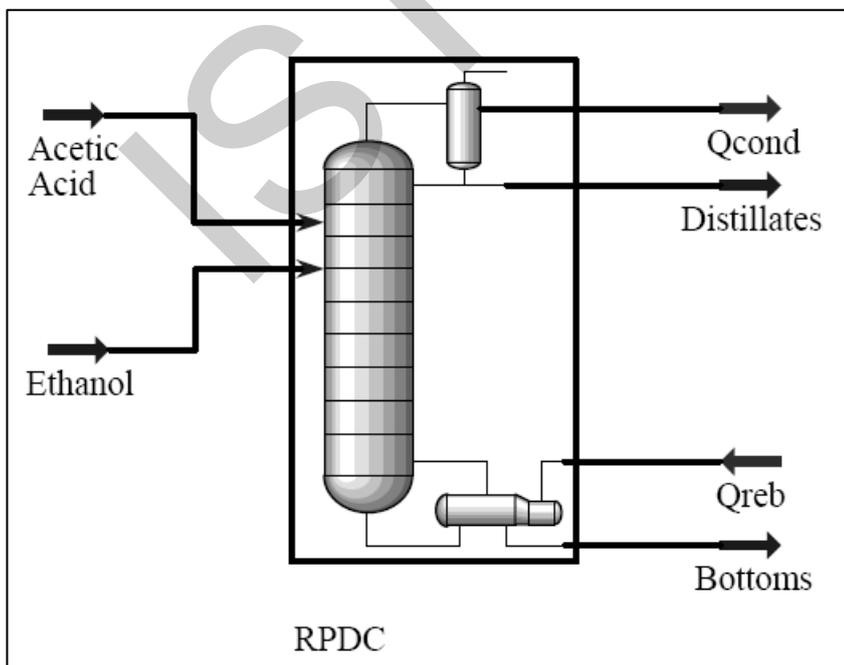


Figure 2 Aspen HYSYS reactive packed distillation steady state simulation flowsheet

Table 1 Simulation operating parameters

Parameter	Value
Fluid Package	General NRTL
Reflux ratio (kmol s <sup>-1</sup> recycled liquid/kmol s <sup>-1</sup> liquid distillate)	1
Feed ratio (mL s <sup>-1</sup> acetic acid feed/mL s <sup>-1</sup> ethanol feed)	1
Reboiler duty (kJ/s)	0.250
<b>Condenser Section</b>	
Type	Cylindrical
Height (m)	0.225
Diameter (m)	0.05
<b>Rectifying Section</b>	
Packing type	Raschig rings
Height (m)	0.4412
<b>Acetic Acid Feed Section</b>	
Packing type	Raschig rings
Height (m)	0.0882
<b>Reaction Section</b>	
Packing type	Amberlyst 15
Height (m)	0.4412
<b>Ethanol Feed Section</b>	
Packing type	Raschig rings
Height (m)	0.0882
<b>Stripping Section</b>	
Packing type	Raschig rings
Height (m)	0.4412
<b>Reboiler Section</b>	
Type	Spherical
Volume (L)	3
Level	50%

**HYSYS Optimization Procedure**

After the steady state simulation, the optimization of the plant was carried using the same HYSYS 3.2 process simulator by incorporating an optimizer into the flowsheet (see Figure 3). Three different algorithms were used for the optimization; they are: Fletcher-Reeves, Quasi-Newton and Successive Quadratic Programming (SQP) algorithms. The objective function of the optimization was chosen to be the maximization of the mole fraction of ethyl acetate in the top segment stream. The ranges of the adjusted variables used for the optimizations are as shown in Table 2 below.

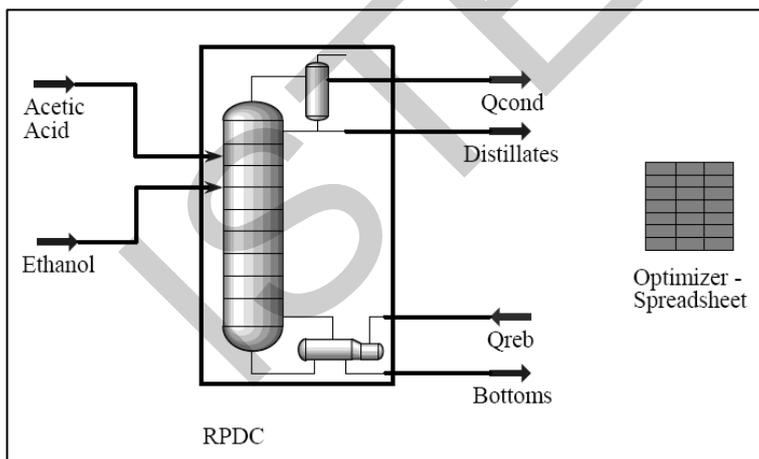


Figure 3 Aspen HYSYS reactive packed distillation optimization flowsheet

Table 2 Parameters used for running the optimizations

Parameter	Low bound	High bound
Reflux ratio (kmol s <sup>-1</sup> recycled liquid/kmol s <sup>-1</sup> liquid distillate)	1	9
Feed ratio (mL s <sup>-1</sup> acetic acid feed/mL s <sup>-1</sup> ethanol feed)	0.5	5
Reboiler duty (kJ/s)	0.050	0.600

After running the HYSYS optimizer, the optimized values of the parameters obtained from one of the algorithms (SQP) were used to run the experimental set-up again for validation.

## RESULTS AND DISCUSSIONS

To simulate and optimize a reactive packed distillation process for the production of ethyl acetate using Aspen HYSYS 3.2 in this work, the entire process column was divided into 17 segments excluding the condenser and the reboiler and its steady state study was carried out by simulating the prototype plant built using the simulator under the conditions of a reflux ratio of 1, a feed ratio of 1 and a reboiler duty of 0.250 kJ/s. The other parameters used for the simulation can be found in Table 1. After the simulation, the temperature and composition profiles obtained are as shown in Figures 4 and 5 respectively.

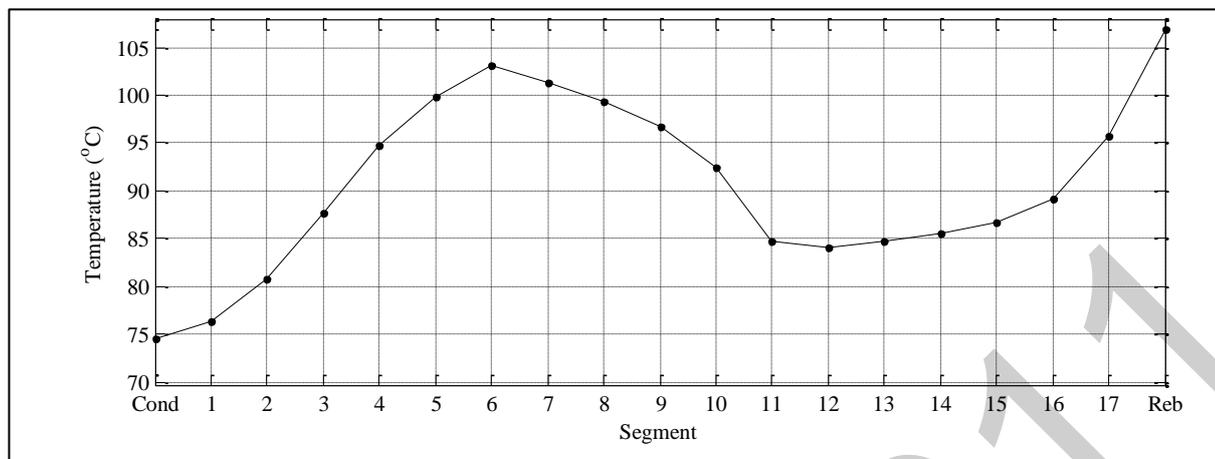


Figure 4 Aspen HYSYS reactive packed distillation column steady state simulation temperature profile (Legend: Cond = Condenser; Reb = Reboiler)

As can be seen from the temperature profile shown in Figure 4, the temperature of the segment near the acetic acid feed section was found to be very high. This was due to the combined effects of the exothermic nature of the reaction occurring in the reaction section of the column, the upward movement of ethanol vapor from the ethanol feed section and the mixed vapor moving upward from the liquid mixture in the reboiler.

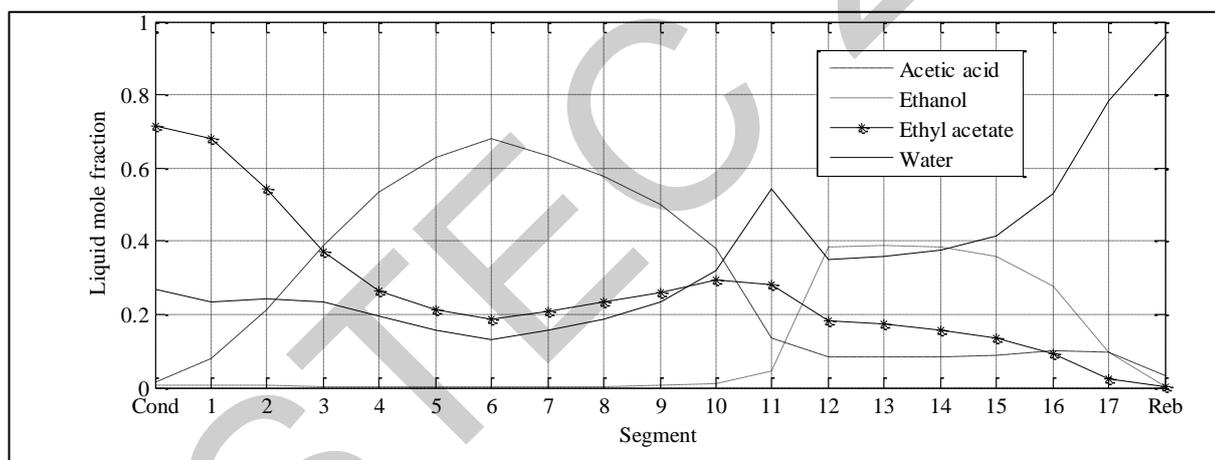


Figure 5 Aspen HYSYS reactive packed distillation column steady state simulation composition profiles (Legend: Cond = Condenser; Reb = Reboiler)

From the composition profile shown in Figure 5, ethyl acetate (the desired product), as expected, was found to have the highest mole fraction of 0.7132 in the top segment of the column followed by water with a mole fraction value of 0.2665. The mole fractions of the other two components (acetic acid, 0.0141 and ethanol, 0.0062), as expected, were found to be very low in the top segment. This was an indication that effective reaction conversion and separation were achieved in the column.

Considering the mole fractions of the various components in the reboiler, water was found to have the highest mole fraction of 0.9597 followed by acetic acid with a mole fraction of 0.0332. The mole fractions of ethanol and ethyl acetate in the reboiler were estimated with the Aspen HYSYS to be 0.0043 and 0.0028 respectively. The very small values of the mole fractions of acetic acid and ethanol in the reboiler were due to high reaction conversion occurring in the column.

When the experimental set-up was run using the same parameters as those used for the HYSYS simulation, taking the top segment temperature as the point of interest to infer the composition of the top segment mixture because it is the one indicating the state and kind of the product obtained from the process, a good relationship was observed from the results of the two (HYSYS simulation and experimental study) cases. For instance, as can be seen from Table 3, the steady state top segment temperature obtained from HYSYS simulation was 74.5338 °C while that of the experimental study was measured to be 74.6600 °C. The percentage error between the results which was calculated to be 0.1690% was found to be very favorable. This is an indication of the fact that the developed HYSYS model for the process is a good representation of the real process.

Table 3 Comparison between Aspen HYSYS simulated top segment temperature and the experimental one

Description	Value
Simulated top segment temperature (°C)	74.5338
Experimental top segment temperature (°C)	74.6600
Absolute residual (°C)	0.1262
Percentage absolute residual (%)	0.1690

Having carried out the steady state simulation of the Aspen HYSYS RPDC and validated using an experimental study, the process was optimized using three different optimization algorithms. As mentioned before, the maximization of the mole fraction of ethyl acetate in the column top segment was set as the objective function of each of the optimizations. The results obtained from the optimizations of the process are as shown in Table 4 below.

Table 4 Optimum parameters

Parameter	Value			
	Steady-State	Fletcher-Reeves	Quasi-Newton	SQP
Reflux ratio (kmol s <sup>-1</sup> recycle/ kmol s <sup>-1</sup> distillate)	1.0000	2.8995	3.0881	2.6103
Feed ratio (mL s <sup>-1</sup> acetic acid/mL s <sup>-1</sup> ethanol)	1.0000	3.3251	3.4565	2.0011
Reboiler duty (kJ/s)	0.2500	0.1076	0.0951	0.1070
Objective function (Top ethyl acetate mole fraction)	0.7132	0.7628	0.7624	0.7608
Top segment temperature (°C)	74.5338	74.3335	74.3356	74.3260

It can be observed from the results shown in Table 4 that the increase, as a result of the maximization, in the mole fraction of ethyl acetate in the column top segment has resulted in a decrease in the top segment temperature. Also, as can be seen from the table, among the three algorithms used for the optimization of the process, Fletcher-Reeves algorithm was found to give the highest mole fraction of ethyl acetate in the top segment of the column by maximizing the objective function from the steady state simulation value of 0.7132 to 0.7628. Quasi-Newton algorithm yielded a very close value (0.7624) of ethyl acetate mole fraction to that of the Fletcher-Reeves algorithm. The optimized ethyl acetate mole fraction (0.7608) gave by SQP algorithm was also found not to be too different beyond acceptance from those of the other two algorithms. The differences in the objective functions given by the three algorithms were accounted for by the differences in the optimum operating conditions given by each of them. For instance, the optimum reflux ratio obtained from the three algorithms could be approximated to one significant figure of 3. However, the situation was not the same in the case of the feed ratio because the approximations to one significant figure of each of the feed ratios obtained from Fletcher-Reeves and Quasi-Newton algorithms were both 3 while that of the SQP was 2. Considering the optimum reboiler duty, the values given by Fletcher-Reeves and SQP algorithms were found to be very close to each other than when each of them was compared to the result given by Quasi-Newton.

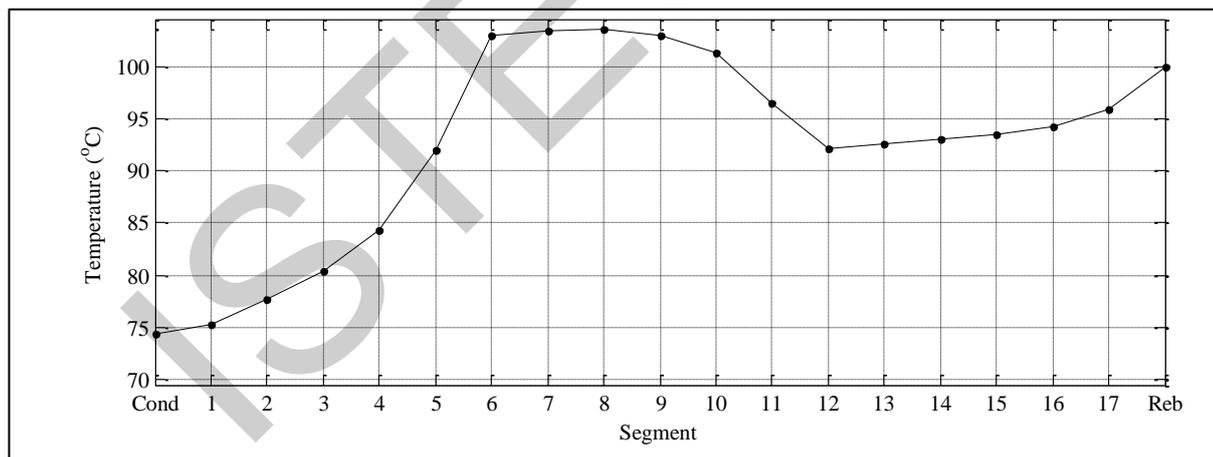


Figure 6 Aspen HYSYS reactive packed distillation column optimization temperature profile

From the temperature and composition profiles of the optimized case of the process shown in Figures 6 and 7 respectively, it was noticed that there were changes between the profiles and those of the steady-state simulation shown in Figures 4 and 5. That is to say that, while trying to maximize the composition of the ethyl acetate in the top segment stream, the changes that occurred in the composition profiles of the components have caused a change in the temperature profile also. The occurrence of the change in the temperature profile owing to the changes in the composition profiles of the components is an indication of the fact that the composition and the temperature of the mixtures present in the column segments are dependent on each other. In other words, column segment composition is a function of column segment temperature and vice versa.

Furthermore, an experiment was carried out for the validation of the optimization using the optimum operating conditions obtained from one of the algorithms. In this case, the optimum operating conditions of SQP were used because the value of its objective function was discovered to be close to those of the other two algorithms and it had the lowest feed ratio among the three. Choosing it (SQP) was considered as an effort to reduce the cost of production.

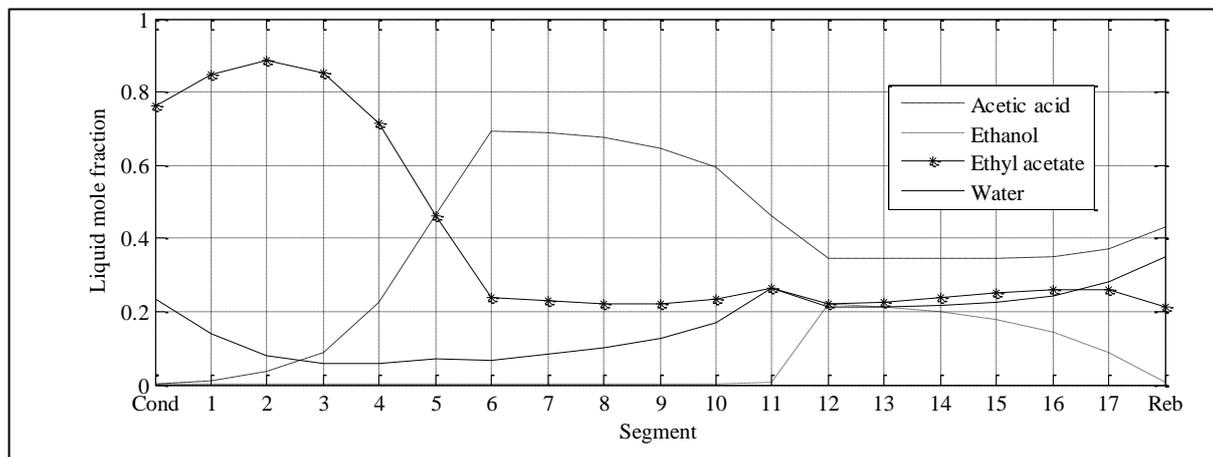


Figure 7 Aspen HYSYS reactive packed distillation column optimization composition profiles

After the experiment was carried out using the selected optimum operating conditions, it was discovered from the results that there was a good conformity between the optimized top segment temperature of the process using HYSYS 3.2 and the experimental one because, as can be seen in Table 5, the Aspen HYSYS and the experimental optimized top segment temperature values were 74.3260 °C and 74.5200 °C respectively.

Table 5 Comparison between SQP optimized top segment temperature and the experimental one

Description	Value
Simulated top segment temperature (°C)	74.3260
Experimental top segment temperature (°C)	74.5200
Absolute residual (°C)	0.1940
Percentage absolute residual (%)	0.2603

In addition, as also shown in Table 5, the percentage error which was also calculated in this case to be 0.2603% was found to be low enough for a good model.

## CONCLUSIONS

The good relationship between the temperature estimated from the simulation using the developed Aspen HYSYS model for the reactive packed distillation process and the experimental ones measured from the pilot plant have revealed that Aspen HYSYS can be used to represent and simulate the process successfully. In addition, the three optimization algorithms investigated were found to produce relatively similar maximized mole fractions of ethyl acetate in the top segment of the column. When the optimum parameters of SQP were used to run an experiment for validation, a good agreement was found between the optimum top segment temperature and the experimental one.

## ACKNOWLEDGEMENTS

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# SMALL ROV TO DETECTION AND IDENTIFICATION OF DANGEROUS UNDERWATER OBJECTS

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## ABSTRACT

A small unmanned underwater vehicle (UUV) to inspection of an undersea space is presented in the paper. Its behavior is controlled by a trained pilot. Correct detection and identification of targets depends on vehicle's precise displacement along a predefined route. Nowadays, the UUVs are equipped with an automatic control system to execute some basic maneuvers without constant human interventions. Hence, in the paper, an autopilot assuring an appropriate vehicle's movement is described. Selected results of computer simulations illustrating a quality of the underwater mission are inserted.

**Keywords:** - underwater vehicle, autopilot, modelling, simulation.

## 1. INTRODUCTION

A described system to detection and identification of dangerous objects located in the underwater space is a floating platform designed and built basis on a special kind of the UUV, called remotely operated vehicle (ROV). It is equipped with a comprehensive set of devices and sensors to achieve a high quality of operational work. The set mounted on the vehicle's body consists of: lamps and TV cameras, a scanning sonar, an inertial navigation unit, a doppler velocity log, a transponder/responder for hydroacoustic navigation and a manipulator (see Fig. 1).

The ROV operates in crab-wise manner in four degrees of freedom (DOF) with small roll and pitch angles that can be neglected during normal operations. Its behaviour is controlled by a trained pilot located on a board of the mother-ship or an offshore structure. A typical mission of detection and identification of dangerous objects consists of two phase. The first one, called a transition phase, is a displacement to a target area from a launch point. During the second phase, called detection phase, a searched object is found by the pilot. A pilot's work is supported by a computer which provides required information, integrating sonar and cameras images with data from a navigation system and other sensors (see Fig. 2 and Fig. 3).

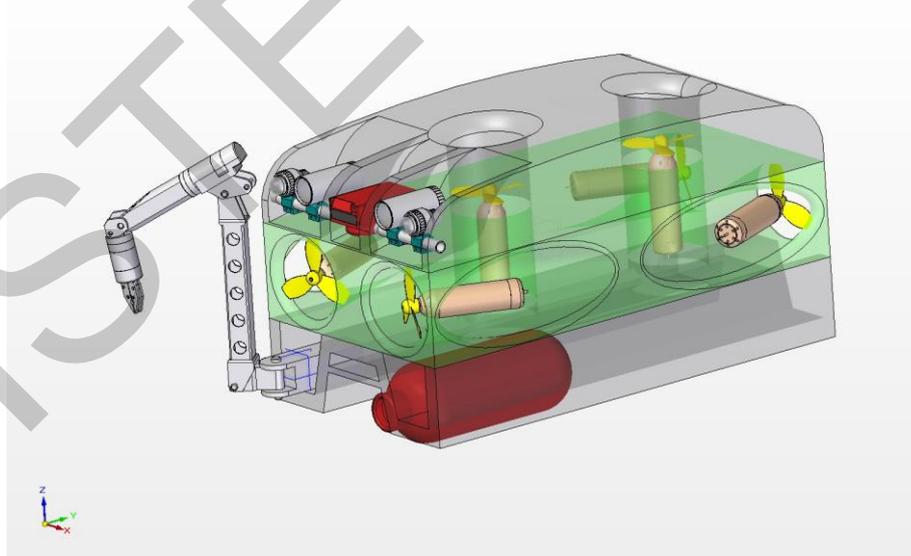


Figure 1. Virtual vision of ROV.

To execute some basic manoeuvres without a constant pilot's supervision, contemporary ROVs are often and often equipped with an automatic control system. An interesting review of classical and modern techniques useful to steering of the UUVs vehicles has been provided in Craven *et al.*, 1998. Automatic control of such underwater apparatus is a difficult problem due to their nonlinear dynamics. Moreover, the dynamics can change according to the alteration of configuration to be suited to the mission. Hence, an autopilot, responsible for keeping desired positions and orientations of the ROV during the transition phase, should be flexible and self-adapting to varying motion conditions.

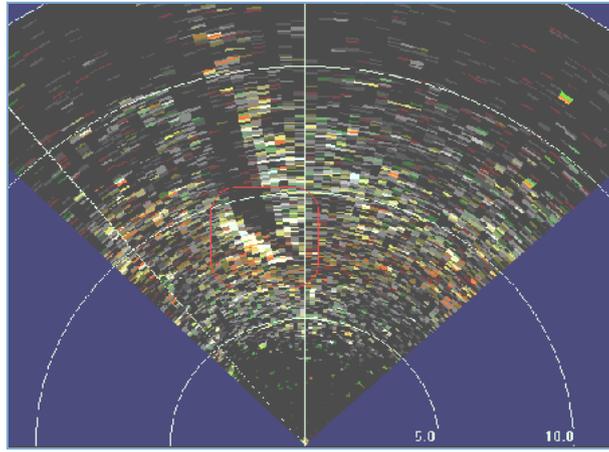


Figure 2. Screen display with sonar image.

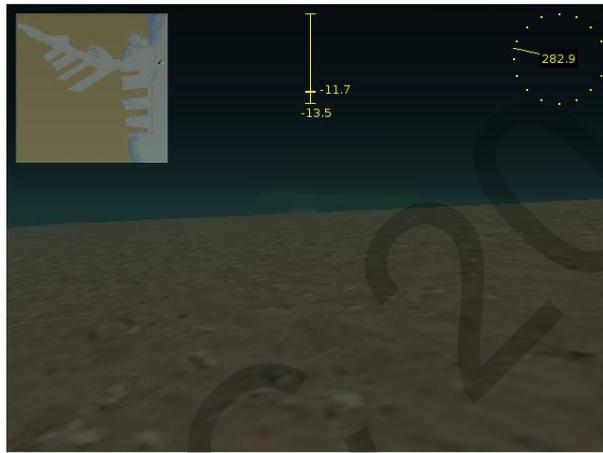


Figure 3. Screen display with TV image and navigation data.

## 2. EQUATIONS OF MOTION

A general motion of the underwater vehicle of six DOFs describes the following vectors (Fossen, 1994; Fossen, 2011) :

$$\begin{aligned} \boldsymbol{\eta} &= [x, y, z, \phi, \theta, \psi]^T \\ \mathbf{v} &= [u, v, w, p, q, r]^T \\ \boldsymbol{\tau} &= [X, Y, Z, K, M, N]^T \end{aligned} \tag{1}$$

where:

- $\boldsymbol{\eta}$  – position and orientation vector in the inertial frame;
- $x, y, z$  – coordinates of position;
- $\phi, \theta, \psi$  – coordinates of orientation (Euler angles);
- $\mathbf{v}$  – linear and angular velocity vector with coordinates in the body-fixed frame;
- $u, v, w$  – linear velocities along longitudinal, transversal and vertical axes;
- $p, q, r$  – angular velocities about longitudinal, transversal and vertical axes;
- $\boldsymbol{\tau}$  – vector of forces and moments acting on the vehicle in the body-fixed frame;
- $X, Y, Z$  – forces along longitudinal, transversal and vertical axes;
- $K, M, N$  – moments about longitudinal, transversal and vertical axes.

Nonlinear dynamical and kinematical equations of motion in the body-fixed frame can be expressed as:

$$\begin{aligned} \mathbf{M}\dot{\mathbf{v}} + \mathbf{C}(\mathbf{v})\mathbf{v} + \mathbf{D}(\mathbf{v})\mathbf{v} + \mathbf{g}(\boldsymbol{\eta}) &= \boldsymbol{\tau} \\ \dot{\boldsymbol{\eta}} &= \mathbf{J}(\boldsymbol{\eta})\mathbf{v} \end{aligned} \tag{2}$$

where:

- M** – inertia matrix (including added mass);
- C(v)** – matrix of Coriolis and centripetal terms (including added mass);
- D(v)** – hydrodynamic damping and lift matrix;
- g(η)** – vector of gravitational forces and moments;
- J(η)** – velocity transformation matrix between the body fixed and the inertial frames.

### 3. ADAPTIVE ALGORITHM OF CONTROL

The algorithm of control worked out basis on a simplified ROV model proposed in Fossen, 1994:

$$\mathbf{M}_d \dot{\mathbf{v}} + \mathbf{D}_d(\mathbf{v})\mathbf{v} = \boldsymbol{\tau} \tag{3}$$

where all kinematics and dynamics cross-coupling terms are neglected, so  $\mathbf{M}_d$  and  $\mathbf{D}_d(\mathbf{v})$  are diagonal matrices. Uncertainties in the above model are compensated by a control system.

The expression (3) for motion in four DOFs, (surge, sway, heave and yaw), takes a form (Garus, 2007):

$$\begin{aligned} m_x \dot{u} + d_x |u|u &= \tau_x \\ m_y \dot{v} + d_y |v|v &= \tau_y \\ m_z \dot{w} + d_z |w|w &= \tau_z \\ m_N \dot{r} + d_N |r|r &= \tau_N \end{aligned} \tag{4}$$

Define the following vectors  $\boldsymbol{\tau} = [\tau_x, \tau_y, \tau_z, \tau_N]^T$  and  $\mathbf{p} = [m_x, d_x, m_y, d_y, m_z, d_z, m_N, d_N]^T$  the expression (4) can be written as:

$$\boldsymbol{\tau} = \mathbf{Y}(\mathbf{v}, \dot{\mathbf{v}})\mathbf{p} \tag{5}$$

where  $\mathbf{Y}(\mathbf{v}, \dot{\mathbf{v}})$  is a known matrix of measured signals, usually referred as the regressor matrix, (for more details see Spong *et al.*, 1998), and has the form:

$$\mathbf{Y}(\mathbf{v}, \dot{\mathbf{v}}) = \begin{bmatrix} \dot{u} & |u|u & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \dot{v} & |v|v & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \dot{w} & |w|w & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \dot{r} & |r|r \end{bmatrix} \tag{6}$$

A structure of the proposed control system is depicted in Fig. 4.

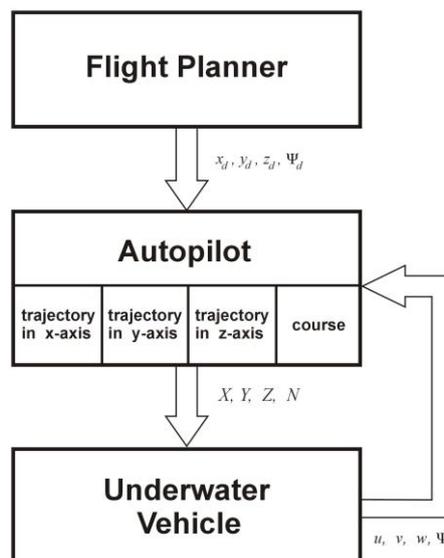


Figure 4. Block diagram showing structure of control system.

#### 4. SIMULATION STUDY

Numerical simulations have been made to confirm validity of the proposed control algorithm under the following assumptions:

1. the ROV can move with varying linear velocities  $u, v, w$  and angular velocity  $r$ ;
2. its velocities  $u, v, w, r$  and coordinates of position  $x, y, z$  and heading  $\psi$  are measurable;
3. the desired route is given by means of set of way-points  $\{(x_{di}, y_{di}, z_{di})\}$ ;
4. segments of the predefined route between two successive way-points are defined as smooth and bounded curves;
5. the command signal  $\tau$  consists of four components:  $\tau_1 = \tau_x = X$ ,  $\tau_2 = \tau_y = Y$ ,  $\tau_3 = \tau_z = Z$  and  $\tau_4 = \tau_N = N$  calculated from the control law (5).

A regulation problem has been examined under interaction of environmental disturbances, i.e. a sea current. To simulate such influence on vehicle's motion its velocity  $V_c$  was assumed to be slowly varying and having a fixed direction. For computer simulations the disturbance was calculated by using the 1<sup>st</sup> order Gauss-Markov process (Song *et al.*, 2003):

$$\dot{V}_c + \mu V_c = \omega \tag{11}$$

where  $\omega$  is a Gaussian white noise,  $\mu \geq 0$  is a constant and  $0 \leq V_c(t) \leq V_{c,max}$ .

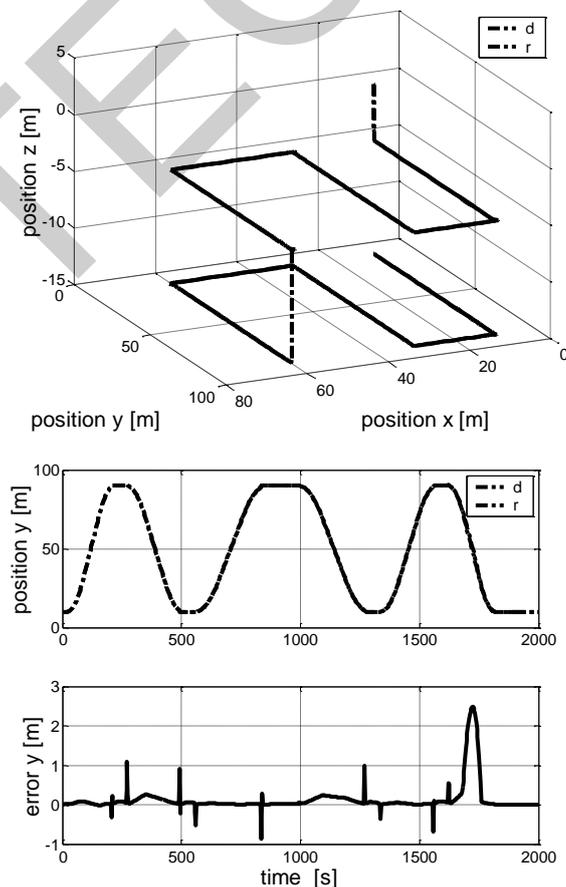
Some results of simulations are depicted in Fig. 5. The case study showed that the proposed adaptive algorithm enhanced good quality of movement along the desired route.

#### 5. CONCLUSIONS

This paper has described the using of the adaptive algorithm for control of positions and orientations of the remotely operated vehicle designed to detection and recognition of dangerous targets in the underwater space.

It can be concluded from the obtained results that the proposed approach provides the automatic control system being robust and having good performance.

Another advantage of the discussed control system is its flexibility with regard to the change of dynamic properties of the ROV according to the alteration of configuration to be suited to the mission.



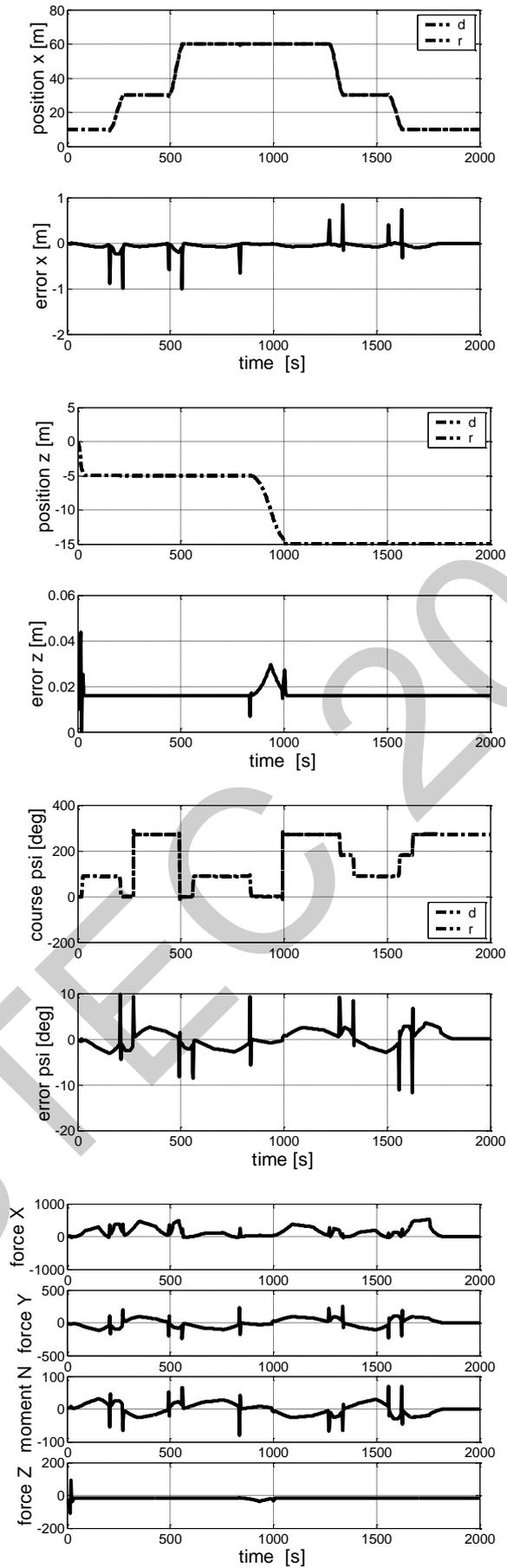


Figure 5. Results of track-keeping control: desired (d) and real (r) path in 3D space (upper plot), x-, y-, z-position and error of position (2<sup>nd</sup> ÷ 4<sup>th</sup> plots), course and error of course (5<sup>th</sup> plot), commands (low plot).

## 6. ACKNOWLEDGMENT

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# SPECIES DISTRIBUTION AND BIODIVERSITY ASSESSMENT OF SEAGRASS AT HAD YONG LUM, HAD CHAO MAI NATIONAL PARK, TRANG PROVINCE, THAILAND

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## Abstract

The Species Distribution and Biodiversity Assessment of Seagrass at Had Yong Lum, Had Chao Mai National Park, Trang Province was investigated during two seasons in 2010 which were dry season in March to April and rainy season in June 2010. Nine species of 6 genera 2 families were reported in both seasons, of which 9 species are *Enhalus acoroides*, *Thalassia hamprichii*, *Halophila ovalis*, *Halophila minor*, *Syringodium isoetifolium*, *Halodule uninervis*, *Halodule pinifolia*, *Cymodocea serrulata* and *Cymodocea rotundata*. The majority found scattered dense seagrass in the middle of the beach. Seagrass that is *Halophila ovalis* spreading most in dry season and *Cymodocea rotundata* are the most in rainy season. And species distribution minimal are *Halophila minor* and *Syringodium isoetifolium* in both season.

When analyzed the index value for biodiversity in dry and rainy season which were species diversity, species richness and species evenness. Species diversity are using the formula of Shannon diversity Index found that area of Had Yong Lum valued biodiversity index for the seagrass are 1.45 and 1.32, which are areas with high biodiversity. When analyzing the value and richness index formula of Margalef's Index found that richness index values are 0.96 and 0.94. And species evenness formula of Pielou's Evenness Index, that found are 0.66 and 0.60. The area from the canal mouth swell Kuan Thung Koo distance is 1.3 kilometers to the richness of seagrass species. It also found that the distribution of seagrass will be distributed according to the characteristics of the soil sediment. The study area are 3 soil characteristics, including a mud-sand soil, soil clay and sandy soil. The seagrass found on a mud-sand soil include *Cymodocea serrulata*, *Thalassia hamprichii*, *Enhalus acoroides*, *Halodule pinifolia*, and *Syringodium isoetifolium*. Soil clay are *Halophila ovalis*, and sandy soil include *Cymodocea rotundata*, *Cymodocea serrulata* and *Enhalus acoroides*.

The water quality were effected to seagrass distribution in dry and rainy season such as Temperature, DO, pH, salinity, transparency and water depth.

## I. INTRODUCTION

Seagrasses, marine flowering plants, are widely distribution along temperate and tropical coastlines of the world. Seagrasses have key ecological roles in coastal ecosystems and can form extensive meadows supporting high biodiversity. The global species diversity of seagrasses is low (< 60 species), but species can have range that extend for thousands of kilometers of coastline (Short et al., 2007).

Seagrasses form a critical marine ecosystem: their role in fisheries production, and in sediment accumulation and stabilization, is well documented (Green and Short, 2003; Larkum et al., 2006), but they contribute to function of ocean ecosystems and have direct value to humanity. Seagrasses are the only submerged marine plants with underground root and rhizome system. The role of roots and rhizomes in binding sediments is highly important, as illustrated in a number of studies that have compared erosion on vegetated versus non-vegetated areas during storm events (Koch et al., 2006). The role of seagrass shoots in this process is also important, as this provides a stable surface layer above the benthos, baffling currents and thereby encouraging the settlement of sediments and inhibiting their resuspension (Short and Short, 1984; Ward et al., 1984)

Seagrasses habitat is critical for a number of threatened species, including sirenians (dugong and manatee), sea turtles and sea horses, all widely perceived to have high cultural, aesthetic or intrinsic values. Other seagrasses functions include the maintenance of genetic variability, with potential biochemical utility, and a possible, though poorly understood, role in supporting resilience of the coastal environment.

Human impacts to seagrasses distribution, diversity and health are profound and occur at several scales, most notably manifesting in the near absence of seagrasses in industrialized ports and other areas of intense human coastal development (Short and Wyllie-Echeverria, 1996; Orth et al., 2006). Seagrasses are being lost rapidly in developed and developing parts of the world (Short et al., 2006), with occasional efforts at mitigation and restoration.

Hat Chao Mai National Park is famous for a variety of organisms and marine resources such as coral reefs, beaches, habitat of dugong and mangrove forests, which are large pieces of seagrasses beds in the country. From a variety of ecosystems and the beautiful scenery in Hat Chao Mai National Park. The attention of tourists to visit a lot and the expansion of tourism activities, sometimes with the invasion area, which has resulted in seagrasses beds have been affected and the degeneracy. The causes, types and biodiversity of seagrasses decline. Therefore, it is essential to study the biodiversity, distribution and environment factors associated with seagrasses in order to management and conservation for the habitat of aquatic animals and sustainable next.

## II. OBJECTIVE

1. To survey species diversity and distribution in Had Yong Lum, Had Jao Mai National Park during the dry and rainy season.
2. To evaluate and compare the seagrasses biodiversity between dry and rainy season.
3. To study and compare the environmental factors affecting the seagrasses biodiversity between dry and rainy season.

### III. METHODS

#### A. Filed Survey

1) Surveyed seagrasses species by line intercept transect technique along Had Yong Lum coastal. Distance between baseline were 100 meter, and between stations were 50 meter. In each station collect data by quadrat (0.5 x 0.5 meter), and 4 repeat. Recorded species, and seagrass bed cover. And use GPS to recorded location (UTM).

2) Collected environmental factors : Salinity, Depth, Water Transparency, DO, Temperature and pH, which were one station to collected seagrasses, by Multi-parameter Water Quality Monitoring System, on period tides . Sedimentology along with data on sea grass at low tide.

#### B. Analysis

1) Seagrasses: to analyze as follow:

- Classification seagrasses species (Kanchanaphat et al., 1991).
- Evaluated percent cover in each species per seasons and per areas.
- Biodiversity assessment: Species diversity as Shannon diversity Index, Species richness as Margalef's Index and Species evenness as Pielou's Evenness Index.
- Mapping distribution by ArcGIS

2) Environmental factors were average values related to the distribution of seagrasses.

### IV. RESULT AND DISCUSSION

#### A. Study area

Had Yong Lum, Had Jao Mai National Park, Tran Province is bay with clam winds. The beach with seagrasses scattered about 5 km long and connected to the mangrove forest and beach favor canal Kuan Tung loans (fig. 1). Which is near the mouth of the canal boat ride through the regular tourist and fishing boats. People use this area for fishing and tourism on regular basic. The coastal characteristic is the nature of the soil, mainly sand, muddy sand and mud were found living in many areas covered include: Dugong, Sea turtle, Sea Star, Swim Stroke shells, Crabs and soldier crabs, fish types etc.

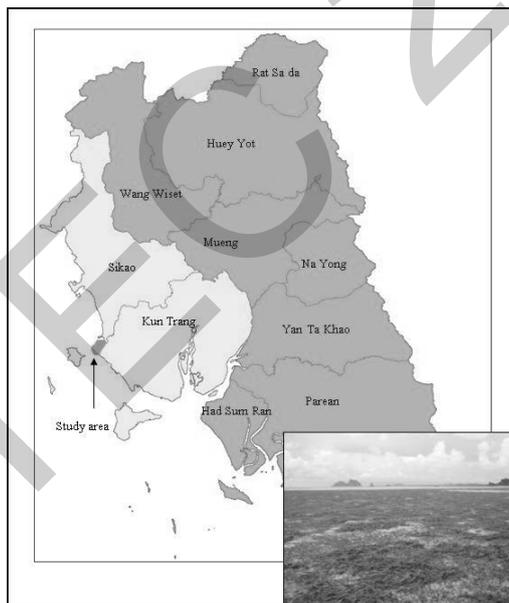


Figure 1. Study area

#### B. Species list

The Species of Seagrasses at Had Yong Lum, Had Chao Mai National Park, Trang Province was investigated during two season in 2010 which were dry season in March to April and rainy season in June 2010. Nine species of 6 genera 2 families were reported in both seasons, of which family HYDROCHARITACEAE are *Enhalus acoroides*, *Thalassia hamprichii*, *Halophila ovalis* and *Halophila minor*.

In addition, of which family CYMODOCEACEAE are *Syringodium isoetifolium*, *Halodule uninervis*, *Halodule pinifolia*, *Cymodocea serrulata* and *Cymodocea rotundata*. But in 2008 found that 7 species excepted *Halophila minor* and *Halodule uninervis* (Nantida et al., 2008).

#### C. Biodiversity

Biodiversity of the seagrasses in the dry and rainy season are similar, have a slightly higher value (Fig 2) . Moreover, there is a high biodiversity and each species were cover regularly. However, in the late of rainy season 2008 were highly

than 2010, which is species diversity by Simpson diversity Index are 1.87 – 4.6 and species richness by Rarefaction Index are 5.09 – 7.00.

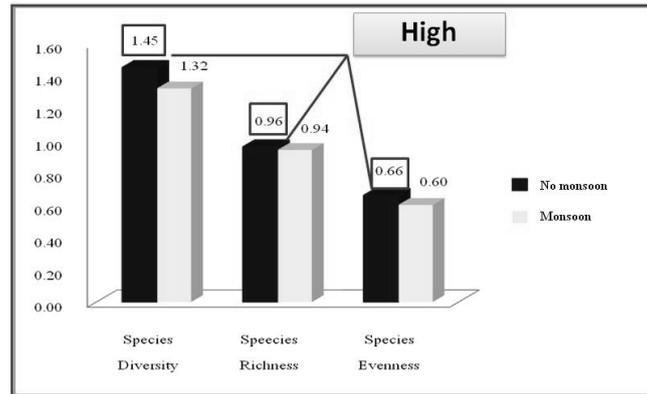


Figure 2. The biodiversity values of seagrasses in Had Yong Lum, Had Jao Mai National Park, in both seasons.

D. Distribution in Had Yong Lum, Had Jao Mai National Park.

Seagrasses distributions at the generic level are remarkably similar between dry and rainy season. The majority found scattered dense seagrasses in the middle of the beach and away from the canal especially in rainy season (fig. 3). Seagrasses that is *Halophila ovalis* spreading most in same in 1999 (Ratthana, et al.) and 2008 (Juthamass), which is *Halophila ovalis* sepeading most in dry season. *Cymodocea rotundata* are the most in rainy season. In addition, species distribution minimal are *Halophila minor* and *Syringodium isoetifolium* in both season (fig. 4). When investigating distribution of seagrasses genera across bioregions found that *Halophila* is genus with the greatest number of species and two species of the genus (*H. ovalis* and *H. decipiens*) are globally widespreas (Vermet et al., 1995), while most other members of the genus are confined to a single bioregion. *Halophila* has one, and possibly two, species that are invasive. Several species of *Halophila* are endermic and have limited distribution, but there are unresolved issues of species designation among these.

A number of genera have congeneric species in the Atlantic and Pacific Oceans; among these, the most notable are *Thalassia*, *Syringodium* and *Halodule*. In general, these three genera occupy the same physical habitat and fulfill similar successional roles in both the Atlantic and the Indo-Pacific.

The survey in dry season found *Halophila minor* is only in the middle zone in line 1. Nevertheless, the rainy season found that only in line 8. Because of their root system is not strong, so the easy to blow them up.

Season affected the distribution of two types of seagrasses which were *Halodule uninervis* and *H. pinifolia*, found in the rainy season than outside the rain. Because of the environment in the non-monsoon period is appropriate to both species for growing better during the rainy season, such as transparency or suspended sediment in the water and depth.

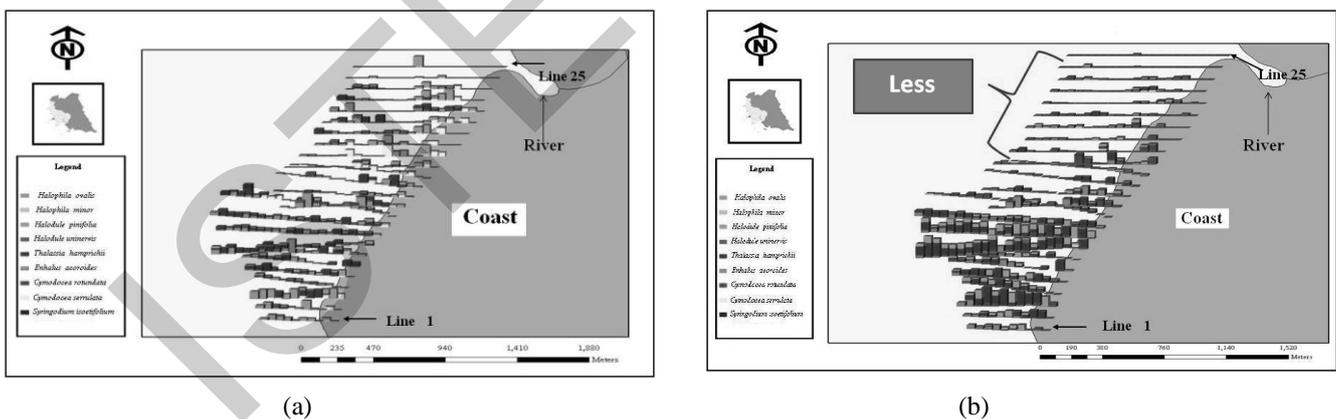


Figure 3. Seagrasses distribution in dry season (a) and rainy season (b).

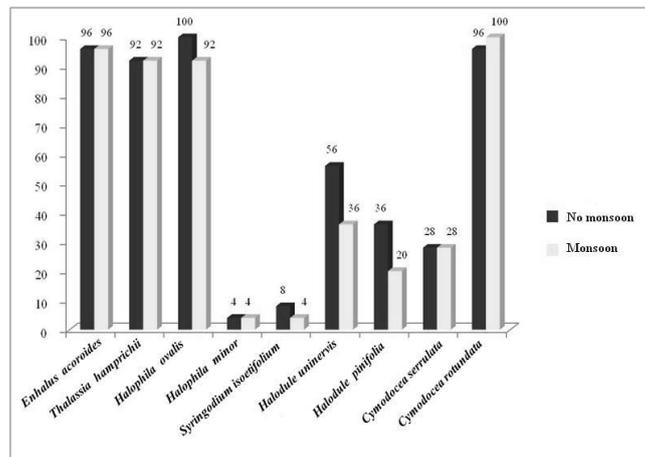


Figure 4. The percentage of Sea grasses cover in dry and rainy season.

## E. Environmental Factors (Table 1)

### a) Air Temperature

Depending on the area of geography that affected the growth of seagrasses in photosynthesis and dry dried, some species and the study of Chatcharee (2000) found that seagrasses in the tropics for more in shallow waters and are often exposed to air during low tide. A tolerance of temperature changes over the sea grass areas in deep water areas and flooded all the time. Some genus are resistant to heat, such as *Halodule* and *Enhalus*. For air temperature measurements Had Yong Lam in both Seasonal changes in the range of 29.86 to 31.84 degrees Celsius.

### b) Water temperature

Water temperature at the optimum growth of each seagrasses species are different. The water temperature will have a role to process of seagrasses as photosynthesis process. Breathing process so that the water temperature measured at Had Yong Lam and both seasons were changing in the range of 27.36 to 29.86 degrees Celsius, consistent with the study of distribution and biomass of seagrasses at Koh Lanta, Krabi province (Chakit et al., 2005) found that water temperature in the range of 27.00 to 32.0 degrees Celsius, and the study of water quality and style sediment optimum fertility of seagrasses in Thailand (Chakit, 2007) found that the temperature water suitable for growth of *Enhalus acoroides*, *Halophila ovalis*, *Halodule pinifolia*, *Cymodocea serrulata* and *Cymodocea rotundata* in the range of 29.28 – 31.10 degrees Celsius.

### c) Dissolve Oxygen (DO)

Both seasons of average DO in Had Yong Lam were changing in the range of 5.23 – 8.21 mg./l, which corresponds to the study of water quality and sediment optimum fertility to seagrasses in Thailand (Chakit, 2007) found that in the range of 5.11 – 11.3 mg./l, which is the amount of dissolved oxygen can affect the process of respiration of aquatic plants and fish. And decomposition of organic matter by water. In addition about oxygen dissolved in water to vary the depth. If the water depth resulted in greater oxygen content along with more water (Krisana and Chutima, 2002).

### d) Depth

The depth of the water affected the growth and spread of some seagrasses species because of the depth differences affected the photosynthesis of seagrasses. And at a depth of more water will decrease the amount of light is not suitable for photosynthesis. Average depth measured from the Had Yong Lam in both seasons were changing in the range of 1.14 to 2.17 meters, the depth will affect the distribution of *Halophila ovalis* directly, found in shallow water are larger leaf size than deeper water, and are scattered a large number. Andaman sea will find *Halophila ovalis* at a depth ranging from 1.0 to 5.4 meters (Changsang and Poovachairanon, 1994).

### e) Transparency

The average of transparency measured from the Had Yong Lam and both seasons were changing in the range of 0.94 to 1.95 m. The survey found that the area near the river mouth will be exposed to water, rather low, because they are influenced by sediment of sediment at the mouth of the river The sediment at the mouth of canals has accumulated a large study found that non-monsoon period is higher than the value of transparency during the rainy season. The transparency of the water will affect the photosynthetic process of some species. And found that the transparency of the water decreases as the depth increased. It was found that the sea grass that grows in areas where water levels are not very deep area is an area that contains the values of transparency, such as *Halophila ovalis* and *Halodule pinifolia*.

### f) pH

pH values measured at Had Yong Lam in both seasons were changing in the range of 7.99 to 8.24, which corresponds to the study of distribution and biomass of seagrasses at Koh Lanta, Krabi (Chakit et al., 2005) conducted during the months of April and October 2548, which covers a range that the dry and rainy season. It was found that pH in the range of 7.9 – 8.45, the value of pH was changed depending on the salinity. When increasing salinity, acidity - alkalinity increased with.

### g) Salinity

The average of salinity measured Had Yong Lam in both seasons were changing in the range of 33.82 - 34.23 ppt. The survey found that along the survey adjacent to Canal Kuan Tung loans get influenced by the river. Results in the area with

seagrasses distribution is less than the area away from the canal to Kuan Tung loans. Like the grass of the Andaman Sea (Kanjapapat et al., 1991) survey found that the first line next to the Canal will have a salinity was 28.43 ppt. Has resulted in the seagrasses in a small number of organizations. From the survey found that in the dry season period, salinity less than a storm Found that the salinity of seagrasses, rather than find some more content with the low salinity, such as *Thalassia hamprichii*, *Halophila ovalis*, *Halophila minor*, *Halodule pinifolia*, and *Cymodocea rotundata*. Rounded ends, which indicates that these seagrasses grow well in water with salt in a wide range.

#### h) Sediment

Sediment characteristics were collected along with seagrasses survey, during the water coming down. The seagrasses will grow well in areas that are similar to the sediment is sandy mud. Sediment characteristics were 3 types mixed mud and sand and mud, the study found that the area is muddy sand mixed. Many seagrasses species can thrive, such as *Halophila ovalis*, *Thalassia hamprichii*, etc. It was found that *Halodule pinifolia* and *Halodule uninervis* will grow well in the sand and coarse sand coral debris. In 2008 were survey found three characteristic sediment types present muddy sand, sand and mud, but some seagrasses species distribution on different sediments, such as *Halophila ovalis* was found on mud, *Thalassia hamprichii* was found on muddy sand, and *Cymodocea rotundata* was found on sand. This is different to this study showed that both three species can grow well in the sediment characteristics and 3 types according to a survey, because of the time difference makes a difference data each other (Juthamass, 2008).

TABLE I. ENVIRONMENTAL FACTORS IN HAD YONG LUM

Factors	Monsoon			
	Phase Change	Means	Phase Change	Means
Air Temperature (c)	30.07 - 33.38	32.78	29.65 - 30.69	30.05
Water Temperature (c)	28.71 - 31.21	29.53	26.00 - 28.51	27.28
pH	8.15 - 8.41	8.3	7.84 - 8.07	7.69
Water Depth (m.)	1.06 - 2.67	1.69	1.22 - 2.08	1.74
Salinity (ppt.)	33.11 - 33.37	33.27	34.54 - 35.10	34.82
DO (mg/l)	6.42 - 12.11	8.23	3.96 - 4.31	4.14
Water Transparency (m.)	1.06 - 2.73	1.69	0.88 - 1.17	1.03

## V. CONCLUSION

### A. Species List

The species of Seagrasses at Had Yong Lum, Had Chao Mai National Park, Trang Province was investigated during two season in 2010 which were dry season in March to April and rainy season in June 2010. Nine species of 6 genera 2 families were reported in both seasons, of which family HYDROCHARITACEAE were *Enhalus acoroides*, *Thalassia hamprichii*, *Halophila ovalis* and *Halophila minor*. Which family CYMODOCEACEAE were *Syringodium isoetifolium*, *Halodule uninervis*, *Halodule pinifolia*, *Cymodocea serrulata* and *Cymodocea rotundata*.

### B. Biodiversity

In dry season there is a biodiversity value a little bit higher than rainy season. Hat Yong Lam valuable biodiversity of the seagrasses high two seasons. And considered to have high fertility

### C. Distribution

The majority found scattered dense seagrasses in the middle of the beach. Seagrasses that is *Halophila ovalis* spreading most in and *Cymodocea rotundata* are the most in rainy season. Moreover, species distribution minimal are *Halophila minor* and *Syringodium isoetifolium* in both season.

### D. Environmental Factor

The water quality were effected to seagrasses distribution in dry and rainy season such as Temperature, DO, pH, salinity, transparency and water depth. Especially, transparency and water depth to effected leave size of *Halophila ovalis*, which is low shallow lager than deeper. In addition, sediment were effected to distribution of seagrasses.

## Acknowledgment

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# SPREADING BEHAVIOR OF HIGHLY-PRESSURIZED SPRAY DROPLETS EXITING FROM AN INJECTOR OF NON-IMPINGING TYPE

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## ABSTRACT

Disintegration characteristics and spatial distribution of the spray emanating from the nozzle orifice in an injector of liquid monopropellant rocket engine are investigated by using Dual-mode Phase Doppler Anemometry (DPDA). Spray characteristic parameters such as droplet mean velocities, Sauter Mean Diameter (SMD), turbulent intensity, number density, and volume flux are measured at various locations along the geometric axis of the nozzle orifice and on its cross-sectional plane. With a view to observing dynamic features of spray droplets, those quantitative data are plotted in radial profile of spray and also mapped onto the velocity to diameter and instantaneous-angle to time domains. Also, evolutionary behavior of the droplets is featured with a reconstruction of the velocity vectors with SMD, number density, and volume flux into three-dimensional space.

**Keywords:** Monopropellant Rocket Engine, Non-impinging-type Injector, Dual Mode Phase Doppler Anemometry, Spray Droplet, Droplet Disintegration

## INTRODUCTION

A better understanding of the evolution and dynamic behavior for fuel spray generated from thruster injector makes it possible to derive the design parameter of brand-new liquid rocket engine. The injector design is intimately linked to the instability mechanism which may result in a significant malfunction of propulsion system. As the first phenomenon which occurs in the combustion chamber of a liquid propellant rocket and the subsequent disintegration of jets into droplets, a study on jet disintegration contributes greatly to the understanding of the development of liquid rocket engine combustors (Reitz & Bracco, 1982).

In this paper configuration of the thruster injector will be introduced first along with magnified-sectional view of nozzle orifice. Also, schematic illustration of measurement positions for dual-mode phase Doppler anemometry (DPDA) will be followed. Quantitative data obtained from DPDA measurement are provided in terms of the mean axial and radial velocities, mean diameter, turbulence intensity, number density, and volumetric flux of droplets emanating from the injector nozzle orifices in order to investigate the characteristic spray behavior of a 5 Newton-class thruster injector. Correlation between SMD (Sauter mean diameter) and turbulence intensity as a function of positional variations will be analyzed. Dynamic behavior of spray droplets at various locations of the axial and radial direction is scrutinized by mapping the populations of droplets onto the velocity and size domain as well as presenting the instantaneous variation for directional angles of droplets passing through a fringe volume. Finally, the mean values are reconstructed onto three-dimensional space so as to examine the spatial characteristics of droplets velocities, SMD, number density, and volumetric flux.

## EXPERIMENTAL SETUP

The thruster injector employed in this study has 8 nozzle orifices, each of which has 30 ° cant angle off from the center-axis of injector face as shown in Fig. 1 and is fabricated by electrical discharge machining (EMD) as likely as in the practical liquid propellant thruster. Length-to-diameter ratio ( $L/d_o$ ) of the each nozzle orifice is 1.67 based on the diameter and the length of nozzle orifice are 0.152 mm and 0.254 mm, respectively. Deionized water (DIW) is used in a laboratory-scale experiment as a simulant that has the liquid properties similar to the propellant of hydrazine ( $N_2H_4$ ). DIW pressurized in the chamber by gaseous nitrogen ( $GN_2$ ), passing through a series of valves and filters is supplied up to injector, and then the injector generates eight (8) spray streams. The geometric axis for one of the eight (8) spray jets generated under the injection pressure of 27.6 bar is carefully aligned to the vertical and DPDA systems are set up with their optical axis perpendicular to the flow direction.

Assuming that  $x$ ,  $y$ , and  $z$  represent each direction for radial, axial, and depth of spray, respectively, data acquisition along the spray stream ( $y$ -axis) is carried out at four (4) locations away from the injector face with 50 mm ( $\Delta y/d_o = 328$ ) of the traversing step as described in Fig. 2. At the each locations of axial distance, cross-sectional ( $x-z$ ) sweeping is sequentially conducted by means of the three-dimensional traverse system within the measurement range of  $6 \times 6 \text{ mm}^2$  ( $x \pm 3 \text{ mm}$ ,  $z \pm 3 \text{ mm}$ ) with a jitter of 1 mm.

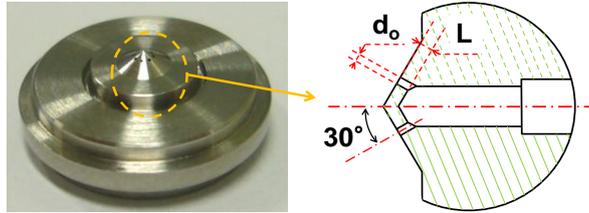


Fig. 1 Configuration of the injector employed in the experiment

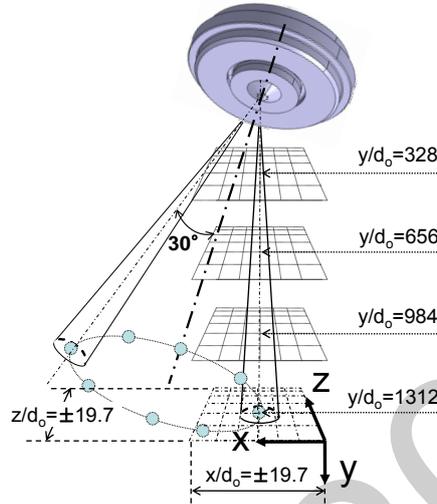
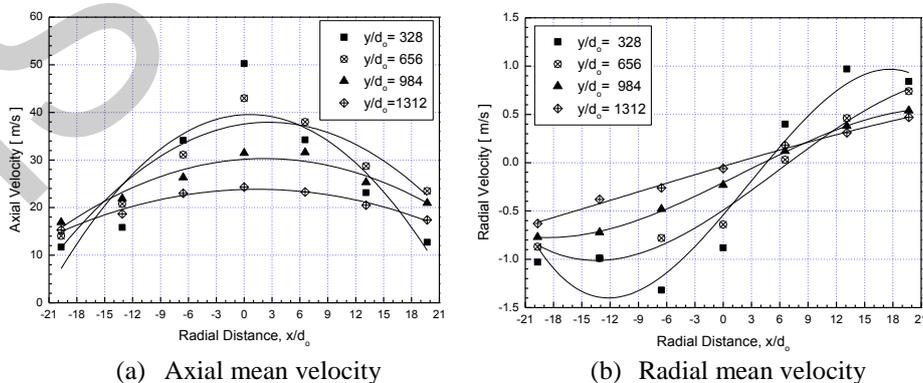


Fig. 2 Positional indication for DPDA measurement

### RESULTS AND DISCUSSION

The radial profiles of the axial and radial mean velocities at the center of depth direction ( $z/d_o = 0$ ) are shown together in Fig. 3. Axial velocity profiles for the all axial locations of spray stream indicate that their maximum values reach at the center of radial direction ( $x/d_o = 0$ ). Velocity at the center of upstream ( $y/d_o = 328, x/d_o = 0$ ) decreases approximately from  $50 \text{ m/s}$  around the nozzle orifice exit down to  $24 \text{ m/s}$  at downstream of spray. The decrease in velocity is attributed to the continuous loss of droplet momentum to surrounding air. Velocity difference between at the center and at the outer ( $x/d_o = 19.7$ ) near the nozzle orifice exit is larger than that of the far downstream. As droplet goes toward outer region, radial velocity at the upstream is featured by decreasing soon after increase, while the increase of velocity is observed just at the downstream. It implies that the spray stream widely disperses in radial direction along the spray downstream. In spite of symmetrical trend of velocities, their absolute values are not symmetric against the center line ( $y$ -axis). This result is consistent with the previous ones (Ganippa et al., 2004) that demonstrated the asymmetric spray resulting from non-symmetric cavity which is caused by differences of nozzle orifice inlet geometry as well as fluid inflow angle.



(a) Axial mean velocity (b) Radial mean velocity  
Fig. 3 Variations of mean velocities with radial position at the different axial locations

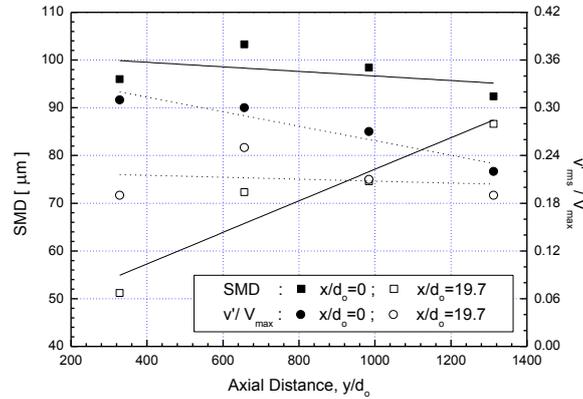
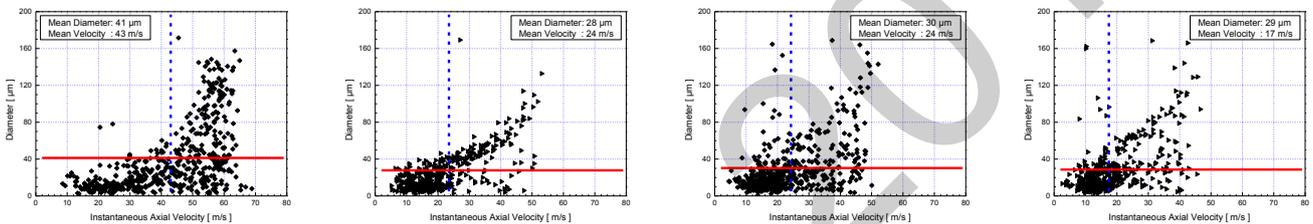


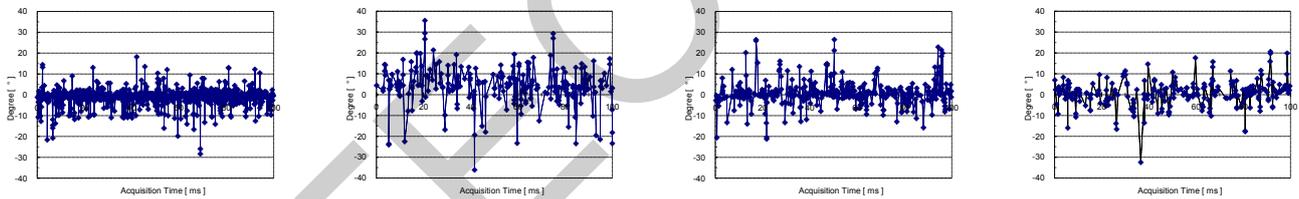
Fig. 4 SMD and turbulence intensity profiles according to axial distance variation

SMD and turbulence intensity along the axial direction are co-plotted as in Fig. 4. Both SMD and turbulence level at the center of radial direction decrease, but have higher values than those at the outer region. It should be pointed out that SMD at the center of upstream ( $y/d_o = 328$ ,  $x/d_o = 0$ ) is inadequate owing to its unreasonable value, which is less than that at the center of further downstream (i.e.,  $y/d_o = 984$ ,  $x/d_o = 0$ ). Also, it is inferred that such an increase in SMD at  $x/d_o = 19.7$  is attributed to the spray dispersion in radial direction caused by its diffusion or dispersion. Dissipation of spray droplets by surrounding air results in diminishment of turbulence intensity as droplet goes toward downstream and outer region.



(a)  $y/d_o = 656$ ,  $x/d_o = 0$  (b)  $y/d_o = 656$ ,  $x/d_o = 19.7$  (c)  $y/d_o = 1312$ ,  $x/d_o = 0$  (d)  $y/d_o = 1312$ ,  $x/d_o = 19.7$

Fig. 5 Cumulative populations for diameter and velocity of instantaneous droplets



(a)  $y/d_o = 328$ ,  $x/d_o = 0$  (b)  $y/d_o = 328$ ,  $x/d_o = 19.7$  (c)  $y/d_o = 1312$ ,  $x/d_o = 0$  (d)  $y/d_o = 1312$ ,  $x/d_o = 19.7$

Fig. 6 Instantaneous variation for directional angle of droplet

Figures 5(a)-(d) delineate the cumulative populations of instantaneous droplets. In order to improve a pictorial clarity, values only for 500 droplets among 10,000 sampled-ones are mapped onto each Velocity-Diameter domain. Horizontally-solid and vertically-dotted lines in each domain, represent arithmetic mean diameter (AMD) and mean velocity, respectively. The reason why axial location of  $y/d_o = 656$  is selected as the upstream is because the aforementioned size information at  $y/d_o = 328$  is unrealistic. As a whole, droplets at the center of upstream (Fig. 5(a)) are featured with their wide ranges of velocity and diameter compared with those at the other locations (Figs. 5(b)-(d)). It means that large droplets with high velocity disintegrate into finer droplets with low velocity as they move toward downstream and outer region of spray.

To observe the instantaneous angular variation of droplets passing through fringe volume at the various locations of axial and radial direction, instantaneous directional angles of droplets are presented in Fig. 6. The figure for each case includes the data acquired within 100 ms since the recording began. Thus how many data are in a figure is directly linked to the data rate of DPDA measurement. High data rate of over 10 kHz as well as vivid angular fluctuation near  $0^\circ$  which is parallel to the spray geometric axis ( $y$ ), is caught at the center of upstream (Fig. 6(a)). As droplets go downstream or toward outer region of spray, their data rate shows decreasing tendency. This implies that there is higher concentration of droplets at the center of upstream than at the others. It is seen that for the location of  $y/d_o = 328$ ,  $x/d_o = 19.7$ , angular variation range is wide and its averaged angle leans toward positive direction. From the macroscopic point of view, it reveals the spray diffusion toward right-outer direction. But this leaning trend does not happen at the downstream because cant angle from the spray axis is smaller than that at the upstream despite of their same radial location ( $x/d_o = 19.7$ ).

Dynamic behavior of spray droplets along the spray stream is presented through the velocity vector projected on to the plane of geometric axis of nozzle orifice ( $y$ ) and streamwise coordinate ( $x-z$ ) as seen in Fig. 7. Velocity difference between at the center and at the outer near the nozzle orifice exit is quite large, but it gets smoothed out at the far downstream throughout the

whole streamwise plane. The high SMD, which is narrowly distributed at the upstream, expands its distribution region in the cross-section as goes toward downstream of spray. It demonstrates the evolution of droplet disintegration accompanying diffusion and also is confirmed through detailed view of SMD and velocity at the center-plane of depth direction ( $z$ ) as depicted in Fig. 8.

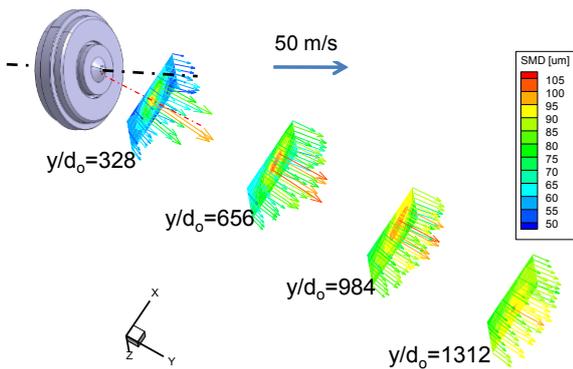


Fig. 7 Dynamic behavior and SMD variation of droplets along the injector-spray stream

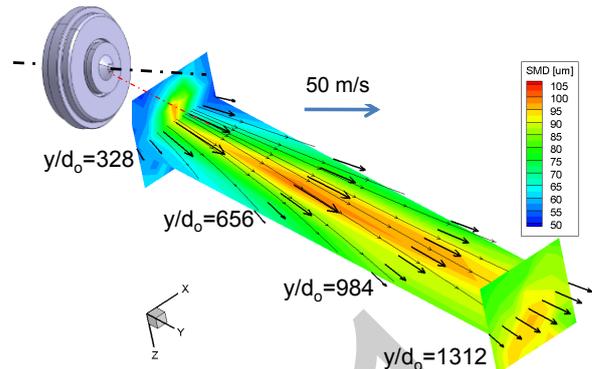


Fig. 8 Distributions of SMD and mean velocity with streamline at the center-plane of depth direction ( $z$ )

Figure 9 shows spatial distribution of the droplet number density which is defined as the number ( $\#$ ) of droplets per unit volume ( $cm^3$ ). As droplets go from upstream to downstream and from center to outer region at the downstream, a decrease in number density is found, indicating diminishment of droplets density caused by atomization and diffusion. The lower number density at the center of upstream than at the outer region is ascribed to the existence of liquid ligaments or largely deformed droplets in that region.

Volumetric flux, which is defined as the volume ( $cm^3$ ) of droplets passing through unit area ( $cm^2$ ) per unit time (sec.) and directly related to combustion rate, is given in Fig. 10. Generally accepted feature is that volumetric flux decreases as moving from upstream / center to downstream / outer region of spray. The result is in good agreement with that through identifying the numerical values on the contour surface in the figure.

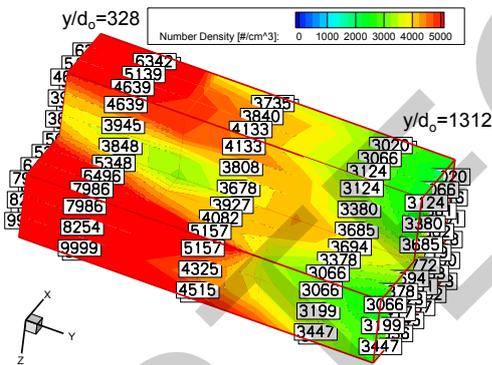


Fig. 9 Spatial distribution of the droplet number density

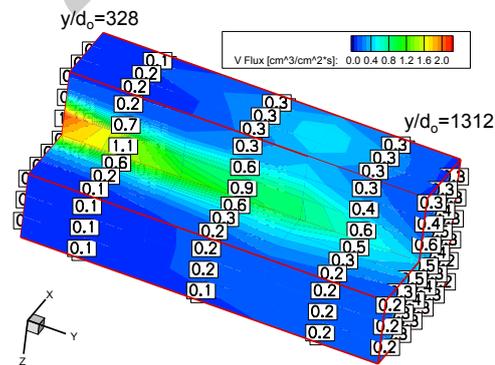


Fig. 10 Spatial distribution of the droplet volumetric flux

## CONCLUSIONS

Spray characteristics of an injector employed in the 5 Newton-class of liquid-propellant thruster have been addressed with evolutionary features of the droplets. Quasi-3D analysis on spray characteristic parameters such as velocity, size, turbulence intensity, number density, and volumetric flux is made in order to investigate a spatial distribution of spray droplets.

Spray characteristic parameters indicate almost symmetric against the center-axis of nozzle orifice, but the absolute value for radial velocity is not so against the center-axis of nozzle orifice. As goes from upstream / center toward downstream / outer region of spray, axial velocity, SMD, turbulence intensity, and volumetric flux decrease. Number density at the center of upstream is even lower than that at the outer region of upstream because of liquid ligaments or largely agglomerated droplets.

Dynamic behavior of droplets and the expansion of spray stream caused by spray diffusion were scrutinized in three-dimensional space by utilizing the droplet mean characteristics parameters and the instantaneous data.

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# STEADY-STATE ELECTRON DRIFT VELOCITY AT DIFFERENT TEMPERATURES IN $\text{Al}_x\text{Ga}_{1-x}\text{N}$ AND $\text{In}_x\text{Ga}_{1-x}\text{N}$ ALLOYS: MONTE CARLO SIMULATION

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## Abstract

The  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys are widely used in optoelectronic devices operating in the visible and ultraviolet. They are also attractive for high power, high temperature and high frequency electronic applications. The specific properties of these materials are the source of the charges induced by the effects of spontaneous and piezo-electric polarizations at the interfaces of quantum wells and super lattices. They are used in heterojunction field effect transistors HFET, modulated doping field effect transistors MODFET, and heterojunction bipolar transistors HBT.

We study  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  in the cubic phases because they would have better electronic and optical performances than in their hexagonal phases. We first present GaN, AlN, InN and their alloys  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . In the second section; we describe the main steps of Monte Carlo simulation method that we use. In the third section; we calculate steady-state electron drift velocity versus electric field for different temperatures and various molar fractions  $x$ . We consider the acoustic, piezo-electric, ionized impurities and polar optical phonon scatterings. We compare our results with published work and are in satisfactory agreement.

**Key words:**  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ,  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , Temperature (T), electric field (E), velocity (v)

## 1. INTRODUCTION

The gallium nitride GaN is the most studied of III-N and even more all other semiconductors. Its large gap and its possibility of alloys with indium nitride (InN) and aluminium nitride (AlN) raised great hopes for these materials as devices in both optical and electronic applications (G. Roosen, 2003). The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys are often used as barriers of confinement in the optoelectronic-based nitrides structures, and in transistors such MODFET, HEMT and HBT. Their lattice parameters can be deduced from those of GaN, InN and AlN by Vegard's law; they are given respectively by equations (1) and (2) whose are linear interpolations but not sufficient to obtain more accurate values (Fabrice Enjalbert, 2004). The usual lattice parameters of binary compounds in their cubic phase are given in Table 1. The difference between experimental and theoretical values is due to differences in the quality and structural constraints existing in the layers.

$$a_{\text{In}_x\text{Ga}_{1-x}\text{N}} = x \times a_{\text{InN}} + (1-x) \times a_{\text{GaN}} \quad (1)$$

$$a_{\text{Al}_x\text{Ga}_{1-x}\text{N}} = x \times a_{\text{AlN}} + (1-x) \times a_{\text{GaN}} \quad (2)$$

Tab.1 lattice parameters of GaN, InN and AlN compounds, in their cubic phase

Material	Calculated $a_0$ (Å) (S. K. Pugh et al. 1999)	Experimental $a_0$ (Å)
GaN	4.423 - 4.462 - 4.452	4.50 (Xu et al. 2000) - 4.53 (R. C. Powell et al. 1993)
InN	4.996 - 4.392 - 4.981	4.98 (M. Guerrero and Esteban, 2002) - 4.97 (F. Dessenne, 1998)
AlN	4.301 - 4.392 - 4.34	4.38 (I. Petrov et al. 1992) - 4.3996 (Okumaru et al. 1998)

The effective masses of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ternary compounds are also often deduced by linear interpolation from those of GaN, InN and AlN. In the  $\Gamma$  valley, they are respectively  $m_e^* = 0.15m_0$ ,  $m_e^* = 0.10m_0$  and  $m_e^* = 0.25m_0$  in the cubic phase ( $m_0$  is the electron mass in vacuum).

At 300K; GaN, InN and AlN admit gaps about 3.2eV, 1.9eV and 6eV in their cubic phases. The variations of the alloys energy band gaps, depending on the composition, are given by equations (3) and (4) where the bowing parameter  $b$  is approximately equal to  $1.13 \pm 0.23\text{eV}$  (Fabrice Enjalbert, 2004).

$$E_{\text{In}_x\text{Ga}_{1-x}\text{N}}^g = x \times E_{\text{InN}}^g + (1-x) \times E_{\text{GaN}}^g - b \times x \times (1-x) \quad (3)$$

$$E_{Al_xGa_{1-x}N}^g = x \times E_{AlN}^g + (1-x) \times E_{GaN}^g - b \times x \times (1-x) \quad (4)$$

## 2. MONTE CARLO SIMULATION

The Monte Carlo method is based on a drawing of lots process of interactions sustained by the carriers during their movement in the compound, from probability laws. The method consists to follow the behavior of each electron in real space and in wave-vectors space. Let us consider an electron which has energy  $\varepsilon(t)$ , wave-vector  $k(t)$ , and which is placed in  $r(t)$ . Under action of an electric field  $E(r, t)$ ; the exchange of energy and momentum with the lattice, and the deviation of its trajectory by impurities, will modify energy, wave-vector and position of the electron. Using mechanical and electrodynamic laws, we determine the behavior of each electron in time and space. To be more realistic:

1. We statistically study possible energy exchange between electrons, modes of lattice vibrations and impurities; this allows us to calculate the probability of these interactions and their effect on the electron energy and wave-vector.
2. We assume that these interactions are instantaneous. We can now do move electrons in free-flight under the only effect of electric field, between two shocks. The free-flight time is determined by drawing lots. When there is interaction, we determine its nature by drawing of lots, and we change the energy and wave-vector of the electron, in this case. The distribution of electrons changes, we then compute the resulting electric field at sufficiently small time intervals. Thus, we can assume the electric field constant between two calculations (Thobel, 1980) – (S. Galden, 1992) – (O. Mouton et al. 1993).

## 3. RESULTS AND DISCUSSION

We consider a simplified model of three isotropic and nonparabolic valleys, with a maximum alloy scattering rate. We consider the acoustic, piezoelectric, ionized impurities and polar optical phonon scatterings. We calculate the electron mass in the higher valleys, by the relationship (5) (A.F.M. Anwar et al. 2001) (where  $m^*$  is their effective mass in  $\Gamma$  valley, and  $\alpha$  is the nonparabolicity factor of the considered valley):

$$m = m^* \times (1 + \alpha\varepsilon) \quad (5)$$

In the steady-state, we calculate the electron drift velocity as a function of applied electric field for different temperatures namely 300, 500 and 700K; and for various molar fractions  $x$ , in the  $Al_xGa_{1-x}N$  and  $In_xGa_{1-x}N$  ternary compounds with an electron concentration equal to  $10^{17}cm^{-3}$ . The results are illustrated respectively by Fig.1 to 6. To validate our results, we compare them with those of reference 14 where the authors study the same ternary compounds, at room temperature.

By increasing the temperature, the gap decreases. That of InN is small; the  $In_xGa_{1-x}N$  ternary compound will have its gap towards zero quickly enough. For this reason, we limit ourselves to a temperature equal to 700K.

- Increasing the molar fraction  $x$  of aluminium in the  $Al_xGa_{1-x}N$  ternary compound, or decreasing the molar fraction  $x$  of indium in the  $In_xGa_{1-x}N$  ternary compound:

- The band gap energy increases.

- The energy separating the upper valleys and the  $\Gamma$  valley increases; then there is an increasing critical electric field for which the velocity reaches its maximum while the peak velocity decreases.

- The electron effective mass increases also, resulting in a decrease of electron drift velocity.

- At room temperature, we obtain respectively for GaN, InN and AlN peaks about:  $3 \times 10^7 cm/s$  for  $E=110kV/cm$ ,  $3.24 \times 10^7 cm/s$  for  $E=50kV/cm$  and  $2.13 \times 10^7 cm/s$  for  $E=400kV/cm$ . Their saturation velocities are respectively about  $2 \times 10^7 cm/s$ ,  $2.35 \times 10^7 cm/s$  and  $1.75 \times 10^7 cm/s$ .

- The increase in temperature allows a higher kinetic energy gain for electrons; they move more and then come into collisions with other atoms by transferring their energy. Then for the same molar fraction  $x$ ; the peak velocity decreases and moves slightly toward the highest fields, and the saturation velocity decreases also.

The alloy scattering mechanism dominates in the ternary compounds under the present simulation conditions; the total scattering rate is higher. Thus a higher field is required to the free carriers for reaching the higher valleys, and the peak velocity occurs at a higher field.

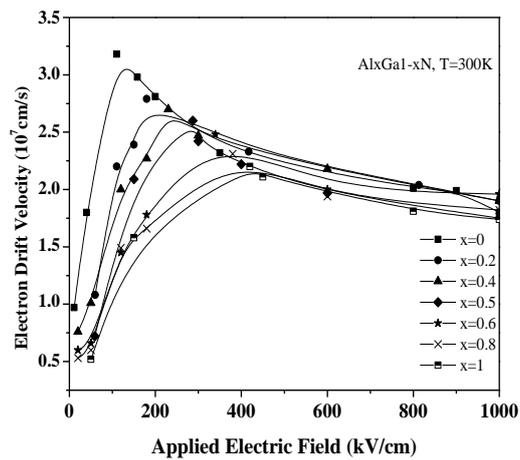


Fig. 1 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 300K, within  $\text{Al}_x\text{Ga}_{1-x}\text{N}$

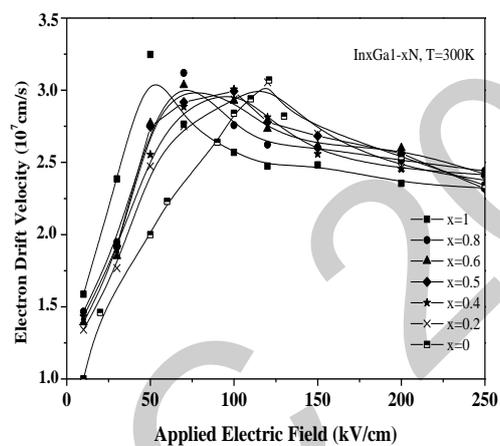


Fig. 2 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 300K, within  $\text{In}_x\text{Ga}_{1-x}\text{N}$

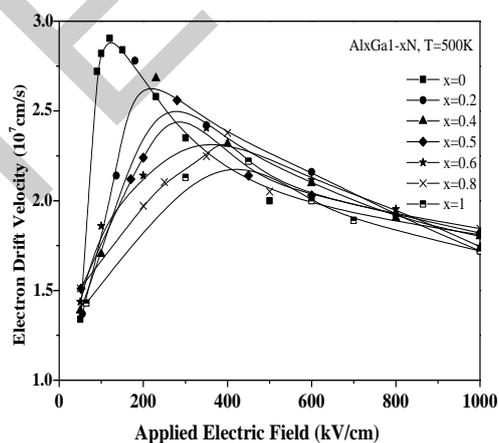


Fig. 3 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 500K, within  $\text{Al}_x\text{Ga}_{1-x}\text{N}$

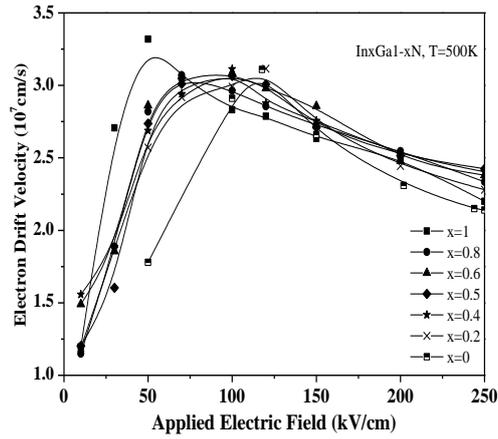


Fig. 4 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 500K, within  $\text{In}_x\text{Ga}_{1-x}\text{N}$

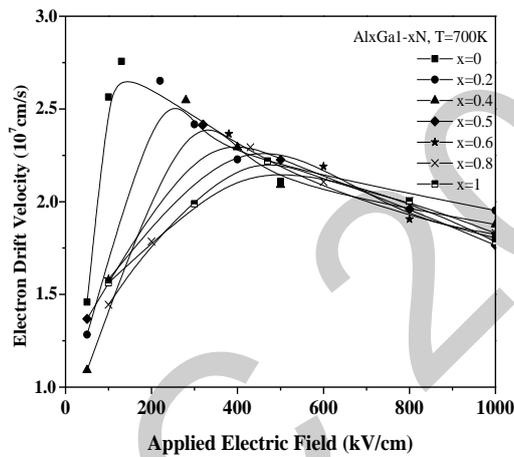


Fig. 5 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 700K, within  $\text{Al}_x\text{Ga}_{1-x}\text{N}$

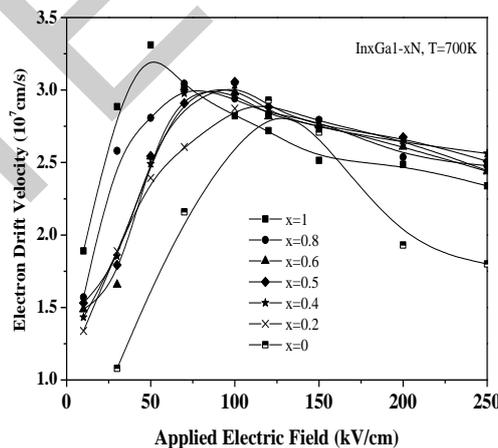


Fig. 6 The electron drift velocity versus applied electric field for different molar fractions  $x$  at 700K, within  $\text{In}_x\text{Ga}_{1-x}\text{N}$

#### 4. CONCLUSION

GaN, InN, AlN, and their alloys, constitute a major research field of electronics in the solid state for microwave applications. They have several advantages: high voltage thanks to their large gaps, high output impedance, high peak and saturation velocities, and large thermal and chemical stabilities.

We studied the electron transport at low field in the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ternary compounds, using Monte Carlo simulation, and considering a simplified model of three isotropic and nonparabolic valleys. We considered the acoustic, piezoelectric, ionized impurities and polar optical phonon scattering mechanisms.

We calculated the steady-state electron drift velocity versus applied electric field for different temperatures and various molar fractions  $x$  of aluminum and indium in the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  and  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys.

The inclusion of alloy scattering influences the transport dynamics changing the peak velocity and the threshold electric field. However, if the alloy scattering is strong, the ternary compounds exhibit peak velocities below that of their constituent binaries.

Calculated at 300K; our results are in satisfactory agreement with those of (M. Farahmand & F. Brennan, 2001) where the authors use a nonparabolic effective mass energy band model, ensemble Monte Carlo simulation.

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# STEREO CAMERA BASED MARKERLESS MOTION CAPTURE BY MORPHOLOGICAL ANALYSIS OF DISPARITY MAP

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**Abstract:** This paper presents a new real-time system to acquire motion information of human articulated objects such as arm and head. The system does not need any marker or device to wear on human body and adopted stereo camera to obtain robust system against for illumination and complex background without position initialization of articulated objects. We present a solution to estimate self-occluded body objects when human model behaves normal action towards the camera. The main idea of the solution is to apply a component labeling techniques on sliced disparity map, and found the arm position when the arm is located in front of basis distance of body and we could also found arm location when the arm is located on the basis distance with Morphological methods. From this approach, we can obtain the full body shape considering self-occlusion. It is simple and fast in comparison with other methods which satisfy real-time performance and accuracy of object tracking at the same time. As the result of experiments, we obtained the reliable motion data of articulated object motion under various costume and body type of models.

**Keywords:** Human Robot Interaction, Stereo-camera, Markerless Motion Capture, disparity map.

## 1 Introduction

Recently the ubiquitous computing which can communicate with the human in anywhere without the user's recognition of the system, has been noticed as the new paradigm of computerization. In the ubiquitous environments, the computer needs to obtain user's intention or information with accuracy. For this reason, the Human Computer Interaction (HCI) has occupied an important position.

Especially, Computer Vision base HCI system has unique advantage which is non-tangency and non-awareness of sensor's existence. In vision-based HCI, there are many perception modalities. These can be divided into six categories such as [2]: people tracking, gesture recognition, facial perception, facial expression, eye orientation tracking and head pose tracking. Especially, Human motion information that combines people tracking and gesture recognition has a unique advantage which is the simple and general approach to obtain user's intention. Information of motion is an intuitive expression cue for estimating user's intention. We can simply obtain user's intention by estimating the human motion information. And human motion information can be obtained analyzing continuous location of articulate body part of human.

Proposed method can be used to ubiquitous system or robot system. When the system understands human needs, they can perform what users want. Moreover, the method can be used in base research skill for human ethology.

Computer vision based motion capture system is can be divided into two sorts of system extensively. First one is Marker based human motion capture system and other one is Markerless motion capture system. Marker based human motion capture system is widely used on computer 3D-graphics and there are many commercial products. The user can obtain accurate result, but user needs to learn how to use it and many pre-calibrating for different body types for targets. On the other hands, Markerless human motion capture system does not need any device which the user wears equipment for the system.

Many of previous researches were proposed on this topic. Leung[3], Kakadiaris[4] and Lerasle[5], have developed an ribbon model, deformable model, full body model for their algorithm. However, they can't cover self-occlusion and complex pose such as the motion hand on user's head. Recently, there are many efforts on this research field to overcome above problems. The method of using stereo camera and multi camera were proposed and using silhouette method was also suggested.

Our method also based on stereo camera. However, we proposed novel algorithm that can estimate self-occlusion on real-time performance. We modify disparity-map from stereo camera and we make it blob with suggested filter. And then, the blob was separated by occlude articulated object section and non-occlude articulated object section. The algorithm is applying different method on each section that we suggested. The each result could merge and we could obtain reasonable results.

This paper is organized as follows: In section 2, our algorithm is presented. First, we describe preprocessing procedure before our algorithm work. Second, the main feature is introduced and explained how to acquire. Then third, we explain human motion capture algorithm in case of self-occlusion and finally, Morphological approach is described in case of without self-occlusion. In section 3, we cover the system setup with detail specification. In section 4, we show the experimental result of our system. And finally in section 5, we evaluate our algorithm and conclude this paper.

## 2 Markerless Motion Capture

The procedure of the system has divided into 4 steps approximately. Every procedure has been performed in computer software on system. The output of the algorithm is left hand, right hand, body center and head position in 3D working space.

### 2.1 Preprocessing

To obtain precision disparity map, we need a fine camera calibration. An accurate intrinsic and extrinsic camera parameter is essential for the disparity matching procedure. In this paper, we used the commercialized library, which is Smallvcal and VidereDesign's camera calibration program [7,9].

### 2.2 Main Feature Extraction from Disparity Map

From the calibration of stereo camera we could obtain accurate disparity map, Videre-Design STH-2 Stereo camera can suggest 3D map information within 1~2cm error rate on about 2M distance in front of stereo camera. And then, We adopt noise blob removal filter on the disparity-map and find body center location by COG(Center of Gravity) consequently. Fig 2. shows overall follow of Main Feature extraction method from disparity map.

First, we use Noise blob removal filter by counting continuous disparity pixels. Count number of pixels mean size of disparity blob and the filter remove 1 or 2 pixel size blob immediately.

Second, we remove background. We assume that there are only one person on the working space and target human stand-up perpendicularly. From this, we could obtain Center of Gravity (COG) of the all disparity map throughout Noise blob removal filter procedure. Then, we remove all disparity map 30cm behind of COG.

Next, we could estimate COG of Human Body, this is different point compare with COG of all disparity map. We find first left and right disparity blob by searching from left and right side of bottom of disparity image and find body area of disparity (red area of Fig. 3).

We assume that only one target human is located in front of camera and stand up toward the cameras. The system can analyze the human body disparity from back ground by histogram of disparity map. The histogram present enough cue to distinguish human body and we could obtain human distance from camera by measuring disparity of body COG(Center of Gravity).

We also could find hand blob when the hand part is located in front of body distance from the stereo camera. Fig .4 shows hand blob parts. Hand blob part number could be 0, 1, or 2. This method was adopted by previous research [10] using component labeling and self-occlusion blob extraction algorithm.

Finally, we could defined the still human motion disparity map image has occlude arm blob or not.

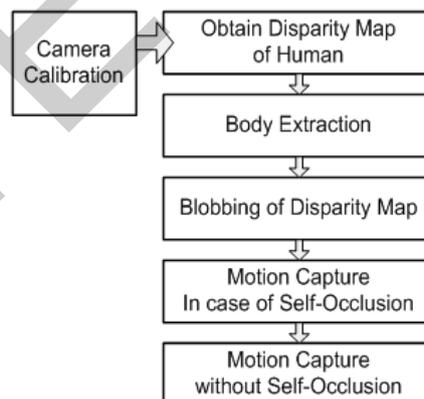


Fig 1. The overall procedure of the system

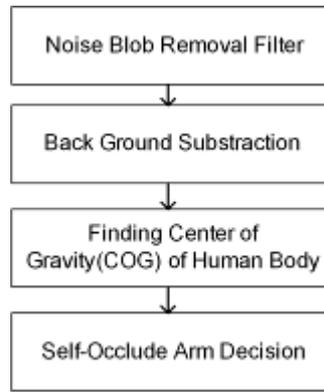


Fig 2. Main feature extraction procedure

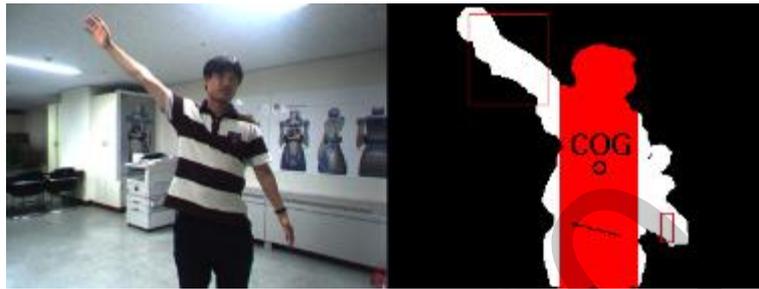


Fig 3. Finding center of gravity (COG) of target human body.



Fig 4. Finding hand blob when the hand is located in front of body distance from the camera.

### 2.3 Human Motion in case of Self-Occlusion

In this case, each hand position is estimated by edge point of blob area which is red rectangular on Fig. 5. And we distinguish left and right hand from the point of opposite diagonal corner point of left and right hand positions by comparing with x location of disparity map image.

We already know human body center position from previous procedure. We also know the body distance from the camera and body size (red part on Fig. 3). From this, we could estimate head center position on disparity map by following equation (1) and (2).

$$Head_{(x,y)} = \begin{cases} X = COG_x \\ Y = (COG_y - L_y) \end{cases} \quad (1)$$

$$L_y = \frac{C \cdot P_n}{D_z} \quad (2)$$

where X and Y is head position of disparity map and COG<sub>x</sub> is center position of target body, P<sub>n</sub> is pixel number of body part of disparity map, D<sub>z</sub> is body COG distance from the stereo camera and C is camera and target dependent constant value by obtaining from experimental trial and errors.

Finally, we obtain 4 positions from disparity map image and we could replace them easily to 3D location in the working space by the function of SmallV[9] of Videre-Design.

## 2.4 Human Motion without Self-Occlusion

We could find up easily on previous section when the self-occlusion was detected. However, many undetectable pose are still remained such as hands up pose and attention pose. In this case, hand is located on same distance of body COG. Thus, we need to use different method to find hand location.

The presented algorithm finds one side of articulated object of human by morphological approach. It can be hand or elbow. We evaluate shape of human body and decide that it is hand or elbow. Finally we could obtain human hand geometry information considering hand like blob which explained section 3.2.

The algorithm compares 3 different morphological states from disparity map in case of non-self-occlusion. Each case detects hand position. It shows on Fig. 7 and the algorithm choices one position by measuring distance from head and COG of body.

Finally we could obtain head center position and body center position, left hand and right hand position in case of non-self-occlusion case.

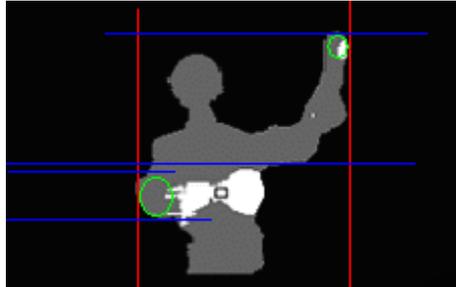


Fig 5. Morphological human motion capture in case of non self-occluded human body

## 3 Experimental Result

We implement our algorithm using C++ under the Pentium 4 PC with Microsoft Windows environment and the Videre Design MEGA-D stereo camera is connected by IEEE1394 cable. We use the Videre Design SVS library to estimate the disparity map on real-time (about 24 frames per second at 320x240 frame resolutions). The camera is fixed vertically on the wall of our experimental studio.

To obtain reasonable experimental result, we used several human models who have different appearance in face color, hair style and gender. All experiments were performed under the different illuminate condition (70~200 LUX).

As the result of experiments, the algorithm estimates articulated body position with small error fewer than 2.1cm in body center, 3.4cm in head center, 0.9cm in left and right hand respectably. All data could obtain in the real time (20frames/sec). Fig. 9 shows measured average error results.

## 4 Conclusion

In this paper, we suggested a new approach of estimating human pose by analyzing morphological feature from the disparity map. From this approach, we can obtain the full body shape considering self-occlusion. It is simple and fast in comparison with other methods which satisfy real-time performance and accuracy of object tracking at the same time. Especially, the HCI on ubiquitous system will be appropriate application for this method.

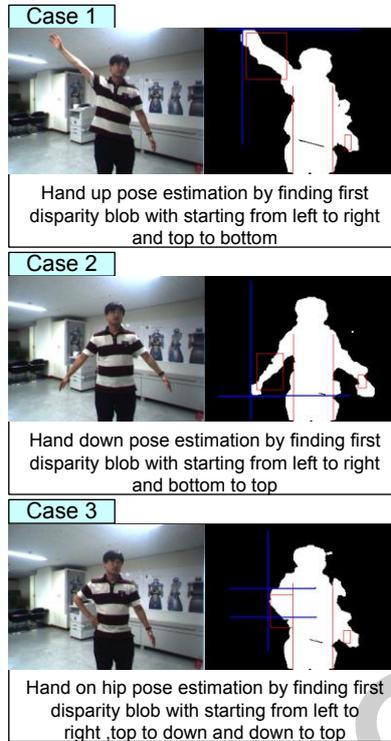


Fig 6. Morphological left hand detection case procedure in case of non self-occluded pose

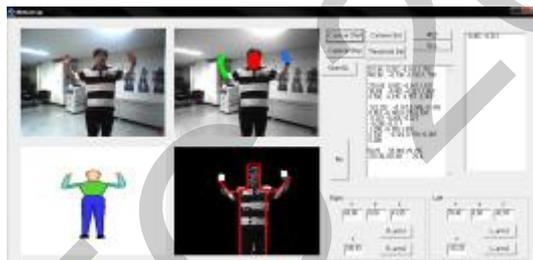


Fig 7. Experimental system setup and implemented human motion capture system.

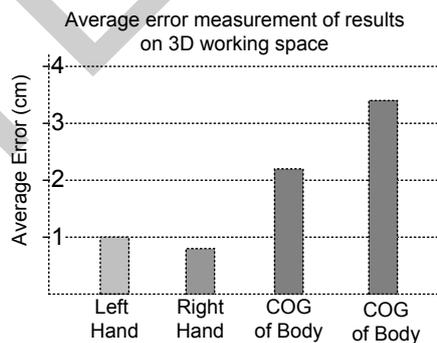


Fig 8. Experimental results; Average measurement of distance errors on each articulated object.

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# STUDY OF SANDBLASTED GLASS SUBMITTED TO CHEMICAL ATTACK BY HF ACID

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## ABSTRACT:

Generally, glass sandblasting erosion is characterised by formation of surface microcracks, chippings and sometimes craters. These defects directly affect the glass properties (optical transmission and mechanical strength). The aim of this work is to seek a way for improving the properties of a soda lime glass eroded by sandblasting. The procedure consists of eroding glass samples using various sand masses) and then to submit them to a chemical attack by fluorhydric acid (3%) using various duration (0÷8h).

The results show that the flexural strength clearly increases with attack duration. In the, the mean value was. After sandblasting, the strength decreases from 123.7 MPa (as-received state) to 46.83 MPa. By chemical attack during 8h, the resistance increases up to 160 MPa. In the same time, the optical transmission marks a minimum (9.5%) at the beginning and then increases to 46.5%. It exceeds the value of the sandblasted glass that is 22.5%.

In order to explain the mechanisms of the chemical attacks, we realized Vickers indentations which are similar to sand impacts on glass surface. Various loads were used. The indented samples were submitted to different chemical attack duration. We observed that this last affects clearly the defects morphology generated by sandblasting. There is a gradual transformation from typical Vickers imprint to cellular structure which accomplished after attack duration of 5 hours

**Key words:** Glass, Sandblasting, Defects, chemical attack by HF

## 1. INTRODUCTION

In the Sahara, sandstorms have a great influence on the environment: dunes movement, desertification, some other problems such as ophthalmic diseases and pulmonary, teeth degradation, snake bites and scorpion...). The sandstorms also affect the everyday lives of people. Among others, this influence leads to a surface damage of a great number of objects, particularly those made of brittle materials such as glasses and ceramics. In the case of glasses, sandstorms can damage vehicles windshields, headlights optics, protection glass sheets of solar panels and sensors, various glazing. There is formation and interconnection of cracks which lead to material removal. This last is governed, in particular, by chipping mechanism.

Several researchers have highlighted the influence of the relevant factors on the brittle materials erosion [1, 2, 3]. They found that the kinetic energy and shape of the particles play a major role in the erosion mechanisms. As a result, it occurs a mass loss leading to a clear drop in mechanical strength and optical transmission. At the same time, the surface roughness increases.

It is well established that glass surface defects are responsible of the light scattering [4, 5]. In the case of vehicles circulating in southern Algeria, the light scattering due to damaged windshields, disturbs the driver's visibility especially during sunset, sunrise or by night when crossing oncoming vehicles.

In his study, Stuart Chambers [6] showed a clear relation between windscreen wear and increased driver reaction time. When meeting an oncoming vehicle while driving in the dark, a driver looking through an extremely worn windscreen may have a detection distance almost 15% shorter compared to a driver looking through a new one. The combination of an extremely worn windscreen and impaired vision means that a driver loses approximately 25% of his detection distance, or up to 20 meters.

To remedy the defects generated on the sandblasted surfaces, several solutions have been suggested:

- by applying a thermal quenching or a thermo-chemical quenching in order to increase the mechanical resistance of the glass surface against erosion [7],
- by depositing thin transparent layers in order to cover the defects and thus regenerate the surface [8]
- by applying a mechanical polishing or a chemical polishing [9]

The purpose of this work is first to erode soda-lime glass samples with a constant mass and a constant speed. Subsequently, the sanded samples are subjected to a chemical surface treatment with hydrofluoric acid HF (3%) for varying durations up to 8 hours. The attacked surface analysis shows that from duration of 5 hours, the defects acquire cell morphology. To explain this phenomenon, glass samples were indented using different loads and then immersed in a hydrofluoric acid solution for different durations. On the other hand and due to the glass brittleness, a part of our study is devoted to the statistical distribution of the biaxial flexural strength using the Weibull method.

## 2- PROCEDURE EXPÉRIMENTALE

### 2.1. Samples preparation and test conditions

An usual soda lime glass of 2.8 mm thick is used. Samples of dimensions 50×50 mm<sup>2</sup> are prepared from the same glass sheet, and eroded on the same side. The sand comes from the region of Ouargla (south of Algeria) and is used in the as-received state. According to figure 1, the grains shape is variable from nearly rounded to angular, and the mean particles size is located between 200 and 300 μm.

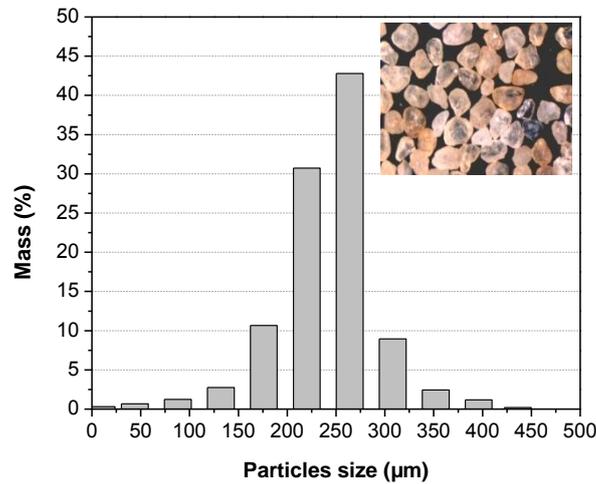


Figure 1: Granulometric distribution diagram and a sample of the sand used.

All samples are sandblasted in the normal position relative to the sand flow. The projected sand mass is kept constant (150 g) for all tests. The speed of the flow is 25 m / s. After sandblasting tests, the samples are subjected to the action of a hydrofluoric acid solution (3%) for various durations (0 and 8h.). Vickers indentation tests are performed on a microhardness tester type Zwick-Roell using loads ranging from 1 to 40 N

The mechanical characterization of the specimens is carried out in biaxial bending with concentric rings. Batches of 30 samples were prepared before and after sandblasting in order to compare the values dispersion. Other batches of 30 samples were also prepared after indentation and etching for 4 durations: 1, 3, 5 and 8. The aim is to show the influence of attack duration on the mechanical strength and optical transmission.

### 3. RESULTATS ET DISCUSSION

#### 3.1. Effect of the sandblasted state

Microscopic observation shows that sandblasted surfaces are first formed of isolated defects of various sizes and distributed randomly on the surface. As the projected sand mass is important, neighboring defects interconnect. It follows a collapse at the surface resulting in the formation of large damaged areas (dark areas in Figure 2).

Average arithmetic roughness  $R_a$  measured in the initial state is 0.035  $\mu\text{m}$ , while that of sandblasted glass with 150 g is of the order of 2.9 microns. The total roughness  $R_t$  for sanded state is equal to 13.15  $\mu\text{m}$ . The optical transmission of the initial glass is 91.6%, but after sandblasting with a mass of 150g, it decreases to 22.4%. This drop is attributed to the presence of surface defects which scatter incident light.

Figure 3 shows the probability of rupture  $P_i$  versus the strength  $\sigma_i$ . It is clear that the resistance values are more dispersed in the case of as-received glass than that of the sandblasted. The average value of the initial state is  $123.7 \pm 23$  MPa. In this case, the pre-existing microcracks are very small size compared to those generated by sandblasting. These microcracks govern the glass strength. However, after sandblasting the strength values and the dispersion becomes much smaller. This gives an average value of about  $46.83 \pm 8.93$  MPa. The mechanical strength decreases because of the effect of the sandblasting defects. The values dispersion is significantly reduced due to the homogeneity of the sandblasted surface especially in the central area which is the most eroded and the most requested.

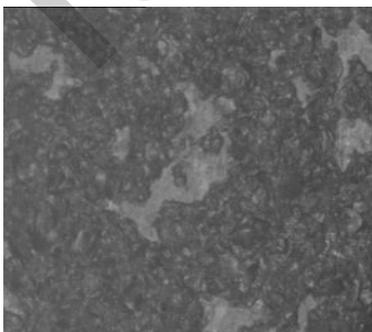


Figure 2: Damaged zones after sandblasting the glass surface.

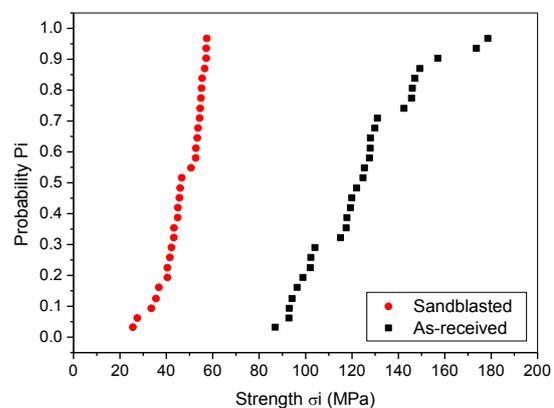
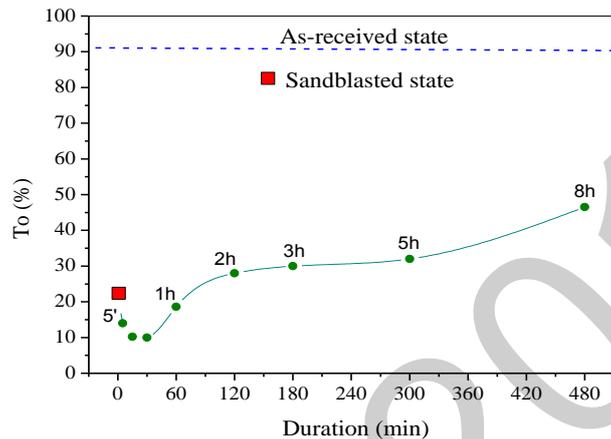


Figure 3: Strength distribution for the two glass states

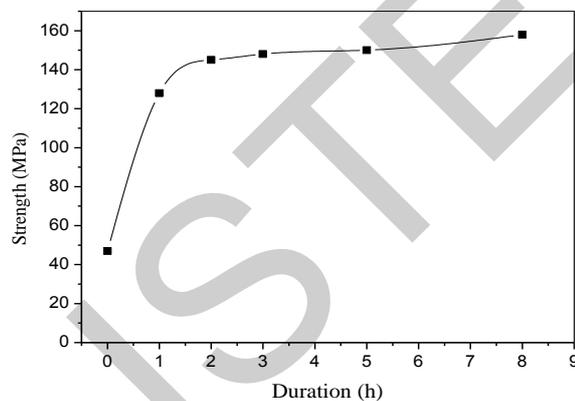
### 3.2. Effect of chemical attacks on eroded samples

**a) Optical transmission  $T_o$ :** Figure 4 shows the variation of the optical transmission versus chemical attack durations. The dashed line corresponds to the initial value of the optical transmission (91.6%). At the attack beginning and during the first minutes, the transmission decreases up to a minimum and reaches a value of about 9.5%. Parallel to this, the drop is accompanied by a sensitive increase of the roughness. This behavior is probably due to the active chemical reaction at the beginning and which become less active after that, because of the deposition of the reaction products (hexafluorosilicic acid  $\text{SiF}_6\text{H}_2$  [9]). This superficial damage leads to a light scattering which affects negatively the optical transmission. From 01 h duration,  $T_o$  increases regularly and reaches 46.5% and it clearly exceeds the sandblasting state value (22.4%). During this period, it happens a cracks blunting (see figure 5) as we can see for attacked indentations (see below) and there is a reduction of the level difference difference between the troughs and peaks. Consequently, the roughness tends to be reduced, and then to improve the optical transmission

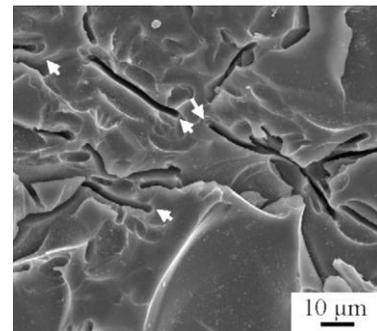


**Figure 4:** Variation of the optical transmission versus chemical attack durations.

**c) Mechanical strength:** Figure 5 shows the variation of the fracture strength  $\sigma_f$  versus chemical attack durations. The strength increases sharply at the beginning and after 2h it tends towards a constant level. The values pass from 47 Mpa for the sandblasted state to approximately 160 Mpa after 8h of acid attack. This value is higher than that of the as-received state. This strength improvement is attributed in particular to crack tips blunting (figure 6). The etching is done on the sides of the cracks and at the same time the cracks tip become rounded.



**Figure 5:** Variation of the mechanical strength versus chemical attack durations.



**Figure 6:** Micrograph showing the cracks blunting

In figure 7, the fracture probability  $P_f$  is plotted against the fracture strength  $\sigma_f$  for different durations. As the attack duration increases, there is a shift of the curves to the right, which corresponds to large values of strength. In other words, the resistance improves gradually. Note also that the values distribution is almost the same for all durations.

The Weibull modulus “ $m$ ” is determined in function of etching durations. The Weibull lines present a unimodal character. This means that in each case, there is a single family of defects governing the mechanical strength of sandblasted and attacked glass. All the values of  $m$  are situated between 5 and 6 indicating that the samples behavior is of brittle nature.

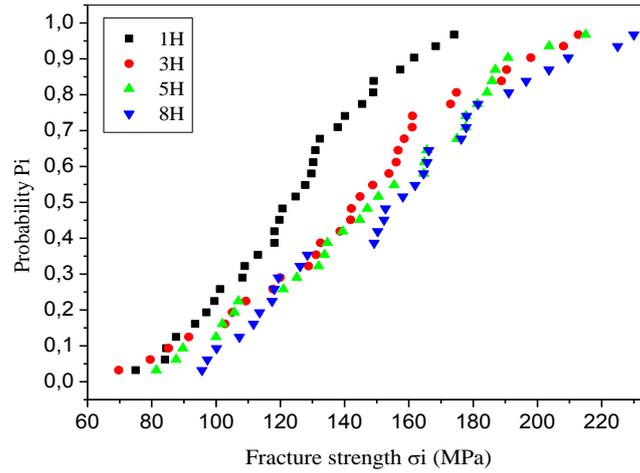


Figure 7: Strength distribution obtained for different durations.

d) Cellular morphology induced by chemical attack

- Below, is represented the morphology of the glass surfaces after sandblasting with 150 g and etching using various durations. We note that there are very distinct morphological changes from the earliest times of attack. With duration increasing, this morphology tends to cover the entire sanded surface. The size cells increases and interacts. Cells size increases with the chemical attack duration and cellular shape is accomplished from 5h.

Table 1: Morphology of the glass surfaces after sandblasting with 150 g and etching using various durations.

Sandblasted	Attacked 1h/HF	2h	3h	5h	8h

In an attempt to explain the cells formation, we used samples of raw glass that we have indented using different loads using various indentation loads (2 to 40 N). These samples were submitted to chemical attack by HF acid for different durations (0 to 15h). In the following table, we present some examples showing the sequences forming the cell structure.

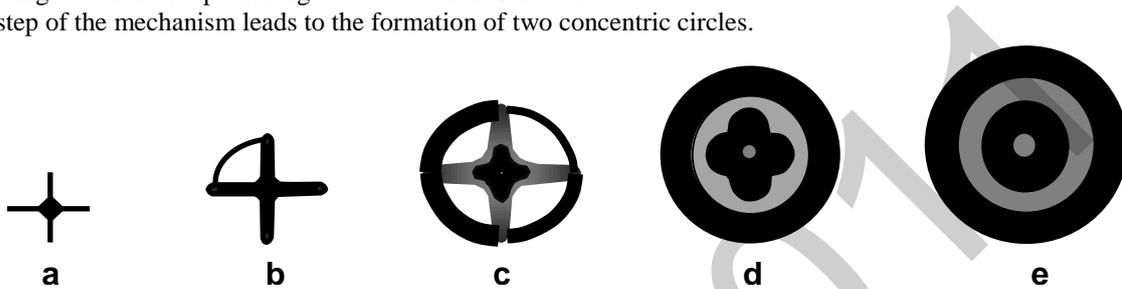
Table 1: Indentation imprints submitted to acid attack for various loads and durations

P (N)	0h	1h	3h	5h	8h	15h
5						
10						
15						

We can see that there are basically two mechanisms which differ depending on the applied loads (imprints size):

- For low loads: as the radial cracks and scales are of small size (tips of radial cracks are near the imprint), there is rapid formation of cells i.e. from the first moments. This formation is in the form of two concentric circles. The inner circle corresponds to the evolution of the imprint and the outer circle corresponds to lateral cracks which emerge in the surface.
  - For high loads: as the radial cracks and scales are much larger sizes (far away imprints), the mechanism of cells formation becomes clearer and demands greater attack durations.
- The following attack mechanism can be proposed (figure 8):

- Presentation of the original Vickers indentation.
- Under the action of chemical attack, the radial cracks begin to grow. There is appearance of some scales, and a clear blunting of the crack front.
- After a certain period, the defects size increases. The limits of lateral cracks form a closed contour more or less regular. The traces of the lateral and radial cracks continue to expand under the effects of chemical attack. The radial cracks tend to disappear and the imprints acquire a cross shape and they become larger.
- The contour grows again and becomes nearly circular. It is slightly distorted at the ends of radial cracks. The imprint presents swelling which the shape is irregular and it tends to become circular.
- The final step of the mechanism leads to the formation of two concentric circles.



**Figure 8:** Schematic diagram representing sequences of the chemical attack mechanism made on a Vickers indent.

## CONCLUSION

The aim of this work focuses on the influence of HF acid solution (3%) on the morphology of sandblasting defects, which are similar to defects induced by Vickers indentation. The study can be divided into two parts: the first part concerning the samples sandblasting and the second part on the chemical etching effect.

- Before sandblasting tests, the optical transmission, the average arithmetic roughness and flexural strength were determined. The values found are respectively:  $T_o = 91.6\%$ ,  $R_a = 0.054 \mu\text{m}$  and  $\sigma_f = 123.7 \pm 23 \text{ Mpa}$ . After sandblasting with a mass of 150 g, we got a remarkable drop in the optical transmission and mechanical strength, while the roughness shows a significant growth. The following values are respectively obtained:  $T_o = 22.4\%$ ,  $R_a = 2.9 \mu\text{m}$  and  $\sigma_f = 46.8 \text{ Mpa}$ . As the values of the mechanical strength present a great dispersion, especially in the case of as-received glass samples, the stress distribution using the Weibull statistical analysis was applied. Weibull modulus obtained for the two cases are respectively 5.80 (as-received) and 5.23 (sandblasted).

After etching the sandblasted surfaces, we noticed a small drop in the optical transmission at the beginning of the attack, followed by a clear improvement as the duration increases. However, the mechanical strength increases from the first moments, in contrast to the roughness which decreases with increasing attack duration. This is explained by the homogenization of the surface.

Weibull statistical analysis showed that the strength is governed by a single family of statistical defects. These are sandblasting defects which predominate. The Weibull modulus  $m$  varies slightly (between 4 and 6 for all the attack durations) and reflects the brittle nature of the chemically treated glass.

The surfaces sandblasted and then submitted to the action of HF solution for different periods, present a morphology that tends to become cellular for important periods. To try to explain this structure, Vickers indentation tests are performed with different loads on a raw glass.

The sequences forming the cellular structure are proposed. It was found that the size of the imprints and that of radial cracks increases with the applied loads. During the attack, lateral cracks emerge on the surface and there is a widening of their contours. When the attack duration is sufficient, arcs of lateral cracks interconnected and the final shape tends to become cellular with two concentric circles.

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## STUDY ON E-MARKETING WEBSITES AND DELIVERY SERVICE TO HOME

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### ABSTRACT

The main idea in this research is a comprehensive survey of e-marketing and delivery service to homes websites. Researchers visited top ten sites according to the most frequently used search engines "Google and Yahoo". Evaluation of these sites according to certain criteria is made to extract advantages and drawbacks. A website about electronic marketing and delivery service to homes was built with avoidance of many negative points that were found at the sites analyzed.

**Keywords:** E-marketing, Home-delivery, website, C#, ASP.NET.

### INTRODUCTION

E-commerce is a new term in the online world. It makes buying and selling, transferring funds, advertising and displaying products easy. E-commerce is a creative idea as it allows companies to offer their goods and products through their websites [2, 5]. E-marketing means using digital technologies such as websites, mobile devices and social networking to help reach your customer base, create awareness of your brand and sell your goods or services. These technologies can be used cheaply and effectively, whatever the size of your company or your business model. [1, 2]

The basics of marketing remain the same - creating a strategy to deliver the right messages to the right people. Though businesses will continue to make use of traditional marketing methods, such as advertising, direct mail and PR, e-marketing adds a whole new element to the marketing mix. Its flexible and cost-effective nature makes it particularly suitable for small businesses.

E-marketing gives businesses of any size access to the mass market at an affordable price and, unlike TV or print advertising, it allows truly personalized marketing. Specific benefits of e-marketing include: Global reach - a website allows you to find new markets and trade globally for only a small investment. Lower cost - a properly planned and effectively targeted e-marketing campaign can reach the right customers at a much lower cost than traditional marketing methods.

This research is aiming at comprehensive survey of e-marketing and delivery service to homes websites. Researchers use top ten sites according to the most frequently use search engines "Google and Yahoo". Evaluation of these sites according to certain criteria is made to extract advantages and drawbacks. A web site about electronic marketing and delivery service to homes was built with avoidance of many negative points that were found at the sites analyzed. The new web site helps customers to shop and use the home delivery services so they can save a lot of time and effort. Customers can use the internet to buy what they need from this website while setting home, simply by logging in to our page and choosing what they want. Then the delivery employee delivers the product to the customer's home and gets the money from the customer. Designed web site focused on security and safety issues for customers money and market rights.

### RELATED WORK

- In [7] This paper presents a framework of website quality evaluation for measuring the performance of government websites. Multiple criteria decision-making (MCDM) is a widely used tool for evaluating and ranking problems containing multiple, usually conflicting criteria. In line with the multi-dimensional characteristics of website quality, MCDM provides an effective framework for an inter-websites comparison involving the evaluation of multiple attributes. It thus ranks different websites compared in terms of their overall performance. This paper models the inter-website comparison problem as an MCDM problem, and presents a practical and selective approach to deal with it. In addition, fuzzy logic is applied to the subjectivity and vagueness in the assessment process. The proposed framework is effectively illustrated to rate Turkish government websites.[ 7]
- In [8] The Content Management Systems (CMS) are widely used on the Internet. They separate the content creation from the site design. Users without having web design or programming knowledge can create a professional website using a ready-made application that allows them to concentrate only over the content creation. A site powered by a CMS is called a dynamic website, because its content (text, images, and animations) could respond in various ways to the visitors' requests. The dynamic content is created using client site programming (JavaScript for example) or server side programming (ASP, PHP). Static websites are made only from HTML files.
- In order to modify them you must edit one by one, Usually CMS are database driven. The visitors will look at the front end, which is the final website displaying your content, while the backend allows you to manage the content that is stored in a database.
- Dynamic sites are easy to update and maintain. When you deal only with static html pages, the updating process could take hours, while the use of a CMS will simplify the content editing process. This is performed from an administration panel

through a simple browser based interface. Another advantage of CMS is the increased interactivity and functionality of your website. Most of CMS have lots of modules that allow you to enhance your website in minutes, website development being faster as compared to creation of static html files. For example you can have a news publishing system, a forum, a blog and an image gallery on the same website due to the CMS modularity. The disadvantages of CMS over static websites (formed only by HTML pages): low pages loading speed on client side due to multiple database requests and the SEO (search engine optimization) process is not always optimal due to the web addresses format, because the pages address names are dynamically generated. These impediments can be eliminated by optimizing CMS using PHP cache optimizers and short URL's names generators. The best practice is to carefully decide when a CMS is necessary, depending of the website size, the time interval when the content is updated and the web hosting services details.

In [14] Author presents six criteria for a thorough evaluation after identifying a number of potential web sources. These selection and evaluation criteria are the following: Visual clues, authority, currency, relevance, accuracy, and objectivity.

### CRITERIA OF WEB SITE ANALYSIS

Researchers access to most popular websites in e-commerce and e-marketing and analyze them by a set of the following criteria:

#### - Architecture and Navigation

**Consistency:** Page layout or style is consistence throughout the website , eg. justification of text , font types , font size, position of the navigation menu in each page .colours are consistent and provide consistent look and feel for navigation and information design ,eg. font colures ,background colures ,use of standard link colures (standard ,blue link color should be used for unvisited pages and purple or red colors for visited pages ).

**Navigation on Support** Navigational links are obvious in each page so that users can explore and find their way around the site and navigate easily ,e.g. index ,or site map, or navigation bar or table of contents.

**Internal search:** Internal search is effective, eg. fast ;accurate; provides useful, concise and clear results which are easy for interpreting.

**Working Links:** Links are discernible, working properly and not misleading so that the user knows what to expect from the destination pages ,eg. links are obvious, no broken links ,link names match page names.

**Resourceful** The site is informative and resourceful, eg.it has links to external useful resources

**No orphan pages** The site has no dead-end pages ,eg. Its easy and obvious to go to the home page from any sub-page of the site ,pages have a clear indication of their position within the site .

**Logical structure of site** The structure of the site is simple and straightforward ,related information is grouped together ,categorization of products is helpful .

Architecture is not too deep so that the number of click to reach goals is not too large.

**Simple navigation menu** Navigation menu is simple and straightforward, the menu choices are ordered logically so it is easy to understand the website.

#### -Content:

**Up-to-date information** The information is up-to-date, current, often update, date of last update is displayed and informs the user when new information is added.

**Relevant information** The information is sufficient and relevant to user needs, e.g. content is concise and non-repetitive, terminology/terms are clear and unambiguous, there are no under construction pages

**Accurate Information** The information is precise, e.g. product measurements ,total price services ,etc

**Grammatical Accuracy** Content is free from grammatical errors, eg. no spelling errors ,no grammar errors ,punctuation is accurate.

**Information About the company** Basic facts about the company or company overview are displayed, eg. year founded , type of business , purpose of its website etc.

**Information about the products** adequate information about the products is displayed ,eg. Description, photographs, availability , prices etc

#### Accessibility and communication:

##### Easy to find and access website

The site is easily identifiable and accessible from search engines, the url is domain related ,not complex , and easy to remember .download time of the pages is appropriate.

**Contact us information** Useful information to enable easy communication with the company is displayed , e.g. .faq,contact us (eg. name, physical address, telephone number, fax number, email details), customer feedback form to submit customers comments .

**Help \customer service** The help \customer service is easy to find ,has a clear and distinct layout ,searching for help \customer service is easy navigating in help\customer service is easy ,amount of information is sufficient ,concise and designed to answer the specific questions users will have in a specific context

**Compatibility** The site works with different browsers and on different monitor resolutions.

#### -Design:

**Aesthetic design** The site is attractive and appealing so that it impresses the potential customer .

**Appropriate use of images** Quality of images is adequate , no broken images, images make a contribution to the understanding and navigation of the site, alternative text is used for images, image size is relevant so that it has minimal effect on loading time.

**Appropriate choice of fonts and colors** Font types are appropriate and easy to read. Choice of colours for both fonts and background is appropriate, combination of background and font colours is appropriate .

**Appropriate page design** Pages are uncluttered, headings are clear page margins are sufficient, minimum or no long pages with excessive white space that force scrolling; particularly on the home page of the website, page title is appropriate, describing the company name and contents of each page.

#### - Transactions

**Easy order process** Registration on site is easy, changing customer information is easy, logging on to the site is easy, ordering process is easy ,changing the contents of the shopping cart(adding, deleting or editing) is easy obvious and accurate.

**Ordering information** Complete information about ordering is displayed and can be accessed easily ,e.g. how to order, payment options ,cancelling an order , return and refund policy ,terms and conditions.

**Delivery information** Information about delivery and dispatch of an order is displayed, e.g. delivery times, delivery costs , delivery areas delivery address options (the ability to deliver the order to another address ) ,delivery options , problems (e.g. non-delivery , late delivery ,incorrect delivery address etc.)

**Order\ delivery status provision** Company informs the customer about order status , e.g. by sending confirmation email to customer after placing an order, by sending dispatch confirmation email to customer when order is sent out, by using online order tracking system.

**Alternative methods of ordering \payment \delivery are available** Alternative methods of ordering (e.g. online )payment (visa ,credit card ),cash on delivery ,cherub by boost ,bank transference) and delivery (standard ,express ,etc)are supported so that the user can select the method that suits him \her.

**Reasonable confidence in security and privacy** The site uses secure socket layer or recognized secure payment methods ,information about security guarantee and privacy policy is clearly displayed.

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## WEBSITES ANALYSIS

Researchers list three websites in this section, and analyzed them depended on the previous criteria, same idea was applied to the other seven sites to get advantages and treat all the drawbacks to obtain a comprehensive website:

### 1- [www.mysupermarket.com](http://www.mysupermarket.com)

My Supermarket is a completely FREE website which allows you to compare supermarket prices as you shopping and get the best possible deal for your groceries figure 1 present the first page of this site.

#### Architecture and Navigation:

##### Exploration Heuristic

Page layout or style is consistence throughout the website , eg. justification of text , font types , font size ,position of the



This

Figure-1 My Supermarket website

navigation menu in each page . Colours are consistent and provide consistent look and feel for navigation and information design ,eg.font colours ,background colours ,use of standard link colours (standard ,blue link color should be used for unvisited pages and purple or red colors for visited pages ) .

**Consistency** Navigational links are obvious in each page so that users can explore and find their way around the site and navigate easily ,e.g. index ,or site map, or navigation bar or table of contents.

**Navigation on Support** Internal search is effective, eg. fast ;accurate; provides useful, concise and clear results which are easy for interpreting

**Internal search** Links are discernible, working properly and not misleading so that the user knows what to expect from the destination pages ,eg. links are obvious, no broken links ,link names match page names .

**Working Links** The site is informative and resourceful, eg. it has links to external useful resources

**Resourceful links** The site has no dead-end pages ,eg. Its easy and obvious to go to the home page from any sub-page of the site .pages have a clear indication of their position within the site.

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**Simple navigation menu**

**Content:**

**Up-to-date information** The information is up-to-date, current, often update ,date of last update is displayed and informs the user when new information is added

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**Accurate Information** The information is precise, e.g. product measurements, total price services, etc

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**Information about the products** Adequate information about the products is displayed ,eg. Description, photographs, availability ,prices etc

**Content:**

**Easy to find and access website** The site is easily identifiable and accessible from search engines, the url is domain related ,not complex , and easy to remember .download time of the pages is appropriate.

**Contact us information** Useful information to enable easy communication with the company is displayed , e.g. .faq,contact us (eg.name, physical address, telephone number, fax number, email details), customer feedback form to submit customers comments .

**Help \customer service** The help \customer service is easy to find ,has a clear and distinct layout ,searching for help \customer service is easy navigating in help\customer service is easy ,amount of information is sufficient ,concise and designed to answer the specific questions users will have in a specific context.

**Compatibility** The site works with different browsers and on different monitor resolutions.

**Foreign language and currency support** The sites content is displayed in different languages and uses more than one currency.

**Design:**

**Aesthetic design** The site is attractive and appealing so that it impresses the potential customer .

**Appropriate use of images** Quality of images is adequate , no broken images, images make a contribution to the understanding and navigation of the site, alternative text is used for images, image size is relevant so that it has minimal effect on loading time.

**Appropriate choice of fonts and colors** Font types are appropriate and easy to read. Choice of colours for both fonts and background is appropriate, combination of background and font colours is appropriate .

**Appropriate page design** Pages are uncluttered, headings are clear page margins are sufficient, minimum or no long pages with excessive white space that force scrolling; particularly on the home page of the website, page title is appropriate, describing the company name and contents of each page.

**Transactions:**

**Easy order process** Registration on site is easy, changing customer information is easy, logging on to the site is easy, ordering process is easy ,changing the contents of the shopping cart(adding, deleting or editing) is easy obvious and accurate .

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**Alternative methods of ordering \payment \delivery are available** Alternative methods of ordering (e.g. online )payment (visa ,credit card ),cash on delivery ,cherub by boost ,bank transference) and delivery (standard ,express ,etc)are supported so that the user can select the method that suits him \her .

**Reasonable confidence in security and privacy** The site uses secure socket layer or recognized secure payment methods, Information about security guarantee and privacy policy is clearly displayed.

2- [www.wairose.com](http://www.wairose.com) : the second website to be analyzed is wairos which represents a Mall site

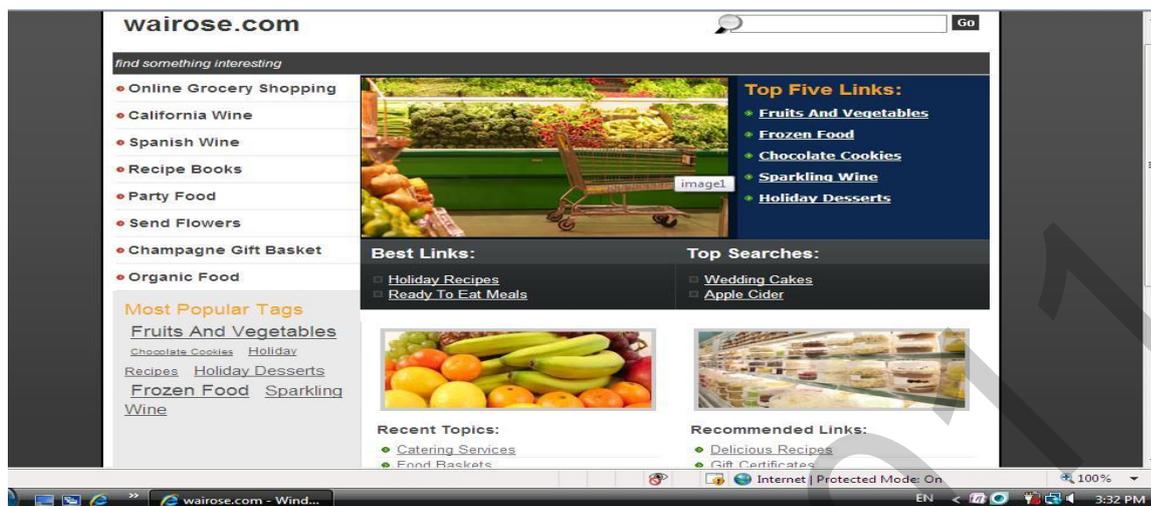


Figure-2 Wairose website

Description the site:- this The following analyses focus on advantages and disadvantages of this site.

#### Architecture & navigation

Content: -Up-to-date information Often update is displayed & informs the user when new information is added.

Relevant information Content is concise & non repetitive. Information is precise; total price; services

Grammatical Accuracy: Very good Information. About the company: overview was displayed and Information about the product.

Consistency Use more than colure of the key; background white & black; good font size. so page layout & style is consistent throughout the web sit

Navigation support Use index; & use table of content; no site map; no navigation bar; Internal search is not understood & very slow.

Working links very clear & link match page name. Resourceful link the site is not informative it has no link to external useful resources.

No orphan page: there is a orphan page because easy to move in the pages Logical structure of site.

Categorization of product is helpful; the architecture is not deep so that the number of click to reach goals not large.

Use simple navigation menu. Description; photograph ; prices

Accessibility & communication: Menu is Simple & choices are ordered, easy to find & access web site

The site is not easy to identifiable & accessible from search Contact us information No information to communication with company. Help-customer service Customer service is easy to find; searching for help

Compatibility site works with different browsers Foreign language & currency The site no different language.

#### Design

Use a very simple aesthetic design. Use appropriate images. Font types are easy to read & color for both font & background is appropriate. Appropriate page design Page are cluttered; heading are not clear

#### Transaction:-

Easy order process Easy to registration in the site ;but not easy to changing the content of the shopping cart

Ordering information No payment option & no return and refund policy

Delivery information Delivery time ; cost ; areas & address

Order-delivery Company not inform the customer about order status

Reasonable security & privacy Not use secure in this site

3- the last site in this research is a mall website in Jordan that represents many activities which contain home delivery the address of the site is : <http://www.safeway.com.jo>

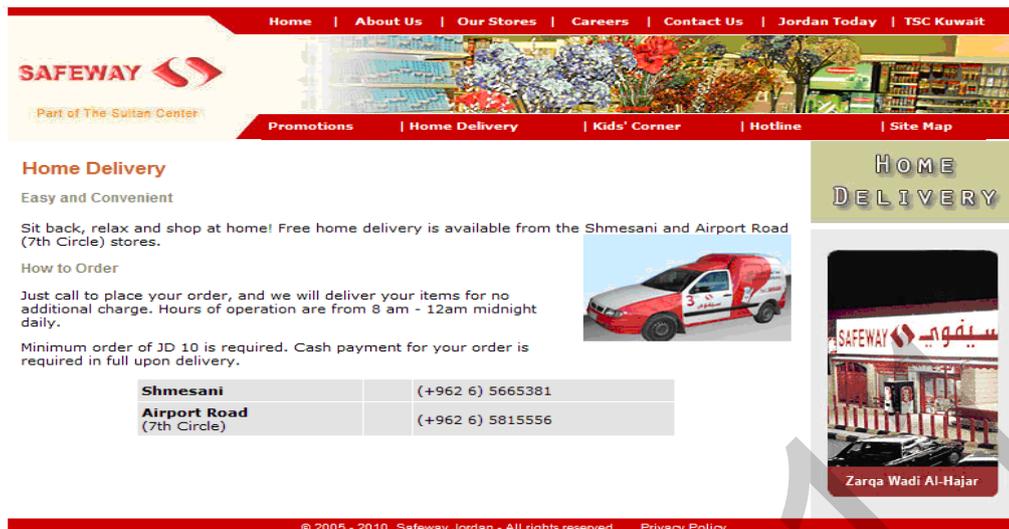


Figure-3 Safeway website

Architecture and navigations:

Consistency: red color keys, The background Color white, font size=16, There is great consistency between the colors because of the color red Intro and the end of the site

Navigation support : have an index but complex and does not have a search function. Working links are very clear, good working ,resourceful links and don't have external links.

Orphan page: site have many orphan pages.

Logical structure of site: understand people easily (usability) but we think developers must reduce the writings and images of more than simple navigation menu

Content: Up-to-date, Relevant and Accurate information, also the site has Information about the company and the product.

Accessibility and communication: Easy to find and access web site

### New website

Devtohome :This website contain many interfaces the most important is the home page which include :index, main gate gory, search, and contact us service and details about every item in the website. The main idea of this site is to allow the user to select goods and requirements from supermarket then request it on line. The problems of electronic money payment were treated. Researchers focus on the security problem by adding a flag for each record to prevent any person with bad history from using the site. Also we use registration procedure and keep phone numbers to prevent the tricks and thrift. Search in our website use optimal algorithms to get the results in short time and give the user many options to make the search in simple navigation menu. Site doesn't have any orphan page and links are used. Figure 3 show the first page of devtohome website.

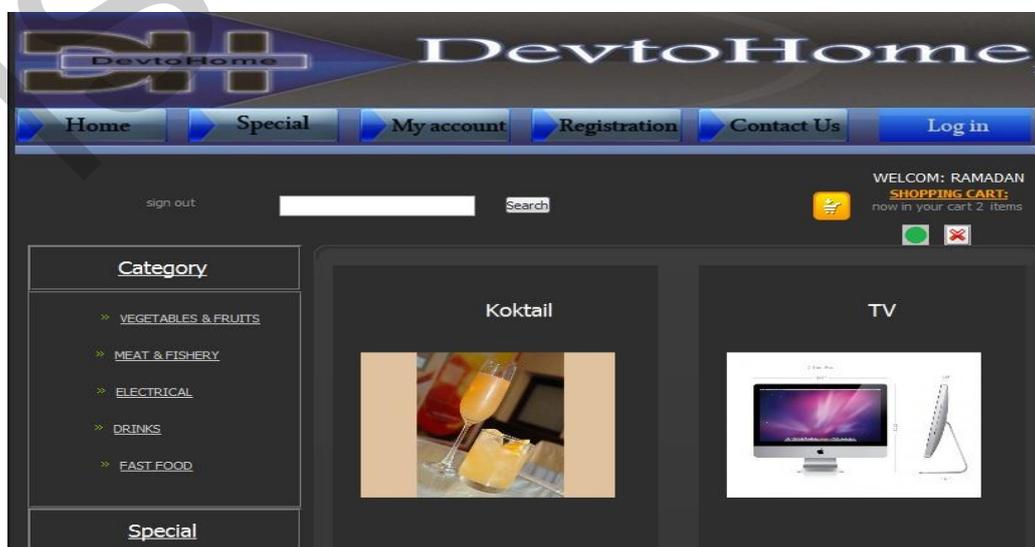


Figure-4 New Designed Website (Devtohome )

This research is funded by the Deanship of Research and Graduate Studies in Zarqa University /Jordan

## CONCLUSION AND FUTURE WORK

In this research, a comparison of ten popular sites related to e-marketing, and home delivery were adopted. More than thirty factors affecting the websites design were used. Research team took advantages and disadvantages from these sites to present a new site for home delivery marketing.

Research team hope to design a questionnaire, to assess new site performance and to compare with other predecessor sites.

### Acknowledgement

This research is funded by the Deanship of Research and Graduate Studies in Zarqa University /Jordan.

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# SYNTHESIS AND ANTIMICROBIAL EVALUATION OF NOVEL 1,2,4-TRIAZOLO[1,5-*a*] PYRIDINE, 1,2,4- TRIAZOLO[3,4-*b*]1,3,4-THIADIAZOLE AND 1,2,4- TRIAZOLO[3,4-*b*]1,3,4 THIADIAZINE DERIVATIVES

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## ABSTRACT

The reactivity of acid hydrazide **2** towards some carbon electrophiles was convenient for synthesis of some novel triazolo[1,5-*a*]pyridone and bispyrazolyl derivatives **8a,b** and **12** respectively. The new 1,2,4-triazole-5-thiol derivative **16** used as a precursors for synthesis of some new 1,2,4-triazolo[3,4-*b*]1,3,4-thiadiazoles **17a,b**, 1,2,4-triazolo[3,4-*b*] 1,3,4-thiadiazine derivatives **18a,b** and **20**. Some of the newly synthesized compounds were tested *in vitro* for their antibacterial and antifungal activities and showed promising results.

**Keywords :** N- alkylazoles, thiadiazoles, thiadiazine, derivatives, antimicrobial activity

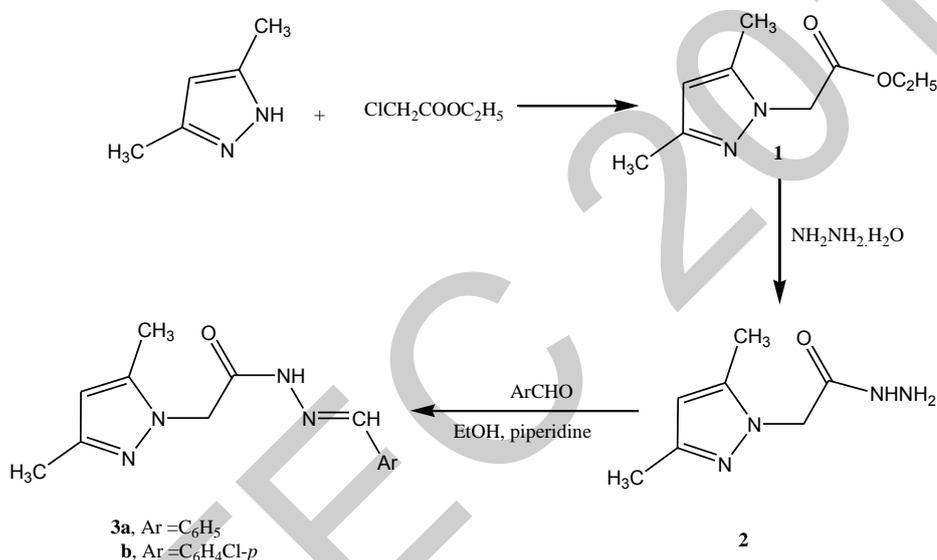
## INTRODUCTION

In continuation of our program in studying the chemistry of substituted N-alkylazoles<sup>1-3</sup> aiming to produce heterocyclic compounds with expected biological activities.<sup>17-18</sup> In this work ethyl(3,5-dimethylpyrazol-1-yl) acetate **1** was used to synthesize triazolo[1,5-*a*]pyridine derivatives which have pronounced biological activity as antidepressants,<sup>19,13</sup> however, their synthetic approaches are rather limited.<sup>13,18</sup> Also, 1,2,4-triazolo[3,4-*b*]thiadiazoles and 1,2,4-triazolo[3,4-*b*] thiadiazine derivatives were synthesized which reported to have good antimicrobial activity.<sup>17,13</sup>

## RESULTS AND DISCUSSION

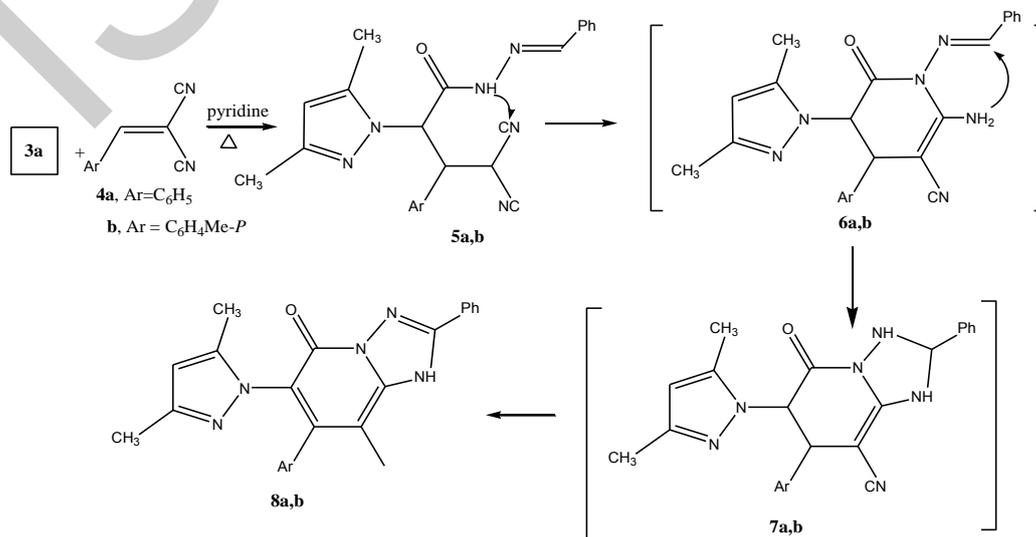
Ethyl (3,5-dimethylpyrazol-1-yl) acetate **1** can be prepared via reaction of 3,5-dimethylpyrazole with ethyl chloroacetate in refluxing toluene and in presence of an equimolar amount of triethylamine. The IR spectrum of **1** revealed absorption band at  $\nu_{\max} = 1675 \text{ cm}^{-1}$  for the carbonyl ester and <sup>1</sup>H NMR showed a triplet at  $\delta = 1.17 \text{ ppm}$  and a quartet at  $\delta = 4.17 \text{ ppm}$  characteristic for ethyl ester group and two singlet signals recognizable for the methyl groups at C-5 and C-3 at  $\delta = 2.01$  and  $\delta = 2.15 \text{ ppm}$  besides two singlets at  $\delta = 4.70$  and  $\delta = 5.83 \text{ ppm}$  for the N- methylene and pyrazolyl4-H. Treatment of compound **1** with hydrazine hydrate in refluxing ethanol for one hour gave the hydrazide product **2**. The structure of product **2** was established based on its analytical and spectral data. IR spectrum revealed bands at  $\nu_{\max} = 3360, 3309$  and  $3193 \text{ cm}^{-1}$  for the NH<sub>2</sub>, NH stretching and band at

1658  $\text{cm}^{-1}$  for carbonyl group,  $^1\text{H NMR}$ , revealed singlet at  $\delta = 4.86$  ppm for (N- $\text{CH}_2$ ), two  $\text{D}_2\text{O}$ -exchangable broad signals at  $\delta = 7.47$  ppm, 8.71 ppm due to  $\text{NH}_2$  and  $\text{NH}$  groups besides the other singlet that appear at their expected positions. Condensation of the acid hydrazide derivative **2** with aromatic aldehydes in refluxing ethanol and few drops of piperidine as a catalyst provide the Schiff's base compounds **3a,b** in good yields (cf. Scheme 1). As a typical example, the structure of **3a** was established based on its analytical and spectral data. The IR spectrum of compound **3a** revealed NH stretching at  $\nu_{\text{max}} = 3415$   $\text{cm}^{-1}$  and CO stretching at  $\nu_{\text{max}} = 1680$   $\text{cm}^{-1}$ . Its  $^1\text{H NMR}$  spectrum revealed two singlets at  $\delta = 1.98$  and 2.19 ppm for two methyl groups at C-3 and C-5 of pyrazole, singlet at 4.76 ppm for (N- $\text{CH}_2$ ), singlet at 5.81 ppm for pyrazolyl 4-H a multiplet at  $\delta = 7.43$ -8.25 ppm for aromatic protons, ylidene CH and a broad singlet at  $\delta = 11.63$  ppm or NH. Moreover, the mass spectrum of compound **3a** showed a molecular ion peak at  $m/z = 256$  ( $\text{M}^+ 100\%$ ), which is compatible with molecular formula  $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}$ .

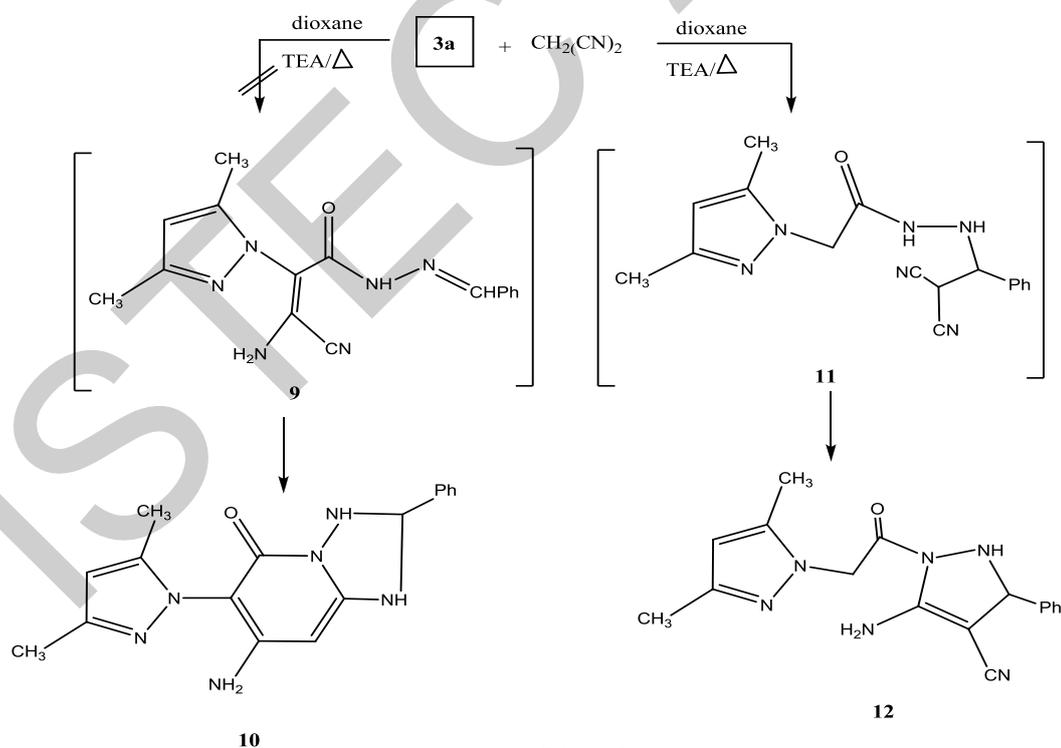


Scheme 1

1,2,4-Triazolo[1,5-*a*]pyridine derivatives **8a,b** can be easily synthesized by facile and efficient route. Thus, compound **3a** reacts with cinnamionitriles **4a,b** in refluxing pyridine to afford **8a,b** respectively via intramolecular cyclization and outoxidation in good yields (Scheme 2). The structure of **8a** was established based on elemental analysis and spectral data.



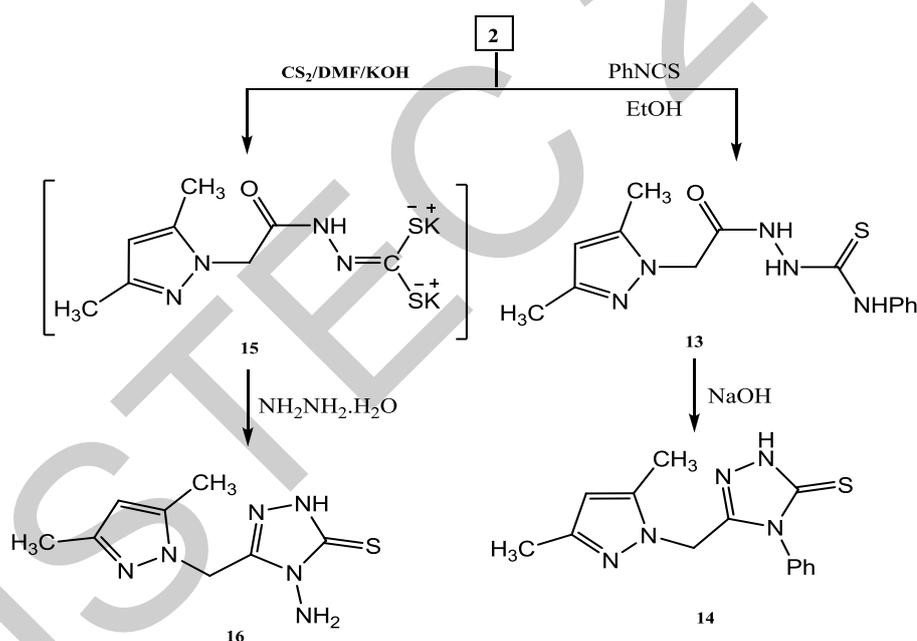
Thus, the IR spectrum revealed absorption band at  $\nu_{\max} = 3186 \text{ cm}^{-1}$  for NH and a band at  $2205 \text{ cm}^{-1}$  for CN group.  $^1\text{H}$  NMR revealed the absence of singlet corresponding to active methylene  $\text{CH}_2$  and appearance of two singlets at  $\delta = 2.09$  and  $2.10 \text{ ppm}$  for two methyl groups at C-3 and C-5 of pyrazole, singlet at  $5.83 \text{ ppm}$  for pyrazolyl 4- H, a multiplet for aromatic protons at  $\delta = 7.43\text{-}8.20$  and  $\text{D}_2\text{O}$ -exchangeable signal at  $\delta = 10.80 \text{ ppm}$  for NH,  $^{13}\text{C}$  NMR also revealed signals at  $\delta = 114.3$  and  $168.9 \text{ ppm}$  which are corresponding to CN and CO groups, respectively, besides the other carbon atoms that appear at their expected positions (cf. experimental part). Furthermore, the mass spectrum of product **8a** revealed molecular ion peak at  $m/z = 406(\text{M}^+, 48 \%)$  corresponding to molecular formula  $\text{C}_{24}\text{H}_{18}\text{N}_6\text{O}$ . The formation of **8a,b** is assumed to take place via *Michael type addition* of methylene group in **3** to the active double bond in **4a,b** to form acyclic nonisolable intermediates **5a, 5b** which are cyclized to pyridine derivatives **6a,b**. The latter undergo further cyclization spontaneously into tetrahydro-1,2,4-triazolo[1,5-*a*]pyridine derivatives **7a,b** which in turn undergo auto oxidation to afford the final isolable products **8a,b**. Similar cyclization have been reported in literature.<sup>18</sup> Compound **3a** reacts with malononitrile in dioxane under refluxing in presence of catalytic amount of triethylamine to give predictable compound **10** or **12**. The bicyclic isomeric Structure **10** was excluded based on spectral data which confirmed the isomeric structure **12**. Thus, the IR spectrum which revealed the presence of absorption band at  $\nu_{\max} = 2218 \text{ cm}^{-1}$  for CN group. and at  $\nu_{\max} = 3368, 3304, 3211, 1642$  for  $\text{NH}_2$ , NH and CO groups. The  $^{13}\text{C}$  NMR showed two signals at  $\delta = 115.3$  and  $160.9 \text{ ppm}$  for CN and CO groups, respectively, beside the other signals appear at their expected positions. (Scheme 3)



Scheme 3

Reaction of the acid hydrazide **2** with phenyl isothiocyanate in refluxing ethanol for two hours afforded the 1:1 adduct of thiosemicarbazide derivative **13** in good yield, which in turn cyclized, by boiling in NaOH (5%) to yield 1,2,4-triazolthiol derivative **14** as shown in (Scheme 4). The structure of compound **14** was confirmed based on its analytical and spectral data. The IR spectrum revealed the absence of any absorption bands for NH stretching at  $\nu_{\max} = 3150 \text{ cm}^{-1}$  and corresponding to CO group,  $^1\text{H NMR}$  revealed a singlet at  $\delta = 12.01 \text{ ppm}$  for SH, a singlet at  $\delta = 4.86 \text{ ppm}$  for N-CH<sub>2</sub> besides the other signals that appear at their expected positions (cf. experimental part).

The new key intermediate **16** was prepared from the reaction of the acid hydrazide **2** with carbon disulphide in the presence of dimethylformamide and a catalytic amount of potassium hydroxide to produce the non isolable intermediate salt **15** which reacted with hydrazine hydrate to afford 1,2,4-triazole derivative **16**. The structure of compound **16** was confirmed *via* inspection of analytical and spectral data. Thus, the mass spectrum shows a molecular ion peak at  $m/z = 224$  ( $M^+$  100%) which is established for molecular formula of  $\text{C}_8\text{H}_{12}\text{N}_6\text{S}$ . Moreover, the IR spectrum revealed NH<sub>2</sub>,NH stretching at  $\nu_{\max} = 3460, 3320, \text{ and } 3150 \text{ cm}^{-1}$  and  $^1\text{H NMR}$  revealed two singlets at 1.09 and 1.10 ppm for two methyl groups at  $\delta = \text{C-3}$  and C-5 pyrazole, a singlet at  $\delta = 4.64 \text{ ppm}$  for CH<sub>2</sub>, a singlet at  $\delta = 5.89 \text{ ppm}$  for pyrazolyl 4- H, and two signals ( $\text{D}_2\text{O}$ -exchangeable) assigned to NH<sub>2</sub> and NH protons at  $\delta = 4.96$  and 13.10 ppm (Scheme 4).

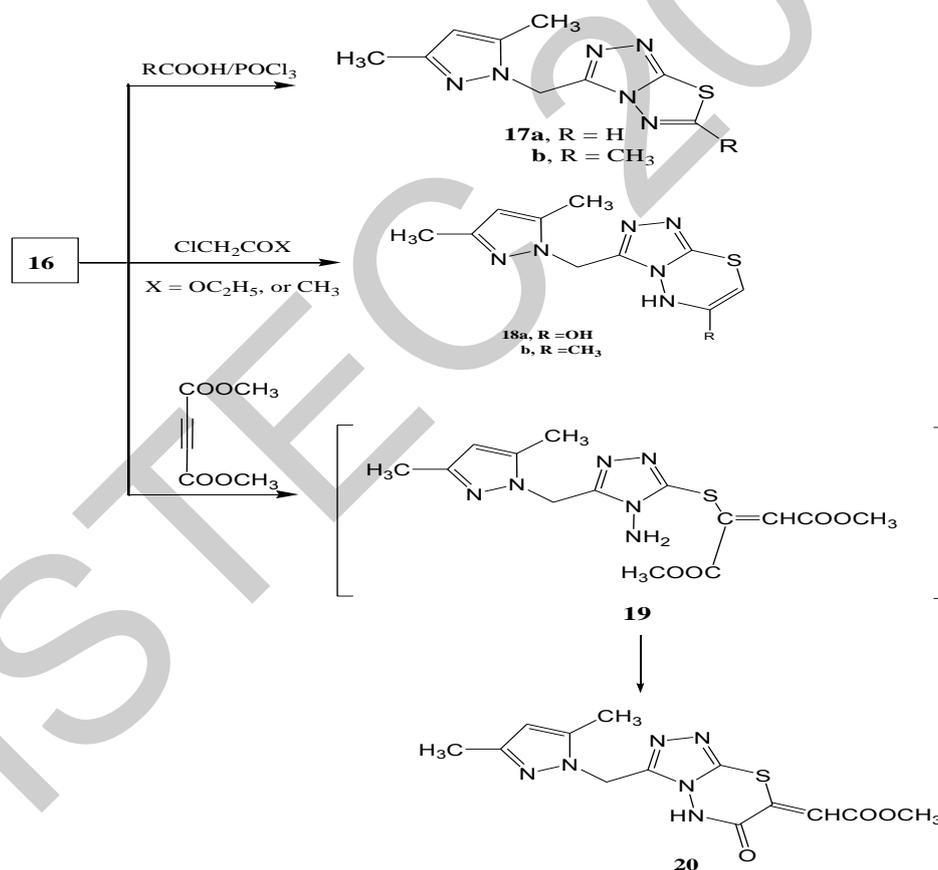


Scheme 4

Compound **16** was considered as starting material for the synthesis of a variety of new compounds (cf. Scheme 5). Thus condensation of **16** with carboxylic acid in presence of phosphorus oxychloride<sup>14</sup> produces the triazolothiadiazole derivatives **17a,b**. Structures of **17a,b** were established based on the analytical and spectral data (cf. experimental part). Also, condensation of **16** with ethyl chloroacetate or chloroacetone in refluxing ethanol in presence of a catalytic amount of triethylamine afforded the 1,2,4-triazolo[3,4-b]1,3,4-thiadiazine derivatives **18a,b**. The products were assumed to be obtained *via* elimination of HCl and ethanol molecules in **18a** or HCl and water in **18b**. The structures of **18a** and **18b** were

established based on the spectral and analytical data. Thus,  $^1\text{H}$  NMR spectrum of compound 18a revealed the absence of any signal corresponding to ethyl ester. (cf. experimental part). Reaction of compound **16** with dimethyl acetylenedicarboxylate (DMAD) in refluxing ethanol in presence of a catalytic amount of acetic acid provided the 1:1 adduct **20**. Compound **20** was assumed to be formed *via Michael addition* of SH to the triple bond of acetylene derivative followed by cyclocondensation with elimination of methanol.

The structure of compound **20** was confirmed based on the analytical and spectral data. Thus, the mass spectrum of the isolated product **20** shows a molecular ion peak at  $m/z = 334$  ( $M^+$  100%) which is compatible for the molecular formula  $\text{C}_{13}\text{H}_{14}\text{N}_6\text{O}_3\text{S}$ . Also, IR spectrum revealed a band at  $\nu_{\text{max}} = 3390\text{ cm}^{-1}$  for NH, absorption bands at 1720 and  $1650\text{ cm}^{-1}$  for the ester and amide carbonyl groups.  $^1\text{H}$  NMR revealed two singlets at  $\delta = 0.89$  and  $1.23\text{ ppm}$  for the two methyl groups in pyrazole at C-3 and C-5, a singlet at  $\delta = 2.41\text{ ppm}$  for methyl ester, two singlets at  $\delta = 4.14$  and  $5.42\text{ ppm}$  for methylene and pyrazolyl H-4, respectively, a singlet at  $7.41\text{ ppm}$  for olefinic CH and a singlet at  $8.21\text{ ppm}$  for NH. Moreover,  $^{13}\text{C}$  NMR revealed two signals at 161 and 169 ppm for the two carbonyl groups, a signal at 44.1 ppm for  $\text{CH}_2$  and signals at 118 and 152.6 ppm for olefinic carbons besides the other signals at their expected positions (cf. experimental part).



Scheme 5

## EXPERIMENTAL

The melting points were determined on a Stuart melting point apparatus and are uncorrected. The IR spectra were recorded as KBr pellets using a FTIR unit Bruker-vector 22

spectrophotometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO- $d_6$  as solvent at 300 MHz and 75 MHz, respectively on Varian Gemini NMR spectrometer using TMS as internal standard. Chemical shifts are reported in  $\delta$  units (ppm). Mass spectra were measured on a Shimadzu GMMS -QP-1000 EX mass spectrometer at 70 eV. The elemental analyses and the biological evaluation of the selected newly synthesized heterocyclic compounds were performed at the Micro analytical Center, Cairo University, Giza, Egypt.

#### ***Ethyl (3,5-Dimethylpyrazol-1-yl)acetate (1)***

A solution of 3,5-dimethylpyrazole (0.96 g, 10 mmol) in dry toluene (30 ml) was treated with ethyl chloroacetate (1.23 g, 10 mmol) in presence of triethylamine (1 ml). The reaction mixture was refluxed for 5 hours. The solvent was evaporated under vacuum and the solid product so formed, was collected by filtration and crystallized from benzene.

Beige crystals; yield (92%); mp 72°C; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  1675 (CO);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  at 1.17 (t, 3H, CH<sub>3</sub>), 2.01 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 4.17 (q, 2H, CH<sub>2</sub>), 4.70 (s, 2H, N-CH<sub>2</sub>), 5.83 (s, 1H, pyrazolyl 4-H). MS: m/z 182 (M<sup>+</sup>100%). Anal. Calcd for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (182.225): C, 59.32; H, 7.74; N, 15.37%. Found: C, 59.26; H, 7.76; N, 15.23%.

#### ***2-(3,5-Dimethylpyrazol-1-yl)acetic acid hydrazide (2)***

Hydrazine hydrate (0.5 g, 10 mmol) was added to a solution of ethyl (3,5-dimethylpyrazol-1-yl) acetate (1.8g, 10 mmol) in ethanol (10 ml). The reaction mixture was heated under reflux for one hour, concentrated in vacuum, the solution was cooled and the solid product formed was filtered and crystallized from ethanol.

Yellowish white crystals; yield 95%; mp 182°C; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3360, 3309, 3193 (NH), (NH<sub>2</sub>) 1658 (CO);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  at 1.07 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 4.86 (s, 2H, CH<sub>2</sub>), 5.87 (s, 1H, pyrazolyl 4-H), 7.47 (br. s, 2H, NH<sub>2</sub>, D<sub>2</sub>O-exchangable), 8.71 (br. s, 1H, NH, D<sub>2</sub>O-exchangable); Anal. Calcd for C<sub>7</sub>H<sub>12</sub>N<sub>4</sub>O (168.20); C, 49.98; H, 7.19; N, 33.31%. Found: C, 49.93; H, 7.21; N, 33.36%.

#### **General procedure for synthesis of 3a,b**

To a solution of 2 (1.68 g, 10 mmol) in (30 ml) ethanol was added aryl aldehyde (1.41 g, 10 mmol) followed by few drops of piperidine. The reaction mixture was refluxed for 3 hours and the solvent was evaporated under vacuum. The solid product so formed, was collected by filtration and crystallized from ethanol

#### ***2-(3,5-Dimethylpyrazol-1-yl) acetic acid benzylidenehydrazide (3a)***

White crystals; yield 90%; mp 140°C; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3415 (NH), 1680 (CO);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  at 1.98 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.19 (s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 4.76 (s, 2H, N-CH<sub>2</sub>), 5.81 (s, 1H, pyrazolyl 4-H), 7.43 - 8.25 (m, 5H, Ar H, 1 H ylidene CH), 11.63 (br. s, 1H, NH); MS: m/z 256 (M<sup>+</sup> 100%) Anal. Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O (256.31): C, 65.60; H, 6.29; N, 21.85%. Found: C, 65.54; H, 6.15; N, 21.65%.

#### ***2-(3,5-Dimethylpyrazol-1-yl)acetic acid (4-chlorobenzylidene)hydrazide (3b)***

White crystals; yield 80%; mp 168°C; IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$  3341 (NH), 1680 (CO),  $^1\text{H}$  NMR (DMSO- $d_6$ ) at 1.11 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 1.18 (s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 5.01 (s, 2H, N-CH<sub>2</sub>), 5.89 (s, 1H, pyrazol 4-H), 6.82-8.05 (m, 4H, Ar H, 1H ylidene CH), 9.85 (s, 1H, NH); Anal. Calcd. for C<sub>14</sub>H<sub>15</sub>ClN<sub>4</sub>O (290.75): C, 57.83; H, 5.20; N, 19.27; Cl, 12.19%. Found: C, 57.65; H, 5.19; N, 19.69; Cl, 12.32%.

### General procedure for synthesis of( 8a,b):

A solution of 3a (2.56 g, 10 mmol) in pyridine was treated with arylidene malononitrile 4a or 4b (10 mmol). The reaction mixture was heated under reflux for 8 hours, then left to cool; the solvent was removed under vacuum, then diluted with water and acidified by concentrated HCl. The formed solid product was collected by filtration, washed with water and crystallized from ethanol.

#### **6-(3,5-Dimethylpyrazol-1-yl)-5-oxo-2,7-diphenyl-1H-[1,2,4]triazolo[1,5-a]pyridine-8-carbonitrile (8a)**

Yellowish white crystals; yield 75% ; mp 182°C, IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3186 (NH), 2205 (CN),  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  ppm 2.09(s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.10(s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 5.83 (s, 1H, pyrazol 4-H) , 7.43-8.20 (m, 10H, Ar H), 10.80 (s, 1H, NH D<sub>2</sub>O exchangeable),  $^{13}\text{C}$  NMR (DMSO- $d_6$ ) :  $\delta$ ppm 10.1, 13.2 (2CH<sub>3</sub>), 114.3 (CN), 106.1 , 120.5, 120.5, 126.2, 128.2, 128.4, 136.1, 139.2,143.1, 147.3, 154.6, 158.7, 168.9 (CO); MS: m/z 406 (M<sup>+</sup> 100%) Anal. Calcd. for C<sub>24</sub>H<sub>18</sub>N<sub>6</sub>O (406.45): C, 70.92; H ,4.46; N, 20.67%. Found: C, 70.93; H, 4.47; N, 20.68%.

#### **7-(4-methyl-phenyl)-6-(3,5-dimethyl-pyrazol-1-yl)-5-oxo-2-phenyl-1-H-[1,2,4]triazolo[1,5-a]pyridine-8-carbonitrile (8b)**

Yellowish white crystals; 85%; mp 205°C; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3390 (NH), 2221 (CN), 1690 (CO);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  at 1.98 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.01 (s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 2.21(s, 3H, CH<sub>3</sub>) 5.61 (s, 1H,pyrazol 4-H), 7.71-8.12 (m, 9H, Ar H), 10.81 (s, 1H, NH); Anal. Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>6</sub>O (420.477): C, 71.41; H, 4.79; N, 19.98; %. Found: C, 71.35; H, 4.87; N, 19.89%.

#### **5-Amino-1-(3,5-dimethylpyrazol-1-yl)acetyl-3-phenyl-2H-pyrazole-4-carbonitrile (12)**

To a suspension of 3a (2.56 g, 10 mmol) in dioxane (20 ml) and a catalytic amount of piperidine was treated with malononitrile (0.66 g, 10 mmol). The reaction mixture was heated under reflux for 5 hours. The solution was evaporated under reduced pressure. The solid product, so formed, was collected by filtration.

Yellow crystals; yield (90%); mp 205°C; IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3368, 3304, 3211, (NH<sub>2</sub>), ( NH), 2218, (CN) 1642 (CO),  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$ ppm 1.03(s, 3H, CH<sub>3</sub>, pyrazolyl 3CH<sub>3</sub>), 1.07(s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 2.2 (br. s, 2H, NH<sub>2</sub>), 4.8 (br. s, 1H, NH); 4.9 (s, 2H, N-CH<sub>2</sub> ); 5.4 (s,1H, pyrazolyl- 4H); 5.75 (s, 1H, pyrazolyl-H-4), 7.39-7.53 (m, 5H, ArH);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  9.91, 10.1 (2 CH<sub>3</sub>), 115.30(CN), 120.56, 120.59, 120.64, 126.21, 128.20, 135.10, 162.91 (CO). MS m/z 322 (M<sup>+</sup>100%) Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>N<sub>6</sub>O (320.35) C, 63.73; H, 5.03; N, 26.23%. Found C, 63.70; H, 5.10; N, 26.29%.

#### **4-Phenyl-1-(1-carbonylmethyl-(3,5-dimethyl-pyrazol-1-yl)thiosemicabazide (13)**

A solution containing (3,5-dimethylpyrazol-1-yl) acetic acid hydrazide **2** (1.68g, 10 mmol) and phenyl isothiocyanate (1.35g, 10 mmol) in ethanol (20 ml) was heated under reflux for 2 hours and left over night at room temperature . The solid product so formed was filtered and crystallized from ethanol.

Yellowish white crystals; yield 90% ; mp 189°C, IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3300 , 3150 (NH) , 1685 (CO),  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  at: 1.13(s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 1.89(s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 4.9 9 (s, 2H,N- CH<sub>2</sub>), 5.65 (s,1H, pyrazol 4-H), 7.12-8.20 (m, 5H, ArH), 8.57, 9.17, 9.98(3 br. s., 3H, 3NH); Anal. Calcd. for C<sub>14</sub>H<sub>17</sub>N<sub>5</sub>OS (303.39): C ,55.42; H, 5.64; N, 23.08; S, 10.56%. Found: C, 55.45; H, 5.61; N, 23.07; S, 10.38%,

**5-(3,5-Dimethylpyrazol-1-ylmethyl)-4-phenyl-2,4-dihydro-[1,2,4]triazole-3-thione (14)**

A suspension of compound **13** (3.3g, 10 mmol) in sodium hydroxide solution (5% 5ml) was heated under reflux for one hour. The reaction mixture was allowed to cool, neutralized with 10% hydrochloric acid. The precipitate formed was filtered, washed with water and crystallized from ethanol.

Yellowish white crystals; yield 70%; mp 298°C; IR(KBr)  $\nu_{\max}/\text{cm}^{-1}$  3150 (NH);  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  at 1.07(s, 3H, CH<sub>3</sub>, pyrazolyl 3CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 4.86 (s, 2H, N-CH<sub>2</sub>), 6.12 (s, 1H, pyrazol 4-H); 7.01-8.20 (m, 5H, Ar-H); 15.01 (s, 1H, NH); Anal. Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>S (285.37) C, 58.92; H, 5.29; N, 24.54; S, 11.23% Found: C, 58.89; H, 5.29; N, 24.51; S, 11.31%.

**4-Amino-5-(3,5-dimethylpyrazol-1-ylmethyl)2,4-dihydro-[1,2,4]triazole-3-thione (16)**

To cold solution of **2** (1.68 g, 10 mmol) in absolute ethanol (25ml) containing potassium hydroxide (0.84 g, 15mmol), carbon disulphide (1.14 g, 10 mmol) was added gradually. The reaction mixture was stirred over night at room temperature, and then hydrazine hydrate (1 g, 20 mmol) was added with stirring and heated under reflux for 2 hours. The reaction mixture was cooled, diluted with water and acidified with 10% hydrochloric acid. The solid product formed was filtered and crystallized from ethanol.

Yellow crystals mp 204°C, IR(KBr)  $\nu_{\max}/\text{cm}^{-1}$  3320, 3150 (NH) and (NH<sub>2</sub>), 1630 (C=N),  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  at 1.09 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 1.10(s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 4.64(s, 2H, N-CH<sub>2</sub>), 4.96 (br. s, 2H, NH<sub>2</sub>), 5.89 (s, 1H, pyrazol 4-H-), 15.10 (s, 1H, NH) MS: m/z 224 (M<sup>+</sup>100%) Anal. Calcd. For C<sub>8</sub>H<sub>12</sub>N<sub>6</sub>S (224.29); C,42.84; H,5.39, N,37.47, S,14.29% Found: C,42.82, H,5.37, N,37.21, S,14.32%.

**General procedure for synthesis of 17a,b:**

A mixture of compound **16** (2.2 g, 10 mmol) and appropriate carboxylic acid (formic acid or acetic acid) (10 mmol) in phosphorus oxychloride (4ml) was heated under reflux at 90°C for one hour. The reaction mixture was cooled, poured over sodium carbonate solution. The solid product formed was filtered and crystallized from dioxane.

**3-(3,5-Dimethylpyrazol-1-ylmethyl)[1,2,4]triazolo[3,4-b][1,3,4]thiadiazole (17a)**

Brown crystals; yield 65%; mp 234°C,  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ ppm 1.22(s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 1.32(s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 4.82 (s, 2H, N-CH<sub>2</sub>), 5.36 (s, 1H, pyrazol 4-H), 8.10 (s, 1H, thiadiazoly 5-H-),  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$ ppm 10.21, 13.10 (2, CH<sub>3</sub>), 59.21(CH<sub>2</sub>), 108.22, 133.11, 136.2, 138.20, 141.31; Anal. Calcd for C<sub>9</sub>H<sub>10</sub>N<sub>6</sub>S (234.28) C, 46.14, H, 4.30, N, 35.87, S, 13.68% Found: C, 45.87, H, 4.69, N, 35.66, S, 13.39%.

**3-(3,5-Dimethylpyrazol-1-ylmethyl)-6-methyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazole (17b)**

Brown crystals; mp 192°C;  $^1\text{H}$ NMR, (DMSO- $d_6$ )  $\delta$ ppm, 1.19 (s, 3H, CH<sub>3</sub>), 2.09 (s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.43(s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 5.2 (s, 2H, CH<sub>2</sub>) 6.01(s, 1H, pyrazol 4-H); Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>6</sub>S (248.31); C, 48.37; H, 4.87; N, 33.84; S, 12.91% Found: C, 48.44; H, 4.58; N, 33.61; S, 12.79%.

**General procedure for synthesis of 18a,b:**

A solution of compound **16** (2.20g, 10 mmol) and ethyl chloroacetate or chloroacetone (10ml) in absolute ethanol (50ml) was heated under reflux for 5 hours, then left to stand over night at room temperature, neutralized by sodium carbonate solution. The solid product formed was filtered and crystallized from ethanol.

**3-(3,5-Dimethylpyrazol-1-ylmethyl)-5H-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazin-6-one (18a)**

brown crystals; yield 65%; mp 239°C; IR(KBr)  $\nu_{\max}/\text{cm}^{-1}$  3250 (NH), 1674 (CO)  $^1\text{H}$  NMR, (DMSO- $d_6$ )  $\delta$  at 1.13(s, 3H, CH<sub>3</sub>, pyrazolyl 3CH<sub>3</sub>), 1.89(s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 4.25 (s, 2H, triazolothiadiazine), 5.19 (s, 1H, pyrazol 4-H), 6.1(s, 2H, CH<sub>2</sub>), 8.51 (s, 1H, NH), MS: m/s 264; (M<sup>+</sup>100)% Anal. Calcd For C<sub>10</sub>H<sub>12</sub>N<sub>6</sub>SO (264.31) C, 45.0044, H, 4.57, N, 31.79, S, 12.13% Found: C, 45.385; H, 4.57; N, 31.61; S, 12.22%.

**3-(3,5-dimethylpyrazol-1-ylmethyl)-6-methyl-7H-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazine (18b)**

Brown crystals; yield 84%; mp 174°C, IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3150(NH), 1625(C=N)  $^1\text{H}$  NMR, (DMSO- $d_6$ )  $\delta$  at 1.81(s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.01(s, 3H, CH<sub>3</sub>, pyrazolyl 5-CH<sub>3</sub>), 2.62 (s, 3H, CH<sub>3</sub>), 3.68 (s, 2H, triazolothiadiazine-yl7-H) 5.61(s, 1H, pyrazol 4-H); Anal. Calcd. For C<sub>11</sub>H<sub>14</sub>N<sub>6</sub>S (262.34) C, 50.36; H, 5.37; N, 32.03; S, 12.22 %. Found: C, 50.41; H, 5.26, N, 32.21; S, 12.15%.

**3-methyl-(3,5-dimethylpyrazol-1-ylmethyl)-6-oxo-5,6-dihydro-[1,2,4]-triazolo[3,4-b][1,3,4]-thiadiazin-7-ylidenacetic acid methyl ester (20)**

To compound **16** (2.2 g, 10 mmol) add dimethyl acetylenedicarboxylate (2g, 10mmol), dissolved them in methanol(50ml) and trace of glacial acetic acid was added. The reaction mixture refluxed for 10 hours. The reaction mixture was cooled, neutralized with sodium carbonate and the solid product so formed was collected by filtration and crystallized from acetic acid.

White crystals m.p 210 °C, (KBr)  $\nu_{\max}/\text{cm}^{-1}$  3390 (NH), 1720, 1685 (carbonyl ester, CO),  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  at 1.23(s, 3H, CH<sub>3</sub>, pyrazolyl 3-CH<sub>3</sub>), 2.09(s, 3H, CH<sub>3</sub>, pyrazolyl 5CH<sub>3</sub>), 3.83 (s, 3H, CH<sub>3</sub>), 4.81 (s, 2H, CH<sub>2</sub>), 5.42 (s, 1H, pyrazol 4-H), 7.41 (s, 1H, olefinic, proton), 8.91 (s, 1H, NH),  $^{13}\text{C}$  (DMSO- $d_6$ )  $\delta$  11.3, 13.4, 44.1, 59.3, 106.3, 118.7, 147.1, 148, 148.7, 152, 152.6, 158.2, 161, 169, (CO), Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>6</sub>O<sub>3</sub>S (334.36), C, 46.69, H, 4.22, N, 25.13, S, 9.59 % Found : C, 46.51, H, 4.12, N, 25.52, S, 9.54%

**Biological activity**

The antibacterial and antifungal activity was carried out in the microbiology revision of micro analytical centre of Cairo University. Using the diffusion plate method<sup>11-14</sup> a bottomless cylinder containing a measured quantity (1ml, mg/ml) of the sample is placed on a plate (9 cm diameter) containing a solid bacterial medium (nutrient agar broth) or fungal medium (Dox's medium) which has been heavily seeded with the spore suspension of the test organism. After incubation (24 hours for bacteria and 5 days for fungi), the diameter of the clear zone of the inhibition surrounding the sample is taken as measure of inhibitory power of the sample against the particular test organism.

Most of the compounds were tested *in vitro* against gram negative bacteria (*Escherichia coli anaerobic* (EC) and *Staphylococcus* (SA) and antifungal activity against *Candida Albicans* (CA) and *Aspergillus Flavus* (AF). The reference antibiotics *Tetracycline* and *Amphotericin B* were used as references to evaluate the potency of the tested compounds under the same condition. The test results are depicted in Table 1 on the following basis;

The solvent used was DMSO.

Concentration of the sample in 100 g/ml

IZD = 2-10 mm beyond control = + (low activity)

IZD = 11-24 mm beyond control = ++ (moderate activity)

IZD = 25-35 mm beyond control = +++ = (high activity)

	<i>Inhibition zone diameter (mm / mg sample )</i>			
Sample	<i>Escherichia Coli( G+) Bacteria</i>	<i>Staphylococcus Albums(G+) Bacteria</i>	<i>Aspergilla's Flavus Fungus</i>	<i>Candida Albicans Fungus</i>
Control: DMSO	0.0	0.0	0.0	0.0
8a	15 ++	18 ++	0.0	0.0
8b	16 ++	18 ++	0.0	0.0
13	13 ++	13 ++	0.0	0.0
14	16 ++	15 ++	0.0	0.0
16	13 ++	12 ++	0.0	10 +
17a	17 ++	19 ++	14 ++	13 ++
17b	17 ++	15 ++	0.0	13 ++
18a	16 ++	15 ++	0.0	9 +

18b	13 ++	12 ++	0.0	10 +
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### CONCLUSION

The tested results revealed that all compounds exhibits moderate activity against *Escherichia Coli* (EC) and *staphylococcus aureus*. Most compounds have no activity against *Aspergillus flavus* (fungus) and *Candida albicans* (fungus) except 16, 17a, b, 18a, b.

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# SYNTHESIS AND CHARACTERIZATION OF NEW LIQUID CRYSTALLINE SALICYLALDIMINES

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## ABSTRACT

Presently, liquid crystal (LC) compounds are materials of marvellous technology products such as cell phones, laptop displays, digital watches and calculators [1, 2]. Schiff bases or imines are widely studied as liquid crystalline materials. The azomethine bond ( $-\text{HC}=\text{N}-$ ) is usually incorporated into the molecular structure to increase the length and polarisability anisotropy of the compound core and consequently enhance liquid crystal phase stability. Moreover, azomethines are very interesting class of organic compounds for investigations of their liquid crystal properties from the point of view of their rich polymorphism [2]. Salicylaldimine derivatives have attracted considerable attention with regard to their structure–property relationships. The vast majority of compounds exhibiting liquid crystalline phases may be regarded as having a rigid molecular central group with one or two flexible terminal alkyl or alkoxy chains [3-6].

The aim of this work is the synthesis and characterization of the new salicylaldimines with two different terminal groups. For this purpose, salicylaldimine derivatives were synthesized and their liquid crystal behaviours were studied. Characterization of the salicylaldimines were performed by using spectroscopic methods (UV-VIS, FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR). New calamitic liquid crystalline salicylaldimines, 5-(10-undecenyloxy)-2-[[[4-tetradecyloxyphenyl]imino]methyl]-phenol (**6**) and 5-(10-undecenyloxy)-2-[[[4-hexadecyloxyphenyl]imino]methyl]-phenol (**7**) were prepared by *p*-toluensulfonic acid catalyzed condensation of 2-hydroxy-4-(10-undecenyloxy)benzaldehyde with 4-tetradecyloxyaniline and 4-hexadecyloxyaniline in toluene, respectively. Crystallization from acetone/methanol gave yellow crystals

The thermal and mesogenic behaviours of these calamitic salicylaldimine compounds were examined by optical polarizing microscopy (PM).

**Key words:** Schiff bases, Salicylaldimines, Liquid crystal

## INTRODUCTION

Schiff bases, named after Hugo Schiff [7-8], are formed when any primary amine reacts with an aldehyde or ketone under specific conditions. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group has been replaced by an imine or azomethine group. Schiff bases are some of the most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizer [9].

Liquid crystals (LC) are an important phase of both scientific and technological aspects. The liquid crystal state is a kind of state whose order between the crystal solid and isotropic liquid states [10]. Research on liquid crystals exploded during the 1970s and 1980s. Liquid crystal synthesis is a field in its own right, especially in investigating structure-property relationships. Technologically, liquid crystal came a part of our daily lives. First time LC were used in wristwatches and pocket calculators but nowadays being used for displayed in all sorts of instruments, including portable computers and televisions. Advantages of liquid crystal displays are their low power consumption and small size [11].

The salicylaldimine's materials feature among the earliest and most widely studied class of liquid crystals. These compounds are stabilized by intramolecular hydrogen bonding [12-15]. The salicylaldimines compounds exhibit mono- and polymorphism. Salicylaldimine derivatives have attracted considerable attention with regard to their structure–property relationships. The vast majority of compounds exhibiting liquid crystalline phases may be regarded as having a rigid molecular central group with one or two flexible terminal alkyl or alkoxy chains [3-6].

In this work is the synthesis and characterization of the new salicylaldimines with two different terminal groups. For this purpose, salicylaldimines were synthesized and their liquid crystal behaviours were studied. Characterization of the salicylaldimines were performed by using spectroscopic methods (UV-VIS, FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR).

The thermal and mesogenic behaviours of these calamitic salicylaldimine compounds were examined by optical polarizing microscopy (PM).

## EXPERIMENTAL

### Metarials

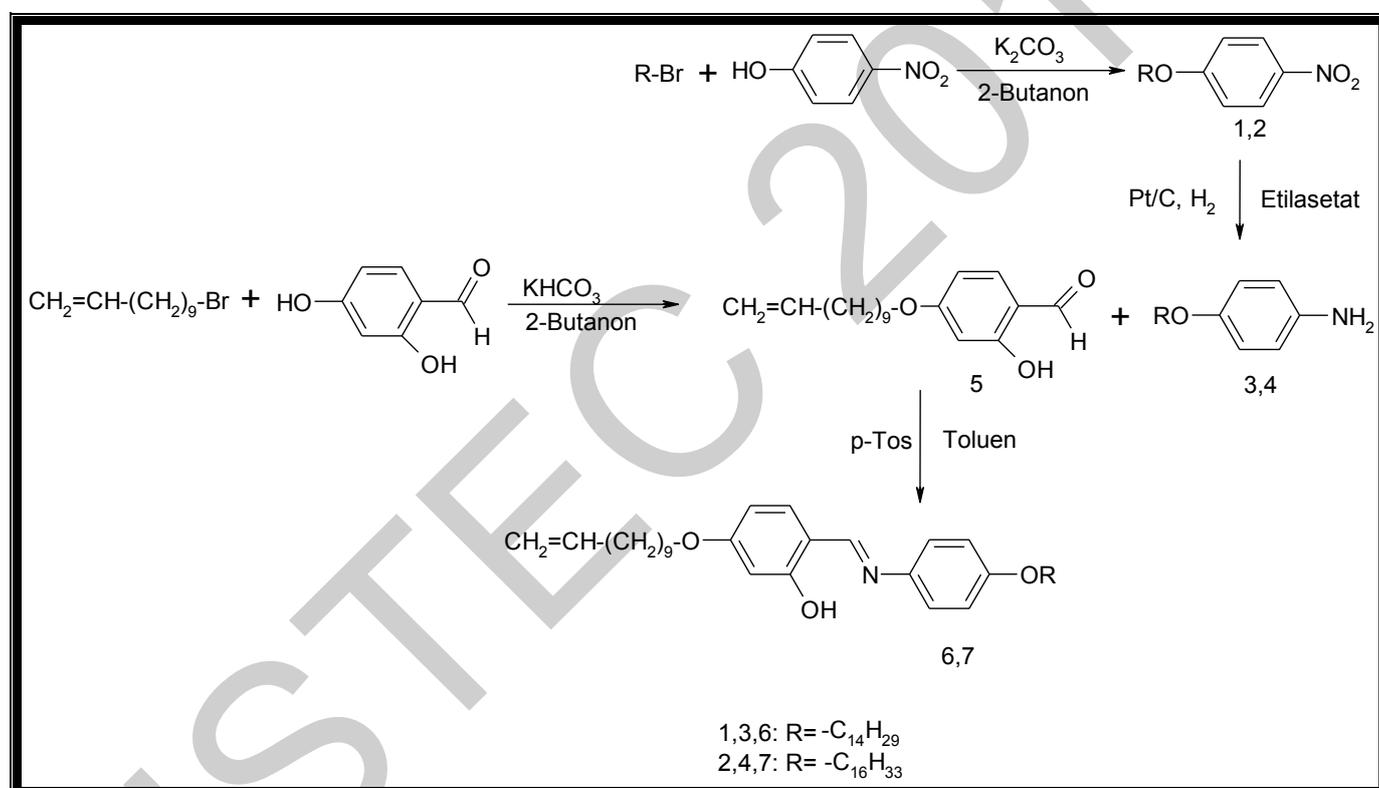
The reagents were purchased from Merck, Aldrich, Alfa Aesar or Fluka and used without further purification.

### Synthesis of Salicylaldimines **6** and **7**

The synthesis of the compounds is presented in Scheme 1. The nitro compounds **1** and **2** prepared reactions of 1-bromotetradecan or 1-bromhexadecan with p-nitrophenol in 2-Butanon to give 4-tetradecyloxynitrobenzene (**1**) and 4-hexadecyloxynitrobenzene (**2**), respectively, as described previously. Compound **1** and **2** were reduced to the corresponding anilines **3** and **4**.

The aldehyde **5** was obtained by the reaction of 2,4-dihydroxybenzaldehyde with 11-brom-1-undecene in the presence of  $\text{KHCO}_3$  as a base and 2-Butanon as a solvent.

p-Toluenesulfonic acid catalyzed condensation reaction of 2-hydroxy-4-(10-undecenyloxy) benzaldehyde (**5**) with 4-tetradecyloxylaniline (**3**) or 4-hexadecyloxylaniline (**4**) in toluene gave the salicylaldimines **6** and **7**, respectively. The reaction solution was reflux for 5 h in Ar atmosphere. The **6** and **7** purified by recrystallization from acetone/methanol. Yellow crystalline product was obtained and dried. (yellow crystals, 1,35 g, %60 yield of **6**, yellow crystals, 0,82 g, %45 yield of **7**). The chemical structures of **6** and **7** were characterized by the common spectroscopic methods (UV-VIS, FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ).



Scheme 1. Synthesis of salicylaldimine compounds **6** and **7**

## CHARACTERIZATION

The chemical structures of salicylaldimine were confirmed by standart methods:

Ultra violet-visible (UV-Vis) studies were performed in quartz cell  $\text{CHCl}_3$  as solvent using a Agilent 8453 spectroscope.

Fourier transform infrared (FTIR) studies were performed by ATR eqment using a Perkin- Elmer FTIR spectroscope at a resolution of  $4\text{ cm}^{-1}$ . The scanned wavenumbers range from  $4,000$  to  $400\text{ cm}^{-1}$ .

$^1\text{H NMR}$  measurements was conducted on Bruker 400 MHz in  $\text{CDCl}_3$  as solvent with tetramethylsilane (TMS) as the internal reference.

$^{13}\text{C NMR}$  measurements was conducted on Bruker 400 MHz in  $\text{CDCl}_3$  as solvent with tetramethylsilane (TMS) as the internal reference.

Liquid crystalline behaviour of the salicylaldimines were investigated by polarising optical microscopy using Leitz Laborlux 12 Pol polarising microscope, equipped with Linkam THMS 600 hot stage and Linkam TMS93 temperature controller.

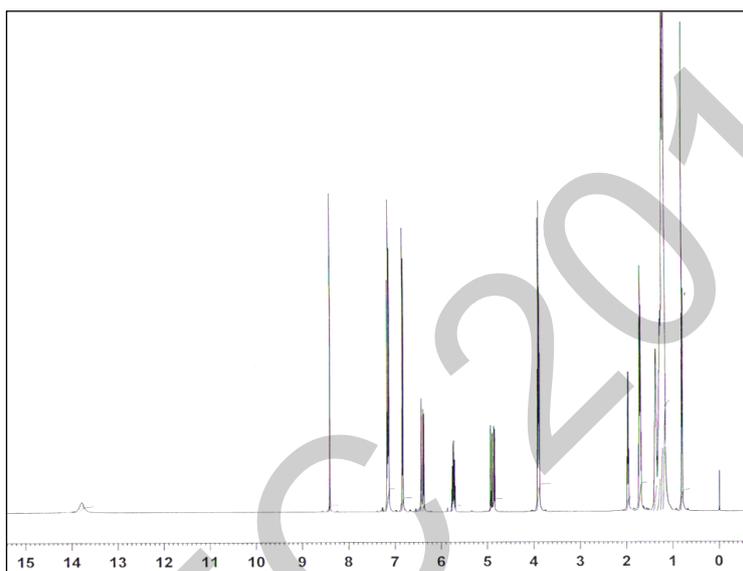
## RESULTS and DISCUSSION

### Synthesis and Characterization of Salicylaldimines **6** and **7**

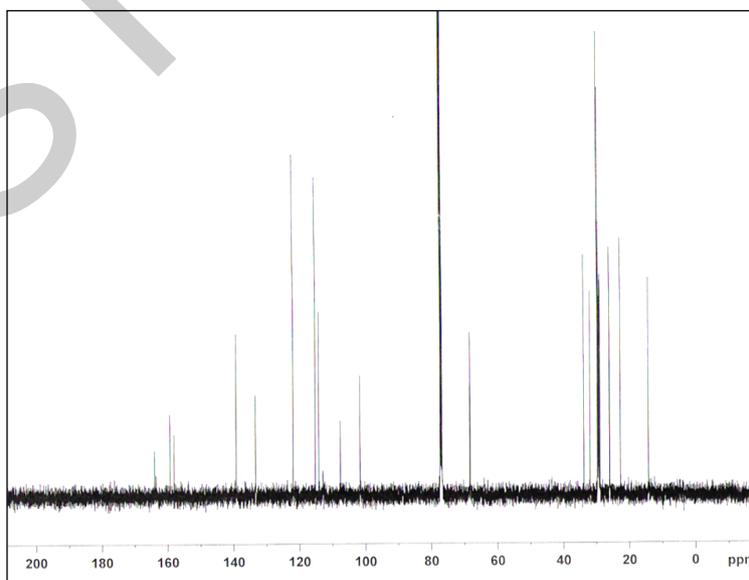
The general reaction scheme for the synthesis of salicylaldimines was given in **Scheme 1**.

The salicylaldimine **6** and **7** were prepared by the *p*-toluenesulfonic acid catalyzed condensation of the 2-hydroxy-4-(10-undecenyloxy)benzaldehyde (**5**) with 4-tetradecyloxyaniline (**3**) and 4-hexadecyloxyaniline (**4**), respectively.

The chemical structure of the **6** and **7** were confirmed by standard methods: UV-VIS, FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ . The proposed structures are full agreement with the all spectroscopic data. The resonance of the salicylaldimine **6** was observed at 13.90, 8.50, 5.95-4.76 ppm which was assigned to  $-\text{OH}$ ,  $\text{HC}=\text{N}$  and  $-\text{CH}=\text{CH}_2$ , respectively. The spectroscopic data of salicylaldimines (**6,7**) are given in the **Table 1**. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectrum of **6** have shown in **Fig. 1** and **Fig.2**.



**Fig. 1** The  $^1\text{H-NMR}$  spectrum of **6**



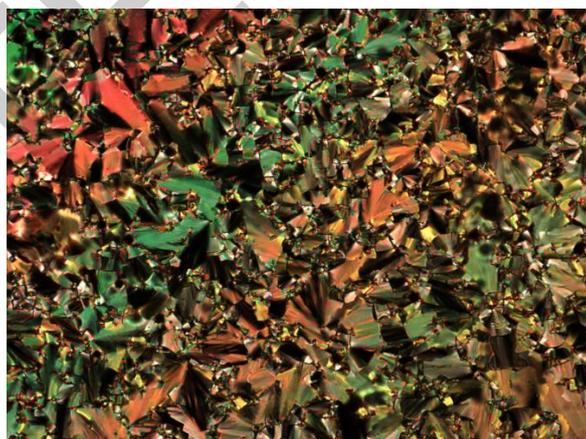
**Fig. 2** The  $^{13}\text{C-NMR}$  spectrum of **6**

**Table 1:** The spectroscopic data of salicylaldimines **6** and **7**

Compound	UV-Vis $\lambda$ (nm)	FT-IR $\gamma$ ( $\text{cm}^{-1}$ )	$^1\text{H-NMR}$ $\delta$ (ppm)	$^{13}\text{C-NMR}$ $\delta$ (ppm)
<b>6</b>	349.1	3076 (-CH=CH <sub>2</sub> )	13.90 (s, -OH)	159.36 (HC=N)
		1619 (C=N)	8.50 (s, HC=N)	139.22 -114.14 (-CH=CH <sub>2</sub> )
			5.95-4.76 (m, -CH=CH <sub>2</sub> )	
<b>7</b>	348.9	3084 (-CH=CH <sub>2</sub> )	13.90 (s, -OH)	159.31 (HC=N)
		1622 (C=N)	8.42 (s, HC=N)	139.23 -114.14 (-CH=CH <sub>2</sub> )
			5.79-4.82 (m, -CH=CH <sub>2</sub> )	

#### Liquid Crystalline Behavior of Salicylaldimines **6** and **7**

The mesomorphic properties of salicylaldimines **6** and **7** were studied by optical polarizing microscopy (PM). Optical polarizing microscopic and morphologic investigations of salicylaldimines showed that the salicylaldimines **6** and **7** exhibit liquid crystalline properties. The compounds **6** and **7** show thermotropic mesophases. The compounds **6** and **7** exhibit smectic mesophase. These mesophases are enantiotropic which are displayed by typical textures of SmC. The texture of **6** showed in **Fig.3** and the texture of **7** showed in **Fig.4**.



**Fig. 3** Optical texture (200 x) observed on cooling from the isotropic phase for the salicylaldimine **6** SmC phase at 115 °C.

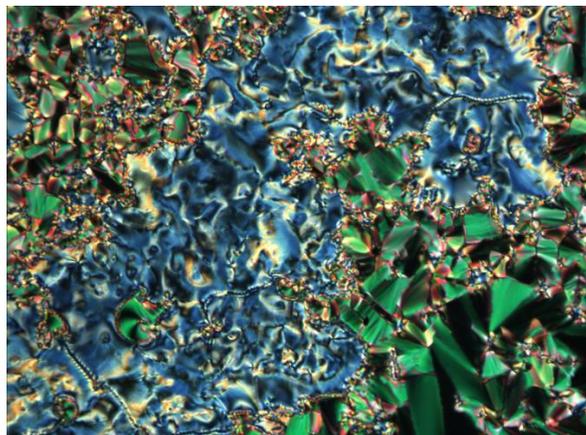


Fig. 4 Optical texture (200 x) observed on cooling from the isotropic phase for the salicylaldimine 7 SmC phase at 110 °C.

The transition temperatures and mesophase types observed for these compounds (6,7) are given in Table 2.

Table 2: Phase transition temperatures T (°C)<sup>a</sup> 6 and 7; Cr: crystalline, Sm: smectic and Iso: isotropic phase

Compound	R	T °C <sup>a</sup>
6	-C <sub>14</sub> H <sub>29</sub>	Cr 79 SmC 120 Iso
7	-C <sub>16</sub> H <sub>33</sub>	Cr 84 SmC 117 Iso

<sup>a</sup> Heating rates are 10.0 °C min<sup>-1</sup> for the melting and for the clearing processes.

## CONCLUSION

Two different liquid crystalline salicylaldimines, 5-(10-undecenyloxy)-2-[[[4-tetradecyloxyphenyl]imino]methyl]-phenol (**6**) and 5-(10-undecenyloxy)-2-[[[4-hexadecyloxyphenyl]imino]methyl]-phenol (**7**) were synthesized and their chemical structures were confirmed by UV-VIS, FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR. The salicylaldimine compound **6** and **7** exhibits liquid crystalline properties and show thermotropic enantiotropic mesophases. POM investigations indicate that the salicylaldimines **6** and **7** exhibit liquid crystalline phases of smectic C textures.

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# SYNTHESIS, BIOLOGICAL ACTIVITY OF HYDRAZIDE-HYDRAZONES AND 4-THIAZOLIDINONES DERIVED FROM ETODOLAC

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## ABSTRACT

Etodolac hydrazone; 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole-1-yl) acetohydrazone [2] and a novel series of new etodolac hydrazone derivatives; 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole-1-yl) acetic acid [(5-nitro-2-furyl/substituted phenyl)methylene] hydrazones [3-15] and 3-(2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole-1-yl)acetyl hydrazono)-2-alkyl/aryl-4-thiazolidinones [16-26] were synthesized in this study. The structures of new compounds were determined by spectral (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, HREI-MS) methods. An anticancer activity of the selected compounds was determined at one dose towards the full panel of 60 human cancer cell lines by the National Cancer Institute (NCI). 2-(1,8-Diethyl-1,3,4,9-tetrahydropyrano[3,4-*b*]indole-1-yl) acetic acid [(4-chlorophenyl)methylene] hydrazone, 9 demonstrated the most marked effect on prostate cancer cell line PC-3 with 41.76% growth percent at 10<sup>-5</sup> M. Because of this result, this compound was evaluated for caspase-3 activation for apoptosis, which plays a key role in the treatment of cancer. The antiproliferative effect of compound 9 was evaluated *in vitro* using the MTT colorimetric method against two human cancer cell lines (prostate cell line PC-3 and melanoma cell line MDA-MB-435).

**Keywords:** Apoptosis, Etodolac, Hydrazone-Hydrazone, 4-Thiazolidinone, Anticancer

## INTRODUCTION

Etodolac [1,8-diethyl-1,3,4-tetrahydropyrano(3,4-*b*)indole-1-acetic acid] is a nonsteroidal anti-inflammatory agent with analgesic, antipyretic, and antiinflammatory properties. The U.S. Food and Drug Administration approved etodolac for the treatment of inflammation and pain caused by osteoarthritis and rheumatoid arthritis. Etodolac has a stronger inhibitory effect on cyclooxygenase-2 (COX-2) activation. Its mechanism of action is inhibition of COX with reduction in the synthesis of prostaglandins and other mediators of inflammation and pain. In recent days, it has been reported that etodolac has antitumor activity on many types of cancer, such as urogenital system cancers (Shigemura *et al.*, 2005; Okamoto *et al.*, 2008); Burkitt's lymphoma (Kobayashi *et al.*, 2005), multiple myeloma, chronic lymphocytic leukemia and prostate cancer. (Carson *et al.*, 2003; Carson *et al.*, 2006a; Carson *et al.*, 2006b)

Etodolac is a commercially available NSAID containing a racemic mixture, in which the *S*-enantiomer has COX inhibitory activity, whereas the *R*-enantiomer does not (Demerson *et al.*, 1983). The two enantiomers very often exhibit different pharmacological activities. The *R*-Etodolac is a novel pro-apoptotic agent with potential anti-tumor activity against B-cell chronic lymphocytic leukemia (Robak *et al.*, 2006; Jensen *et al.*, 2008) and hepatocellular cancer (Behari *et al.*, 2007). The behavior of etodolac shows that the use of optically pure drugs is very considerable for their applications.

Prostaglandins are thought to play an important role in the proliferation of prostate cancer and are highly expressed in prostate cancer tissue. COX-2 inhibitors such as etodolac, suppress proliferation, induce apoptosis in prostate cancer cells and have no effect in normal prostate stromal cells (Kamijo *et al.*, 2001; Shigemura *et al.*, 2005).

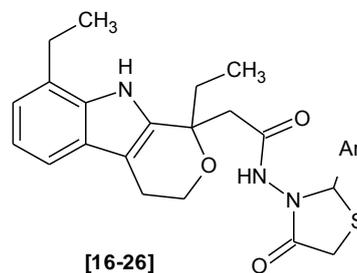
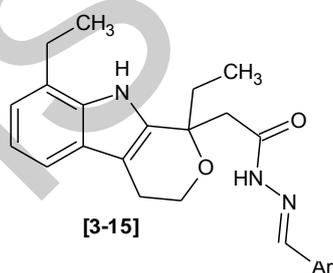
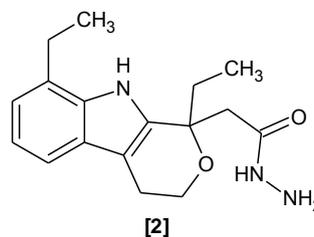
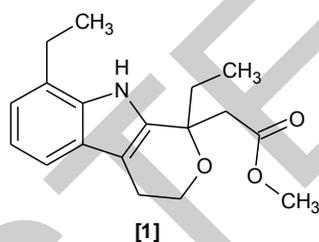
There is need to develop the new, potent, fast-acting antitumoral drugs with low toxicity. Hydrazones possessing an azometine -NHN=CH- proton constitute an important class of compounds for new drug development. Therefore, many researchers have synthesized these compounds as target structures and evaluated their biological activities (Rollas and ŞG.Küçükgül, 2007). The search for more effective and less toxic antitumoral drugs, led to the discovery of hydrazide-hydrazones containing new compounds having antitumoral activity (Hofmann *et al.*, 2006.) In previous studies, it has been reported that hydrazide-hydrazones possess antitumoral activity (Terzioğlu and Gürsoy, 2003; Gürsoy and Karali, 2003; Demirbaş *et al.*, 2004; El-Hawash *et al.*, 2006; Jin *et al.*, 2006; Vicini *et al.*, 2006; Gürsoy and Güzeldemirci, 2007; Liu *et al.*, 2009). There is also a report on the discovery of a hydrazone derivative as an apoptosis inducer that caused a high degree of growth inhibition in A549 lung cancer cells (Zheng *et al.*, 2009).

Another important scaffold is 4-thiazolidinone which possesses a wide range of promising biological activities. (Verma and Saraf, 2008). The 4-thiazolidinone derivatives have demonstrated significant anticancer activities (Chimirri *et al.*, 1986; Vigorita *et al.*, 1992; Gududuru *et al.*, 2004; Abdel Hafez *et al.*, 2009; Hafez and El-Gazzar, 2009).

In view of these findings, the synthesis of novel hydrazide-hydrazones and 4-thiazolidinones derivatives starting from etodolac were aimed at investigating their antitumoral activities of these compounds as discussed below. The characterization of these compounds synthesized from etodolac, were identified by the help of elemental analysis, UV, IR, <sup>1</sup>H-NMR, API-ES and HR-MS spectral data while the purities of them were proved by TLC.

## EXPERIMENTAL

### Chemistry



**Synthesis of methyl (1,8-diethyl-1,3,4,9-tetrahydropirano[3,4-b]indole-1-yl) acetate [1]:** Etodolac (0.01 mol) was refluxed in methanol (16 ml) containing concentrated H<sub>2</sub>SO<sub>4</sub> for 3 hours. The contents of the flask were subsequently cooled and neutralized by using NaHCO<sub>3</sub> (5%). The resulting precipitate was filtered, dried and recrystallized twice from ethanol. Yield, 66%; m.p., 127-130°C. This compound has been previously reported by Vincenzo and Franco 1997; Raghavan *et al.*, 2001 (m.p. 128-130 °C).

**Synthesis of 2-(1,8-diethyl-1,3,4,9-tetrahydropyran[3,4-b]indole-1-yl)acetohydrazide [2]:** To methanolic solution of compound **1** (20 mL, 0.01 mol) was added hydrazine-hydrate (80%, 7 mL) and refluxed for 3 h. The reaction mixture was then

cooled, diluted with water and allowed to stand overnight. The precipitated solid was washed with water, dried and recrystallized twice from petroleum ether.

**Synthesis of 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indole-1-yl) acetic acid [(5-nitro-2-furyl/substituted phenyl)methylene] hydrazide [3-15]:** A solution of compound **2** (0.01 mol) and equimolar amounts of appropriate aromatic aldehyde in absolute ethanol (30 mL) was heated under reflux for 3 h. The obtained precipitate was filtered off, dried and recrystallized twice from ethanol.

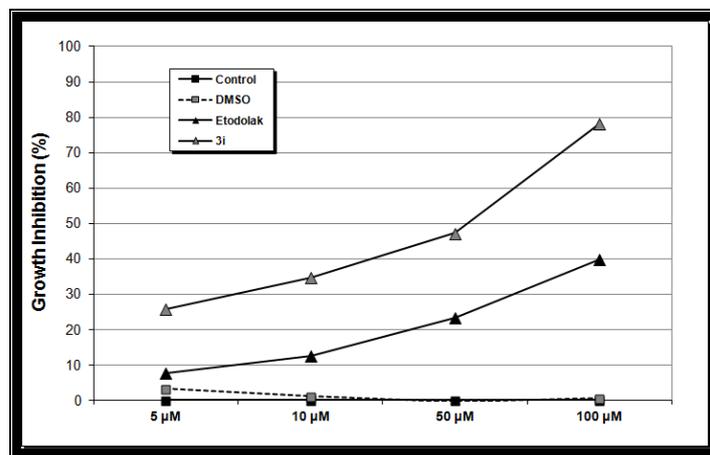
**Synthesis of 3-(2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetyl hydrazono)-2-alkyl/aryl-4-thiazolidinone [16-26]:** A mixture of compounds [3-15] (0.01 mol) and thioglycolic acid (0.2 mol) was refluxed in dry toluene (100 ml) using a Dean–Stark water separator. Excess toluene was evaporated under vacuo and the flask content was neutralized by addition of NaHCO<sub>3</sub> (5%) until CO<sub>2</sub> release was completed. The precipitated solid was washed with water, dried and recrystallized from ethanol-water.

## PHARMACOLOGY

### Evaluation of Anticancer Activity *in vitro*

Primary anticancer assay was performed in accordance with the protocol of the Drug Evaluation Branch, National Cancer Institute, Bethesda (Grever *et al.*, 1992; Alley *et al.*, 1988; Boyd and Paul 1995; Shoemaker 2006). The cytotoxic and/or growth inhibitory effects of the compounds were tested *in vitro* against the full panel of 60 human tumor cell lines derived from nine neoplastic diseases at 10-fold dilutions. The percentage of growth was evaluated spectrophotometrically versus controls not treated with test agents. Briefly, effect of the compounds on the growth parameters of the different cancer cell lines was evaluated relative to equivalent amounts of DMSO treated controls and expressed as percent growth rate. The compounds were added at 10<sup>-5</sup> M concentration for 48 h. Compounds **1, 9, 10, 20, 21** chosen as prototypes were evaluated against the full panel of 60 human tumour cell lines at one dose in NCI *in vitro* primary anticancer assay. Anticancer screening data at a concentration of 10<sup>-5</sup> M was summarized in Table 1. The most potent derivative was identified as 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indole-1-yl) acetic acid [(4-chloro phenyl)methylene] hydrazide, compound **9** which demonstrated the most marked effect by 41.76% growth percent on prostate cancer cell line PC-3 amongst the *in vitro* screens using NCI's 60 human tumor cell lines. Moreover, compound **9** had a strong cytotoxicity against melanoma SK-MEL-28 cell line.

On the basis of the above results, cell viability and cytotoxicity effects were performed by measuring the levels of surviving cells after incubation for 48h with compound **9**, using MTT colorimetric assay (Woerdenbag *et al.*, 1993). Cell viability and the antiproliferative effect utilizing the standard MTT colorimetric method against panel of three human cell lines, L-929, MDA-MB-435 melanoma cancer cell, PC-3 prostate cancer cell line for 48 hr. Viability was estimated as the percentage of living cells after incubation of the cells for 48 h with four concentrations (5, 10, 50 and 100 µg/mL) of the molecule tested (100 indicates no activity; 0 indicates complete cell death) with final DMSO concentration of 0.1-0.05%. For compound **9**, results appeared to be indicative of a dose-dependent inhibition, with a clear inhibition of the percentage of living cells after exposure to 100 µg/mL of substance. It can be understood from Fig 1 that compound **9** has a strong growth inhibitory activity (78.15%) against PC-3 cancer cell line at 100 µg/mL.



**Fig. 1.** Growth inhibition (%) of compound **9** towards PC-3 cancer cell line.

For this compound **9**, further bioassay was conducted and caspase-3 activity was followed by incubation for 18 hours. Because caspase-3 has been described to be essential for drug-induced apoptosis (Porter and Jänicke, 1999). We evaluated effects of compound **9** on caspase-3 activation to reveal the possible mechanisms responsible for apoptosis at PC-3 prostate cancer cell line for 18 hr incubation. When compound **9** was compared with the control group and etodolac for caspase-3 activity, it has been found that compound **9** had higher caspase-3 activity at concentration of 50  $\mu\text{M}$ . On these preliminary results of caspase-3 activity, we planned further studies that it would be evaluated caspase-3 and other apoptotic markers activity after 24,48 and 72 –hours incubations.

**Table 1:** Anticancer screening data at  $10^{-5}$  M concentration

Compound	NCI code	Mean Growth	% Range of growth	The most sensitive cell line	Growth Inhibition %	Promotion of cell growth %
1	D-750934/1	100.14	47.01	Prostate cancer PC-3	28.07	71.93
9	D-750935/1	84.37	84.03	Prostate cancer PC-3	58.24	41.76
				Renal cancer UO-31	49.34	50.66
				Non-small cell lung cancer HOP-92	53.13	46.87
10	D-750936/1	99.68	64.78	Prostate cancer PC-3	39.58	60.42
20	D-756798/1	93.39	88.46	Leukemia MOLT-4	56.97	43.03
21	D-756799/1	92.01	63.89	Leukemia MOLT-4	31.43	68.57

## CONCLUSION

In this study, etodolac hydrazide and a series of novel etodolac hydrazide derivatives were synthesized and evaluated for anti-cancer activity. The selected compound **9** by NCI showed significant inhibition of prostate cancer cell line PC-3. In this study, we have identified compound **9** as a promising anticancer agent. It might be of great interest to combine etodolac with hydrazone and 4-thiazolidinone groups to prepare novel derivatives. This study has been indicated that synthesis of hydrazone and 4-thiazolidinone derivatives of etodolac resulted in more effective compounds compared to the starting

compound, etodolac. Based on these studies, we are now in the process of synthesizing modified analogues of the lead compounds in order to generate more effective anti-proliferative agents.

### Acknowledgements

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# SYNTHESIS, CHARACTERIZATION AND ACTIVITY OF COPPER-HMS-n CATALYSTS IN THE HYDROGENATION OF BENZALDEHYDE

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## ABSTRACT

The series of copper-containing hexagonal mesoporous silica with different Cu contents have been prepared following the pathway type  $S^{0T}$ . The obtained solids have been calcined at 500°C and characterised by chemical analysis, BET surface area, XRDiffraction and FTInfra-Red spectroscopy. These materials (Cu-HMS-n) have been tested in the gas phase reduction of benzaldehyde at atmospheric pressure in the range temperature of 120°C-240°C under hydrogen flow. The obtained products were benzylalcohol, toluene and benzene with yields depending on the Si/Cu ratio in the precursor and reaction temperature. The products of benzaldehyde hydrogenation (benzylalcohol and toluene) and hydrogenolysis (benzene) were preferentially formed at low/middle and high reaction temperature respectively. The observed selectivities also suggested the existence of bifunctional sites for both the hydrogenation and hydrogenolysis reactions. These sites were believed to be involved as acidic/cationic centers for the adsorption of the oxygenate molecules and metal center for the hydrogenation or hydrogenolysis step.

Keywords: copper; HMS; benzaldehyde; hydrogenation; benzylalcohol.

## 1. INTRODUCTION

In the past few years, considerable effort has been devoted to develop a heterogeneous catalytic system able to perform selective hydrogenation of the carbonyl function of aldehydes and ketones into corresponding alcohols with a high yield [1,2]. The discovery of the new family of mesoporous silica molecular sieves with pore diameters in the 2.0–10 nm range, designated as M41S, is of considerable interest for heterogeneous catalysis and material science [3,4]. Depending on the synthesis conditions, different phases could be obtained, like the hexagonal phase MCM-41, the cubic one MCM-48 as well as the lamellar compound MCM-50 [5]. Furthermore, another pathway was proposed by Tanev et al. [6] to prepare mesoporous silica at room temperature by neutral templating route ( $S^{0T}$ ). These materials denoted hexagonal mesoporous silica (HMS), reveal excellent catalytic capacity for macro molecular reactions and suggest new opportunities for transition metal incorporation into silica frameworks [7-10].

Heterogeneous catalytic studies of benzaldehyde hydrogenation have been largely devoted to the liquid phase medium [11,12] whereas relatively few studies have been reported for the gas phase medium [2,13]. In the latter case, metal [1,2,14-16] and metal oxide [17] supported catalysts were used but no work have been reported using metal-containing hexagonal mesoporous silica as catalysts. It was shown that benzene and toluene by-products were formed directly from benzaldehyde and benzyl alcohol, respectively, and a Langmuir–Hinshelwood model, with the addition of the second hydrogen atom as rate determining step, fits the data satisfactorily.

The hydrogenation of benzaldehyde and *o*-tolualdehyde to the corresponding alcohols was studied over Ni/SiO<sub>2</sub> in the temperature range of 110–300°C [14,15]. No ring hydrogenation was detected and the by-products arose from the direct hydrogenolysis of the aryl–carbonyl C–C bond [15,16]. As to metal oxides as catalysts, one of us have shown that their catalytic properties in the hydrogenation of benzaldehyde to benzyl alcohol depends on their reducibility and, also, on their surface acid–base properties [2]. Toluene and benzene by-products arose from benzylalcohol and benzaldehyde hydrogenolysis, respectively [17].

In the present study, we report synthesis, characterization of such solids incorporating copper and the results of the catalytic studies of the selective reduction of benzaldehyde over copper-mesoporous molecular sieves materials (HMS).

## 2. EXPERIMENTAL

- The Cu-HMS-n catalysts (where n is the Si/Cu ratio in the precursor gel = 50, 25, 15) have been prepared following the pathway type  $S^{0T}$  using a protocol reported by Tanev et al. [6]. In a representative preparation, hexadecylamine was added to a solution containing water and ethanol and the mixture was stirred until homogeneous. Then tetraethyl orthosilicate was added under vigorous stirring. The metal precursor (copper nitrate) dissolved in TEOS itself. This solution was then stirred at room temperature for 24 h to obtain the products. The solids were recovered by filtration, washed with distilled water, and air dried at 120°C. Organic molecules occluded in the mesopores were removed by solvent extraction. The obtained solids were calcined at 500°C in air for 6 h.

- The chemical compositions of the samples were determined by a combination of wet chemical methods and atomic absorption spectrometry. The surface areas determined using the BET method on a Coultronics 2100E apparatus and the data were interpreted using the BET equation and an effective cross-sectional area of 16.2 Å for N<sub>2</sub>. Powder X-ray diffraction (XRD) patterns were recorded on Siemens D500 diffractometer with CuK $\alpha$  radiation. They were recorded with 0.02° (2 $\theta$ ) steps and 1s counting time per step over two angular domains from 1° to 10° (2 $\theta$ ) and from 10° to 80° (2 $\theta$ ). The FTIR spectroscopy analysis has been carried out on a Phillips 9800-FTIR spectroscopy type. The Ni-HMS-n catalysts have also been examined with a scanning electron microscope (SEM), a JEOL2000 electron microscope.

- Benzaldehyde (Aldrich, 99.88%) was degassed under nitrogen purge before use. The catalytic performances were carried out in the same reactor with 0.2 g samples at atmospheric pressure and a total flow rate of 50 cm<sup>3</sup>.min<sup>-1</sup>. Before testing, the catalysts were in situ pre-treated for 2 h at 350°C in a current of dihydrogen (H<sub>2</sub>) with a flow rate of 20 cm<sup>3</sup>.min<sup>-1</sup>. Benzaldehyde hydrogenation (Aldrich, 99.88%) was performed in dihydrogen flow at atmospheric pressure and in the whole range of reaction temperature 120-240°C. Gaseous benzaldehyde (3.2 torr) was obtained by bubbling N<sub>2</sub> (250 torr) in liquid benzaldehyde maintained at constant temperature (50°C) in a suitable saturator. The gaseous reactant and products were heated up-stream and outstream in order to avoid their condensation and analyzed on line by a FID gas chromatograph (Delsi IGC 121 ML) equipped with a CP-Sil8CB/Chromosorb WAW column.

### 3. RESULTS AND DISCUSSION

#### 3.1. Catalysts characterization

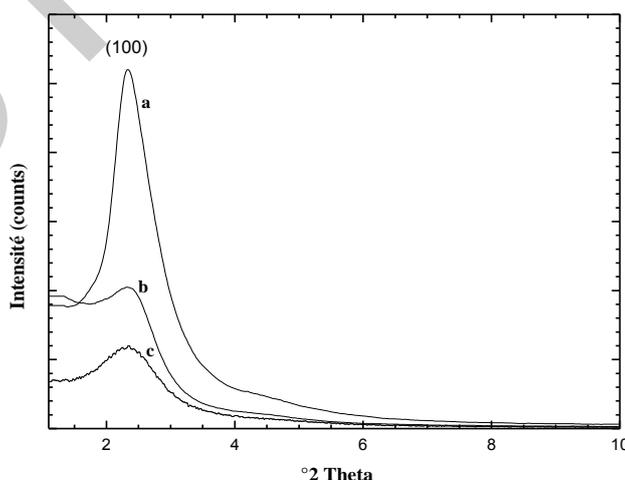
The results of the chemical composition and characteristics of the catalysts are summarised in Table 1. The copper compositions of the solids corresponded relatively well to those fixed for the synthesis, except at low copper content (Cu-HSM-50) where a loss of copper was observed. Most of the values of the specific surface areas of the solids were larger than 900m<sup>2</sup>/g, which was typical of mesoporous materials [18]. When the copper content increased, the BET surface area decreased from 1140 m<sup>2</sup>/g (Si/Cu=50) to 910 m<sup>2</sup>/g (Si/Cu=15). The BJH method of the samples showed a uniform pore size with values between 33Å and 37Å.

**Table 1** : Copper-based catalysts and their properties. Cu-HMS-n (n = 50, 25, 15)

Catalyst characteristics		Cu-HMS-50	Cu-HMS-25	Cu-HMS-15
Chemical analysis	n = Si/Cu	64	27	16
	Cu (wt%)	1.00	3.3	6.3
Catalyst S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )		1140	1010	910
Pore volume of the catalyst* (cm <sup>3</sup> .g <sup>-1</sup> cat)		0.90	0.85	0.77
Pore diameter (Å)*		36	37	33

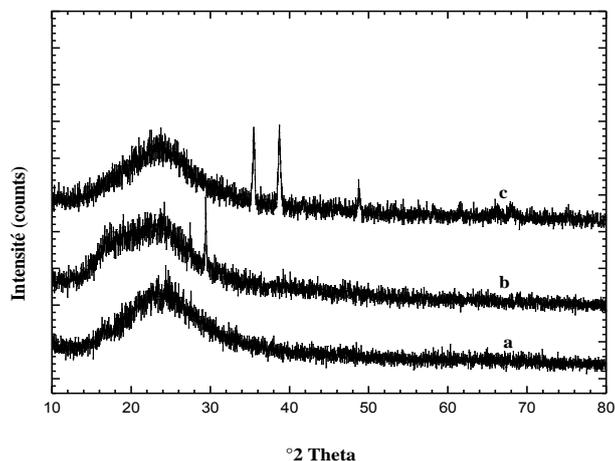
\* Determined after calcination step by BJH method.

The X-ray powder diffraction pattern of the pure siliceous HMS mesoporous molecular sieve (not showed) gives one broad peak at low angle region corresponding to d<sub>100</sub> reflection. This result indicates the presence of uniform mesoporous channels. Compared to the pure siliceous HMS material, the copper-containing mesoporous silicas Cu-HMS-n showed a similar broad peak at 2 $\theta$ =2.2° (Fig. 1). The intensity of the peak decreased as the copper content increased showing that the addition of copper has a negative effect on the crystallinity [19]. At the same time, very small peaks corresponding to CuO phase appeared in the 30–80° (2 $\theta$ ) for Cu-HMS-15 (Fig. 2).



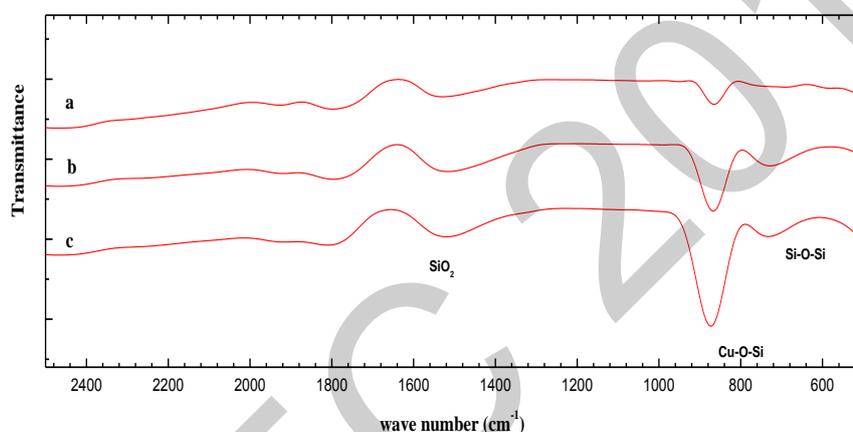
**Figure 1**: XRD patterns of Cu-HMS-n catalysts in the domain of 1-10° (2 $\theta$ ). n = Si/Cu = (a) 50, (b) 25, (c) 15.

On the other hand, when the copper content increased from n=Cu/Si=50 to 15, clear diffraction peaks of CuO phase appeared (Fig. 2). In fact, the Cu-HMS-50 did not showed any XRD peaks of metal oxide. Indeed, the Cu-HMS-15 showed more intense reflection than Cu-HMS-25. This result indicated that the increase of copper content favoured the formation of larger CuO particles extra framework.



**Figure 2 :** XRD patterns of Cu-HMS-*n* catalysts in the domain of 10-80° (2 $\theta$ ). *n* = Si/Cu = (a) 50, (b) 25, (c) 15.

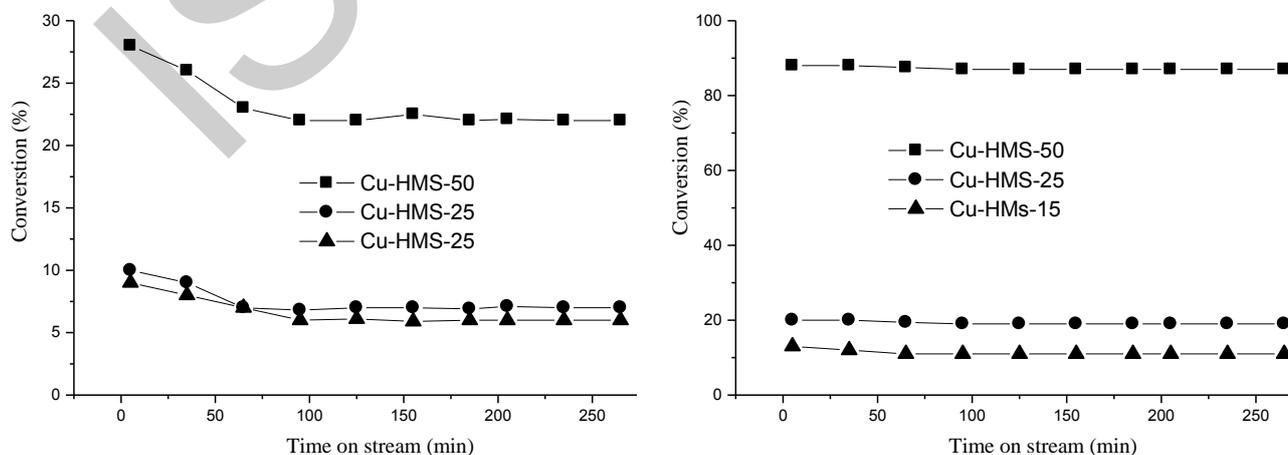
The IR spectra of Cu-HMS-*n* catalysts with different Cu contents are characteristic of the copper-containing hexagonal mesoporous silica. Characteristic wave number of bands of Cu-O-Si (870-890 $\text{cm}^{-1}$ ) and Si-O-Si species (740-760 $\text{cm}^{-1}$ ) were identified (Fig. 3).



**Figure 3:** FTIR spectra of Cu-HMS-*n* catalysts. *n* = Si/Cu = (a) 50, (b) 25, (c) 15.

### 3.2. Catalytic activity

The pure siliceous HMS mesoporous molecular sieve was almost inactive in benzaldehyde hydrogenation in the whole range of reaction temperature. However, the copper-hexagonal mesoporous silica catalysts were active and exhibited low initial deactivation (5%-20%) before the steady-state was established. The duration (1-2 h) of deactivation, the level and order of conversion depended on the copper content and reaction temperature. Figure 4 reports conversion results with time on stream at 120°C and 240°C. It can be noted that no initial deactivation occurred at 240°C for all catalysts but, for the latter, a low drop of conversion from 28% to 22% is observed at 120°C for Cu-HMS-50.



**Figure 4:** Conversion of benzaldehyde with time on stream at 120°C and 240°C respectively.

In stationary conditions, the reported data of the various catalysts shown that the reaction is catalytic and the products obtained were: benzyl alcohol, toluene and benzene (Table 2).

**Table 2 :** Catalytic results for gas phase hydrogenation of benzaldehyde over Cu-HMS-n (n=50 ; 25 ; 15) catalysts.

Catalysts	T <sub>reaction</sub> °C	W <sub>0</sub> <sup>a</sup>	W <sup>b</sup>	Selectivity <sup>b</sup> %		
		Conversion %		BOL	TOL	BENZ
Cu-HMS-50	120	28	22	100	-	-
	160	63	60	98	02	-
	200	82	80	85	15	-
	240	88	87	83	17	-
Cu-HMS-25	120	10	07	91	09	-
	160	15	10	50	50	-
	200	18	17	30	70	-
	240	20	19	-	100	-
Cu-HMS-15	120	09	06	-	100	-
	160	11	08	-	100	-
	200	12	10	-	94	06
	240	13	11	-	86	14

<sup>a</sup> Initial rate, W<sub>0</sub> : measured from the conversion-contact time dependencies and extrapolated to zero conversion.

<sup>b</sup> Steady-state conversion and selectivity measured after 6h of reaction time.

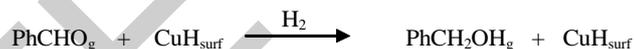
BOL : Benzylalcohol, TOL : Toluene, MECH: Methylcyclohexane, BENZ: Benzene.

Under H<sub>2</sub> flow, the results showed that the steady-state conversion increased with reaction temperature for all catalysts. In range temperature reaction 120-240°C, the Cu-HMS-50 catalyst showed the high activity whereas Cu-HMS-25 and Cu-HMS-15 catalysts were less active in the hydrogenation of benzaldehyde (table 2). The maximum of conversion was obtained at 240°C from Cu-HMS-50 catalyst, whereas it reached lower values for the other catalysts.

At high reaction temperature (240°C), the Cu-HMS-50 catalyst was by far the most active and the order of activity was as follows: Cu-HMS-50 >> Cu-HMS-25 > Cu-HMS-15. Such an order seems to be related to the specific surface area and pore volume of the catalyst.

On the other hand, the elevation of copper content on HMS structure was not favourable to increase the catalytic activity. In fact, the results showed that the activity decreased with the copper loading catalysts. At the same reaction temperature, the maximum of conversion was high for the low copper content Cu-HMS-50 catalyst.

Benzyl alcohol was produced only on the Cu-HMS-50 and Cu-HMS-25 catalysts in the range of 120-240°C. At 120°C, much higher selectivity to benzyl alcohol was obtained on Cu-HMS-50 (100%). Its selectivity decreased with increasing reaction temperature (from 100% to 83%) and with the copper loading. The probably presence of weak copper content favoured the reduction of the carbonyl compound to the corresponding alcohol. The chemical process of benzyl alcohol formation is believed to be a 1-2 nucleophilic addition, with a high polarization of the transition state [1]:



Cu-HMS-15 catalyst does not formed the alcohol product in the gas phase as a consequence of adsorption phenomena probably chemically converted before desorption.

High selectivity to toluene was observed for Cu-HMS-15 catalyst while Cu-HMS-50 catalyst exhibited lower selectivity values (<20%). On the other hand, the results showed that toluene selectivity increased with the reaction temperature for all catalysts except Cu-HMS-15 (not formed the alcohol product) and the order depended on copper loading. It is now well established that toluene is the product of the consecutive reaction of hydrogenolysis of benzyl alcohol and/or benzoxy species [1,13]. The complex site would be bifunctional in nature, implying the metal cation and hydride entities interacted with oxygen and carbon atoms of the alcohol molecule respectively:



Low selectivity to benzene was obtained only on Cu-HMS-15 (<20%) and at high reaction temperature. Gas phase kinetic study of benzaldehyde over copper [13] catalysts showed that benzene was produced directly from reactant molecule and not from the alcohol or toluene intermediates. Carbon monoxide was identified as co-product of benzene [13,17]. The results significantly show that benzene was formed by an independent way from that of the products of the C=O double reduction:



#### 4. CONCLUSION

This study shows that copper-containing hexagonal mesoporous silica structure with different Cu contents is obtained using a protocol reported by Tanev et al. and exhibited excellent activities in benzaldehyde hydrogenation. Catalysts characterizations demonstrate that increasing copper content favoured the formation of larger particles resulting the decrease of specific surface area.

On the other hand, our results showed that the hydrogenation of benzaldehyde over catalysts depended on the copper loading and reaction temperature. Indeed, the benzaldehyde conversion increased with reaction temperature but decreased with copper content. For weak benzaldehyde conversion, benzyl alcohol was formed at low temperature over Cu-HMS-n ( $n=Si/Cu=15, 25$ ). Toluene was obtained for all catalysts. Few of benzene was formed at high reaction temperature over Cu-HMS-50 (<15%).

The present results can be also discussed in the light of the relative importance of the reducibility and the acid-base properties of the considered solid, that's the variation of these properties as a function of copper content. The mechanistic features of our results are discussed.

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# THE DISCOVERY OF AN ENTERPRISE NETWORK TOPOLOGY CREATED IN A VIRTUAL ENVIRONMENT WITH SNMPv3

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*Keywords: Topology Discovery, Snmpv3, GNS3, VMWARE Workstation*

## ABSTRACT

To design network management systems in a best way, network topology have to be discovered with every features of network such as connectivity, device type, etc. Our goal is to discover an enterprise network which is created in a virtual environment (GNS3 and VMWARE Workstation) with SNMPv3. An algorithm which is used in previously academic researchs is redesigned according to features of virtual environments which are used in project.

## 1.INTRODUCTION

Nowadays enterprise networks have become more complex and wide because of huge number of users and a lot of applications that work in networks [1-4]. To benefit from this growing enterprise networks more effectively and efficiently, network management concept which means management and maintenance at the highest level has occurred. Network management systems have some kind of basic concepts such as security, topology discovery, monitoring, controlling, coordination and schedule. To benefit from these concepts of network management more effectively, first of all, topology discovery and connection of between devices have to be detected in a best way. And then network management system can be designed according to these results.

There are several techniques in network topology discovery such as ping mechanism, trace-route, DNS (Domain Name System) and SNMP (Simple Network Management Protocol) [1-4]. But only SNMP can provide better performance than others and also it pulls a lot of queries in completely and a secure way like as name of device, device type or connectivities between devices.

In this paper, an enterprise network topology that has been created in virtual environmet (GNS3 and VMWARE workstation) is going to be discover through an algorithm which uses SNMPv3 that is security version of SNMP. Due to work in virtual environment, the proposed algorithm is going to finish topology discovery more less time than a real environment.

## 2. SNMP

SNMP is a network management protocol for managing IP (Internet Protocol) networks. SNMP has a three structure; agent software which runs on managed devices, SNMP manager which communicates between NMS (Network Management System) and agent, and finally NMS which manages all network operations. SNMP'working mechanism is like as sending request and reply to request and to make these operations, UDP (User Datagram Protocol) is used [5,6]. By means of SNMP, data can be pulled from device easily and configurations on device can be changed easily. For example, device can be restarted or a configuration file can be send to device. Hereby, we realize that SNMP is more important protocol in network management.

When SNMP pull data from the device, SNMP uses some kind of identifier to pull data. These identifiers are called as MIB (Management Information Base) values and these values are represented with numbers. For instance, 1.3.6.1.2.1.1.5.0 variable means device name [6,7]. The requested values in MIB are called also OID (Object Identifier) variables. Values of MIB and OID are existed in reference numbered [8] .

SNMP uses some criterias in for network security. Some more important criterias are given in below [8];

- Authentication: It provides data integrity and authenticate source of data.
- Community name: It is used for authentication parameter during message transmission between SNMP and managed devices.
- Encryption: It encodes SNMP packages.
- Privacy: It provides to keep content of SNMP packages in network in hidden.
- Security Level: This means an algorithm which is used on every SNMP packages. HMAC, MD5 or SHA are used.
- Data Integrity: It means not divided data situation of a message package.
- SNMP User: This is a user who manage the SNMP system. According to SNMP messages that comes from network management system, user can make any related changes about situation of network.
- Security Model: This is a security strategy that is used by SNMP agent. There are 3 version: SNMPv1, SNMPv2c, SNMPv3.

Unfortunalety, all of SNMP version can't support all these security criterias. There is a comprasion of SNMP version about security in table 1.

Table 1: SNMP Security Models and Levels [8]

	Model	Level	Authetication	Encryption
1	v1	noAuthNoPriv	Community name	No
2	v2c	noAuthNoPriv	Community name	No
3	v3	noAuthNoPriv	User name	No
4	v3	authNoPriv	MD5 or SHA	No
5	v3	authPriv	MD5 or SHA	DES, AES

As we see in above, SNMPv3 made SNMP queries are used in secure way with encryption algorithms during data communication because of supporting all security levels. So SNMP packages are encrypted during all communication and network security is ensured.

### 3.APPLICATION OF NETWORK TOPOLOGY DISCOVERY

Network topology discovery is very big and comprehensive area and there are also a lot of academic research about it [1-4]. In addition, there are a lot of applications about network discovery in both academic and commercial environment [9-10]. Most of these studies are made in real environment. In our study, we have referenced to number [1] academic research which is made with using SNMPv2c. But in our study, both an enterprise network is created in virtual environment and the topology is discovered with SNMPv3 in securely.

With this goal, in the following sections, firstly information with related to modelling environment is going to be given and then information of algorithm in used will be given.

### 3.1 Modelling Environment

To modelling a network topology, we use a well-known program called as GNS3 (Graphical Network Simulator) that is a modelling program for network modelling simulator. Since GNS3 can model Cisco devices exactly, it has been used for this study [11]. To run the application codes, at first a virtual machine is created in VMWARE Workstation that is a well-known program in virtualization environment, and then this created virtual machine is attached to network topology that is created in GNS3 program with making related configurations [12].

An enterprise network means to connect all isolated departmental or workgroup networks into an intracompany network, with the potential for allowing all computer users in a company to access any data or computing resource. And also it would provide interoperability among autonomous and heterogeneous systems and have the eventual goal of reducing the number of communication protocols in use. In brief, it integrates all the systems within an organization.

Depending on the information given in above, for network topology discovery which is purpose of this study, an enterprise network structure which is created with GNS 3 and VMware programs, is chosen as a sample model. In this model, part 1 is given a form as backbone of the network and for this part, Cisco 6509 switches are used. In part 2, cloud describes the virtual machine in VMWARE Workstation which we developed our application in. In part 3, 4, 5 and 6, different departments of the enterprise network are shown. One of the main backbones manages DMZ (Demilitarized Zone) which is shown in part 7. DMZ exposes an organization's external services to a larger untrusted network (usually internet). The other one manages VPN (Virtual Private Network) servers which are shown in part 8. VPN provides remote offices or traveling users access to a central organizational network securely. On the other hand, the rest of topology consist of call managers and access points.

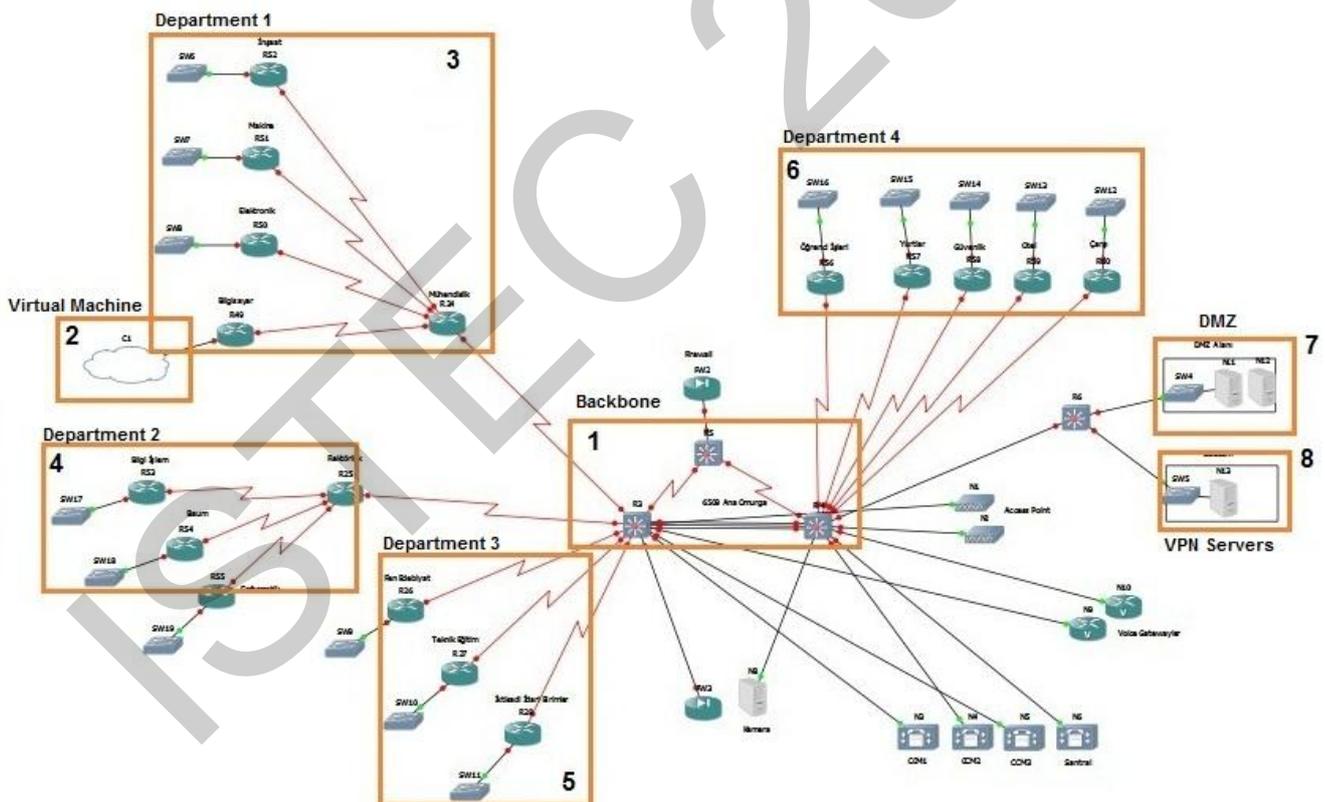


Figure 1: An Example of An Enterprise Network Topology

After finishing all required configurations (such as enabling SNMP, router configurations etc.) in GNS3 program, modelling of an enterprise network is completed. The part that application codes and algorithm run in, is created in VMWARE Workstation program and attached to topology as a cloud which is shown in part 2 of Figure 1.

### 3.2 Configuration

This proposed algorithm consists of a lot of subjects such as device type, connectivity of devices, routing table etc.

Before we start to run the algorithm, we have to check all configuration on devices are ok. To pull out datas from devices, we use SNMPv3 which is shown in row number 5 of Table 1. For enabling SNMP on each device, we have to observe these rules in below [7,8];

- Group is created: The security model and level that is given in row number 5 of Table 1 is selected. “grup1” is created for devices in same area in command line in below. This group is set to “read” feature and security level is selected as “v3”. And then “grup1\_oku” is created for “read” feature.

```
snmp-server group grup1 v3 priv read grup1_oku
```

- User is created: According to security criterias, users are added to group. For user names, “kullanici” is used. To add security criterias, “md5” algorithm is used for authentication, “aes 256” algorithm is used for encryption. And this security criterias are set to “grup1”.

```
snmp-server user kullanici grup1 v3 encrypted auth md5 cisco priv aes 256
```

- Features is created: “read, write and notify” features can be set to group. Our study’aim is only about topology discovery, “read” feature ise enough for us. And “read” feature is related to “view” command. “izle” is created for “view” feature.

```
snmp-server view izle system included
```

### 3.3 The Used Algorithm and Implementation

After all of the configurations have been completed, the algorithm is ready to start. As we told, SNMP mechanism is send request and reply to the request [4]. All values (such as system situation of device, routing table on device, mac address table of device, package that flows over device) are identified by MIB values. So when you want to pull out data from device, you have to add related MIB values to end of the SNMP query.

According to this SNMP MIB value responses from device, the algorithm is created and also in every step of algorithm, related MIB values are used.

The used algorithm for the project is shown in Figure 2. Since GNS3 doesn’t support some features in swithes and logical topologies, this proposed algorithm is the renewed version of the algorithm that is given in academic research called number [1]:

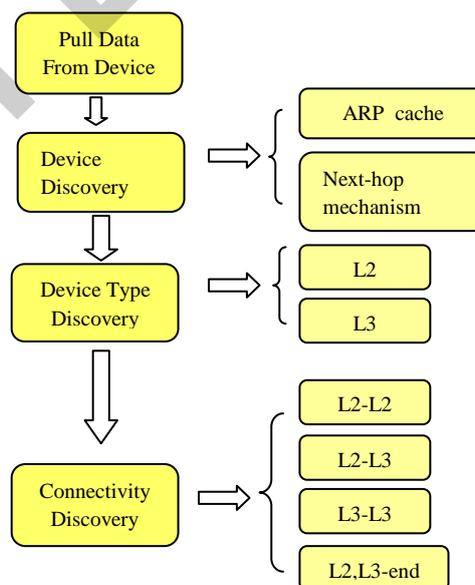
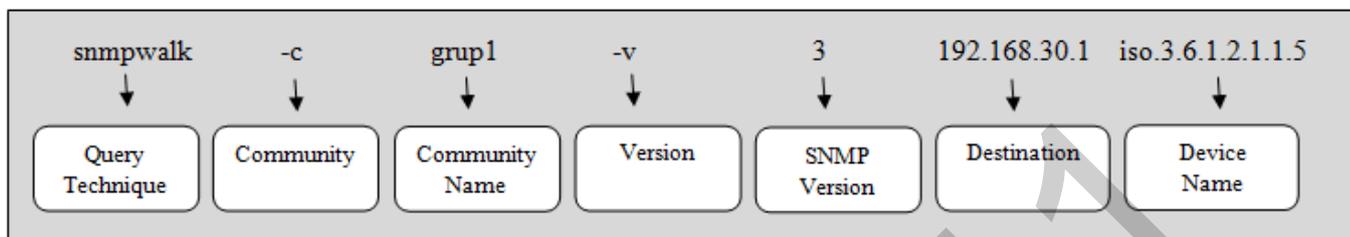


Figure 2: The Used Algorithm

Steps of the algorithm:

- **Pull data from device:** After creating network topology on virtual environment, we configure device and then we can pull data from devices with SNMP queries. For pulling out data from device, we use “snmpwalk” query technique of “net-snmp” library which includes all SNMP PDU’s (Protocol Data Units). For example, to get the name of device name, we have to add this query to our application:



- **Device discovery:** “ipNetToMediaNetAddress” and “ipRouteNextHop” values are pulled out from devices with using ARP caching and Next-hop mechanism [13,14]. Firstly, we find out our subnet, then we start to ping all the subnet. After pinging all the subnet, we can find all alive devices. And then we send query of “sysServices” to all the alive devices. If the response that comes from device is equal to “78”, we realize that device is a router and we look at the routing table of that device with query of “ipRouteNextHop”. This tables includes all subnets of the network. Finally we ping again all of the subnets of the network. Hereby, we can find all alive devices. With ARP caching, we can find IPs of layer 2 devices with using query of “ipNetToMediaNetAddress”.
- **Device type discovery:** According to “sysServices” value that is pulled from device, system decides that device is L2 or L3 device. After completing the device discovery part of the algorithm, system sends to query of “sysServices” to all of the alive devices. According to response comes from device, we can realize device is a what kind of device.
- **Connectivity discovery:** According to result of matching of ip and mac address that comes from device, we system decide that connectivity between devices is L2 or L3 connectivity. For finding L3-L3 connectivity, we use query of “ipRouteNextHop”. According to the result of query, we can check out the routing table. In routing table, we can see only “direct” or “indirect”. Direct means that ip is an interface of that router. Indirect means that ip is destination route of that router. For L2-L2 connectivity, we check out AFT (adres forwarding table) of L2 devices. If there is an match of this tables, we can realize these devices are connected to each others. For L2-L3 matching, we check out all the entries of mac tables of switches. If any entry is the same mac of any router’s interface, we realize that router is connected to that switch.

Project is coded with C# programming language in Visual Studio. As a database, MySql is chosen for this study. For SNMP libraries, Web SNMP API.Net Edition 4 is used [15]. After running the program, we have a network view in Figure 3. In Figure 3, we have run the algorithm only on these parts of Figure 1.

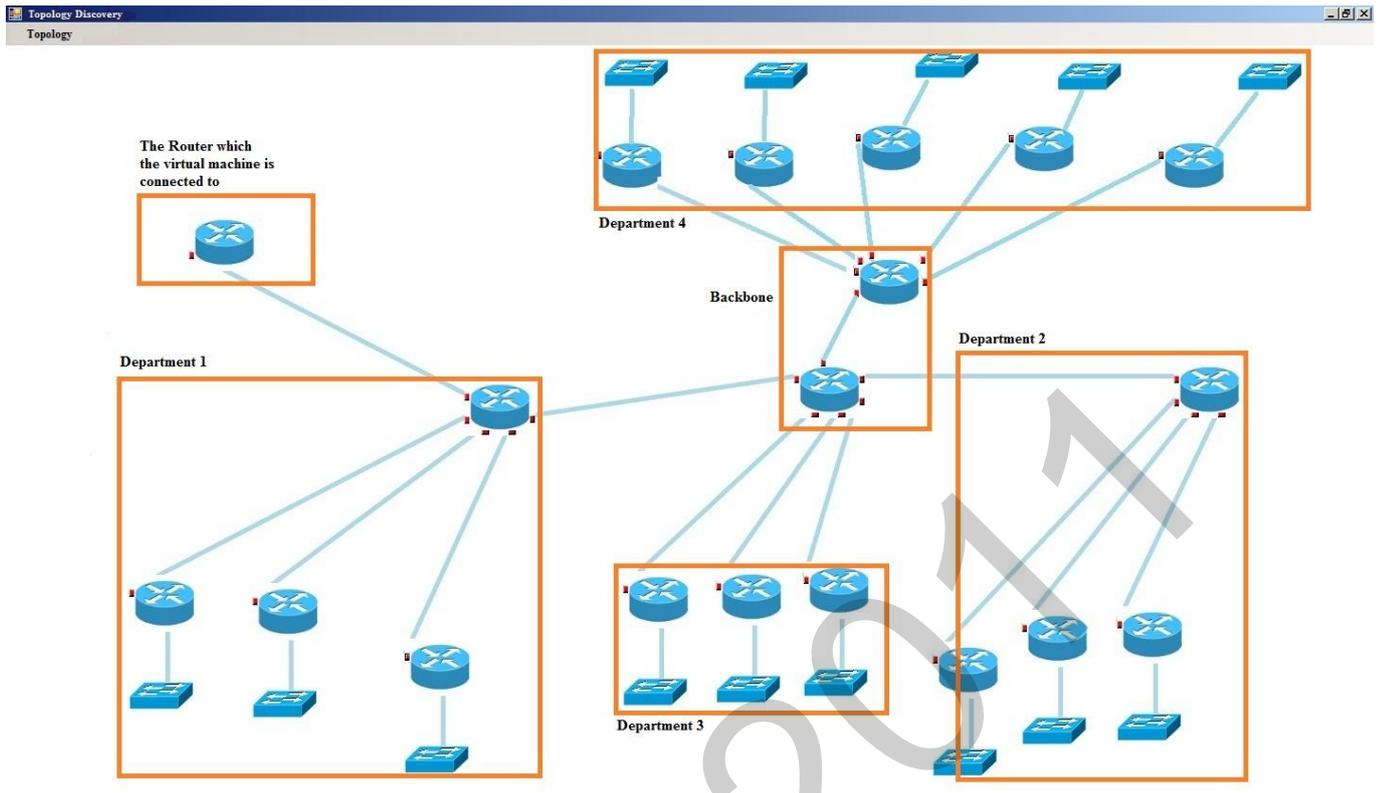


Figure 3: Graph View of Network

#### 4. CONCLUSION

In this study, we have chosen a virtual environment instead of real environment in order to not come up some problems in real environment for network topology. For virtual environments, GNS3 and VMWARE programs are used, related configuration are made on this programs. Because of security features, we have chosen SNMPv3 for network discovery. Since network discovery is made in different virtual environments which communicate with each other, this study can be an example for future works.

#### 5. ACKNOWLEDGMENTS

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# THE EFFECT OF HYPERGRAVITY ON THE GERMINATION AND GROWTH OF *ERUCA SATIVA* MILL.

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## ABSTRACT

Many environmental factors such as soil, temperature and gravity influence plant development. The aim of this research was to evaluate the effects of hypergravity on *Eruca sativa* Mill. (Rocket plant). A centrifuge was used to perform hypergravity experiments. Rocket plant seeds were placed on germination paper followed by the addition of water, and subsequently subjected to intermittent hypergravity (8h hypergravity followed by 16h rest), repeated over four days. Total germination and size of seedling were evaluated before and after being cultivated in soil in a natural environment. Results showed that root growth was greater in the centrifuge group than the control group. The growth of shoots after transference to soil was also found to be higher than the control group. Additionally, the centrifuge group of rocket seeds germinated 1% more and had a material mass of almost 20% more than the control group.

## INTRODUCTION

One of the main problems faced by food, pharmaceutical and perfume companies working with vegetal materials is the maintenance of access to good quality and quantity of supply in order to keep continuous production of their products. The quality of vegetal material produced depends on cultivation conditions as well as the specific germination time of each species. The environment interferes with the physiological mechanisms of plants (Arimura et al., 2005) and consequently on the substances they produce. Among these environmental factors are soil, temperature, altitude, luminosity and gravity (Leite, 2009; Martins-Ramos et al., 2010). Gravity is one of the most important cues and plants respond to it by growing shoots upwards (negative gravitropism) and roots downwards in the direction of gravitational pull (positive gravitropism). Gravitropism is a coordinated response composed of four sequential processes: gravity perception, signal formation, intracellular and intercellular transduction and transmission of the signal, and asymmetric cell elongation between the upper and lower sides of the responding organism (Morita et al. 2007). Researchers have been investigating the application of different technologies to plant growth aimed at producing greater volumes of vegetal material in shorter time periods, whilst maintaining a good quality of plant. Rocket plant (*Eruca sativa* Mill. or *Eruca vesicaria* L.) is widely distributed all over the world, is usually consumed fresh (leaves or sprouts) and is known for its typical spicy taste. It contains a number of health promoting agents including carotenoids, vitamin C, fibers, flavonoids, and glucosinolates. Rocket plant has been used in traditional pharmacopoeia for various purposes: antiphlogistic, astringent, depurative, diuretic, digestive, emollient, tonic, stimulant, laxative, and rubefacient (Barillari et al., 2005). All of these aspects, in addition to its short germination time, stimulated the investigation of the effect of hypergravity on *Eruca sativa* Mill. Therefore, the aim of this research is to evaluate the effects of hypergravity on the germination and growth of *Eruca sativa* Mill.

## MATERIAL AND METHODS

### Hypergravity conditions

A small centrifuge was built at the Microgravity Centre/PUCRS in order to perform hypergravity experiments. It consists of two main structures and an electromechanical motor system. The base structure is made from carbon steel (120mm height, 350mm length, 230mm width) and holds the electromechanical motor system within. Connected over this via a rotary shaft, is a round plastic formation with a diameter of 660mm (Figure 1) and this holds the plant containers. This structure can carry 12 sample holders of 65mm in diameter for each test (Figure 2). Each sample holder allows the plant container to lean during centrifuge tests to ensure that the acceleration is applied to the desired axis.

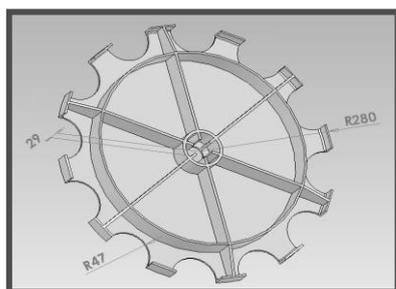


Figure 1. Schematic view of the round structure used to support plant containers (n=12)

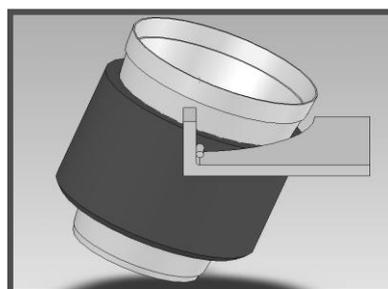


Figure 2. Schematic view of the plant container.

The electromechanical system consists of one electric motor that is connected to a reduction pulleys and gears system capable of delivering a continuous rotation up to 200rpm on the samples support structure. Rotation of the system is controlled by a DC power supply that is directly connected to the DC motor. The desired rotation in revolution per minutes (rpm) is established by changing the voltage of the power supply and measuring the rotation frequency with a contactless optical tachometer. A Digital Timer is used to control the schedule for turning the system on and off, by programming it for a period of 4 cycles of 16 hours off and 8 hours on.

For this study the centrifuge was set to run for a determined rotation frequency that would result in an acceleration equivalent to +7Gz. To calculate the rotation frequency for the desired acceleration the following procedure was used.

Using the schematic of acceleration in the centrifuge (Figure 3) and all the known parameters:

- Length of the arm (Length): 0.33m
- Desired Resultant Acceleration ( $a_r$ ): +7Gz
- Earth's Gravity Acceleration ( $a_{G_z}$ ): +1Gz

Then the parameters to be determined:

- Centripetal Acceleration ( $a_{cent}$ )
- Resultant Sample Angle ( $\alpha$ )

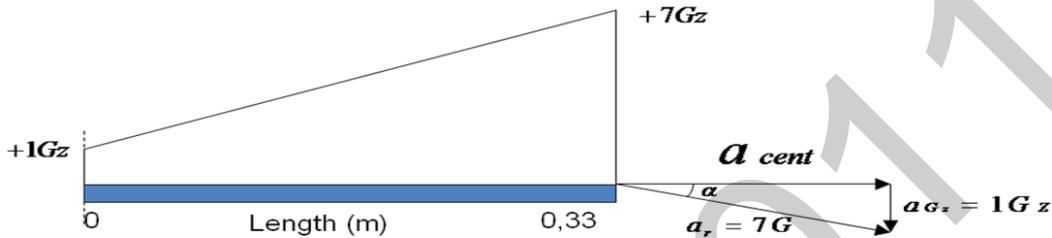


Figure 3. Schematic of acceleration of the sample in the centrifuge.

The  $\alpha$  angle can be determined using a rectangle triangle formed by the  $a_r$  as hypotenuse and the  $a_{G_z}$  as the opposite side and the Equation 1.

$$\sin \alpha = \frac{a_{G_z}}{a_r} \text{ Equation 1}$$

Applying the values  $a_r = 7$  and  $a_{G_z} = 1$  on the Equation 1:

$$\sin \alpha = \frac{1}{7} = 0.143$$

It is then possible to have the  $\alpha$  angle using the Equation 2:

$$\alpha = \arcsin(\sin \alpha) \text{ Equation 2}$$

Resulting in:

$$\alpha = 8.21^\circ$$

The  $\alpha$  angle is then used to determine the value of  $a_{cent}$  by applying the cosine relation, Equation 3:

$$\cos \alpha = \frac{a_{cent}}{a_r} \text{ Equation 3}$$

Applying the values  $a_r = 7$  and  $\alpha = 8.21^\circ$  on the Equation 3:

$$\cos 8.21^\circ = \frac{a_{cent}}{7}$$

$$a_{cent} = 0.989 \times 7$$

$$a_{cent} = 6.923G$$

To determine the rotational frequency of the centrifuge needed to produce calculated  $a_{cent}$  the value was converted to meters per square second ( $m/s^2$ ) multiplying it by the Earth's Gravity  $9.81m/s^2$ :

$$a_{cent} = 6.923 \times 9.81$$

$$a_{cent} = 67.914 \text{ m/s}^2$$

The  $a_{cent}$  can be described in the Equation 4, where  $\omega$  is the rotational speed in radians per second (rad/s):

$$a_{cent} = \omega^2 \times \text{Length} \text{ Equation 4}$$

It is then possible to determine  $\omega$ , using:

$$\omega = \sqrt{\frac{a_{cent}}{Length}}$$

$$\omega = \sqrt{\frac{67.914}{0.33}}$$

$$\omega = 14.346 \text{ rad/s}$$

Then convert this value to frequency  $f$  in revolutions per minute (rpm):

$$f = \omega \times \frac{60}{2\pi}$$

$$f = 14.346 \times \frac{60}{2\pi}$$

$$f = 137 \text{ rpm}$$

### Hypergravity experiment

*Eruca sativa* Mill (Rocket plant) seeds from Isla Pak (Batch:18708/10), were submitted to hypergravity experiments. The centrifuge described above was used to simulate hypergravity. Three rolls of germination paper, previously humidified with water and seeded with fifteen seeds each (forty five seeds in total), were placed in each of six of the twelve recipient containers. The hydration of the seeds was maintained by the addition of 80mL of distilled water to each container, and subsequently, each was covered by a plastic film containing holes to allow air exchange, yet reducing the loss of water by evaporation. The experiment was performed in an intermittent form, 8h in a centrifuge rotating at a +7Gz velocity speed, followed by 16h of rest, repeated over a four day period. The same procedure and number of samples were used to prepare a control group. At the end of the allotted time the number of germinated seeds were evaluated for both groups, and all seeds then removed from the germination paper and measured individually for the total size of seedling (shoot + root). The results of the experimental and control groups were compared by applying Student's  $t$ -test on the average, using an SPSS statistics program.

### Natural environmental cultivation

After being submitted to hypergravity simulation in an intermittent form over four days, the seedlings from both groups were transferred to plant pots containing soil and kept outside on a terrace for continued cultivation in a natural environment. Water was added to each to keep the soil humidity at 80%.

## RESULTS AND DISCUSSION

Many studies about the effect of hypergravity on plants have been done (Kasahara et al., 1995; Soga et al., 1999; Hoson and Soga, 2003). According to Kasahara *et al.*, (1995) gravitational forces greater than +1G have been useful to study the influence of gravity on the growth of plants. The stems of the seedlings from the centrifuge group were verified by this present study as being less flexible than those of the control group. These findings are in agreement with experiments conducted by Hoson et al. (2002), who demonstrated that the hypergravity produced by centrifugation increased the stiffness of the cellular wall due to the gravitational force. Research performed by Tamaoki et al. (2009) has shown that the content of matrix and cellulosic polysaccharides in unit length increases in shoots when under hypergravity conditions. Some authors have also mentioned that hypergravity increased the amount of cell walls per unit length of shoot in radish, cucumber, cress, azuki bean, and maize seedlings (Wakabayashi et al., 2005). These observations could explain the weight difference observed between the two groups in this experiment, whereby the total weight of *Eruca sativa* Mill seedlings submitted to hypergravity simulation was 25.72g, as compared to 20.89g for the control group, an increased vegetable mass of almost 20%.

Upon analysis of the shoots and roots of the *Eruca sativa* Mill seedlings, it was seen that growth was greater in the centrifuge group than the control group ( $p < 0.001$ ) (Figure 4 and 5). When subsequently being transferred to the pot containing soil, the aerial part of the plant grew more in the experimental group than the control group, probably due to the greater root development during the hypergravity simulation. These results are very important, considering that the active substances of *Eruca sativa* Mill. are presents in its the aerial part. (Leite, 2009). Additionally, it is important to mention the germination of the Rocket plant seeds in the centrifuge group was 1% more than for the control group.

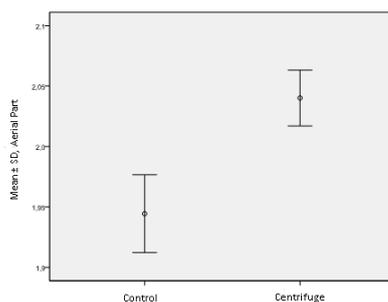


Figure 4. Growth of Aerial Part

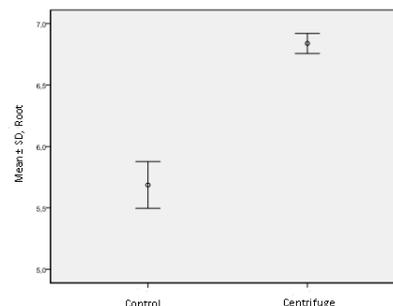


Figure 5. Growth of Root

## CONCLUSION

The results suggest that hypergravity simulation increases the germination and growth of *Eruca sativa* Mill. The roots of those seeds subjected to hypergravity simulation developed more than those in Earth's gravity, but in addition, after continued cultivation in a natural soil environment, an increase in growth rate for the experimental group plant shoots as compared to the control group would suggest that the effect of the hypergravity simulation on the rocket plants is ongoing and will consequently produce a greater volume of vegetal material for use by industry. Further qualitative analysis must be conducted to evaluate if any modifications to the secondary metabolites occur for plants subjected to hypergravity simulation. More studies are also necessary in order to increase understanding of the influence of hypergravity on plants.

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# THE EFFECT OF MONKS IN THE HUNGARIAN URBAN DESIGN AND LANDSCAPE FORMING

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## ABSTRACT

Hungary has a specific history. The monks were settled after the settlement of the Magyars in Hungary. The appearance of the new monks and the continuous proselytization were able to make the country become an elemental part of the Catholic Europe. Therefore the monks had a great role in the urban design and landscape forming. The orders can be divided into three groups based on the relations between the location, activity and landscape forming. In the first category there are those orders which were present in Hungary, but are not substantial in the landscape forming. In the second group there are those orders which settled in large free areas, had significant donations, their main activity was farming, so their impact on the landscape was outstanding. In the third group there are monks who settled in towns, built monasteries, so they had an important role in the formulation of the city structure. I am describing these orders in my essay.

## 1. INTRODUCTION

The environment has been formed by the humans. The landscape changes continuously because of the socio-economic conditions. The landscape changes because of the extent and nature of the influence. In the Hungarian history, the landscape history and landscape forming was important due to the maturation of the settlements in the time of Saint Stephen. The defensive-, central- and economic affairs had significant role in the settlements' establishments. The administrative-, commercial- and information functions have increased the central role of the settlements. This central role was advanced by the education-, health- and cultural institutions. The emergence of the monks had a further impetus on the cities. We can know the burden of the landscape forming, via the landscape forming activity of the humans, the humans' ideas in the land-usage. We can see the conscious activities in the landscape forming via the examples of landscape forming, landscape history and landscape ecology. (Csemez, 1996) So my choice was the orders. I will describe the effects of the monks on the urban design and landscape forming.

## 2. ORDERS IN HUNGARY

Christianity conquered Europe very quickly. Its spreading was influenced by many factors. The early Cistercian persecutions hindered the advancement of the belief all across Europe. The turning point was in 380 AD. on 28<sup>th</sup> February, when Emperor Theodosius decreed that everyone had to follow Jesus 's teaching in the Roman Empire. Then, the religion's spreading was unstoppable. (<http://hu.wikipedia.org/wiki/Kereszt%C3%A9ny%C3%A9g>) The orders were formed. The Hungarians encountered the Christianity at the first time during their migration. The first order was the Benedictine in Hungary in 960. The first reimbursements were the period of Taksony (913?-972), but the first successes were during Géza (972-997). According to the great legend of Saint Stephen (1077) the monks were provided: "Everywhere they established the holy foundations of the churches, they raised the cloister of the canons, the monastic communities began flourishing. (SRH. II. 383. Leg. ford. 26-27.) The first monastery was founded in Saint Márton hill in 996, during Géza, in Pannonhalma. The foundation of monastery grew then. After Saint Benedict's sons, the Cistercians came to our country. They were called by Géza II. (1141-1162). Their first monastery was in Cikádor (1142) (today: Bátorfő). They were followed by the Premonstratensians, who followed Saint Augustine's canon. Then different orders came to our country: the Carthusians, the Dominicans, the Franciscans, the equestrian orders. As a result of our specific historical events the monks' history was different and specific in Europe. The initial recovery was interrupted by the Mongol invasion (1240-1242) in the middle ages. The next low point was the Turkish occupation (16<sup>th</sup>-17<sup>th</sup> century), when the monks disappeared. Because of secularization of the Regulation of Joseph II (1782) the most monasteries were closed. They returned to Hungary in the early 1800s, and they worked again, but after 150 years, they were forced to leave again in the time of communism. After the regime they returned and they started to advocate the idea of monasticism again. (Török, 1990)

## 3. LANDSCAPE FORMING AND URBAN DESIGN

The landscape forming of the monks depended on several factors. The orders can be divided into three groups based on the relations between the location, activity and landscape forming. In the first category there are those orders which were present in Hungary, but are not substantial in the landscape forming. In this group there are the knightly orders whose members were not monks, but secular knights who lived under monastic regulations. These are the Templars, the Hospitallers and the smaller nurse orders. They had a significant role in the Crusades and the surveillance of borders, they were always moving. (Török, 1990) In the second group there are those orders which settled in large free areas, had significant donations, their main activity was farming, so their impact on the landscape was outstanding. They settled down in solitary, uninhabited places, they lived for God, but they had to cultivate the land to live on. The landscape changed thanks to their farming. In the third group there are monks who settled in towns, built monasteries, so they had important role in the formulation of the city's structure. In this group we can find the begging orders, the teaching orders and the healing orders. (Gecse, 1995)

The landscape forming activity of the orders is characterized by these two citation.

*“Who gives us back the days when we worked all day together? When we cut trees, we made extraction of stone, and other time we planted saplings or watered?” (Nazinia Saint Gergely wrote a letter to Saint Basileios)*

*„:” First of all /we have to choose/ farming, because it provides the food for our existence...” (I. Aszk 38.)*

At first I will write about the farming orders because of the citation and after that, about the urban design of the monks.

### 3.1. The farming orders

*“But the servants of the Church were not only the providers of spiritual goods. They were educators, leaders of the people at farming, too... They destroyed forests, dried out marshes, dug channels... Villages were generated. “- wrote Menyhért Érdújhelyi. (Érdújhelyi, 1903, 3.)* In Hungary, the three main farming orders are the Benedictines, the Cistercians and the Premonstratensians. Not only was their farming successful, but also the landscape was changed. The Pauline and the Basilian should also be mentioned.

The members of the Cistercian order established flourishing agriculture everywhere, contributing to the reviving of the tillage and the fruit- and grape cultivation, raising the standards. (Gecse, 1995) The agriculture of the order was successful, because they organised the duties better, they pre-planned the utilization of soil, compared to the feudal farming. They worked themselves, and their life and their future depended on the success of their work. They made farming subunits, grangias. In those places, where the climatic and soil conditions allowed, vineyards were established. The gardens were created both on flatlands and the hilly country; on the hillsides they made terraces which eased the cultivation. (Lékai, 1991)

The centre of the Hungarian male Cistercian life is Zirc. King Béla III founded the abbey in 1182. (Hervay, Legeza and Szacsavay, 1997) From the beginning the agriculture was significant and dominant; the continuous change of the original landscape was the result of that. The landscape forming has been visible since the years of 1700.

A 1776 depiction demonstrates the monastery's building and the regular parcels on its neighbourhood. We can see that in this place there are only the monastery and the soil that became cultivated, because the forests were fall by the monks. The lands were surrounded by the remaining forest. The first military survey originates from 1784 (Figure 1). The settlement was due to the presence of the order, because the viable places had power to modulate the settlement which suffered from the shocks but did not disappear, but were re-populated, and they were blooming again duly owing to the presence of the order. (Tóth, 1998)

The appearance of a settlement means a considerable change in the landscape, as the settlement appears as a new landscape element. The fishing ponds were created by the monks by swelling the brooks up. It is visible that between the two depictions what kind of considerable changes ensued in the landscape, thanks to the work of monks. The next detailed depiction originates from 1805 (Figure 2), on which the increase of the settlement and the usage of the areas are clearly discernible, the number of the fishing ponds decreased, and the ornamental garden and the arboretum, which are in the monastery's direct environment, had already appeared here. The abbey's donations were in Bakony, Fejér county and Mezőföld. On each area they adapted to the local conditions, so they cultivated and shaped the landscape.



Figure 1: The first military survey of Zirc (1784)  
(The first military survey, 1784, IX 17)



Figure 2: Zirc from 1805  
(Veszprém County Archives)



connected to the city wall, because of security reasons. These were the most prominent building in the city. The schools were in the neighbourhood of the bishop's palace or the cathedral. The churches and monasteries of the different orders were scattered within the city wall. (*De Cevins, 2003*)

I would lift a city from medieval Hungary's area. Bratislava. Due to its location, Bratislava was in the focus during the history. It was a royal and religious centre, royal city and place of the Hungarian parliament. ([http://hu.wikipedia.org/wiki/Pozsony\\_t%C3%B6rt%C3%A9nelme](http://hu.wikipedia.org/wiki/Pozsony_t%C3%B6rt%C3%A9nelme)) When we see the medieval description (*Figure 5*), the first number is the royal church, number seven is the Franciscan church and monastery, and the number nine is the town hall around the market place. Outside the city wall there are three churches. These medieval town structure has been preserved to this day with the buildings, too. If we look at the various-age maps (*Figure 6-10*), they show that the structure of the city have not change anything around the religious building.

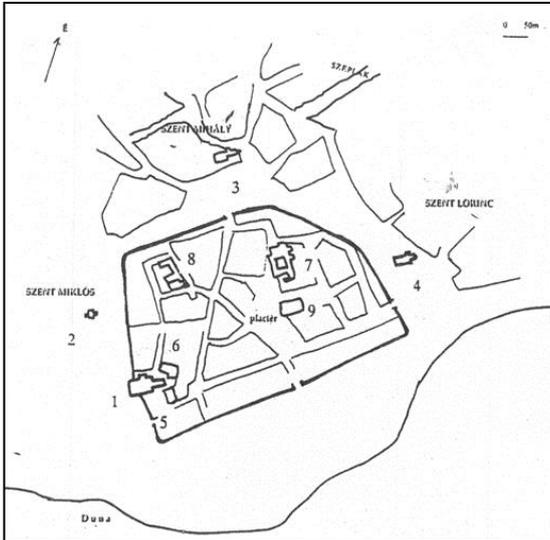


Figure 5: Bratislava in the medieval ages  
(*De Cevins, M. M., 2003*)



Figure 6: Bratislava in the first military survey  
(*The first military survey, 1782-85, VI 8*)



Figure 7: Bratislava in the second military survey  
(*The second military survey, 1840-47, XXIV 45*)



Figure 8: Bratislava today  
(*Google Earth*)



Figure 9: The Franciscan church and monastery today  
(Own photo)



Figure 10: The market place today  
(Own photo)

#### 4. SUMMARY

As you can see the orders' activity and its settlement is closely connected to each other, and through this change their impact on the landscape varied the urban design. At first via the demonstrated domestic and foreign example it can be seen, that farming and landscape forming are connected to each other, but its significance and extension change continuously. Initially the aim was, the interest of the assurance of the self-sufficiency, the more land was feature of under cultivation, this activity in the case of the farming orders was well-organized and planned, for all works it had the aim and its way. The initial changes were the biggest changes in the landscape, because, where earlier forest or barren was, the monastery was built, and they made tillages. In the course of the centuries the landscape changed, because of the habits, the values and the order it-self working was transformed, so the farming, which was the main source of living, was sidelined into 20<sup>th</sup> century, the neighbourhood was populated duly for the processes of urbanization, and other revenue sources were provided for the living of the order. I have examined several cities in the urban design of the monks. I can conclude that the religious buildings have had structure-forming impact. The developed medieval urban structure was preserved around the religious building throughout the centuries. More and more religious and secular buildings were built around the square. The building is preserved for posterity, or disappeared, but the urban structure survived until the present day.

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# THE INFLUENCE OF BACTERIAL CELL WALL PREPARATIONS AND SOME OF THEIR COMPONENTS ON ANTIBIOTIC ACTIVITY OF CRY1A PROTEINS FROM *BACILLUS THURINGIENSIS*.

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## Abstract

Cry1A proteins from parasporal crystals of *Bacillus thuringiensis* subsp. *kurstaki* display antibacterial activity relative *Streptomyces chrysomallus*. The preincubation of Cry1A proteins with preparations of cell walls (CW) from micrococci and streptomycetes have been shown to stimulate this effect in 2,1 and 1,7 times, respectively. Also some components of CW *S. chrysomallus*, such as murein, teichoic acid, N-acetyl-D-galactosamine, have been shown to stimulate the antimicrobial action of Cry1A in 1,7 – 2,5 times. Sodium and potassium ions added to incubation buffer were shown to increase the value of antibacterial activity of the Cry1A. But stimulating effects on antibacterial activity of the Cry1A of CW and some of its components are decreased in 1,4 – 1,9 times in the presence 0.2M sodium chlorides in incubation buffer. We suggest the possibility, that the preincubation of Cry1A proteins with CW and some of its components could stimulate protein oligomerization, and thus increasing their antimicrobial activity. The dependence of this effect from concentrations of some ions is discussed.

## Introduction

The entomopathogenic bacterium *Bacillus thuringiensis* produces protein parasporal crystals -  $\delta$  endotoxins. Cry proteins, composing crystals of more than 80 subspecies of the bacterium, are receptor-specific toxins for some insects, nematodes and ticks larvae. More than 300 Cry proteins, subdivided into 54 classes, depending on their amino acid sequences, are known at the moment. The  $\delta$  endotoxins of *Bacillus thuringiensis* are divided into two families: the insect-specific Cry toxins and Cyt toxins, which are generally cytolytic in vitro. Cry and Cyt proteins have a different three-dimensional structures and mechanisms of action. Cry-proteins of different classes are known to differ in their binding with the sensitive invertebrates' midgut. The Cry1 subclass represents a group of proteins in the 120 -140 kDa range that are primarily toxic towards lepidopteran larvae. The Cry1Aa, Cry1Ab and Cry1Ac proteins, which share more than 85% amino acid sequence identity as protoxins, are selectively toxic to some lepidopteran insect pests. These Cry1A toxins bind to the same receptor molecules suggesting they have a similar mode of action [3, 12]. Cry proteins must go through several structural changes before reaching their functional pore-forming. The Cyt proteins are toxic in vivo to the larvae of members of the order Diptera. The cytolytic effect of the Cyt1A toxin does not require binding to a membrane receptor, but rather is mediated by direct binding to the lipid [3, 4]. Also Cyt protein can to be the receptor for Cry proteins [5].

$\delta$ -Endotoxins from parasporal crystals of some subspecies of *B. thuringiensis* also display an antibiotic (bactericidal or bacteriostatic) effect on some microorganisms. The results show that these proteins are less specific for the studied prokaryotes, as they suppress – with different intensity – the growth of the different test-cultures. The ability of  $\delta$ -endotoxins from many subspecies of *B. thuringiensis* to affect representatives of *Micrococcus*, *Staphylococcus*, *Nocardia*, *Streptomyces*, as well as some fragments of these proteins, are capable of antimicrobial action, also killing anaerobic bacteria and Archaea was reported earlier [15, 16]. However, the effect of Cry-proteins on bacteria is not characterized by such a high specificity as their insecticidal effect.  $\delta$ -Endotoxins act on the microorganisms as and other different antibiotics [10, 18 – 22]. Previously, we also found, that the Cry1D-like toxin from crystals of *B. thuringiensis* subsp. *galleriae* has been put forward as an example of the supposition that cell wall and some of its components like teichoic acid and N- acetylgalactosamine have possible influence on Cry toxins, enhancing their antimicrobial activity [22].

This work presents the results of studies on the antibiotic effects of Cry1A proteins produced by *B. thuringiensis* ssp. *kurstaki* and the effect of the preincubation of Cry1A proteins with preparations of cell walls (CW) from micrococci and streptomycetes, also some components of CW *S. chrysomallus*, such as murein, teichoic acid, N-acetyl-D-galactosamine, on antibacterial activity of these proteins.

## Materials and methods

*B. thuringiensis* subsp. *kurstaki* strain VKPM B-9032 were from Collection of Industrial Microorganisms (VKPM), Scientific Research Institute for Genetics and Selection of Industrial Microorganisms (Moscow, Russia). The test culture *Streptomyces chrysomallus* strain 257 was obtained from the collection of Microbiology Department of Lomonosov Moscow State University (MDMSU).

*B. thuringiensis* was incubated in liquid medium with 1% tryptic casein (Human, Budapest, Hungary), 0.2% yeast extract (Serva, Heidelberg, Germany) and 0.6% glucose, pH 7.4, at 28<sup>o</sup>C with shaking (220 rpm), until complete lysis of sporangia occurred. Parasporal protein crystals were separated from spores and cell wall debris, using a xylene–water biphasic system.

Isolation of  $\delta$ -endotoxins from *B. thuringiensis* and determination of their antibacterial activity made, as was reported earlier [20,22].  $\delta$ -Endotoxins were isolated from the crystals using selective extraction and ion exchange chromatography on MonoQ. Cry1A toxins were obtained by dissolving VKPM B-9032 strain crystals in 0.1M carbonate buffer (pH 10.5) with 10mM dithiothreitol and mixing them for 1 h at 20°C. For tryptic cleavage, this solution was subjected to dialysis against 0.05M Tris-HCl buffer (pH 8.8) with 0.15M NaCl, and then exposed to trypsin (ratio of enzyme-protein was 1:100, w/w) for 1 h at 37°C. During tryptic hydrolysis, Cry1A endotoxins of the B-9032 strain split into 66 and 61 kDa fragments (true toxins). The purity of mentioned proteins was determined by SDS-PAGE [22]. The protein concentration was determined by absorption at  $X = 280$  nm using a Shimadzu spectrophotometer (Shimadzu Corp., Kyoto, Japan).

To determine the antibiotic activity, the test microorganism *S. chrysomallus* was grown on medium, which contained 0.5% triptose medium (Ferak, Berlin, Germany), 0.2% NaNO<sub>3</sub>, 0.1% K<sub>2</sub>HPO<sub>4</sub>, 0.05% MgSO<sub>4</sub>, 0.01% FeSO<sub>4</sub>, 0.05% KCl, and 1.5% Bacto agar (pH 7.4). Microorganism was cultivated at 30°C for 1-2 days.

The antibiotic activity was determined using the diffusion into agar with some modifications. The test-microorganism was grown and then was placed with the transfer loop into sterile water and maintained for 1-2 days at 4°C to allow the removal of the nutrient medium. The cell suspension was introduced into the melted medium, which was poured into Petri dishes (15 mL), and after the medium setting, wells of 6 mm in diameter were made in the agar. The agar was dried in a laminar oven, and the wells were injected with 10 - 30 mkl of the protein solutions under study of 0,02 M tris-HCl buffer pH 8,2 with 0,2M NaCl or without it. After diffusion of the specimens for 4-12 h at room temperature, the Petri dishes were placed into a thermostat at 30° for 1-2 days. Then, a width of the growth inhibition zone was measured. The ratio of the width (mm) of the microorganism growth inhibition zone to the protein amount (mkg) introduced into the well obtained in the proportional region of the dose-response curve was taken as the specific antibiotic activity (U). The minimal concentration of the protein solution tested resulting in a distinct zone of the growth inhibition was taken as the minimal inhibiting concentration (MIC) [6, 20].

Determination of the influence of CW and their components on the antimicrobial activity of Cry proteins The commercial preparation of CW of *M. luteus* (Sigma, USA) as well as the preparations of CW and their components (teichoic acid), isolated from *S. chrysomallus* cells according to the developed method, were used. The washed cells of *S. chrysomallus* with 0.01% SDS were frozen and disrupted by ultrasonication followed by heating at 90 °C for 5 min. All further preparations were carried out at 20°C. CW, separated from intact mycelium, was washed several times with deionized H<sub>2</sub>O and then lyophilized. Peptidoglycan (PG) was obtained, using treatment of this CW sample with tryptic cleavage (for 20 h at 37°C), then 2% SDS (for 5 min at 100°C). Teichoic acid was obtained, using treatment of this CW sample with trichloroacetic acid and ethanol. Electrophoresis, chemical, analytical and spectroscopic methods were used for the control of quality and purity of obtained samples [6, 7, 9, 22]. The effects of CW and teichoic acid on antibiotic activity of Cry toxins were detected after incubating the reaction mixtures at +20°C for 90 min. RESS

For scanning electron microscopy the washed cells and exospores of streptomycetes after their incubation with Cry1A solution with supplement 0,05% peptone were fixed with 2.5% glutaraldehyde for 2h; then the material was dehydrated by successive incubations in ethanol solutions of increasing concentrations (30, 50, and 70% for 30 min), then in 96% ethanol, absolute ethanol, and absolute acetone for 1 h and dried in the critical point. The specimens were evaporated with platinum using an LKB device (LKB Products, Bromma, Sweden). The scanning was performed with Hitachi Ltd. (Tokyo, Japan) microscopes at the accelerating voltage of 20 kV. For transmission electron microscopy the exospores of *S. chrysomallus* were contrasted with 2% aqueous solution of uranyl acetate according to standard techniques [6] and were studied in transmission electron microscope JEM 1011, Jeol Ltd (Japan) at the accelerating voltage of 80 kV.

### Results and discussion.

The MIC value determined for Cry1A proteins solution against *S. chrysomallus* was obtained as 20 - 25 mkg/ml. Antibacterial action of Cry1A proteins on streptomycetes was characterized by value of the specific antibiotic activity (U) at 3 mm/mkg (Table). The preincubation of Cry1A proteins with preparations of cell walls (CW) from micrococci and streptomycetes have been shown to stimulate this effect in 2,1 and 1,7 times, respectively. Also some components of CW *S. chrysomallus*, such as murein - peptidoglycan (PG), teichoic acid (TA), N-acetyl-D-galactosamine, have been shown to stimulate the antibacterial action of Cry1A in 1,7 - 2,5 times. The stimulating effect of teichoic acid and N-acetyl-D-galactosamine (GalNAc), on antibacterial activity of Cry1A proteins was the highest: in 2,3 - 2,5 times higher, respectively. The similar results for Cry1Ab from *B. thuringiensis* subsp. *alesti* were also found.

Table

**Effect of cell wall preparations of *Micrococcus luteus*, *Streptomyces chrysomallus* and some of their components on the antibiotic activity of Cry1A from *B. thuringiensis* subsp. *kurstaki* crystals against *S. chrysomallus***

Variant of solution injected to well in agar medium	Specific antibacterial activities of Cry1A U (mm/mkg):
0.02 M Tris-HCl buffer, pH 8.2, (control-I)	0
I with 200 mkg/mL preparation of cell wall (CW) of <i>M. luteus</i>	0
I with 200 mkg/mL preparation of cell wall (CW) of <i>S. chrysomallus</i>	0

I with 200 mkg/mL teichoic acid (TA) of <i>S. chrysomallus</i>	0
I with 200 mkg/mL peptidoglycan (PG) of <i>S. chrysomallus</i>	0
I with 200 mkg/mL GalNac	0
(I+Cry1A, 50 mkg/mL) -II	3,0 ± 0,31
II + CW of <i>M. luteus</i>	6,3 ± 0,67
II + CW of <i>S. chrysomallus</i>	5,0 ± 0,52
II + TA of <i>S. chrysomallus</i>	6,9 ± 0,75
II + PG of <i>S. chrysomallus</i>	5,0 ± 0,57
II + GalNac	7,5 ± 0,69

Results of the scanning electron microscopy study on the action of Cry1A on *S. chrysomallus* cells and exospores are presented in Fig. 1. As seen in the microphotograph in (Fig.1, photo 1), the initial *S. chrysomallus* culture consists of hyphae and rectangle exospores, i.e., the surface spores that are characteristic of a thickened peptidoglycan layer. After exposure to Cry1A, the majority of extended hyphae vanish (as a result of lysis), and surface spores lose their rectangle shape, Streptomycete hyphae are lysed rather rapidly. Lysis of exospores, which are characterized by the thickened cell walls as compared with vegetative cells, is slower, with protrusions also covering their surface. (Fig.1, photo 2). The lysis of the cells and exospores was most effective after the preincubation of Cry1A proteins with preparations of CW from *S. chrysomallus* (Fig. 1, photo 3).

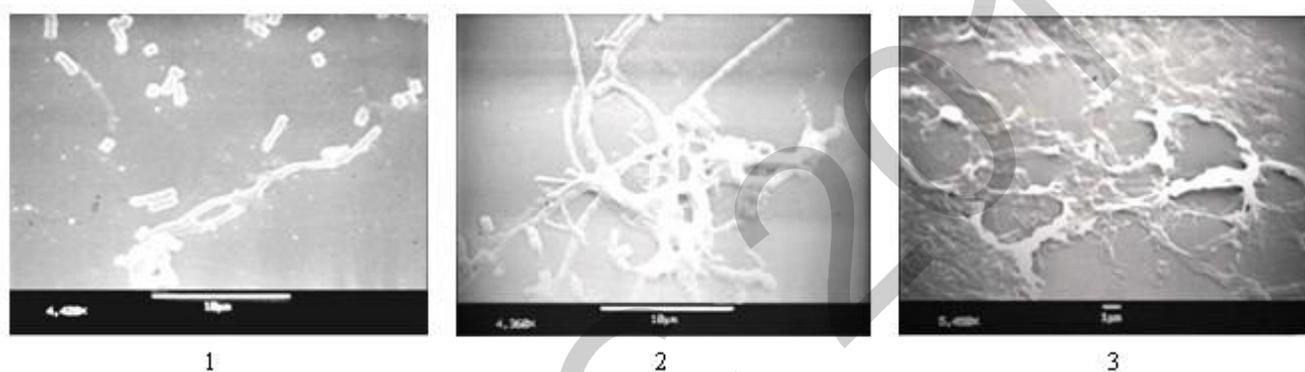


Fig. 1. Scanning electron microscopy of cells and exospores *Streptomyces chrysomallus* treated with the Cry1A endotoxins, 1) Endotoxin-untreated cells; 2) adhesion, swelling, and lysis of hyphae and rectangle exospores 60 min after the addition of the Cry1A proteins at 30°C; 3) the full lysis of hyphae and exospores 60 min after the addition of the Cry1A proteins preincubated with preparations of cell walls from streptomycetes.

Transmission electron microscopy (TEM) microphotographs of contrasted *S. chrysomallus* exospores undergoing lysis after Cry1A proteins treatment (Fig. 2).

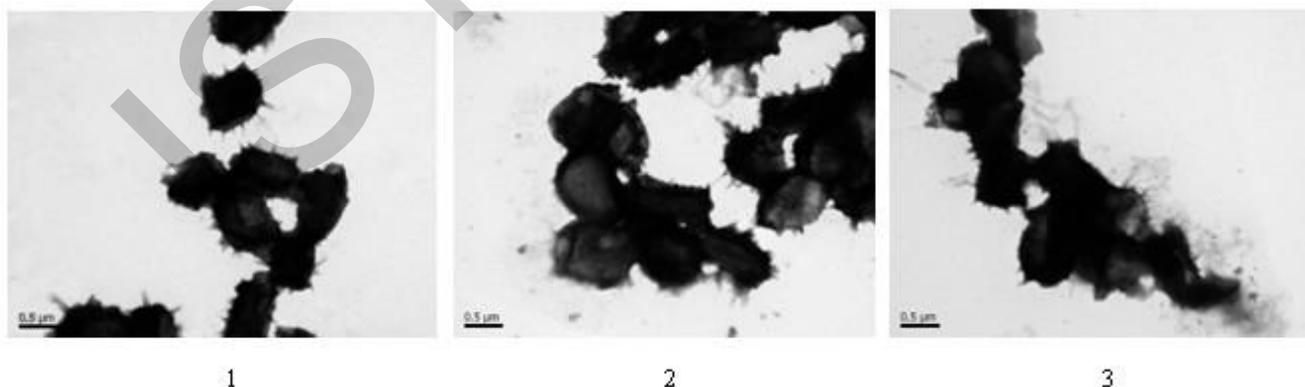


Fig. 2. Transmission electron microscopy of *S. chrysomallus* contrasted exospores of the Cry1A proteins undergoing lysis: 1 – control, endotoxins-untreated exospores; 2, 3 – adhesion, swollen and lysis of exospores 60 min after the addition of the Cry1A proteins at 30°C.

The addition of 0,2M NaCl to incubation buffer with Cry1A were shown to increase the value of antibacterial activity against *S. chrysomallus* (Fig. 3).

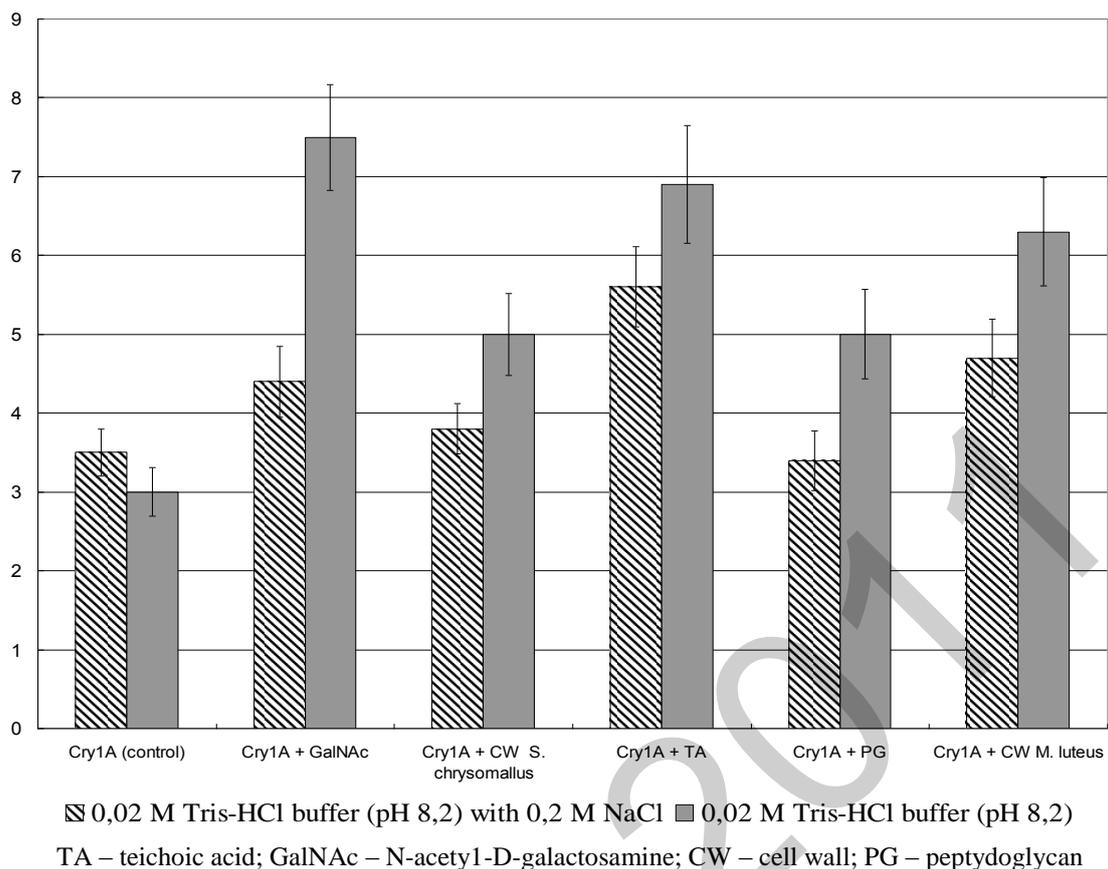


Fig. 3. Effect of cell wall preparations of *Micrococcus luteus*, *Streptomyces chrysomallus* and some of their components on the antibiotic activity of Cry1A proteins from *B. thuringiensis* subsp. *kurstaki* crystals against *S. chrysomallus* in 0.02 M Tris-HCl buffer, pH 8.2, with 0.2M NaCl.

Sodium and potassium ions added to incubation buffer to increase the value of antibacterial activity of the different  $\delta$ -endotoxins *B. thuringiensis* ssp. *israelensis* as was reported earlier [8]. The entomocidal effect of Cry-proteins is based on generation of ion channels, most often  $K^+$ , in the membrane of epithelial cells. The influence of potassium and sodium salts on the cytolytic effect have been shown in varied model systems [3, 12]. In the present work, we have found an increase in the antimicrobial effect of the Cry1A on bacterial cells in the presence of cations of alkaline metals ( $Na^+$ , and also  $K^+$ ). Thus, perhaps the death of a microbial cell should be associated with the generation of ion channels in the plasma membrane (CM).

In the present work, we have also found that stimulating effects of CW and some of its components on antibacterial activity of the Cry1A are decreased in 1,4 – 1,9 times in the presence 0,2M sodium chloride in incubation buffer (Fig. 3).

The influence of ionic strength, buffer composition and pH on the multimerization of Cry toxins over time and the subsequent effects of the different multimers on receptor binding models was very important. Thus, in carbonate buffer at pH 10.5, Cry1Ac and Cry1C assumed a monomeric state. After 24 h, a complete conversion of monomeric toxin to a dimeric or trimeric form was observed only for Cry1Ac under low ionic strength condition. Cry1C and Cry1Ac in high ionic strength buffer remained monomeric. Substitution of pH11 for carbonate buffer suppressed this Cry1Ac oligomerization effect. Once Cry1Ac toxin was in an aggregated form, increases in ionic strength failed to revert the aggregated toxin back to a monomeric form. Although high pH and low salt conditions promote Cry1Ac aggregation, this observation cannot be applied universally to other members of the Cry family. This means that action mechanisms of Cry proteins can be different due to the great number of possible changes within the molecules of Cry proteins. Investigations of different Cry1A toxins showed that one of the most important stages of Cry protein toxic effect is the binding of Cry toxin molecule to protein receptors located in the sensitive insects' mid with further oligomerization [3, 8]. It was shown [14, 20] that some *B. thuringiensis* crystal proteins or their fragments are able to destroy bacterial CM.

Many data concerning the relationship between the prokaryotic CW and CM functions have been described. Some important processes depend upon these structural interrelations, like the synthesis of bacterial peptidoglycan, which is a basic CW component. Change in the state of CW leads to changes in the state and functions of CM, and vice versa [2, 11]. The Cry proteins activity acts on permeability of CM [3], which is protected by CW in almost all prokaryotes [2, 7]. Outside the cytoplasmic membrane of Gram-positive bacteria the fundamental polymer is peptidoglycan (PG), which is responsible for the maintenance of cell shape and osmotic stability. The cell walls of Gram-positive bacteria usually contain a variety of polysaccharides, a significant proportion of which are covalently linked to peptidoglycan, the major scaffolding structure of the cell wall. In addition, typical essential cell wall polymers such as teichoic or teichuronic acids are linked to some of the peptidoglycan chains. These compounds are considered as 'classical' cell wall polymers. In the course of recent investigations of bacterial cell surface layers (S-layers) a different class of 'non-classical' secondary cell wall polymers has been identified,

which is involved in anchoring of S-layers to the bacterial cell surface. Comparative analyses have shown considerable differences in chemical composition, overall structure and charge behaviour of these. Different members of CW so that their interaction with some antimicrobial proteins having and with different lysins can be measured [7, 11]. Some parts of antimicrobial proteins may play an important role in interacting with the negative charge(s) of teichoic acids on the outer surface of the peptidoglycan [13].

We supposed that bacterial CW and some of their components are able to influence Cry toxin, enhancing its antimicrobial activity. We suggest, therefore, that the preincubation of Cry proteins with CW and some of its components could stimulate protein oligomerization, facilitating their interaction with CW, and thus increasing their antimicrobial activity. The increased antimicrobial activity could be the result of changed conformation of Cry protein molecules during their interaction with CW preparations. This means that action mechanisms of Cry proteins can be different due to the great number of possible changes within the molecules of Cry proteins.

It is possible to suppose that antibiotic effect of Cry proteins depends not only on their action against CM of microorganisms as it was discussed earlier [3, 20], but also against CW. Transmission electronic microscopy data obtained [15, 20] about the destruction of prokaryotic CW in the presence of Cry toxins confirm this supposition. We have shown also that the sensitivity of micrococci to the antibacterial action of Cry3A protein depended upon the thickness of its CW [17].

We supposed that polyfunctional Cry-proteins, apparently, could destroy the CW either by activating autolyzins, or by themselves, or by performing both functions at the same time. It also seems possible that such mechanisms of toxicity have differences depending on protein concentrations [22].

Other researchers discussed three probable mechanisms to explain the antibacterial action: (1) lysis of cells due to binding of antibiotic protein to a potential target inducing autolysin mediated death, (2) membrane permeabilization leading to cell lysis and (3) non-lysis mediated mode due to interference of membrane function as a consequence of antibiotic protein binding at the surface [1].

### Conclusions

Cry1A proteins from parasporal crystals of *Bacillus thuringiensis* subsp. *kurstaki* display antibacterial activity relative *S. chrysomallus*. The preincubation of Cry1A proteins with preparations of cell walls (CW) from micrococci and streptomycetes have been shown to stimulate this effect, also some components of CW *S. chrysomallus*, such as murein, teichoic acid, N-acetyl-D-galactosamine, But stimulating effects on antibacterial activity of the Cry1A of CW and some of its components are decreased in 1,4 – 1,9 times in the presence 0.2M sodium chlorides in incubation buffer. We suggest the possibility, that the preincubation of Cry1A proteins with CW and some of its components could influence protein oligomerization, and thus increasing their antimicrobial activity. But in high ionic strength buffer Cry1A proteins remained monomeric.

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# THE MATHEMATICS OF CENTRAL PLANNING AND SMALL TO MEDIUM BUSINESS

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## ABSTRACT

The most severe negative impact of the current financial crisis is the significant increase of the unemployment rate all over the world. In this respect, a vital alternative to the failed economies, if not the only one, is the economic concept of Central Planning (CP) and, at the same time, a very controversial one. The controversy is based on emotions, historic bias and conflict of interests, ideology and propaganda.

This presentation tries, from a formal point of view, to prove that CP, applied in its modern form, de-centralises the economy, creating a hierarchical structure of independent economic layers. Small to Medium Business (SMB) becomes an active component of the structure and significantly contributes to the development of the national economy as a whole.

The main method of the formalisation is a parallel procedure of Linear Programming which allows direct evaluation of the importance of the optimisation constrains to the final solution. Consequently, a new phenomenon is identified, named as The Technology - Economics Conflict, which is the cornerstone of the required de-centralisation.

## HISTORIC REVIEW OF CENTRAL PLANNING AS A MAJOR ECONOMIC MODEL

Central Planning was introduced by the Socialist Philosophical School in an attempt to improve the working and living conditions of ordinary people worldwide. The achievement of such a goal requires the chaotic and crises prone Capitalist system of economic management to be arguably replaced by a better model of collective planning. Since such a change is aimed at the heart of the Capitalism, the overwhelming opposition to the new model was immediate and without any compromise, with clear class orientation.

The de-centralisation of the CP is not a new idea and it was one of the major work areas of a few outstanding mathematicians and economists of the late 20<sup>th</sup> century, Nobel Prize winners. It is enough only to mention the Prize Lecture of Prof. L. Kantorovich (Nobel Prize in Economics, 1975), especially the following paragraph:

*In planning the idea of decentralization must be connected with routines of linking plans of rather autonomous parts of the whole system. Here one can use a conditional separation of the system by means of fixing values of flows and parameters transmitted from one part to another. One can use an idea of sequential recomputation of the parameters, which was successfully developed by many authors for the scheme of Dantzig-Wolfe and for aggregative linear models.* (Kantorovich, 1975)

After the World War I (about 1920) the most outspoken critics of Central Planning were the leading Austrian economist Prof. Ludwig von Mises and some of his followers, mainly Prof. Friedrich August von Hayek (Nobel Prize in Economics, 1974). Their chief opposition was related to the impossibility of Monetary calculations in the Socialist Commonwealth (von Mises, 1920) and the physical and psychological limitations of central planners to acquire and process all necessary data for the management of a rational, optimised economy (Hayek, 1945).

Modern objections to Central Planning are mainly derived from the Nine Lectures given by Prof. Mises at the San Francisco Public Library in 1952 (Foundation for Economic Education, 2006). A few titles could show view points of emotions, historic bias and conflict of interests, ideology and propaganda:

- The Violence of Central Planning (Rockwell Jr. L., 2003)
- Central planning and the parasites it creates (Bonner Bill, 2010)
- Why Central Planning Fails (Perry Mark, 2009)
- The Fallacy of Central Planning (TrueBlood David, 2010)

Of course, many more examples could be provided demonstrating triviality or just ignorance. Some strange cases are even blaming Central Planning for natural disasters (mud slides, droughts, gas explosions, etc.).

From the above one might conclude the Central Planning is dead, but nothing could be further from the truth.

On 5<sup>th</sup> April 2011 some Republican senators introduced the National Manufacturing Strategy Act of 2011 at the American Congress, the heart of the world Capitalist system, the on-line letterhead follows (Congress Legislation, 2011):

govtrack.us

HOME

CONGRESS > LEGISLATION

## H.R. 1366: National Manufacturing Strategy Act of 2011

112<sup>th</sup> Congress: 2011-2012

To require the President to prepare a quadrennial national manufacturing strategy, and for other purposes.

The British Independent of 7<sup>th</sup> December 2010 recommended Central Planning in their editorial “Britain needs to revert to central planning of market” (The Independent, 2010).

Curiously, the biggest social, economic and political endeavour in the American history – Apollo 11 landing on the Moon – is a centrally planned project of NASA. The ideological paranoia and the mindless bureaucratic manoeuvring, in order to stop the project, are remembered, quite humorously, by the wonderfully written book “One Giant Leap: Apollo 11 Remembered”, e.g. excerpts from page 38 follow:

.....*In 1963, an alarmed senator, William Proxmire, told Congress: “The space program is probably the most centralized government spending program in the United States. It concentrates, into the hands of a single agency, authority over an important sector of our economy. It could well be described as corporate socialism.”* .....  
*And in the end, the sums of money involved were not so terrifying as Proxmire made out. A simple comparison between the population census figures and NASA’s expenditure during the 1960’s tell us that it reached the moon for less than two dollars a month from each American citizen. Per day, it was the price of a stick of gum* (Bizony P., 2009).

## MAIN ASSUMPTIONS AND OBJECTIVE OF THE PROPOSED FORMALISATION

The proposed formalisation is based on the neoclassical interpretation of the term “rational” as meaning “optimal” (McCain R., 2011)

This paper is not going to discuss in detail or argue against the claims of Prof. von Mises and Prof. Hayek respectively, but will try to answer one of their principle problems – the necessary data, its processing and the dynamics of information flows of the Central Planning model.

Since “The Use of Knowledge in Society” is considered one of the most important works of modern economics, the discussed formalisation is oriented to the definitions of this essay. In addition, the Prize Lecture of Prof. Hayek - The Pretence of Knowledge - could be considered the natural conclusion of the above work of him. The relevant paragraphs are as follows:

..... *It is about this question that all the dispute about “economic planning” centers. This is not a dispute about whether planning is to be done or not. It is a dispute as to whether planning is to be done centrally, by one authority for the whole economic system, or is to be divided among many individuals. Planning in the specific sense in which the term is used in contemporary controversy necessarily means central planning—direction of the whole economic system according to one unified plan. Competition, on the other hand, means decentralized planning by many separate persons. The halfway house between the two, about which many people talk but which few like when they see it, is the delegation of planning to organized industries, or, in other words, monopoly.* .....  
*If we can agree that the economic problem of society is mainly one of rapid adaptation to changes in the particular circumstances of time and place, it would seem to follow that the ultimate decisions must be left to the people who are familiar with these circumstances, who know directly of the relevant changes and of the resources immediately available to meet them. We cannot expect that this problem will be solved by first communicating all this knowledge to a central board which, after integrating all knowledge, issues its orders. We must solve it by some form of decentralization. But this answers only part of our problem. We need decentralization because only thus can we insure that the knowledge of the particular circumstances of time and place will be promptly used. But the “man on the spot” cannot decide solely on the basis of his limited but intimate knowledge of the facts of his immediate surroundings. There still remains the problem of communicating to him such further information as he needs to fit his decisions into the whole pattern of changes of the larger economic system* (Hayek F.A., 1945).

Before all, this paper fully supports the conclusions of the above mentioned prominent economists related to the necessary planning data and its dynamics. Even more, the concept of the “man on the spot” is actively used in the proposed presentation.

Following the interpretation of the famous economists some sort of divine power should be given to central planners to properly perform their duties and such a claim could be confirmed by the Sûrat 6, Verse 59 of The Holy Qur’an as follows (The Noble Qur’an, English version):

*59. And with Him are the keys of the Ghaib (all that is hidden), none knows them but He. And He knows whatever there is in the land and in the sea; not a leaf falls, but He knows it. There is not a grain in the darkness of the earth nor anything fresh or dry, but is written in a Clear Record.*

Obviously, mortals cannot possess such unlimited power and the basic interpretation of CP clearly concludes – CP cannot work.

However, the proposed method is trying to prove that Central Planning **does not** require omnipotence, **does not** require a plan to be completed, “after integrating *all* knowledge”. Therefore, the main objective is to show in a formal way that Central Planning, considered as an optimisation procedure, requires de-centralisation of the planning structure in order to accommodate various types of data depending on “particular circumstances of time and place”.

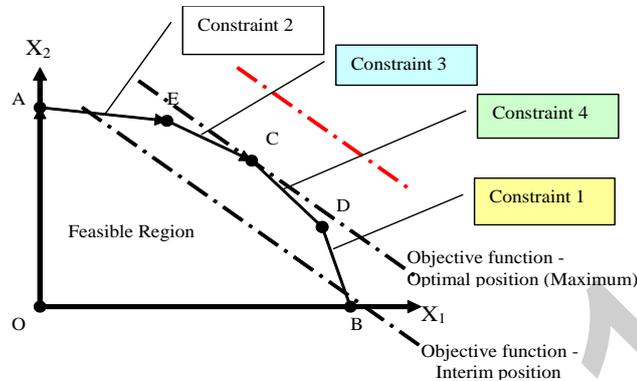
## BRIEF DESCRIPTION OF THE PARALLEL LINEAR OPTIMISATION ROUTINE

The proposed Routine does not need specialised hardware, it could be run on single core processors, but some of the steps could be done simultaneously/independently from each other. It means the basic information could come from digital statistical databases (archives) as input data to the Routine in a de-centralised manner, without the direct intervention of CP office. One

typical application is e-Planning as part of e-Government activities when the input data of the Routine is independently provided by various community centres and branches of the economy.

The proposed method (Africa Method) is developed and named in support of the tendency for a change from mere utilisation, even reckless exploitation (deforestation, soil degradation, etc.), of natural resources to their optimisation and, consequently, the diversification of Africa economies (Chakalisa P., et al, 2008).. A typical application of the new procedure could have been Energy Management, in general, and the feasibility study of the Second Thermal Power station in Botswana in particular (Chakalisa P., et al, 2005).

Geometrically, the Linear Programming (LP) problem could be interpreted in the following way (for the sake of simplicity a two-dimensional case is given below, **Fig. 1**):



**Fig. 1**

The proposed method is based entirely on the theoretical foundations of LP and its modifications (Integer Programming), as introduced in 1947, but it interprets the constraints and the edges of the convex/Simplex (the Feasibility Region) in a different way, which brings certain advantages in terms of simplicity (no need of Slack variables), computational time, and analysis of the processed macroeconomic model. The extreme points of the Feasibility Region (Simplex) are divided into two groups:

- Axis points lying on the coordinate axes, e.g. A and B (**Fig. 1**).
- Constraint Cross-points defined by the intersection of model limitations (problem constraints), e.g. C, D, and E (**Fig. 1**).

The two types of solution require the introduction of Partial Contribution Fractions (PCF) and the Cross-points Operator (CPO).

The fraction, called the Partial Contribution to the Satisfaction of a Constraint (PCSC), is calculated as the limit of the constraint is in the numerator and the constraint coefficient of a variable in the de-nominator.

The fraction, called the Partial Contribution to the Improvement of the Objective function (PCIO), has its numerator to be the variable coefficient of the Objective function (OF) and the de-nominator is the coefficient of the same variable, but from a constraint.

CPO allows comparisons between constraints and it could be used either to construct/minimise the Simplex or find a solution to a simultaneous system. The CPO is directly related to the de-centralisation of the economic model.

An Axis point could be calculated using the Knapsack criterion (Winston, W.L., 1995), borrowed from the Integer Programming. The essence of this criterion is the possibility to calculate and choose a variable of a certain constraint which contributes most to the improvement of the OF.

Of course, the variable, called The Best should not violate any limitation of the model. In the same manner, all other variables of a constraint could be processed and a list be compiled in terms of their significance to the improvement of the OF (e.g. starting with The Best variable). Since the variables are independent of each other, such calculations could be done in parallel. Constraint Cross-points need the introduction of a new criterion - Closeness criterion. The idea is based on the fact that the optimal solution is defined by constraints that are closer to the OF in the optimal point, comparing with the other ones.

Naturally, the Closeness criterion is the angle (Smyrl, J.L., 1989), between a constraint and the OF. The smaller the angle is, closer the respective constraint to the OF is as well. Accordingly, a list of constraints could be compiled reflecting their closeness to the OF, starting with the Closest constraint, for example. The angles in question could be calculated independently, which allows parallel processing to be applied relatively easy.

On the other hand, both solutions (Axis points solution and Cross-points solution) could be computed in parallel too, which additionally reduces the necessary processing time. The better solution is the final one to the LP problem. Obviously, the parallel approach saves time in addition to that one resulting from the elimination of slack variables - an essential concept of the classic LP method.

### CENTRAL PLANNING APPLICATION OF AFRICA METHOD

The proposed method is applied to the compilation of the draft centralised plan of the following macroeconomic model :

"Steelco manufactures two types of steel (steel 1 and steel 2) at two locations (plant 1 and plant 2). Three resources are needed to manufacture a ton of steel: iron, coal, and blast furnace time. The two plants have different types of furnaces, so the resources needed to manufacture a ton of steel depend on the location " (Winston, W.L., 1995).

"Each plant has its own coal mine. Each day, 12 tons of coal are available at plant 1 and 15 tons at plant 2. Coal cannot be shipped between plants. Each day, plant 1 has 10 hours of blast furnace time available and plant 2 has 4 hours available. Iron ore is mined in a mine located midway between the two plants; 80 tons of iron are available each day. Each ton of steel 1 can be sold for \$170/ton, and each ton of steel 2 can be sold for \$160/ton. All steel that is sold is shipped to a single customer. It costs \$80 to ship a ton of steel from plant 1, and \$100 a ton from plant 2" (Winston, W.L., 1995).

The following variables should be defined:

"X<sub>1</sub> = tons of steel 1 produced daily at plant 1  
 X<sub>2</sub> = tons of steel 2 produced daily at plant 1  
 X<sub>3</sub> = tons of steel 1 produced daily at plant 2  
 X<sub>4</sub> = tons of steel 2 produced daily at plant 2" (Winston, W.L., 1995).

The linear macroeconomic model could be formalised as follows:

$$\begin{aligned}
 \text{"max } Z &= 90X_1 + 80X_2 + 70X_3 + 60X_4 \\
 \text{s.t.} \quad &3X_1 + X_2 \leq 12 \quad \text{(Plant 1 coal constraint)} \quad (1) \\
 &2X_1 + X_2 \leq 10 \quad \text{(Plant 1 furnace constraint)} \quad (2) \\
 &3X_3 + 2X_4 \leq 15 \quad \text{(Plant 2 coal constraint)} \quad (3) \\
 &X_3 + X_4 \leq 4 \quad \text{(Plant 2 furnace constraint)} \quad (4) \\
 &8X_1 + 6X_2 + 7X_3 + 5X_4 \leq 80 \quad \text{(Iron ore constraint)} \quad (5) \\
 &X_1, X_2, X_3, X_4 \geq 0 \quad \text{" (Winston, W.L., 1995).}
 \end{aligned}$$

The compilation of **Table 1** of PCIOs is a very important step of the solution, because it is a tool to examine the original Simplex and minimise it, if it is possible.

**Table 1**

Constraint No	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>
(1)	X <sub>1</sub> <sup>(90/3)</sup>	X <sub>2</sub> <sup>(80/1)</sup>		
(2)	X <sub>1</sub> <sup>(90/2)</sup>	X <sub>2</sub> <sup>(80/1)</sup>		
(3)			X <sub>3</sub> <sup>(70/3)</sup>	X <sub>4</sub> <sup>(60/2)</sup>
(4)			X <sub>3</sub> <sup>(70/1)</sup>	X <sub>4</sub> <sup>(60/1)</sup>
(5)	X <sub>1</sub> <sup>(90/8)</sup>	X <sub>2</sub> <sup>(80/6)</sup>	X <sub>3</sub> <sup>(70/7)</sup>	X <sub>4</sub> <sup>(60/5)</sup>

⇔ **Inside the Simplex**

⇔ **Inside the Simplex**

⇔ **Inside the Simplex**

Now CPO is applied to **Table 1** and the results are on its right side. For example, since a maximisation problem is the issue, when the corresponding PCF of constraints (1) and (2) are compared, the values of (1) are less or equal to those of (2), which means constraint (1) is below/behind (2) and contributes less to the OF. Therefore, such a constraint is considered "Inside the Simplex" and, apart from being a limitation, it does not contribute to the economic model at all. In case of minimisation the output of CPO, under similar circumstances, is "Outside the Simplex". The optimised model is given below:

$$\begin{aligned}
 \text{max } Z &= 90X_1 + 80X_2 + 70X_3 + 60X_4 \\
 \text{s.t.} \quad &2X_1 + X_2 \leq 10 \quad \text{(Plant 1 furnace constraint)} \quad (2) \\
 &X_3 + X_4 \leq 4 \quad \text{(Plant 2 furnace constraint)} \quad (4) \\
 &X_1, X_2, X_3, X_4 \geq 0
 \end{aligned}$$

In line with the optimisation of the Simplex, a classification of the constraints could be introduced as well. Constraints that form the Simplex are the Active ones and they make-up the economic level of the processed model. Constraints imposing limitations only are the Passive ones and they are components of other economic layers of the same system. The limitations are the links between the layers of the de-centralised economy, providing for the application of Prof. Hayek's vision that "the knowledge of the particular circumstances of time and place will be promptly used".

Now, to prove the correctness of the optimised Simplex, the original problem will be solved, obtaining the same Simplex minimisation as already calculated by CPO, **Table 1**.

**Step 1.** Compiling the Closeness list between the OF and each of the constraints (the original numbering of the constraints is used in the following table). The list is sorted out in descending order, starting with the Closest constraint to the OF - Z as per **Table 2**.

**Table 2**

Constraint No	C l o s e n e s s				
	Closest				
	(4)	(5)	(3)	(2)	(1)

**Step 2.** The first operation here is the modification of **Table 1** to reflect the order of **Table 2**. After that, PCF of variables should be sorted out in descending order (**Table 3**), starting with The Best variable.

**Table 3**

Variable >>>	Partial Contribution to the Improvement of the Objective function (PCIOs)			
Constraint No	Most			Least
(4) The Best >>>	-	-	X <sub>3</sub> <sup>(70/1)</sup>	X <sub>4</sub> <sup>(60/1)</sup>
(5)	X <sub>2</sub> <sup>(80/6)</sup>	X <sub>4</sub> <sup>(60/5)</sup>	X <sub>1</sub> <sup>(90/8)</sup>	X <sub>3</sub> <sup>(70/7)</sup>
(3)	-	-	X <sub>4</sub> <sup>(60/2)</sup>	X <sub>3</sub> <sup>(70/3)</sup>
(2)	X <sub>2</sub> <sup>(80/1)</sup>	X <sub>1</sub> <sup>(90/2)</sup>	-	-
(1)	X <sub>2</sub> <sup>(80/1)</sup>	X <sub>1</sub> <sup>(90/3)</sup>	-	-

A variable partially contributes Most if the value of the corresponding fraction is the highest.

**Step 3.** The main idea, behind the calculation of Axis points as already mentioned, is the use of the most promising constraints and their best variables to get the maximum value of **Z**. So, the solution starts with the Closest constraint (4) as per **Table 3** and its Best variable  $X_3$ . Therefore,  $X_3 + X_4 \leq 4$ ;  $X_4 = 0$ ;  $X_3 = 4$ ; no violation of any limitation of the problem.

Since the set of variables  $X_1$  and  $X_2$  is not part of the Closest constraint, the second closest/next one should be processed, if the variables in question are there.

Therefore, constraint (5) should be used, starting with its Most contributing (MC) variable  $X_2$ .

$8X_1 + 6X_2 + 7X_3 + 5X_4 \leq 80$ ;  $X_2 = 13.33$ ;  $X_1 = X_3 = X_4 = 0$ ; not possible, because limitations/constraints (1) and (2) respectively are not satisfied. Thus, the second best variable, considering the set of  $X_1$  and  $X_2$ , should be tried -  $X_1$ . Therefore  $X_1 = 10$ ;  $X_2 = X_3 = X_4 = 0$ ; not possible, because limitations /constraints (1) and (2) respectively are not satisfied.

Obviously, with respect to variables  $X_1$  and  $X_2$ , the problem is still unresolved, which requires the next constraint, where  $X_1$  and  $X_2$  are involved, to be processed - (2), in accordance with **Table 3**.

$2X_1 + X_2 \leq 10$ ;  $X_2 = 10$ ;  $X_1 = 0$ ; pair{ $X_2 = 10, X_3 = 4$ } violates constraint (5) and a new variable of lower priority -  $X_1$  should be tried (if available), but  $X_1 = 5$ ;  $X_3 = 4$  does not satisfy (1). Therefore, if available, a new constraint of lower rating, should be involved-(1). There  $3X_1 + X_2 \leq 12$ ;  $X_2 = 12$ ;  $X_1 = 0$ ; pair{ $X_2 = 12, X_3 = 4$ } violates constraint (5) and, respectively,  $X_1 = 4$  should be examined. Pair{ $X_1 = 4, X_3 = 4$ } is acceptable by all other constraints and the corresponding value **Z = 640**. Since there is a calculated value of **Z**, the next iteration is to check if lower priority constraints/variables do not generate a better solution. A reference to **Table 3** shows there are no more constraints to be tried and the new iteration should start from the very beginning, but now the second MC variable of (4) is tried:  $X_4 = 4$ ;  $X_3 = 0$ . After that the iteration continues with variables  $X_1$  and  $X_2$  as the above, checking for no violation of the limits and, at the end of the iteration, the Axis points solution is **Z = 1040**. Since an improvement of **Z** has been identified, another iteration is necessary to confirm or reject its value, following the order of **Table 3**. Now constraint (5) plays a leading role and its MC variable  $X_2$ . At the end, the iteration yields **Z = 1040**, which value confirms the result of the previous iteration. Therefore, finally the Axis points solution is  **$X_1 = 0, X_2 = 10, X_3 = 0, X_4 = 4$  and  $Z = 1040$** .

The main observation of the analysis of **Step 3** is that constrains (1), (3) and (5) respectively do not actively influence the optimal solution at all, as predicted by the optimised Simplex.

**Step 4.** This step utilises the main observation of **Step 3** related to constraint (1), (3) and (5) respectively – they are excluded from Cross-points solution, but in such a case **Step 4** becomes quite similar to **Step 3**. To prove again the importance of the optimised Simplex let consider constraint (5) as an Active one and try to find Cross-points solutions.

The Cross-points solutions, if any, require systems of linear equations. Since there are four variables, four equations, if available, are necessary to form a simultaneous system. In accordance with **Table 2** a new table (**Table 4**) should be drawn to reflect PCSIs of the constraints. In this case there are three equations and four variables which means to one of the variables should be assigned a value in order to solve the simultaneous system. From **Table 3** it could be seen variable  $X_3$  is The Best of constraint (4) which is the closest to the OF and it is logical to give this variable as big a value as possible, without violating any other constrains (in our case (5) and (2) respectively). Thus  $X_3 = 4$ . After the fixture, **Table 4**, is modified and the changes are in **Table 5**.

**Table 4**

Constraint No	$X_1$	$X_2$	$X_3$	$X_4$
(4)	-	-	4/1	4/1
(5)	80/8	80/6	80/7	80/5
(2)	10/2	10/1	-	-

**Table 5**

Constraint No	$X_1$	$X_2$	$X_3$	$X_4$
(4)	-	-	4	0
(5)	52/8	52/6	-	0
(2)	10/2	10/1	-	-



Crossing point

The Crossing Point is easily identified looking at the corresponding PCSIs of constraints (5) and (2). Some are bigger, but others are smaller and the following simultaneous system should be considered:

$$8X_1 + 6X_2 = 80 - 7x_4 = 52$$

$$2X_1 + X_2 = 10$$

For the time being the Cross-points solution is  $X_1 = 2, X_2 = 6, X_3 = 4, X_4 = 0, Z = 940$ . Now, a new iteration should examine from the very beginning of the **Step**, going down the priority order with variables  $X_4$ , whether the solution is final or not.

The new solution is **Z = 1040**, but it should be checked if there is not even a better one. The next iteration is processing constraint (5), but all its PCF disagree with the model limitations. After processing in this way, the final iteration gives  $X_1 = 0, X_2 = 10, X_3 = 0, X_4 = 4, Z = 1040$ , confirming the result of the second iteration.

The result clearly demonstrates that considering together Active and Passive constraints reduces the economic achievement of the system as a whole and creates unnecessary data processing problems. This solution is another illustration of the advantages of the CP de-centralises procedures, as recommended by Prof. Kantorovich in his Nobel lecture.

**Step 5.** Both solutions (values of **Z**) should be compared and the better one is considered the final solution to the Steelco problem as follows:  **$X_1 = 0, X_2 = 10, X_3 = 0, X_4 = 4$  and  $Z = 1040$** . Such findings should not come as a surprise, because they could be clearly seen on **Fig. 1** where there are a few constraints, but only two of them define the optimal solution of the two dimensional case.

At this point the easiest part of the Central Planning is over, based on well established statistical facts. Obviously, certain recommendations, concerning the model (steel manufacturing technology) itself, should be made, because the Passive constraints provide essential components (coal, ore) of the technological process and the required investment for developing the necessary plant coal/ore mines should somehow affect the optimisation of the whole industrial complex. Therefore, a new planning phenomenon, for reference purposes called Technology - Economics Conflict (TEC), emerges – the technology requires certain equipment, but the planners do not know how to evaluate it economically, because the investment in question does not directly affect their plans and models. The answer to the question what should be done, if something does not economically contribute to the achievement of certain goals, is that the information related to it is not necessary at all and naturally such data is not available either. Therefore, Central Planners are not going to be buried under the piles of unnecessary information, but they have to organise a new hierarchical level of planning to accommodate such economic events. This could be done integrating similar businesses at regional/provincial levels or to offer them to SMB, subject to another planning procedure. Obviously, the claim that Central Planning is based on “one size fits all” approach sounds, at least, ridiculous. In such a way, “the man on the spot” is not just a private individual, but the operational planner at her level. The dynamics of the day-to-day running “the cog of a bigger machine” is in its hands, e.g. a flat tyre, a broken drive shaft, dereliction of duties, etc. This is how individuals could participate in the planning process in a de-centralised way, without necessity of chaotic and resource wasting endeavours like competition in its classic format. But it should not be forgotten that the personal responsibility is much higher in comparison with the traditional private ownership and the consequences in case of professional misconduct are much more severe.

The dynamic links between different layers of the economy could be illustrated by the re-calculation of some of the Passive constraints which contributes to the improved performance of the respective economic branches, e.g. the Department of Mines.

$$3X_1 + X_2 \leq 10 \quad \text{original value} = 12 \quad (\text{Plant 1 coal constraint}) \quad (1)$$

$$3X_3 + 2X_4 \leq 8 \quad \text{original value} = 15 \quad (\text{Plant 2 coal constraint}) \quad (3)$$

If the number of variables is equal to the number of constraints, the model, if feasible, is the extreme case of CP or Pure CP and planning hierarchical structure cannot be formed.

The other extreme case is the Free market model when a planning hierarchical structure starts from grass-root level progressing up, but the final outcome is not known in advance. Therefore, the Free market case could be considered a particular case of Central Planning, when the Objective/optimisation function is randomly chosen.

## CONCLUSION

Assuming the modern definition of Central Planning Model and the critiques on its applicability in real life, the proposed approach proves the major attribute of the Model is to be a de-centralised hierarchical planning system, reflecting the dynamics of the relevant information flows. The essence of the proof is the new planning phenomenon TEC which defines and justifies the necessity of a de-centralised economy.

All discussed considerations do not impose significant limitation on the classic Libertarian principles within the framework of modern socio-economic conditions, especially when it comes to the increased social and professional responsibility of “the man on the spot”. The discussed Method contributes to the proper administrative structure of a state, because each economic layer might require a separate managerial body, reducing the unnecessary bureaucracy.

Pure CP and Free market models could be easily explained as specific cases of the proposed Model.

Such a planning system converts SMB into a fully-fledged and unique component of the national economy.

Finally, some misconceptions, myths and hear-say stories of Central Planning should be considered dismissed.

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# THE PHYTOCHEMICAL AND ANTIMICROBIAL EVALUATION OF THE EXTRACTS FROM THE DOG ROSE BUSH '*ROSA CANINA* L'

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## Abstract

The family of the Rosaceae is an important as the number of species (over 3000) and by the vegetative diversity, floral and fruit of its representatives. This family is distributed geographically in all parts of the world, but it's especially abundant in temperate regions of the Northern hemispheres.

Our work is focused on a kind of this family known as *Rosa canina* L. This practical study with the objective phytochemical analysis which involves the identification of different active ingredients present in the leaf powder of *Rosa canina* L. followed by extraction of essential oils, flavonoids, tannins (leaf) and vitamins (of fruit). Finally an evaluation of the antimicrobial activity of the extracts was tested on 05 microbial strains including 04 bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Bordetella bronchiseptica*, *Klebsiella pneumoniae* and 01 references yeast *Candida albicans*. Our preliminary results allow us an overall assessment of the medicinal value of the species studied in this case *Rosa canina* L.

Keywords: *Rosa canina* L., flavonoids, essential oils, tannins, vitamins, Antimicrobial activity

## 1. Introduction

The Rosaceae includes all vegetative forms available from grasses to trees, some herbs such as strawberries; others are shrubs such as roses, brambles, raspberries. Their hair epidermal massive lignified, are transformed into spines and hooked spines. This nature is easily verifiable epidermal: the stings are easily detached from the stem, often resulting in shreds of skin.

Finally, many Rosaceae are trees such as cherry, plum (*Prunus* species, including *Lauro-cerasus*, or cherry laurel, which is widely used in pharmacy), peach, apple and pear. Some of their branches' frequently become thorns. The leaves are alternate and always stipulated. Originally, they are made, imparipinnate, leaflets with toothed (sometimes alternately large and small: Meadowsweet, Agrimony) (Guignard, 1983).

*Rosa canina* L. is native to Europe, Asia Minor and Central (in temperate regions of Asia) and North Africa. The Eglantier is common in hedges, scrub and wasteland, the plant has been naturalized in the eastern part of North America (Wicht and Anton, 2003; Kokh and Hans, 2007).

The species is commonly found on hillsides, along hedges, along roadsides, in wastelands and filled (Iserin, 2001). In Algeria, we find in the bushes of low and medium mountains, in areas well watered and semi-arid.

The *Rosa canina* is made up of several vitamins such as vitamin C (up 1.25%), A, B1, B2, P and K. The L-ascorbic acid is the major constituent, according to the original maturity of pseudo-fruit and the care taken in drying, 0.2 to 1.2% in *Rosa canina* and 0.5 to 2.0% in *pendulina* Rosa, but its values are never reached by the commercial varieties. Other constituents such as pectins (15%), sugars, fruit acids (malic, citric acid), tannins (gallic acid derivatives), an essential oil (about 0.03%), flavonoids and anthocyanins, of red and yellow dyes with especially various isomers of rubixanthine, lycopene, zeaxanthin and B-carotene, the latter being the precursor of vitamin A; of flavinodiols (catechol, épicatechol, gallacatéchol, leucopéonidine ...) of organic acids: citric, malic, quinic and gallic (Iserin, 2001; Wicht and Anton, 2003).

## 2. Materials and Methods

### 2-1 - Biological material:

The plant: the plant material studied consists of leaves and fruits of *Rosa canina* L., collected at Lake Réghaia (Algiers).

Microorganisms: microbial strains used for testing of antimicrobial activity are represented by four bacteria, *Escherichia coli*, *Staphylococcus aureus*, *Bordetella bronchiseptica* and *Klebsiella pneumoniae* and a yeast *Candida albicans*.

### 2-2- Methods

#### 2.2.1 Preparation of plant material:

We made two crops for *Rosa canina* L. at Lake Réghaia: in January 2011 for fruit and March 2011 for the leaves. It is at these times that the fruits are mature and growth of young branches is.

Drying was carried out in the shade in the open air and at room temperature to prevent oxydation of natural substances and the growth of mold.

Grinding and conservation: we used a grinder to get the fine powder. Prior to the whole plant was crushed using a conventional mortar.

#### 2-2-2- Dosages

Determination of water: the water content in medicinal plants is an important indict characterizing the quality of it. For 1g of powder, the expression of results is done according to the formula: % water = (mass of water ÷ weight drug test) × 100. Determination of ash: This is to assess the amount of residual substances not volatilized when the drug is completely burned. Using the formula: % = Total ash (ash mass / mass drug test) × 100.

#### 2.2.3- Reactions characterization

The characterization of bioactive chemicals implements tube reactions either by precipitation or by staining for the identification of various chemical substances present in plants, tests are performed either on the leaf powder them or the infused 20%, methods for characterizing these secondary metabolites is described by Paris and North (1987).

The reactions of characterizations conserne: the anthocyanins, the tannins, the saponins, alkaloids, flavonoids and mucilage.

#### 2.2.4-Extraction of the active ingredients

Extraction of essential oils from the leaves: the condensation of the essential oil was obtained by hydrodistillation in a device that connects the water vapor with a cooler. The essential oil is collected in small glass vials, sealed and stored in the dark at 4 ° C.

Extraction of tannins of the leaves: in 100 ml of benzene and 100 ml of chloroform, we put 60 g of the powder of the leaves. The mixture is macerated for 24 hours. After filtration, the filtrate is removed containing lipids and chloroform and the residue is kept.

In the latter, 100 ml of diethyl ether for the removal of phenols, catechins and oxybutirique acid and then filtered. Similarly, 200 ml of methyl alcohol and maceration is carried out for 45 minutes. The filtrate contains tannins and methyl alcohol. Finally, we realize a vacuum evaporation by Rotavapor at a temperature between 40 ° C and 60 ° C to recover the tannins. The extract of tannins is obtained as a dry bottom of the ball.

Extraction of flavonoids is based on their solubility in alcohols (ethanol, methanol) depending on whether fresh or dried material. To 30 g of dry plant powder made placed in a glass container, you put 100 ml of methanol, allowed to macerate for 72 hours. After filtration, the solution is evaporated under vacuum with a rotary evaporator and the resulting extract is treated with 50 ml of hot distilled water. After cooling, the procedure is a series of liquid / liquid extraction, settling, with solvents immiscible with water.

The solids content of flavonoids was obtained by vacuum evaporation of the extract terminal butanol at a temperature between 50 ° C and 85 ° C. The solids content of flavonoids was finally obtained at the bottom of the balloon.

### Extraction of vitamins from fruits:

Sample preparation: The preparation is done on the following samples of rose hip, ground and weighed. They will then be put in maceration in extraction solvents. The method is required to extract the compounds that exist in the fruit, namely vitamins.

Extraction with a nonpolar organic solvent (chloroform) and extraction with a polar organic solvent (ethanol).

#### **2.2.5-The antimicrobial test:**

We tested our extracts tannins and flavonoids by the method of agar diffusion or disc method is a technique used in medical bacteriology, called sensitivity. With regard to the essential oil obtained, we used the aromagram which is also based on the same principle.

Principle: The diffusion method on agar medium, is to look for in vitro antibacterial antibiotics (the study of the action of antibiotics on the growth of micro-organisms and the sensitivity of the latter) (Duva and Soussy, 1990). This method is suitable for testing of other antimicrobial agents.

### **3. Results and discussion:**

Our study in the laboratory of the Faculty of Science (UMBB) on *Rosa canina* L, a plant of the flora of Algeria harvested in the middle of hunting licenses Réghaia to highlight the presence of different chemical groups in the powder of the leaves and the fruits of the wild rose, and the evaluation of the biological activity of the latter. The phytochemical analysis revealed the presence of tannins, flavonoids, saponins and mucilages, which was confirmed in reactions characterization. The absence of anthocyanins and alkaloids is confirmed by previous theoretical studies.

During the extractions, the highest yield was obtained with tannin extract which is 8.99%. However, the butanol extract and that of diethyl ether and the oils have a low yield. Evaluation of the antibacterial activity of the extracts of leaves allowed us to conclude that: Regardless of the extraction solvent, all pure extracts are extremely active in the bacterial strains of *Staphylococcus aureus*, *Escherichia coli* and *Bordetella bronchiseptica*, so they are more sensitive, compared with *Klebsiella pneumonia*. As against the extract of essential oils is not of great activity.

Thus, the butanol extract flavonoids and tannins in methanol were most active in *Escherichia coli*, with inhibition diameters of 15.5 and 15 mm respectively, *Bordetella bronchiseptica* with inhibition zones of 18 and 22.5 mm in diameter. Both extracts showed a moderate inhibitory activity with diameters of inhibition zones have exceeded the 20 mm on the strains (*Staphylococcus aureus*, *Bordetella bronchiseptica*).

However, in our experiments, the extract of essential oils has no antifungal activity (against *Candida albicans*) and antibacterial except against *Staphylococcus aureus* and *Klebsiella pneumonia* moderately active, this small antimicrobial activity of species *Rosa canina* L, may be due either the low dose extracts, it is not a broad spectrum against bacteria and fungi and depends on the composition of the essential oil itself. The butanolic extract flavonoids and tannins have methanolic our results almost the same spectrum and the same areas of growth inhibition (have almost similar antimicrobial activity against the strains respectful), improves twice the antibacterial activity of the extract the essential oils obtained by steam distillation of water.

The largest zones of growth inhibition were obtained with *Staphylococcus aureus*, responsible for most cases of skin infections is the most sensitive strain. The yeast *Candida albicans* is the most resistant vis-à-vis all the extracts.

The antimicrobial activity of tannins analyzed can be attributed mainly to its main constituent gallic acid which was identified by chromatography, according to Chung et al., (1998) the inhibitory effect of tannic acid on the growth of intestinal bacteria such as *Escherichia coli* can be caused by the binding capacity of iron from the middle and make it unavailable to microorganisms need iron for a variety of functions, including reduction of ribonucleotide precursor of the DNA, the formation of heme, and other basic needs.

In addition, our results show that the antibacterial activities are related to the nature of the solvent and the test strain. Indeed, the extract obtained with methanol is the most active, followed by the extracts with butanol. The latter could be explained by the fact that the methanol (the most polar solvent) is able to extract the maximum ingredients.

This anti-microbial action can be explained by the fact that the plant produces various secondary metabolites belonging to certain classes known to have this type of activity.

The susceptibility testing different extracts of *Rosa canina* L, we revealed the presence of antibacterial activity of different extracts. This result at least partly explains the effectiveness of the plant in traditional medicine for the treatment of various diseases.

#### 4. Conclusion

Our results agree with those of the Team Panizzi et al. (2002), which demonstrated that the antimicrobial activity of polyphenols extracted from *Rubus ulmifolius* seven microbial strains (*Staphylococcus aureus*, *Escherichia coli*, *Bacillus cereus*, *Pseudomonas aeruginosa*, *Aspergillus Niger*, *Saccharomyces cerevisiae*, *Candida albicans*). The results obtained showed that the flavonoids, are also effective against Gram-positive than Gram -, and tannins showed activity in almost all strains.

All data obtained, it appears that the species studied (*Rosa canina* L) appears to be a plant rich in secondary metabolites, not widely used in traditional medicine in areas of Algeria to combat and cure various ailments. Exploitation of its pharmacological properties implies further investigation of its active ingredients. It should be accompanied by development of vegetative propagation of this species.

So we can confirm that the antibacterial and antifungal activities of extracts of the strains studied offers opportunities to substitute at least partially so, the conventional antibiotics by their use. All the results obtained in vitro are only a first step in the search for substances naturally occurring biologically active. Additional tests are required and must be able to confirm the performance highlighted.

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# THE POTENTIAL FOR CLIMATE CHANGE MITIGATION IN SOLID WASTE DISPOSAL: A CASE STUDY OF LAGOS LANDFILLS

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## ABSTRACT

Solid waste disposal sites account for up to 20% of global emissions of methane the second most significant greenhouse gas. However, under proper management landfills can in fact have a positive carbon balance, by capturing the methane-rich landfill gas (LFG) produced from the dumpsites. This paper assesses the potential for implementing such a project in the Olusosun waste disposal site in Lagos, Nigeria. Data regarding municipal solid wastes (MSW) generation and composition, regulations as well as relevant aspects of the Nigerian energy market and its regulations and climate change policies were evaluated. This is employed to assess the potential for a viable implementation of a landfill gas to energy project at the site. The analyses revealed that the flaring only scenario was observed to be the most economically feasible. The cost of producing electricity from LFG (approx. US\$50/MWh) is higher than the estimated long term cost from natural-gas fed thermal plants (at US\$39/MWh).

## 1. INTRODUCTION

Mounting scientific evidence linking climate change to anthropogenic greenhouse gas (GHG) emissions has given more urgency to the calls for adopting less carbon intensive economic growth (Watson, 2001). Increasing attention is being directed at developing countries where much of such future growth is expected. While it is recognized that economic growth is necessary for poverty reduction and sustainable development in these regions, global opinion leader and policy makers from both developing and developed countries agree that it would be undesirable for such growth to be sustained at current levels of carbon intensity.

There is therefore, general consensus on the need to integrate climate concerns into sustainable development objectives in all sectors of the economy; energy, transport, agriculture and waste management. Municipal solid wastes (MSW) contribute significantly to global GHG emission and are a major challenge to public health especially in lower income countries. Where proper management of solid waste disposal sites (SWDS) can be taken for granted in many developed countries, it still is a major problem for their less developed counterparts as many of these countries lack the funding and in most cases the technology to improve their disposal systems.

Emission trading schemes like the Kyoto protocol's Clean Development Mechanism (CDM) serves as a platform for overcoming such financial and technological barriers. Under the mechanism, investors or governments in developed countries can invest in projects in poorer countries, transferring environmentally sustainable technology to help these countries reduce their GHG emissions and contributing to their sustainable development. In the process these investors are allowed to offset the certified emission reductions (CER) generated from such projects against their own emission reduction targets as set by their various countries. Many developing countries are taking advantage of this opportunity already. By 2004, India, Brazil and China, already had 42 such projects between them at different stages of implementation (Ellis, Corfee-Morlot and Winkler, 2004). This paper investigates the potential of implementing a viable landfill gas to energy project (LFGTE) in Lagos, Nigeria under the CDM mechanism. To do this, the technical potential of the project (climate, waste generation quantities, etc) as well as the relevant regulatory and socio-economic environment will be analyzed.

## 2. METHODOLOGY

### 1.1 Conceptual Approach

This study straddles three policy sectors, MSW, energy and climate and has clear and established benefits to sustainable development objectives in these sectors. Assessing the potential performance of an intervention such as proposed in this study requires the identification of the components and relations that could be potentially affected by that intervention (Villavicencio, 2003). In this case, introducing a technology like LFG capture will be influenced by the existing regulations and practices in the MSW, energy and climate sectors as well as physical and socio economic characteristics of the immediate environment and their dynamic interactions (Figure 1).

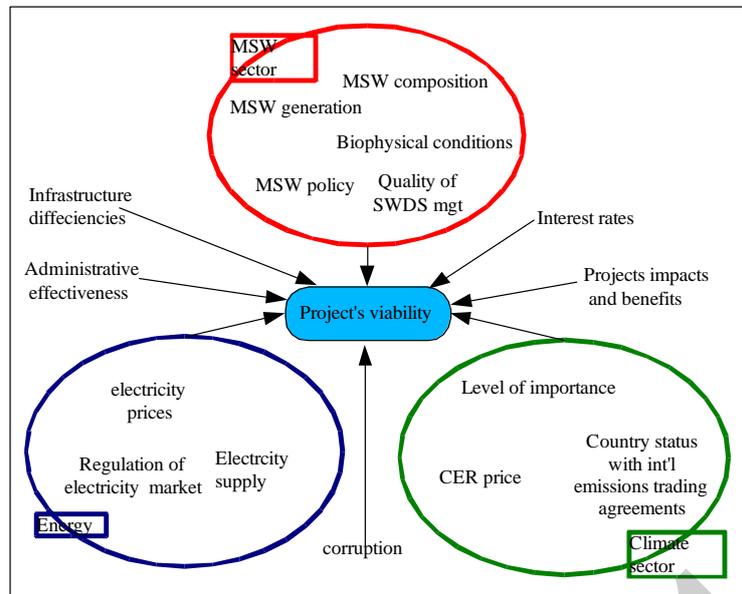


Figure 1: Conceptual map of system structure to be studied

The systems dynamics approach was used for much of the analysis done in this study. It is a method that aims to enhance the understanding of complex dynamic systems (Sterman, 2000) - dynamic, in the sense that the system variables evolve over time as the result of previous interactions (Ruth & Hannon, 1997). These variables and their interactions make up the structure of the system and determine the systems behavior. If those variables and relations can be identified, the system’s behavior can then be simulated with reasonable levels of confidence (Bossel, 1994). Various permutations and combinations of the variables can also be simulated and the likely outcomes evaluated. System dynamics is here applied in analyzing the sectors shown in the conceptual map. Components within each sector interact dynamically with each other and with components in other sectors and influence the key outcome of interest i.e. the projects potential viability.

2.2 LFG Estimation Models

Many methods and models have been developed for projecting LFG generation potential from SWDS. The IPCC recommends two of these methods for LFG generation estimation for the purpose of establishing national GHG inventories – default and first order decay methodologies (World Bank, 2004). The first order decay method is the more accurate of the two and was employed in this work.

3. STATUS OF MSW MANAGEMENT AND CLIMATE CHANGE POLICY IN NIGERIA

1.2 MSW Management in Lagos, Nigeria

According to Bamgbose , Arowolo, Oresanya and Yusuf (2000), 70% of total waste generated in Lagos was from domestic sources and the rest from industry (Table 1). There are widely divergent views on waste generation in Lagos. A World Bank sponsored study reported a daily generation of about 0.21 kg per capita (Bamgbose *et al.*, 2000). This figure is very likely an underestimation because it was based on records of waste received at the various disposal sites across the city. In reality about 30% of waste generated never gets to disposal sites (Agunwamba, 1998). Another study reports daily per capita waste generation rates as 0.35kg (Cynet Services Limited, 2002).

Table 1: Waste composition in Lagos obtained from different studies

Waste Composition (%)	(Bamgbose et al., 2000)	Rushbrook, Pugh, & Mundial (1999)	Cynet Services Limited, (2002)
Paper	10		10
Textiles	4	14	2
Plastic	7		22
Non food putrescibles e.g. garden waste			
Wood or straw		60	45
Food waste	68		5
Others	11	19	14

1.3 Olusosun SWDS

LAWMA currently operates 3 dumpsites; Olusosun, Solus and Abule-Egba. The focus of this work is the Olusosun SWDS which is the largest in Lagos. It is the only one fit to host an LFGTE project because it has a remaining life span left of more

than 10 years, it receives a large amount of waste and, has the right depth. It was constructed under a World Bank loan secured in 1988 to use the trench system. It is at 60m above sea level and lies on a high density clay deposit under which there are two water aquifers (Bamgbose *et al.*, 2000). The average daily tonnage received in Olusosun between March and June 2004 is given in the Table 2.

**Table 2: Average daily tonnage of refuse received at Olusosun site between March and June 2004 (Source: LAWMA)**

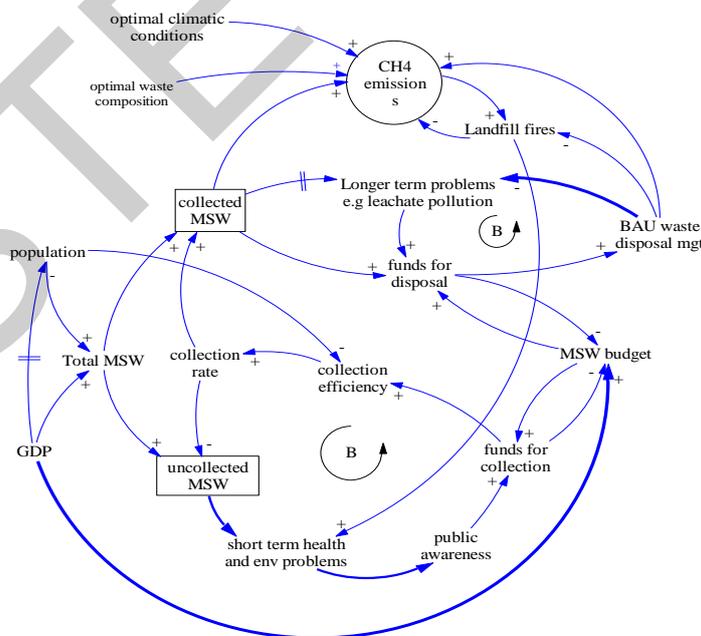
Type of waste		Mon.	Tues	Wed.	Thurs	Fri	Sat	Sun	Weekly Averages
Domestic Waste	LAWMA	730	850	890	820	815	1130	610	835
	Local Government Sanitation Agencies	150	135	150	210	100	2665	60	
	Private Collectors	1340	1325	1215	1360	1220	1610	1140	
Commercial waste (from markets, non-hazardous waste from institutions etc)	LAWMA	220	190	210	170	180	130	180	835
<b>Total domestic and commercial waste</b>		2440	2500	2465	2560	2315	5535	1990	2829.29
Industrial waste and metal scraps	LAWMA, NAFDAC and SON	230	250	270	225	220	250	270	245.0

**4. RESULTS AND DISCUSSIONS**

The focus of the analysis is the assessment of the viability of a LFGTE plant in Olusosun SWDS in Lagos. This is done in two stages. First an analysis of the technical viability as determined by the availability of the methane resource is conducted, followed by a socio economic analysis of the project's survivability. Relevant factors and their interactions in each of these stages are first depicted in Causal Loop Diagrams (CLD), then the results of the STELLA analysis for that stage is presented along with the assumptions under which they were made. The model takes a modular design. The full structure and description of model can be obtained from Aboyade (2004).

**1.4 Assessment of Resource Potential**

The major factors affecting LFG and hence CH<sub>4</sub> emissions from MSW are mainly the amount of waste generated, the composition of the waste, the conditions under which the waste is disposed, and the climate of the region under study. All the factors, save the last, are dependent one way or the other on the socio-economic characteristics of the region. The CLD in Figure 2 captures the interactions that affect CH<sub>4</sub> emissions from MSW in Lagos.



**Figure 2: CLD showing factors affecting CH<sub>4</sub> emission from MSW disposal sites**

The generated waste is either collected or littered as shown in the CLD. The amount of waste collected depends basically on the collection efficiency of LAWMA as dictated by its own administrative effectiveness, which in the past years has been poor.

Where littered waste gets to the point where it becomes aesthetically unpleasant, and presents directly perceptible dangers to public health, public awareness influences government to increase the flow of funds for collection services. Such increase is of course limited by the municipality's budget which in itself is a direct function of the economic prosperity of the state. The poor economic status coupled with the low quality management enjoyed in public services ensures that such increased effort at collection services is hardly sustained. Usually however the limited successes of such efforts at least in reducing the amount of littered waste soon causes public pressure to relax. Also the ever increasing quantities of waste coupled with lack of sustained political will and increasing administrative inefficiencies ensures that the collection rates soon drops and uncleared waste again begins to mount. Interestingly, according to officials in LAWMA, this cycle (represented by the balancing loop in the CLD) very often coincides with the election or appointment of new leaders in the state. This is because in a bid to impress its constituents, the new administration (usually military controlled) pumps money towards reducing the amount of littered waste, only to relax after a while for the same reasons aforementioned.

#### 1.4.1 Methane emissions from Olusosun SWDS

The results of the emission modeling for methane are as shown in the Figure 3 under the following assumptions:

- $L_0$  – Methane generation potential (estimated using the formula,  $MFC \times DOC \times DOC_F \times 16/12$  to be equal to  $150\text{m}^3/\text{mg}$ ). A conservative estimate when compared with  $190\text{m}^3/\text{Mg}$  for Brazil which has a similar waste composition (Mailly, 2004).
- K- methane generation constant for lack of data is assumed to be the default suggested by IPCC - 0.05

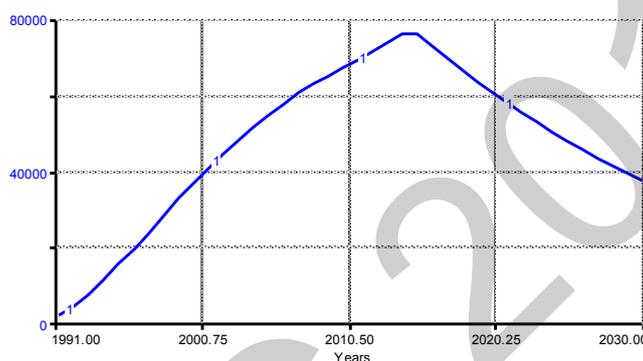


Figure 3: Methane emissions from Olusosun SWDS

The graph shows methane emission from Olusosun reaching its peak of about 76,000 tonnes of methane in 2014 thereabouts with an average annual emission of 63,000 tonnes during the project's lifetime. It also shows that Olusosun will still be generating emissions well beyond 2030. A sensitivity analysis varying  $k$  and  $L_0$  by  $\pm 15\%$  shows that this varies from a low of 47,000 tonnes to a high of 78,000 tonnes  $\text{CH}_4$ .

### 1.5 Assessment of Economic Viability

The economic viability of the proposed project is governed by policies in three different sectors; the MSW, energy and climate or emissions trading sectors. MSW policy and practices especially regarding, MSW collection efficiencies, choice of disposal method and so on are crucial to the waste stream which in turn forms the resource for LFG and electricity production. Energy policies relevant to the electricity prices and the level of regulation of electricity sales will to a large extent will ascertain how much income is to be expected from electricity generated from the site. Furthermore, the existence or not of a climate policy is important to determine if CER's can be sold. Economic viability as measured by net present value (NPV) and internal rate of return (IRR) is a direct consequence of the costs associated with the project and revenues accruing to it; all other factors that affect the projects viability e.g electricity price, CER price and interest rates could be said to feed in through these two components.

#### 1.5.1 Assumptions

Cost estimates for this analysis both capital and operational were obtained from representative estimates given in the US EPA's landfill gas-to-energy project development handbook (EPA, 1996). Apart from these, other important cost items are the transaction costs associated with CER sales; monitoring costs, verification and validation costs as well as registration and approval costs. Taking into account the value of emission reductions possible from this project (25 million  $\text{tCO}_2\text{e}$  over a 20 year crediting period) this project would qualify as a very large CDM project (UNFCCC, 2004) and according to Krey & Welt-Wirtschafts-Archiv (2004), the transaction costs associated with registering and validating emissions from the project under the CDM would be about US\$0.123/ $\text{tCO}_2\text{e}$ .

The revenue stream derives mainly from electricity and CER sales. In general it is assumed that the electricity generated from the project would be sold to the municipality for street lighting. Electricity prices in the analysis will be varied according to current obtainable rates. CER prices have typically been within the 3 to 6US\$/ $\text{tCO}_2\text{e}$  range (Haite & Seres, 2004). Project lifetime of 20 years as consistent with projects of this nature (US EPA, 1999), and tax rate on all profits of 30% which is the

prevalent corporate tax rate in Nigeria (NIPC, 2004). The analysis includes capital costs in the year they are incurred and as such it was not necessary to include depreciation (Barish, 1962).

Cash flow analysis of the viability of the project was done under three scenarios: a) Funding from local sources at current discount rates. b) Funding from foreign sources such as the World Banks Carbon Fund. c) Flaring only option (no electricity generated). The major distinguishing factor between the first two scenarios is the cost of capital for the project as determined by interest and discount rates. According to Barish (1962), high interest rates is one major impediment to project finance in developing countries.

### 1.5.2 Scenario 1: Local funding

Consultations with officials from the state ministry of environment revealed that the government is investigating the possibilities of handing over operation of the landfills to private interests. This scenario simulates the project viability assuming the new private owner decides to borrow from local banks to implement the project. Interest rates in local financial institutions are pegged to the Central Bank's minimum discount rate for treasury bills which is set at 18%. In this scenario it is assumed the local investor borrows from local banks at 22.5% interest.

Putting all these parameters in the STELLA model yield the following results for NPV of the project after 21 years:

**Table 3: NPV (in US\$) under different CER and electricity price ranges**

		Electricity prices US\$/MWh		
		21	50	65
CER price (US\$)	0.00	-1,595,909.44	-874,063.87	-498,834.31
	3.00	-1,004,164.81	-279,299.14	95,631.38
	6.00	-384,284.00	340,581.67	715,512.19

Results show that the project cannot be viable under the price regimes given in the table, without additional revenue from CER's. The prices selected in the Table 6 are based on different assumptions under which electricity price for the project could be negotiated. US\$21 is the lowest price for which the national utility (Power Holding Company of Nigeria – PHCN) sells to its customers, US\$50 is the highest PHCN buys from IPP and US\$65 is the price municipalities pay for electricity for street lighting (all per MWh). Personal communication with PHCN officials revealed it is unlikely for PHCN to buy at higher price than US\$50/MWh given its recent attempts at commercialization. Even assuming that price could be negotiated, the project still isn't viable when CER's are sold for US\$3 as the project still returns a negative NPV. Also the IRR in this case is 13.5% which is clearly below local interest rates. The table shows the project can only be viable (i.e. returns positive NPV) at CER price of up to US\$6. Then IRR is at 23%, still too close to the interest rates.

### 1.5.3 Scenario 2 foreign funding

In the general, the cost of funds from foreign sources are cheaper than that from local sources especially in Nigeria where interest rates are generally on the high side. This is especially true when the sources of the funds are public or non profit institutions, or specialized funds like the World Bank's Carbon Fund. In this scenario a simplified assumption that the project is funded at 8% interest rates yield the following

**Table 4: NPV (in US\$) under different CER and electricity price ranges with 8% interest rates**

		Electricity prices US\$/MWh		
		21	50	65
CER price (US\$)	0.00	-9,019,252.88	-3,366,784.37	-443,093.76
	3.00	-4,217,324.06	1,435,144.45	4,358,835.06
	6.00	736,240.20	6,442,369.50	9,366,060.11

Even here it is still obvious that the project cannot break even without additional revenue from CER's during the stipulated project life. However with IRR raging between 12 to 13%, i.e about 5% higher than the cost of funds, represented here by the interest rates, one can argue that the project stand a much better chance of been profitable under this scenario.

### 1.5.4 Scenario 3 Flaring Only

Further analysis of the first two scenarios point to the fact that CERs makes up between 35% to 53% of revenues depending on whether it is sold for US\$3 or US\$6. The fact that CER revenues account for so much of the total is combined with the fact that the energy generation part of the costs actually accounts for 67% of the projects capital costs and 90% of the operation and maintenance costs suggests higher rates of return if the project is run without electricity generation. Under this scenario therefore, the project's capital costs is reduced to US\$6,354,000 and maintenance costs to US\$299,000. This then yields an IRR of about 27% when CERs are sold for US\$3 per tCO<sub>2</sub>e. This implies the project has much higher returns even when the

source of funding is local. This result in essence shows that the most commonly touted direct benefit of LFG capture – energy generation – holds little prospect as a driving force for such an intervention in Nigeria.

## 5. CONCLUSIONS

The result of this study has shown that the cost of the local private funding is too high to allow the reasonable rate of return for a LFGTE project. Funding from foreign sources at lower lending rates increases the chances of the project being viable, but even that would be by only a slight margin. The flaring only option, without electricity generation on the other hand is the best scenario, as the bulk of the projects revenues are from CER sales. This is just as well, considering that electricity generated from the project will not be able to compete with conventional sources because the costs at which electricity from LFG is produced (approx. US\$50/MWh) is slightly higher than the marginal cost for which electricity from natural gas will be produced in the long term (US\$39/MWh). This conclusion is not very different from that arising from similar studies in countries where electricity prices are low.

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## THE POTENTIAL POWER OF NUMEROLOGY TO HELP IN MATHEMATICS STUDIES

Donna Kakonge

Birth data:

The Potential Power Of Numerology To Help In Mathematics Studies  
December 2, 1972

### Abstract

The Potential Power Of Numerology To Help In Mathematics Studies has the ability of turning the best lawyers and real estate agents into expert mathematicians. It has the potential of helping young students who are gifted with music, and who may struggle with math to be able to achieve mastery with the important life and learning skills of understanding and excelling at math. Math should not be seen as a routine, rudimentary and boring subject, however should be afforded the same creative expression credibility that the arts receive when a student draws a painting, or produces a documentary. Ultimately, the education systems around the world should be producing balanced students who are well-rounded – and mathematics and learning it through numerology is one of the skills that can help to achieve these goals.

**Keywords:** Donna Kakonge, Numerology and Mathematics, Education and Math and Numerology, OISE/University of Toronto, Creative Expression of Math

### INTRODUCTION

Numerology is an ancient science that is based on the power of numbers. The idea behind it is that each number has a significance to it. One is new beginnings, two is a couple, a duo, or also indicates diplomacy, three is creative and self-expressive, four knows right from wrong and is a foundational number, such as the four legs of a table. Five is a number of resourcefulness, travel and change. Six is the number of love, and people who are lawyers, real estate agents and also teachers tend to be associated with this number. Seven is the number of spiritual pursuits, resurrection and perfection. Eight is a number of balance, and eternal life according to The Bible. Nine is a number of completion, as well as the end of good things with the start of ten being broken down to a one for new beginnings. Thus, through this connected understanding of the significance of numbers – this science being taught to children can help them better understand that when you connect one – new beginnings with two – couples – you get three – self-expression as well as happiness. The latter example could also be compared to the base unit of a traditional family.

For a brief overview of how numerology works, there is a life path number, a major expression number, as well as a heart's desire number. These three main numbers are what guides you throughout your life, based on the science of numerology. The following will discuss

the theory behind how this relates to the potential power of numerology to help in mathematics instruction.

### LIFE PATH

The time of a student's birth is a transformative time. The most important number according to the science of numerology that would help all students succeed in mathematics instruction, would be an analysis of their birthdate – which would create the number of their life path – again, the most important number (Decoz, 2003).

With an electronic numerology report with the help of Hans Decoz, who is a foremost numerologist, when the name of this conference: International Science And Technology Conference 2011 [ISTEC], Turkey, is analyzed, the following is interpreted for the life path:

You have ultimate freedom to do with your life as you like: To fulfill its potential completely, or to make some smaller version of yourself. It all depends upon your effort and commitment. You make the decisions to fulfill, to whatever extent, the potential life that exists within you. That is your choice. In this sense, the possible you is implicit during the moment of your birth (Decoz, 2003, pg. 4).

This number was calculated on the day of this particular conference: December 2, 2011. The life path number turned out to be a six. This is an excellent number for anything related to teaching, education, real estate, law, etc. Here is how Hans Decoz's computerized analysis reads:

International Science And Technology Conference 2011, Turkey [ISTEC], you possess great compassion and seek to be of service to others. You have concern for the weak and the downtrodden. You are a healer and a helper to others. You are capable of giving comfort to those in need and will frequently offer a shoulder for others to cry on.

Your task in life is to develop the tools necessary to be truly helpful to others, rather than to simply be a sympathetic ear. You must find the balance between help and interference. In the same way, you must learn the delicate art of the counselor who knows when to leave the struggle to others and when to avoid taking away the necessary experiences and lessons of life.

You are naturally balanced. Therefore, you are well equipped to support and ground others in times of trial.

It is in your nature to take on responsibility – you often fill the void left by others – and do not turn away from personal sacrifice. At times, you may feel overburdened by the travails of others. However, the love others bestow upon you is your well-deserved reward (Decoz, 2003, pg. 4).

So, according to this analysis, the life path of this conference is a good one. If we take an example of a child who was born on August 12, 1972, their life path number would be a three. This would mean that the child would have a natural tendency to the arts, rather than towards mathematics, however since the child also has links and ties with compatible numbers, such as six and nine – the child could do very well with mathematical equations, or even teachers/professors of mathematics that also have similar and compatible life path numbers.

Let us get down to understanding how this can also be implemented in the classroom. When a student is given an equation, such as this:

$$203 + 90 = [\text{answer}]$$

Understanding numerology as explained in the introduction can help. Nine is an ultimate number and everything nine is added to – becomes that number. Everything that is multiplied by nine, equals nine. Let us take a few examples, as well as answer the question above using numerology:

203 = breaks down in numerology to a five

90 = breaks down in numerology to a nine

Definitely, a student of any age can know that the answer to this question is going to be five when broken down to the numerological scientific number.

The answer of  $203 + 90 = 293$ . Indeed, If you add the  $2 + 9 + 3 =$  in numerology = it equals five. This can help a student, using numerology to understand how to get to answers quickly on mathematical examinations.

### CONCLUSION

Numerology is an ancient science that can be used for powerful and fun instruction in mathematics. Basic mathematics instruction can be achieved and taught extremely effectively by keeping in mind three basic rules of how numerology and mathematics connect:

1. Knowing the life path number of a student can help to better instruct that student.
2. Teaching the basics of numerology to students in schools all over the world will not only help them with math, it can also help with every educational discipline there is.
3. Breaking down mathematical equations to basic understandings of numerology, using a one through nine calculation scale – can help you solve any mathematical equation.

About the Author: Donna Kakonge is a PhD student/teacher/writer living in Toronto, Canada. Her official website is: [www.donnakakonge.com](http://www.donnakakonge.com). Although she is a writer, she does her own taxes and was in enriched math in high school. She did not take mathematics beyond high school, although at one time she had aspirations of being a medical doctor. Meeting teachers who were not compatible life path numbers with her own, deterred her from entering the field of medicine. However, meeting many, many professors and teachers who had a very compatible life path number to hers in the area of journalism, communication and writing – led to her present day pursuits – as well as many colleagues and friends.

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# THE ROLE OF DESALINATED WATER IN INTEGRATED WATER RESOURCE MANAGEMENT IN ABU DHABI EMIRATE-UAE

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## ABSTRACT

Water resources components in Abu Dhabi encompass the conventional sources (rain, springs, ponds and groundwater), and unconventional sources (desalinated water and reclaimed wastewater). The latter represent the most important resources for the time being, since ground water is brackish or salty and the annual rainfall is very low in Abu Dhabi Emirate. Thus conventional water resources are considered under severe depletion and exceeded their natural recharging capacity by 24 times. Per capita water consumption is considerably high, since the average daily domestic consumption in Abu Dhabi Emirate is estimated as 350 liters per person but it is intended to be slashed by 200 liters per day in the next few years, as proposed by the Environmental Authority. This should be accompanied by intensive awareness program. This article is aiming at discussing water resources components in Abu Dhabi and their Integrated Water Resources Management (IWRM) Plan.

## INTRODUCTION

United Arab Emirates (UAE) is the world's second largest consumer of water per capita after the United States and the first country in the world in the Ecological Footprints (WWF, 2008). The demand on water is increasing year-on-year due to rapid population growth, growth in hotel industry and rapid expansion of orchards and green areas in addition to the weak awareness of water scarcity and the weak water saving attitudes. All together, had led water issue in UAE to reach an alarming level, particularly because water scarcity issue could only be resolved through establishment of desalination industry which has many advantages and disadvantages (EAD 2009, Abdul-Wahab 2005) (Agashichev and Al-Nasher 2005).

According to the Environmental Agency of Abu Dhabi, water policy in the Emirate has principally emphasized on increasing water supply rather than improved demand management (EAD 2006a). This tendency has a great risk on both groundwater availability and seawater quality. Particularly, if we recall that the former is expected to be completely depleted in next 50 years (EAD 2006a) and the latter is already subjected to the threat of salinization.

It is estimated that the average daily domestic consumption in Abu Dhabi Emirate is ranging between 350-550 liters per person (EAD 2006) which is considered as considerably high rate as compared to 425 liters in the U.S. Flat residents consume on average from 170 to 200 liters of water per day, which may be considered as a reasonable range, but villa dwellers' water consumption is 270 to 1,760 liters per person per day (Teodrova 2009). On average, each Abu Dhabi resident uses 550 liters of water per day. However the Environmental Authority is planning to slash the rate of consumption by 200 liters per person per day in the next few years. On the other hand, water for agricultural uses is mostly ensured through groundwater (Dawoud 2007), whereas the rest of water demand particularly as drinking and household is fulfilled through desalination of seawater from the Arabian Gulf using multistage flash process (MSF) with a total capacity of 683 million gallon per day (MGD) (ADWEC 2011). Most of these plants are planning to expand their production capacities, exposing in this way the fragile ecosystem of the Arabian gulf to a greater risk due to discharge of warm brine water (Elshorbagy 2007).

This article is aiming at discussing water resources components in Abu Dhabi and their Integrated Water Resources Management (IWRM) Plan.

## The Study Area

Abu Dhabi Emirate is the largest of seven United Arab Emirates (UAE). It lays on the southwestern coastline of the Arabian Gulf (Fig. 1) with a coastline extending about 350 km. Total population of UAE is estimated to be 8 million

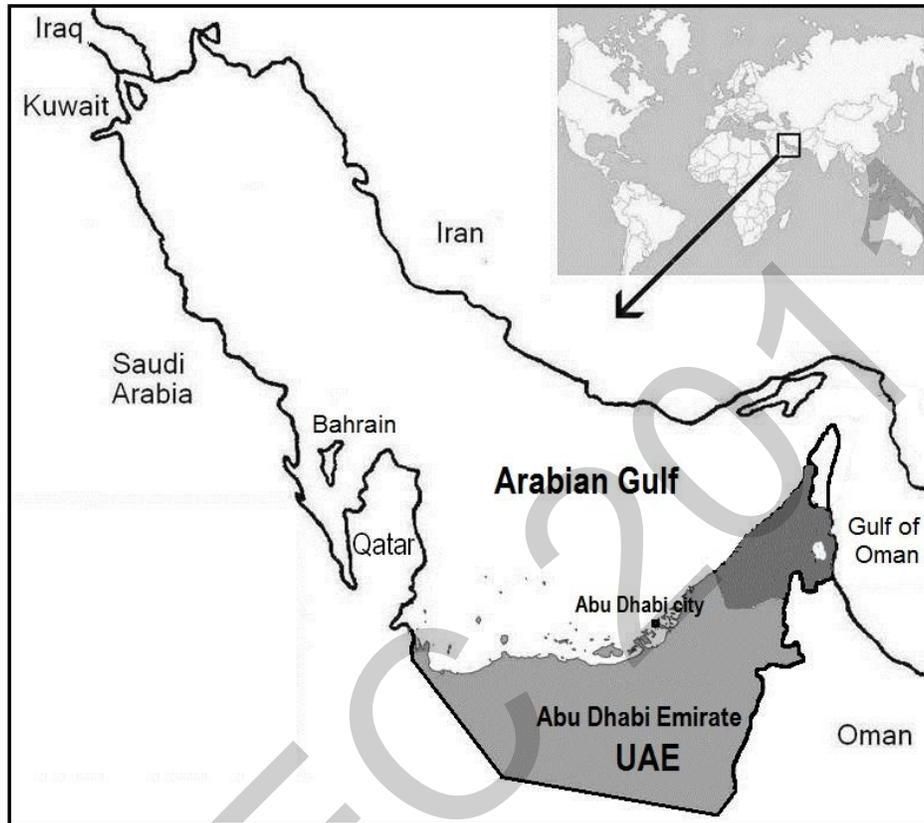


Figure 1 Location of Abu Dhabi Emirate (marked in light grey) with respect to UAE in Arabian Gulf.

in 2011, only 12% are nationals and the rest are expatriates, while Abu Dhabi population is estimated to be 1,305,060 with approximately the same percentage of nationals to expats. Population in Abu Dhabi is steadily increasing at an annual rate of 3.7% (EAD 2006b). Being part of a desert land in the Arabian Peninsula; climate is arid with prolonged hot summer and relatively short winter. The lowest atmospheric temperature was reported as 10.6 °C whereas the maximum temperature was reported as 47.4 °C (EAD 2006a). Relative humidity is considerably high and may reach more than 90% very often.

The majority of water demand is secured through the use of groundwater (brackish 38%), which is mainly used in agriculture, followed by desalinated water (23%), then freshwater (13%). The former type is used for drinking or household and amenity (Fig. 2). Reclaimed water represents only 6% of the total and is only used in landscaping and forestry.

These water resources are generally categorized into two major groups of resources: conventional and unconventional water resources as follow:

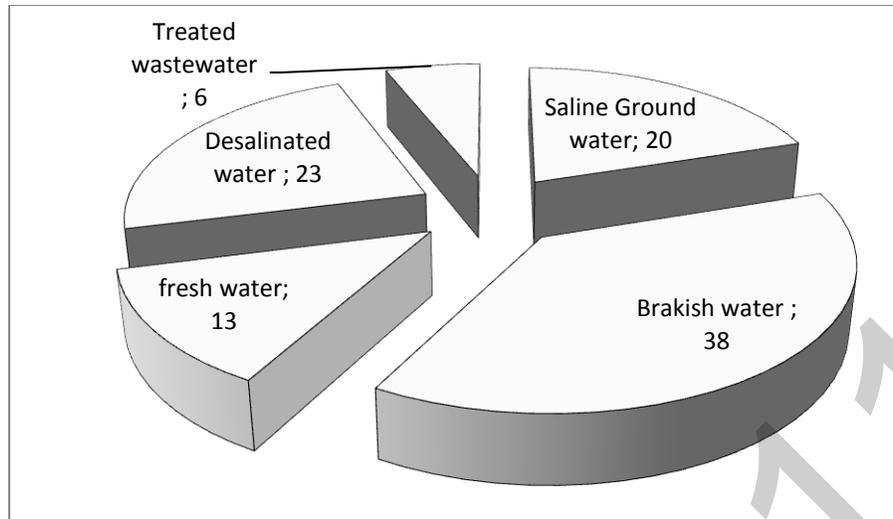


Figure 2 Sources of water in Abu Dhabi Emirate.

### 1. Conventional Water Resources

These are rainfall, springs and groundwater resources:

**Rainfall:** The reported Annual Rainfall is considerably low, reaching 20.4 mm in Abu Dhabi City and 33.8 mm in Al Ain city (EAD 2006). Most of rainy days occur during February, however in a cycle of 4-5 years, rainfall may raise the rate above these average values. On the contrary, annual evaporation rate is relatively high reaching about 2,000 mm (EAD 2009). In general rain water stock is estimated to be 24 million cubic meter (Mcm) per year according to 2007 estimates. (EAD 2009)

Ground water falls into three different categories of salinity whose available stocks according to 2007 estimates are as follow: freshwater 26,000 Mcm, moderately brackish 89,000 Mcm and brackish 132,000 Mcm (EAD 2009).

Ground water contributes to 71.2% of total water demand, yet it is being over-exploited at a rapid rate. Groundwater supply had fallen by 18 % since 2003, while the consumption of water resources in the emirate exceeded their natural recharging capacity by 24 times. (Teodorova, 2009). Therefore it is envisaged that this resource can barely last for the next 50 years. Abu Dhabi's groundwater reserves stand at 641 Mcm. However, more than 97% is brackish, its reserves of sweet or moderately brackish water that can be easily tapped can last only 20 to 40 years, the study says. It is estimated that about 630 well fields exist in Abu Dhabi however the operating wells are only 363. Springs are confined to Al-Ain area. Water in both wells and springs is brackish, moreover water of springs is hot and run at a constant temperature of 39.3° C. It is worthy to mention that groundwater is not used for drinking due to the presence of relatively high levels of boron and nitrate.

### 2. Unconventional Water Resources

Seawater desalination represent the only source of potable water in Abu Dhabi Emirate, it is produced by five Giant power and desalination plants whose locations and capacities are shown on the map (Fig. 3). ADWEA oversees four of the power and desalination plants are located in Abu Dhabi Emirate and uses multistage flash (MSF) and multi-effect systems (MED), whereas the fifth is in Fujairah Emirate and uses hybrid MSF and reverse osmosis (RO). The total annual water production has escalated from 66,772.58 million gallon (MG) in 1998 to 183,560.79 MG in 2010 in addition to 28,232.49 MG imported from Fujairah power and desalination plant (ADWEC 2011). As peak daily water supply, capacity was increased from 220MGD in 1999 to reach 673 MGD in 2010 (Fig. 4) (ADWEC 2011).

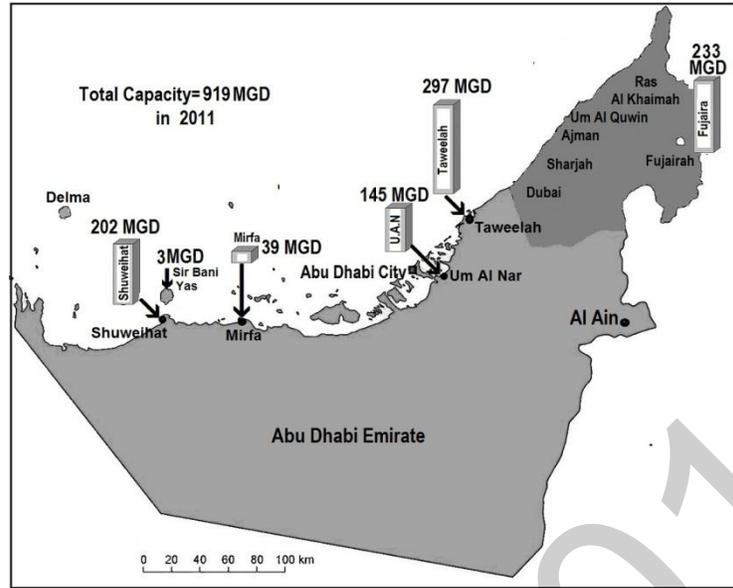


Figure 3 Map of Abu Dhabi Emirate-UAE showing locations and capacities of desalination plants.

Desalination plants are in process to expand their capacities so that the daily production rate is to be doubled in 2030 to cope with the increasing demand. Nevertheless, environmentally, this expansion shall adversely affect marine environment in the Arabian Gulf by the discharge of hot brine water, which is already under great environmental stress.

A smaller desalination plant is located in Delma island has a total capacity of 3 MGD, among which one MGD is produced by MED and the rest is produced by reverse osmosis in addition to similar or smaller RO units owned by different entities or communities among them is the one in Sir Bani Yas which has only 2 MSF units of 0.28 MGD amounting to a total capacity of 0.56 MGD.

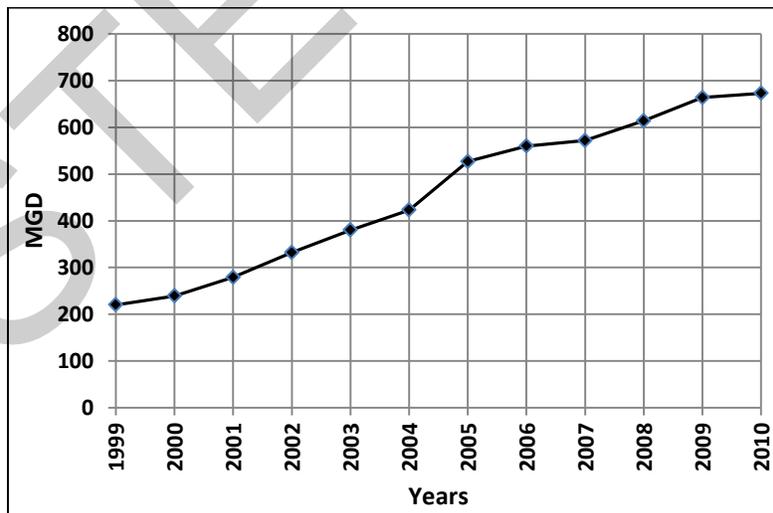


Figure 4 Increase in daily desalinated water production capacity during 1999-2010

Majority proportion of desalinated water (43%) is consumed mostly as potable and household water. The second major use is for livestock 21%. Amenity water (public facilities) is mostly used for landscaping and roadside plantations

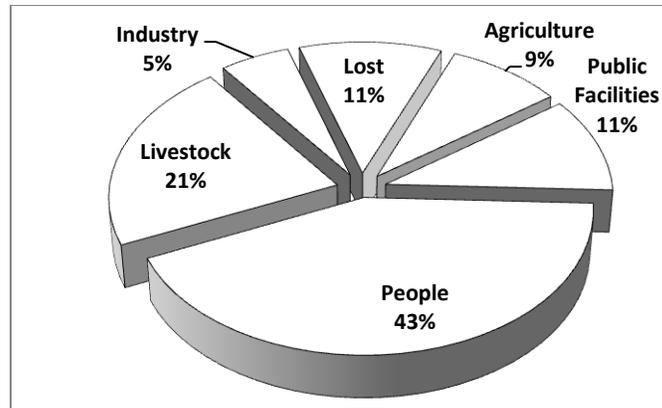


Figure 5 Major uses of desalinated water in Abu Dhabi Emirate

which account 11%, other uses are demonstrated in Fig. 5. Loses in about 11% of water is attributed to breakage of pipes, and physical leakage.

The second unconventional water resource in Abu Dhabi is the reclaimed wastewater. There are two main sewage treatment plants in Abu Dhabi City and Al Ain city, both treat almost 95% of sewage and work slightly over their design capacity (EAD 2009). In the year 2003, population of Abu Dhabi Emirate was 1.3 million; a total of 140.8 Mm<sup>3</sup> of treated wastewater was reclaimed, representing 4% of the total water consumed that year (EAD 2006b) (ADSSC 2007). However, in 2005 a new sewage treatment plant was commissioned rising the total sewage effluents (TSE) to a level of about 139 Mm<sup>3</sup>/year, (Fig. 6) and about 182 Mm<sup>3</sup> in 2007 (EAD 2009). Abu Dhabi collects 146 Mm<sup>3</sup>/year whereas Al Ain collects 36 Mm<sup>3</sup>/year. The rest of 5% is treated by smaller units to serve smaller communities. TSE per person per day is estimated to be 130 based on the served population of 1.4 Million. Currently 35% of TSE (i.e. 51 Mm<sup>3</sup>) is disposed of into the Gulf, the rest is used for landscaping.

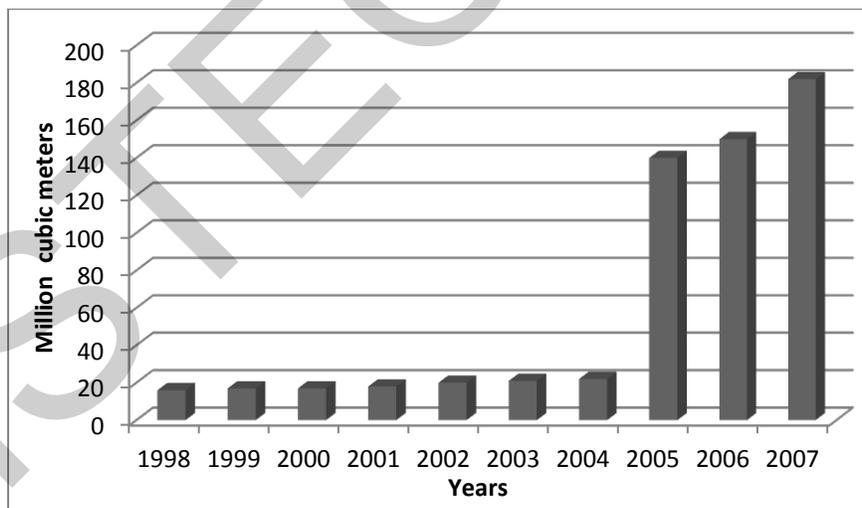


Figure 6 Quantities of reclaimed water from sewage in Abu Dhabi Emirate.

### Water Scarcity Awareness

A couple of years ago, a survey of 2,363 people in the emirate showed that water conservation was the area of least concern. Only 42.8% of respondents were aware that water scarcity should be a concern in the UAE (Teodorova 2009). Taking into consideration that ground water is already under excessive extraction, surface water resources are

scarce. Therefore water conservation should be considered as an essential practice disregarding its abundance or availability. Planners, engineers and policy makers are encouraged to shift toward green technologies (low-flow taps and showers as well as low flush" toilets)...etc. Also to promote environmental awareness towards water saving behavior. On the other hand only 10 % say the task is exclusively the responsibility of consumers. (Gornall and Todorova, 2009)

## CONCLUSIONS

Per capita water consumption in Abu Dhabi Emirate is considerably high, with limited resources and continuously increasing population and agricultural practices. All these factors had led desalination plants to increase their production capacities in order to meet the demand. On the other hand desalination has different adverse effect of the fragile marine environment of the Arabian Gulf. Therefore, water conservation should be considered as an essential practice and people should made aware of its importance. Per capita daily water consumption should be slashed by 200 liters per day in the next few years to come.

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# THE SHELL CHARACTERISTICS OF LAND SNAIL *EOBANIA VERMICULATA* (MÜLLER, 1774) FROM CROATIA

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## ABSTRACT

The land snail genus *Eobania* P. Hesse, 1913 in Croatia consists of four taxons. The mean shell largest diameters (D) of the 13 samples ranged from 19,99 mm to 31,78 mm and the mean shell height (H) from 17,31 mm to 25,66 mm. The shell morphology confirms that all islands populations are smaller with examples of nanism on outside islands Palagruža and Sušac. Molecular analysis (16S rDNA and COI sequence data) showed no significant differences between the South – Adriatic population from the mainland and islands, thus providing no molecular–genetic evidences for classification of a single *E. vermiculata* species into separate subspecies. The observed differences could, probably, be attributed to ecological influences. The mean size of the largest population was approximately 1,5x larger than the mean size of the smallest population. The low variance between the size variation within populations and variation in shell shape were not expected.

## INTRODUCTION

*Eobania vermiculata* (Müller, 1774) or chocolate banded snail is a wide distributed land snail. The nearest countries to Croatia in which *Eobania vermiculata* is registered are Italy, Bulgaria (Dedov, 1998), Greece (Welter-Schultes & Willians, 1999) and Turkey (Örstan et al., 2005). By a review of the available literature we determined that *E. vermiculata* has been recorded in Croatia only in general terms in Dalmatia (Jaekel et al., 1957), on The Island Dugi otok (Štamol 2004; Štamol & Kletečki, 2005) and as subspecies *Eobania vermiculata pelagosana* (Stossich, 1877) from the Islands of Palagruža and Sušac (Berberović 1963, 1967). Molecular phylogeny and biogeography for the species *E. vermiculata* from Croatia are unknown.

The previous studies on a terrestrial gastropods *Helix aspersa* and *Eobania vermiculata* (Sacchi, 1957; Berberović 1963, 1964, 1967) in Croatia were based only on morphometric characteristics of the shell. The results showed that all shells from the adriatic islands are smaller than the average values for land specimens. Those „nanism“ is especially expressed in populations of the Island of Palagruža and Sušac (open sea islands close to the italian seaside) so Berberović (1964) described new subspecies *Helix aspersa pelagosana* and Stossich (1877) *Eobania vermiculata pelagosana*. The basic survey on *Eobania vermiculata* shell morphometry made Berberović (1963) on land and island populations from the Middle Dalmatia (Croatia). He distinguished three separated groups: 1. group Palagruža and Sušac; 2. group „Biševo“ and 3. group „Lastovo“. The shell characteristics of group Palagruža and Sušac showed the nanism caused by geological origin of those islands, vegetation and abundance. The group Biševo is more similar to those from the Island of Gali (Gulf of Salerno). He also divided all examined populations in morphological groups in relation to populations from Palagruža and Sušac to „continental type“ ( H/D ratio lower than Palagruža and Sušac; middle adriatic islands except island of Vis and lastovo archipelag). Lastovo archipelag and the Island of Vis are „lastovo type“ (H/D ratio same or bigger than Palagruža and Sušac) and „biševo type“ consists of populations from Island of Biševo, Korčula and Hvar (H/D ratio much lower than Palagruža and Sušac). The contact zone between types are Island of Vis with neighbouring islands. The land populations divided on populations north from the river

Cetina, between the river Cetina and the river Neretva and south from the river Neretva. In this paper we examined the same shell parameters as Berberović (1964) and represent the morphometric characteristics of 15 different populations of *E. vermiculata*. The aim scope was to determine if any changes in shell size took place in a period from Berberović (1964) till today. Molecular analysis (16S rDNA and COI (Puizina et al., unpublished sequences GenBank Accession Numbers JF277380– JF277396 and JF802030 - JF802030) showed that there is no molecular–genetic evidences for classification of a single *E. vermiculata* species into separate subspecies.

## MATERIAL AND METHODS

The sampling design we used for morphological and molecular analysis followed the pattern of Berberović (1963) (samples for Middle Adriatic) as well as from North and South Adriatic, thirteen sites in total (Figure 1).



Figure 1. Sampling sites along The Adriatic coast.

For shell measurement we collected 20 specimens per site and a total of 300 specimens with a reflected lip because this indicates cessation of growth and maturity of the snail. The measurements were made on the field.

The shell features we measured were shell high (H), shell width (D) and aperture high (h). After that we compared the results as relative shell high (H/D) (ratio between high and width in percents) and ratio between aperture high (h) and shell high (H) in percents. The intrapopulation variation was calculated with the coefficient of variation (CV) of all the morphometric characters of the examined populations. Geographical variation and qualitative data of the shell were subjected separately to principal component analysis (PCA). The UPGMA analysis was used to calculate similarities between the 13 populations based on morphometric data. All statistic calculations were made by Statistica 8.0 and XlstatPro softwares.

## RESULTS

The mean shell largest diameters (D) of the 13 samples ranged from 19,99 mm (sample from island of Sušac) to 31,78 mm (Šibenik, seaside) and the mean shell height (H) from 17,31 mm (Sušac) to 25,66 mm (Island of Šolta). The mean size of the largest population was approximately 1,5 x larger than the mean size of the smallest population. Coefficient of variation (CV%) values of H, D and h ranged from 11,02% to 11,72% and shows the low variance for the size variation within populations. The H/D ratio ranged from 0,78 (sample from Island of Palagruža) to 0,86 (sample from Island of Sušac). The low variance between the size variation within populations and variation in shell shape were not expected. The PCA analysis based on morphometric data of the shell characteristics of *Eobania vermiculata* confirmed that the populations from Islands of Palagruža and Sušac are clearly separated from the other populations (Figure 2).

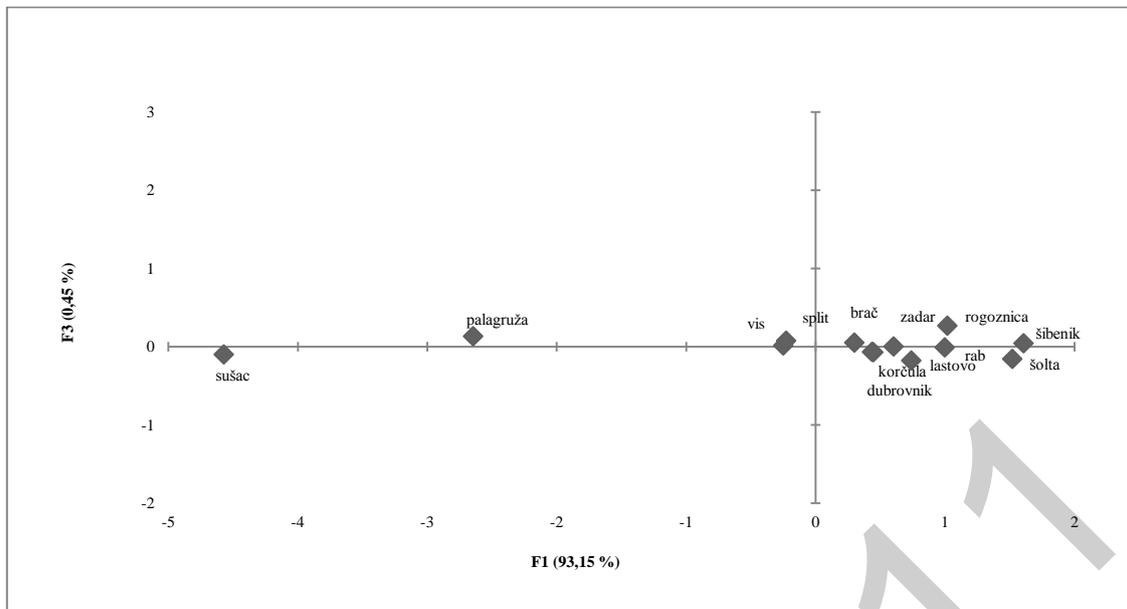


Figure 2. The diagram of PCA analysis.

The variables which mainly contributed to the first discriminant function (squared canonical correlation 0,98%) were shell height (H) and for the second discriminant function (squared canonical correlation 0,94%) shell width (D). The populations from the island of Palagruža and Sušac constituted homogenous group (76,71%), populations from the island of Šolta and Šibenik (coast) constituted more or less homogenous group at the level of 13,57% and those from other sites were heterogenous (0-3%). The first factor (H, 93,15) and the second one (h, 0,45%) separated populations in seven groups according to their geographic proximity. The first group is characterized by two populations: Palagruža i Sušac; second group by population from the Island of Vis; third by Split (seaside); fourth by the Island of Šolta and Šibenik (seaside); fifth by the Island of Rab and Rogoznica (seaside); sixth by the Island of Korčula; seventh is divided in three subgroups: Zadar (seaside), Island of Lastovo and Island of Brač and Dubrovnik (seaside) (Figure 2). UPGMA cluster analysis based on Euclidian distance (Figure 3) was consistent with PCA results.

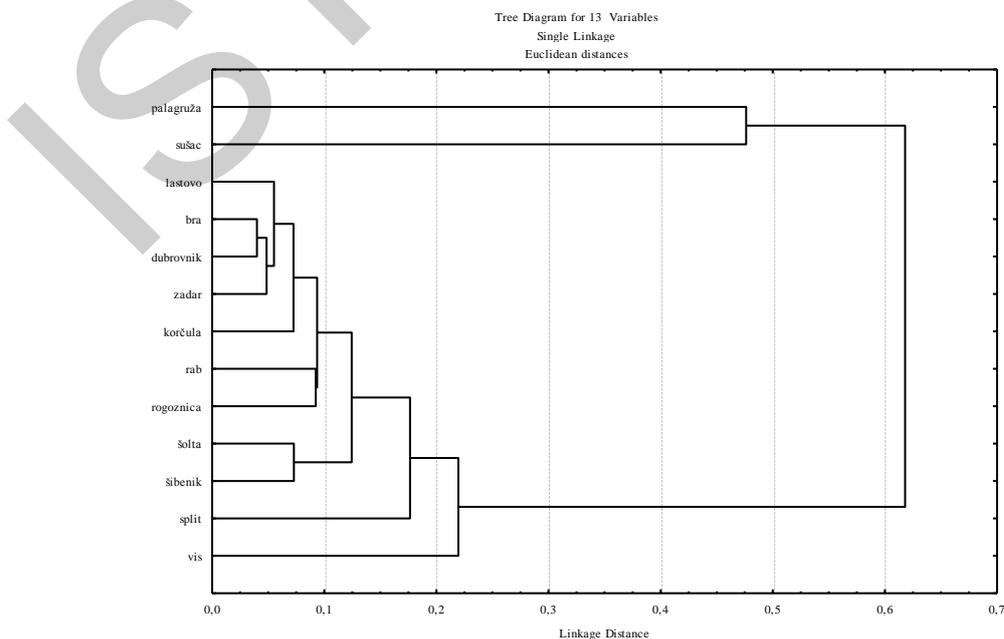


Figure 3. UPGMA cluster analysis.

## DISCUSSION

This study of morphometric characteristics of the shells revealed that populations exposed to antropogenic activity showed multivariate intrapopulation variation. The populations were grouped according to their geographical origin and cluster analysis support that thesis. Populations on open sea islands Palagruža (68 miles S from Split) and Sušac (25 km W from the Island of Lastovo) keep their „nanism“ as Berberović (1964) stated in his research. The main reason for “nanism” on those islands is geographic isolation (took place approximately 10 000 years ago) and extreme ecological conditions. Namely, according to Köppen the Island Palagruža is included in the Csa type of climate - Mediterranean climate with hot summers (only 309,7 mm of rain; high relative humidity of air of 74%-77% with low precipitation of 304 mm) (Trošić et al., 2003). Such climate characteristics are directly reflected on plant communities in which xerophytes are dominant floral component (Pavletić, 1978) and they are not suitable for snail ingestion because of essential oils and silicates in plant tissue. Compared to the starting morphological variation, our shells showed the greater similarity to the sizes of the islands Tremiti (Sacchi, 1957). Lazaridou et al. (1994) stated that the largest shell diameter and the aperture area are negatively related to the mean minimum annual monthly temperatures and Cook and O'Donald (1971) confirms that smaller snails survived better in unshaded and warmer conditions. Ecological conditions in the outer islands (limited amount of food, temperature and humidity) could be the reason of increased body size because those islands are known for extremely unfavourable environmental conditions. The mean annual air temperature is 16,7°C. Total of 85,3 days per year minimum air temperature is 20°C or higher. Annual precipitation is 289,5 mm (Trošić et al., 2003). So, this climate type known as mediterranean arid climate type with long dry period (more than three months per year) with extremely high temperature cause longer hibernation in poikilotherms such as terrestrial snails than in mainland. Also, the resource availability is reduced. The *Eobania* snails are polyfagous herbivores and the amount of suitable plants (herbs and grasses) is limited (Trinajstić, 1973). The Island of Palagruža and Sušac are uninhabited offshore islands app. 68 miles away from the mainland and continuity of such contributions appears perfectly stable nanism. Taking into consideration the formation of these islands it is quite certain that the species *E. vermiculata* is native species here. The populations of inner islands showed greater morphological polymorphism in a way that some individuals reach the standard shell size, almost the same as continental populations. The geographic isolation of those islands is not so long as in outer ones, and the antropogenic influence is obvious. The environmental characteristics are quite different from those on islands Palagruža i Sušac because the most of the land is agricultural; more water and higher humidity as well as unlimited quantity of food are the main reason why those individuals are bigger than on the islands of Palagruža and Sušac. The populations from the islands Lastovo and Korčula according Berberović (1963) were grouped together with continental populations south to the river Neretva. Our survey confirms such shell sizes as Berberović (1963) but in that group are also the populations from the island of Brač. The continental populations from that group are populations from Zadar and Dubrovnik. The continental populations north from the river Cetina are similar with populations from the island of Rab and Šolta which is in accordance with Berberović (1963). The continental populations from the area between the rivers Cetina and Neretva are in the same group with populations from Split and island of Vis. The populations from the Island of Vis is according Berberović (1963) defined as the mixed zone of different types of shell sizes. Our survey confirm this statepoint. The reduction of shell size towards continent-inner islands-outer islands our survey did not confirmed. We found enlargement of shell sizes except on outer islands probably caused by antropogenic influence and changes in environmental conditions. Molecular analysis of two mitochondrial genes (Puizina et al. GenBank unpublished sequences) didn't support subspecies status of *E. vermiculata pelagosana* on molecular level so those samples could be define as ecotypes or forms.

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# THEORETICAL PREDICTION OF THE STRUCTURAL, ELASTIC AND ELECTRONIC PROPERTIES OF THE MAX PHASES $X_2SiC$ ( $X=Ti$ AND $Cr$ )

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## Abstract

Using first-principles calculations, the structural, elastic and electronic properties of the MAX phase  $Ti_2SiC$  and  $Cr_2SiC$  are studied for the first time by means of the pseudo-potential plane-wave method within GGA and LDA. The effect of pressure on normalized lattice constants  $a/a_0$  and  $c/c_0$  and the internal parameter  $z$  is investigated. Our results of lattice constants, internal parameter, elastic constants, sound velocities and Debye temperature are predictions. The  $Ti_2SiC$  and  $Cr_2SiC$  compounds behave as ductile material and shows a stronger anisotropy. The analysis of the band structure and density of states show that these compounds are electrical conductors, having a strong directional bonding between  $Ti$  and  $C$  and  $Cr$  and  $C$  atoms assured by the hybridization of  $Ti-d$  and  $Cr-d$  atom states with  $C-p$  atom states.

**PACS:** 61.50.Ah; 71.15.Mb; 71.20.-b

**Keywords:** A. Ternary carbides; B. Ab initio calculation; C. Crystal structural; C. Electronic structure

## 1. Introduction

The ternary layered carbides called Hagg phases [1] were discovered by Nowotny and co-workers. The compounds with chemical formula  $M_{n+1}AX_n$  were also called MAX phases, where  $M$  is an early transition metal,  $A$  is an IIIA and IVA elements and  $X$  is either  $C$  or  $N$  and  $n$  varies from 1 to 3 and having some of the best metals and ceramics properties [2]. Like metals, they are electrically and thermally conductive, not susceptible to thermal shock and plastic at high temperature. When considering as ceramics, they are elastically rigid, lightweight, creep and fatigue resistant and maintain their strengths to high temperatures [3-8]. Many compounds were reported for  $n = 1$  (the so called 211 phases), the members identified with  $n = 2$  (the so-called 312 phases) and other compounds synthesized for  $n = 3$  (the so-called 413 phases) [9].

The physical properties of MAX phases vary from phase to another depending on  $M$ ,  $A$  and  $X$  elements present in compounds. To our best knowledge, there are no theoretical and experimental studies have been done to investigate the fundamental properties of  $Ti_2SiC$  and  $Cr_2SiC$ . So, it is timely to investigate in the present work some of these properties. We report mainly a first-principles study on structural, elastic, electronic and thermal properties of  $Ti_2SiC$  and  $Cr_2SiC$  compounds using the state of the pseudo-potential plane wave method (PP-PW) in the framework of the density functional theory (DFT) within the generalized gradient approximation (GGA) and local density approximation (LDA). This paper is organized as follows: in section 2, we briefly describe the computational techniques used in this work. The results obtained for the structural, elastic and electronic properties of  $Ti_2SiC$  and  $Cr_2SiC$  compounds are presented and discussed in section 3. Finally, conclusions and remarks are given in section 4.

## 2. Computation details

We optimized the lattice constants, internal parameter and calculated the ground state structure by using the standard *CASTEP* code [10], which is a plane wave pseudo-potential total energy calculation method based on the density functional theory (*DFT*) [11]. The plane wave energy cutoff and the Brillouin zone sampling were fixed at 400 eV and  $9 \times 9 \times 2$  special  $k$ -point meshes. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudo-potential [12]. The exchange correlation potential was calculated within the local density approximation (*LDA*) developed by Ceperly and Alder and parameterized by Perdew and Zunger [13, 14] as well as the generalized gradient approximation (*GGA*) of Perdew, Burke and Ernzerhof [15].

The crystal structure was fully optimized by independently modifying lattice constants and internal atom coordinates. The Broyden-Fletcher-Goldfarb-Shanno (*BFGS*) minimization scheme [16] was used to minimize the total energy and internal forces. The tolerance for geometry optimization was set as the difference of total energy within  $5 \times 10^{-6}$  eV/atom, maximum ionic Hellmann-Feynman force within 0.01 eV/Å and maximum stress within 0.02 eV/Å<sup>3</sup>.

## 3. Results and discussion

### 3. 1. Structural properties

The MAX phases  $M_2SiC$  ( $M = Ti$  and  $Cr$ ) crystallize in the  $Cr_2AlC$  structure, with space group P63/mmc (#194). Its unit cell contains two molecules and the atomic positions are C: (0, 0, 0), Si: (1/3, 2/3, 3/4) and the four  $M$  atoms at (1/3, 2/3,  $z$ ). The structure is defined by two lattice constants  $a$  and  $c$  and the internal parameter  $z$ . We performed a full optimization of all parameters  $a$ ,  $c$  and  $z$ . The computed lattice constants  $a_0$  and  $c_0$ ,  $c_0/a_0$ , equilibrium unit cell volume  $V_0$ , bulk modulus  $B_0$  and its pressure derivative  $B'$  and the internal parameter  $z$  as determined from geometry at zero pressure within *GGA* and *LDA* are given in Table 1. The values of  $B_0$  and  $B'$  are evaluated from the fitting of the pressure–volume data to a third-order Birch–Murnaghan *EOS*. To date, no experimental or theoretical data for these parameters were available to be compared with our theoretical results. Fig. 1 plots the variation of normalized lattice constants ( $a/a_0$  and  $c/c_0$ ) and the internal parameter  $z$  versus applied hydrostatic pressure. The lattice constants decrease monotonously with increasing pressure. This is due to the fact that the atomic bonding along the  $c$ -axis is stronger than that along the  $a$ -axis. While the internal parameter increases monotonically when the pressure is enhanced.

### 3. 2. Elastic properties

The computed elastic constants  $C_{11}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{13}$ ,  $C_{12}$  for the MAX phases  $Ti_2SiC$  and  $Cr_2SiC$  at equilibrium within *GGA* and *LDA* were reported in Table 2. We remark that no experimental and theoretical elastic constants are available to be compared with our results. Future measurements will provide a comparison for our calculated predictions. The elastic constant  $C_{11}$ , which provides a measure of rigidity against unidirectional deformation along  $a$ -axis, is slightly lower than the elastic constant  $C_{33}$ , which provides an estimation of the elastic response of the material to a unidirectional pressure along  $c$ -direction, this is in accordance with the response of  $a$  and  $c$  under hydrostatic pressure (Fig. 1). The condition for mechanical stability of a structure is that its strain energy must be positive against any homogeneous elastic deformation.

For a hexagonal crystal, the mechanical stability under isotropic pressure is judged from the following conditions:

$$\left. \begin{cases} C_{11} > 0 \\ (C_{11} - C_{12}) > 0 \\ C_{44} > 0 \\ (C_{11} + C_{12})C_{33} - 2C_{12}^2 > 0 \end{cases} \right\} \quad (1)$$

It is found that the elastic constants  $C_{ij}$  of  $Ti_2SiC$  and  $Cr_2SiC$  satisfy these criteria, thus these compounds are mechanically stable.

The elastic anisotropy of crystals has an important implication in engineering since it is highly correlated with the possibility to induce micro cracks in the materials [17]. Essentially all known crystals are elastically anisotropic, and a proper description of such an anisotropic behaviour has, therefore, an important implication in engineering science as well as in crystal physics. To quantify the elastic anisotropy of  $Ti_2SiC$  and  $Cr_2SiC$ , we have calculated the shear anisotropic factor ( $A$ ) for the

$\{10\bar{1}0\}$  shear planes between  $\langle 0111 \rangle$  and  $\langle 01\bar{1}0 \rangle$  directions, which is identical to the shear anisotropy factor for the  $\{01\bar{1}0\}$  shear planes between  $\langle 1011 \rangle$  and  $\langle 0001 \rangle$  directions [18]:

$$A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (2)$$

The calculated shear anisotropic factor of  $Ti_2SiC$  and  $Cr_2SiC$  within *GGA* and *LDA* are given in Table 2. For an isotropic crystal, *A* is equal to 1, while any value smaller or larger than 1 indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. According to this,  $Ti_2SiC$  and  $Cr_2SiC$  are characterized by a strong anisotropy for the shear planes described above.

The  $C_{ij}$  elastic constants are estimated from first-principles calculations for  $Ti_2SiC$  and  $Cr_2SiC$  monocrystal. However, generally the elaborated materials are polycrystals, therefore it is useful to estimate the corresponding parameters of the polycrystalline specie from the elastic constants of the single crystal. To this aim we utilise the Voight-Reuss-Hill approximation [19-21]. The calculated Voigt's bulk modulus  $B_V$ , Reuss's bulk modulus  $B_R$ , effective bulk modulus  $B$ , Voigt's shear modulus  $G_V$ , Reuss's shear modulus  $G_R$ , effective shear modulus  $G$ , Young's modulus  $E$ , and Poisson's ratio  $\sigma$  of  $Ti_2SiC$  and  $Cr_2SiC$  are given in Table 2. The calculated value of bulk modulus from elastic constants has nearly the same value as that obtained from the *EOS* fitting. This might be an estimate of the reliability and accuracy of our calculated elastic constants for  $Ti_2SiC$  and  $Cr_2SiC$  compound.

We have calculated the ductility index  $\mu_D$ , due to Pugh [22], given by  $\mu_D = B/G$  and the machinability index  $\mu_M$ , due to Sun et al. [23], which is defined as  $\mu_M = B/C_{44}$ . These two indices show high tensile strength combined with low shear resistance leads to good machinability. The two indices give measures of this ratio, with one using  $C_{44}$  as the measure of shear resistance while the other uses  $G$ . The values of  $\mu_D$  and  $\mu_M$  are listed in Table 2. The obtained  $B/G$  ratio for  $Ti_2SiC$  and  $Cr_2SiC$  is equal to 2.06 (2.12) and 2.79 (2.78) using *GGA* (*LDA*). According to the Pugh criteria, these compounds behave as ductile material. A ductile material is resistant to thermal shocks; their mechanic properties decrease slowly with increasing temperature. The large value of the internal parameter  $z$  of  $Ti$  and  $Cr$  atoms may be contributed to the ductility of  $Ti_2SiC$  and  $Cr_2SiC$ .

In Fig. 2, we present the pressure dependence of the elastic constants and bulk modulus of  $Ti_2SiC$  and  $Cr_2SiC$ . The dots show the first-principles results for the given pressures. The lines are the second-order polynomial fit to the results. We can see quite different behaviors depending on the elastic constants considered. All the elastic constants are increasing with pressure. The  $C_{12}$  curves downwards (upwards) for  $Ti_2SiC$  ( $Cr_2SiC$ ), while all the others upward for  $Ti_2SiC$  and  $Cr_2SiC$ . We observe that  $C_{11}$ ,  $C_{33}$ ,  $C_{13}$  and  $B$  are more sensitive to the pressure than  $C_{44}$  and  $C_{12}$ .

### 3.4. Electronic properties

The computed band structure of  $Ti_2SiC$  and  $Cr_2SiC$  at equilibrium lattice parameter, along the high symmetry directions in the Brillouin zone are shown in Fig. 3. The valence and conduction bands overlap considerably and there is no band gap at the Fermi level and the *DOS* has a large finite value at the Fermi level. Once again, this finding confirms the metallicity of this material. The valence band maximum is situated at *A* (*M*) point at 0.17 (0.64) eV above the Fermi level for  $Ti_2SiC$  ( $Cr_2SiC$ ) and the minimum of the conduction band is located at *H* point (between *K* and *F* points) at 2.7 eV below (0.04 eV above) the Fermi level for  $Ti_2SiC$  ( $Cr_2SiC$ ). The calculated partial density of states (*PDOS*) shown in Fig. 4 requires the understanding of the chemical bonding. The computed number of states at the Fermi level  $N(E_F)$  is 3 and 8.25 states per unit cell per eV for  $Ti_2SiC$  and  $Cr_2SiC$ . Therefore, we expect that  $Cr_2SiC$  show higher electrical conductivity than  $Ti_2SiC$ . We can see that the *d* bands of the transition metal play the dominant role in the *DOS* and thus in electrical transport. Carbon does not contribute to the *DOS* at the Fermi level and therefore is not involved in the conduction properties. *Ti-d* (*Cr-d*) electrons of  $Ti_2SiC$  ( $Cr_2SiC$ ) are mainly contributing to the *DOS* at the Fermi level and should be involved in the conduction properties. *Si-p* electrons do not contribute significantly at the Fermi level.

The strong *Ti* 3d, *Cr* 3d, *Si* 4p and *C* 2p hybridization may stabilize the structure of  $Ti_2SiC$  and  $Cr_2SiC$

#### 4. Conclusion

A summary of our results follows:

- (i) Our calculated structural parameters and elastic constants are predictions.
- (ii) We have found a quadratic dependence of the normalized lattice constants  $a/a_0$  and  $c/c_0$  and internal parameter as a function of pressure.
- (iii) We calculated the shear modulus  $G$ , Young's modulus  $E$ , and Poisson's ratio  $\sigma$  and derived the sound velocity and the Debye temperature for polycrystalline  $Ti_2SiC$  and  $Cr_2SiC$  aggregate.
- (iv) These compounds are electrical conductors and the conductivity is assured by the  $d$  electrons of the transition metal.
- (v) The pressure dependence of the bond lengths shows that the  $Ti-C$  ( $Cr-C$ ) bonds are stiffer than the  $Ti-Si$  ( $Cr-Si$ ) bonds.

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Table 1. Lattice constants  $a_0$  and  $c_0$ ,  $c_0/a_0$ , equilibrium unit cell volume  $V_0$ , bulk modulus  $B_0$  and its pressure derivative  $B'$  and internal parameter  $z$  of  $Ti_2SiC$  and  $Cr_2SiC$  at zero pressure.

		$a_0$ (Å)	$c_0$ (Å)	$c_0/a_0$	$V_0$	$B_0$ (GPa)	$B'$	$z$
<b>Ti<sub>2</sub>SiC</b>								
TW	GGA	3.0353	12.8028	4.217	102.15	165.76*	4.221	0.092
	LDA	2.9906	12.6950	4.245	98.33	185.273*	4.128	0.091
<b>Cr<sub>2</sub>SiC</b>								
TW	GGA	2.8496	11.8494	4.158	83.33	213.37*	4.335	0.090
	LDA	2.8084	11.7649	4.189	80.36	241.50*	4.022	0.090

\*From equation of state

Table 2. Calculated elastic constants  $C_{11}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{13}$ ,  $C_{12}$  (in GPa), bulk moduli  $B_V$ ,  $B_R$  and  $B$  (in GPa), shear moduli  $G_R$ ,  $G_V$  and  $G$  (in GPa), Young's modulus  $E$  (in GPa) and Poisson's ratio  $\sigma$  for  $Ti_2SiC$  and  $Cr_2SiC$  compounds.

	<b>Ti<sub>2</sub>SiC</b>		<b>Cr<sub>2</sub>SiC</b>	
	GGA	LDA	GGA	LDA
$C_{11}$	291	329	305	347
$C_{33}$	303	344	385	427
$C_{44}$	138	157	64	66
$C_{12}$	99	114	132	147
$C_{13}$	100	107	172	184
$B_V$	164.7	184.2	216.3	239
$B_R$	164.7	184.2	210.1	234
$B$	164.7**	184.2**	213.2**	236**
$G_V$	113.4	129.2	77.5	86.8
$G_R$	45.8	43.9	75.4	82.8
$G$	79.6	86.5	76.4	84.8
$E$	205.7	224.5	204.9	227.3
$\sigma$	0.29	0.29	0.33	0.33
$A$	1.40	1.36	0.73	0.65
$B/G$	2.06	2.12	2.79	2.78
$B/C_{44}$	1.19	1.17	3.33	3.57

\*\* From elastic constants

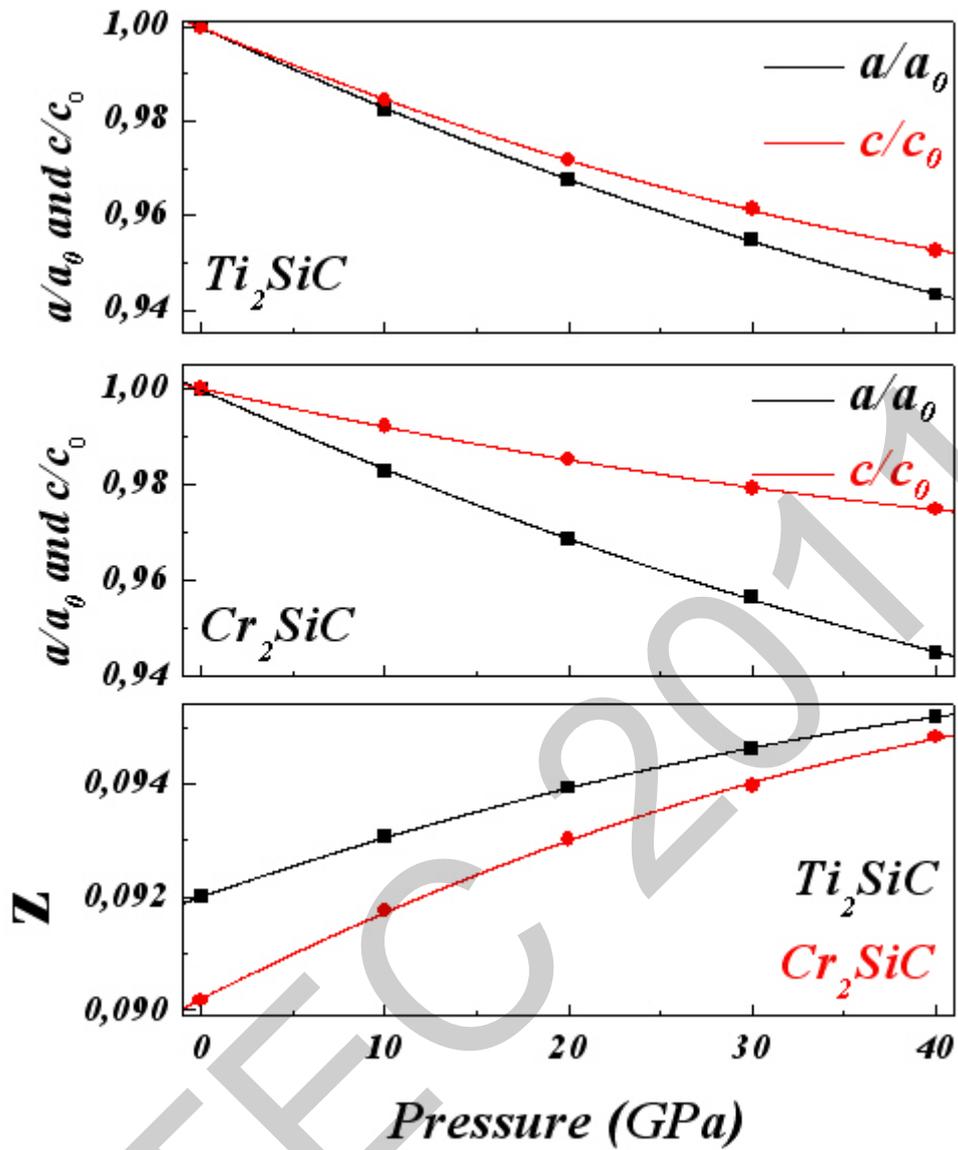
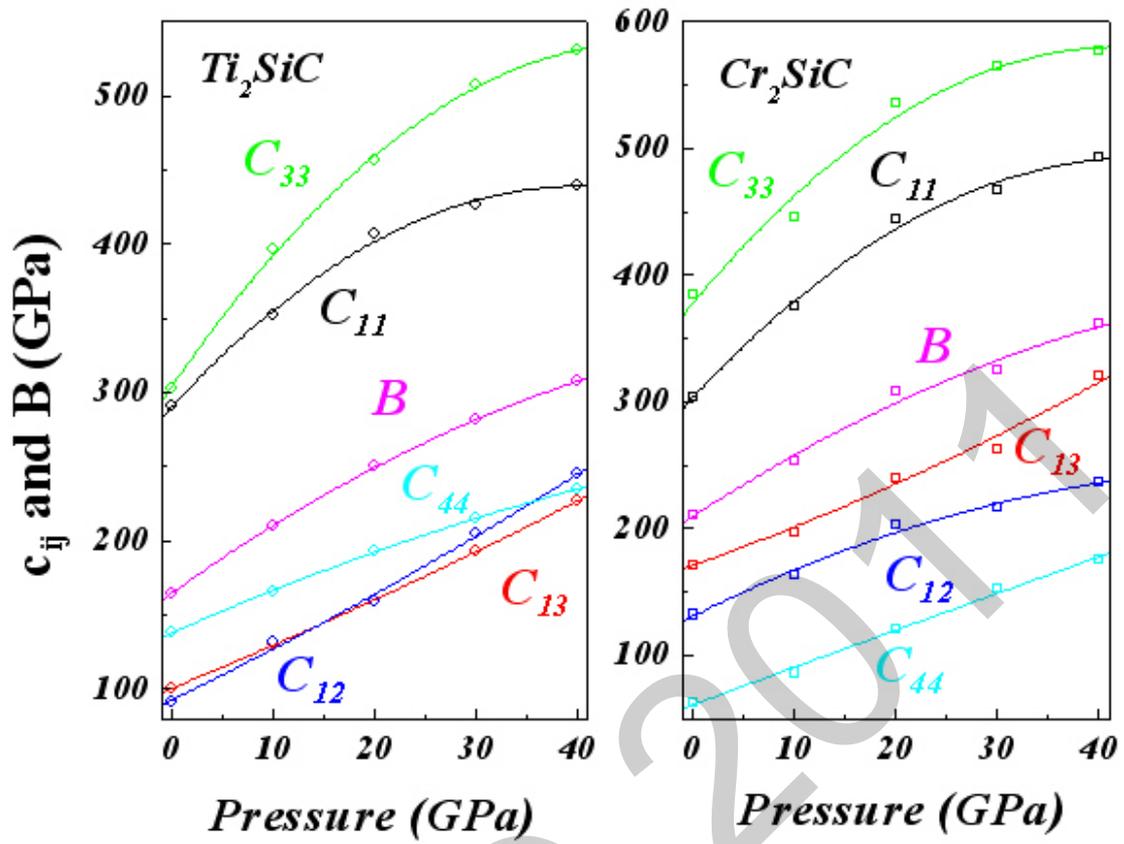
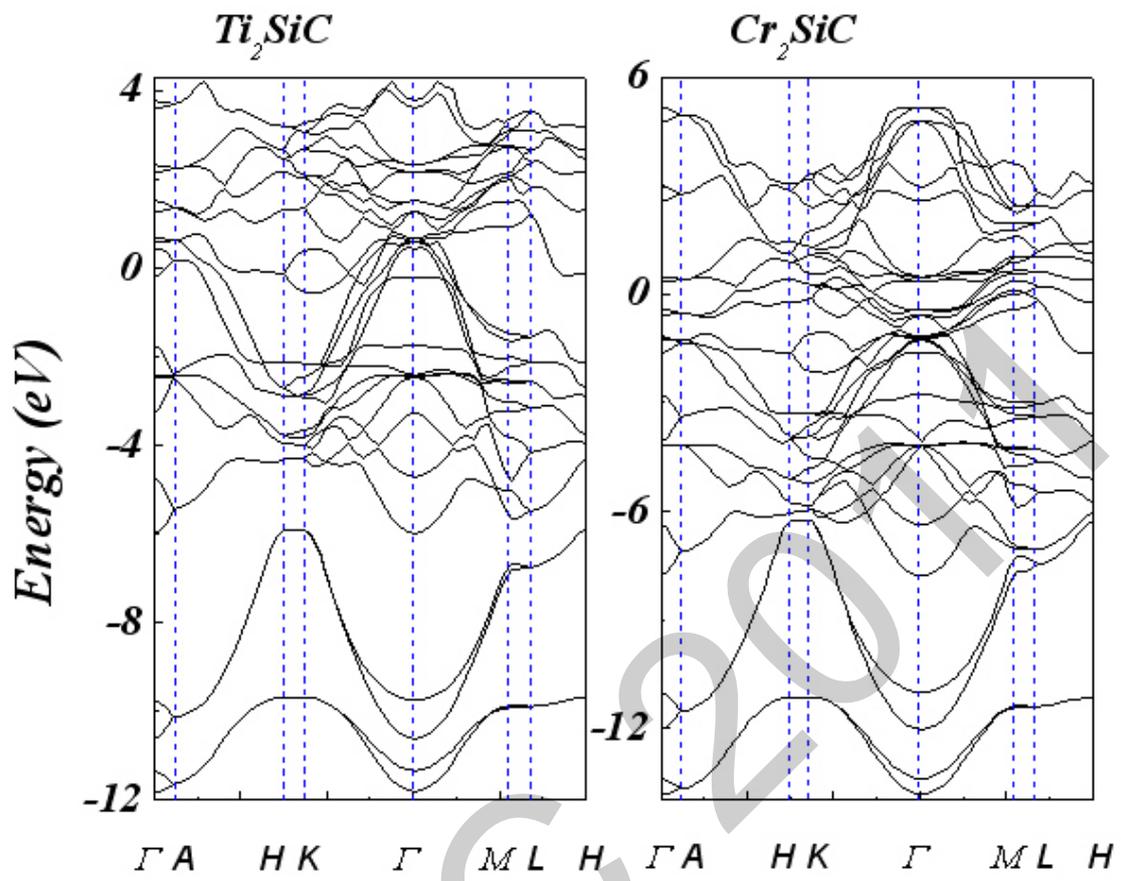


Fig. 1. Plots of normalized lattice constants and internal parameter as a function of pressure.



**Fig. 2.** Pressure dependence of the elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$  and  $C_{44}$  and the bulk modulus  $B$  for  $Ti_2SiC$  and  $Cr_2SiC$ .



**Fig. 3.** Band structure along the principal high-symmetry directions in the Brillouin zone and total density of states of  $Ti_2SiC$  and  $Cr_2SiC$ .

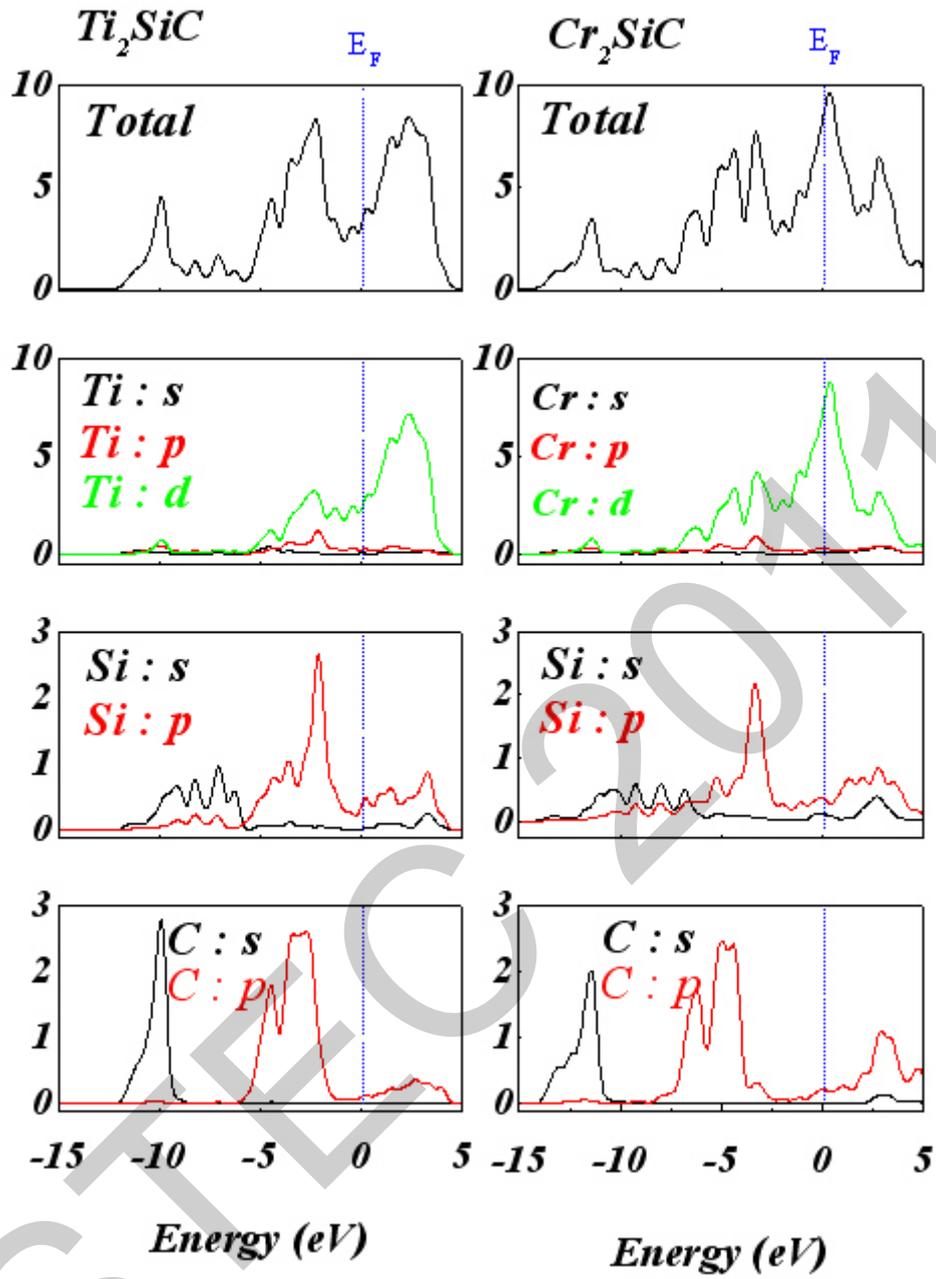


Fig. 4. Partial density of states of  $Ti_2SiC$  and  $Cr_2SiC$ .

# THERMO-ACOUSTIC PROPERTIES OF HYDROCARBON FLUIDS

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**Abstract:** In the present study we investigate the acoustic wave velocities and densities in different hydrocarbon fluids procured from oil wells located in different producing regions of Oman. Using the density data, measured as a function of temperature, the oils are classified, according to the API gravity, as light medium and heavy. The acoustic velocity in the ultrasound frequency of 3 MHz was measured as a function of temperature using an interferometer. A decreasing linear relation is observed between the ultrasonic velocity and the temperature for the samples. Velocity and the density are used to compute the compressibility ( $\kappa_s$ ), coefficient of volume expansion ( $\beta$ ) and the acoustic impedance ( $Z$ ).  $\kappa_s$  and  $\beta$  increase with increasing temperature whereas  $Z$  has been found to decrease with increasing temperature. The results are discussed in term of its applicability in the production and processing of crude oil.

## 1. INTRODUCTION

In order to effectively utilize many new seismic technologies and interpret the results, acoustic properties of reservoir fluids must be well understood. Reliable data of thermo-physical properties of crude oil as a function of temperature and pressure are useful to provide a basis for engineering and technical solutions for exploration, transportation and refinement processes. These are widely used in crude oil processing such as refining operations, optimization of equipment design and in-situ reservoir simulation. Thermo-physical characterization is also of considerable significance for geological and geophysical analysis (see for example, Anderson 1988, 1998).

The present work reports the studies on three crude oil samples obtained from three different producing regions (*viz. Lekhwair, Fahud, and Karim*) of Oman. The density of oils was measured using an oscillating U-tube method. The density data was used to identify the API number of the crude oil samples and classify them as light, medium and heavy. The velocity of propagation of compressional waves in crude oils was measured as a function of temperature using an ultrasound interferometer. The thermo-acoustic properties such as adiabatic compressibility, acoustic impedance and coefficient of volume expansion are computed using density and ultrasound data.

## 2. EXPERIMENTAL TECHNIQUES

Ultrasound velocities in the three samples of the Omani crude oil have been measured at a frequency of 3 MHz in the temperature range from 20°C to 70°C. A high frequency generator excites the quartz crystal at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid. These waves are reflected by the movable metallic plate kept parallel to the quartz crystal. If the separation between the two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator reaches a maximum. If the distance is now increased or decreased and the variation is exactly half wavelength ( $\lambda/2$ ) or multiple of it, the anode current reaches another maximum.

The measuring cell is a specially designed double walled jacket which enables the temperature of the experimental liquid maintained constant by circulating water at the desired temperature. The temperature of the cell was controlled to  $\pm 0.1^\circ\text{C}$  using a circulation thermostat. The measuring cell was kept in an insulated jacket to minimize the heat losses during the measurement. The reflector is slowly moved either clockwise or anticlockwise till the anode current is the maximum and the position of it is noted using the micrometer attached to it. The reflector position is varied to cover  $n = 5$  maxima and its position is noted again. From the known distance moved by the reflector, the wavelength of ultrasonic wave is estimated using the relation,  $d = n(\lambda/2)$ . The process is repeated for several peaks and the average value of  $\lambda$  is obtained, hence the velocity,  $v = f\lambda$  is determined. The accuracy of the velocity measurement is  $\pm 1 \text{ m s}^{-1}$ .

The temperature dependence of the density of the various specimens of crude oil was obtained using the *Anton Paar* density meter based on the law of harmonic oscillation. The oil sample contained in the U-shaped oscillating tube is vibrated at constant frequency using an array of electronic excitation devices. The volume of the sample was kept constant

and the frequency was counted and displayed. A thermostat in the density meter maintained the temperature within  $\pm 0.01^\circ\text{C}$ . The density was calculated by measuring the samples oscillation in conjunction with the temperature. Viscosity errors are minimized by measuring the damping of the oscillations in the U-tube. The technique allows density to be measured within an accuracy of  $\pm 5 \times 10^{-3} \text{ kg/m}^3$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Ultrasound Velocity

The ultrasonic velocity values as functions of temperature for *Lekhwair*, *Fahud* and *Karim* oil samples are plotted in Fig. 1. A decreasing linear relation is observed between the ultrasonic velocity and the temperature for all three samples. The linear dependence of velocity on temperature for the three oil samples is described by the following equations respectively:

$$\text{Lekhwair:} \quad v(t) = 1460.26 - 3.37t \quad (1a)$$

$$\text{Fahud:} \quad v(t) = 1467.36 - 3.30t \quad (1b)$$

$$\text{Karim:} \quad v(t) = 1533.86 - 3.32t \quad (1c)$$

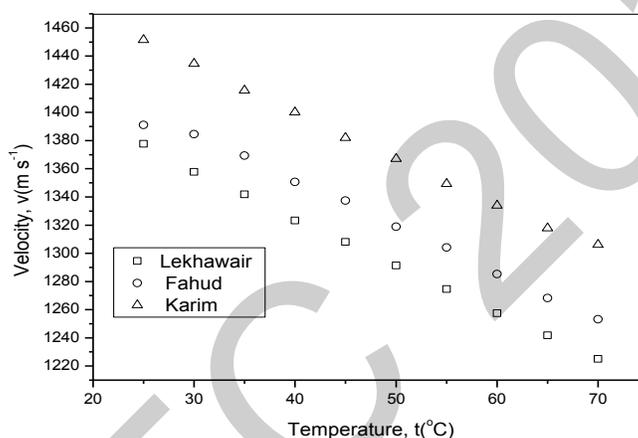


Fig 1. Plot of ultrasonic velocity versus temperature for the Oil Samples.

A similar trend has also been reported for other organic fluids (typical of crude oil) studied as a function of temperature and pressure (Rao and Rao 1959, Wang and Nur 1986). Generally, away from the phase boundary, the velocities and densities are found to be quite linear with temperature and pressure.

For comparison, velocity of pure water is also measured ( $V_m = 1497.0 \text{ m s}^{-1}$ ) at room temperature. It may be noted that the velocity of a compressional wave in Lekhwair and Fahud oils is less by about 8%, and about 3% less for Karim sample than in water. The propagation of a compressional wave causes small local perturbations in the medium. Hence density and inter-atomic forces both control the local fluctuations and hence affect the propagation of sound waves. The microscopic forces of the constituent species in crude oil are of much more complex nature than the water. All such complex forces can be included by considering the viscosity and thermal conductivity of the medium.

#### 3.2 Density

The density measured for the oils as a function of temperature is found to decrease linearly with increasing temperature. The data for one of the samples (Fahud oil) is presented in Fig. 2. The density data is further used to estimate the API gravity (Streeter, 1961) using:

$$API = \frac{141.5}{\rho_{oil}(at 15.6^\circ C)} - 131.5 \quad (2)$$

The values of API determined are:

$$\text{Lekhwair sample} \quad : \quad API = 32.14^\circ$$

Fahud sample : API = 26.71°  
 Karim sample : API = 22.14°

As per specifications given above, Lekhwair sample falls under the category of light crude oil, Fahud belongs to medium oil and Karim is very close to the upper range of heavy oil.

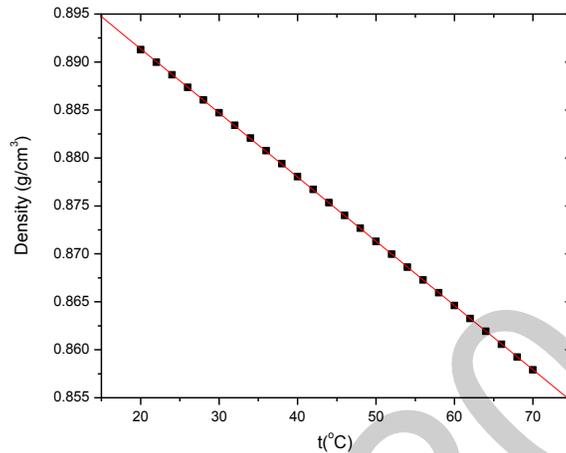


Fig. 2: Plot of density versus temperature for Fahud Oil Sample.

### 3.3 Adiabatic Compressibility

If a compression wave is produced at one place in a medium, it will travel with a constant speed depending on certain properties of the medium. Sound wave causes oscillations in pressure but the oscillations are fast enough so that heat cannot move from compressed regions to rarified regions in order to keep the temperature constant. Before the heat can be conducted away from the compressed regions, the compression has moved on so that sound propagation is adiabatic. An ultrasound wave traveling with a velocity  $v$ , is directly related to its adiabatic compressibility  $\kappa_s$ , by the relation:

$$\kappa_s(t) = v^{-2}(t)\rho^{-1}(t) \tag{3}$$

Both compressional wave velocity  $v(t)$  and density  $\rho(t)$  as function of temperature has been measured. The computed values of adiabatic compressibility are plotted in Fig. 3.

The adiabatic compressibility  $\kappa_s$  of all samples increases with increasing temperature. The dependence of  $\kappa_s$  on temperature can be represented by the following equations:

$$\text{Lekhwair} \quad \kappa_s(t) = 5.45 \times 10^{-10} + 1.59 \times 10^{-12}t + 3.28 \times 10^{-14}t^2 \tag{4a}$$

$$\text{Fahud} \quad \kappa_s(t) = 5.22 \times 10^{-10} + 2.13 \times 10^{-12}t + 1.87 \times 10^{-14}t^2 \tag{4b}$$

$$\text{Karim} \quad \kappa_s(t) = 4.48 \times 10^{-10} + 2.79 \times 10^{-12}t + 4.62 \times 10^{-15}t^2 \tag{4c}$$

where  $\kappa_s$  is in Pa<sup>-1</sup> and  $t$  in °C. The adiabatic compressibility of Lekhwair sample is about 4.5% and 17.8% higher than that of Fahud and Karim respectively at  $t = 25^\circ\text{C}$ . With increasing temperature the difference between the values of  $\kappa_s$  of the samples increases. It is clear from equation (3) that  $\kappa_s$  does not approach zero as  $t$  approaches zero. At low temperatures, however,  $\kappa_s$  almost becomes independent of temperature.

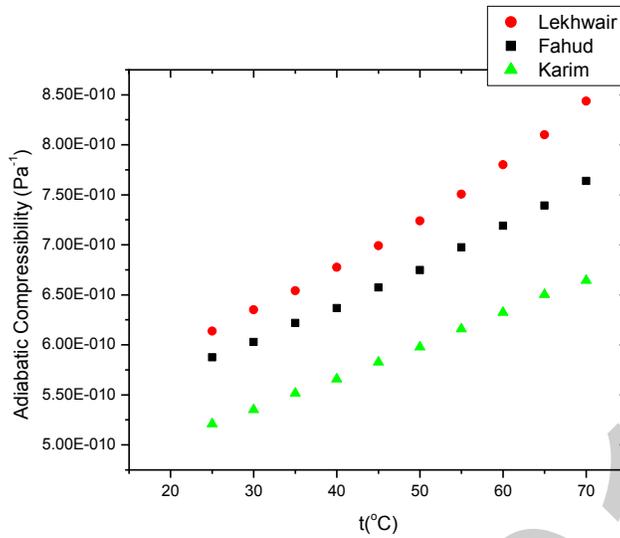


Fig. 3: Temperature dependence of adiabatic compressibility of the crude oil samples

### 3.3 Coefficient of Volume Expansion

The relations describing the dependence of density on temperature allows us to compute the coefficient of thermal expansion

$$\beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial t} \right) \tag{5}$$

The coefficient of volume expansion  $\beta$  is plotted in Fig. 4 as a function of temperature. The linear relations of  $\beta$  as a function of  $t$  for the three samples are represented by the following equations:

Lekhwair:  $\beta = -1.40 \times 10^{-4} + 4.23 \times 10^{-5} t$  (6a)

Fahud:  $\beta = 7.39 \times 10^{-4} + 5.87 \times 10^{-7} t$  (6b)

Karim:  $\beta = 6.90 \times 10^{-4} + 5.1 \times 10^{-7} t$  (6c)

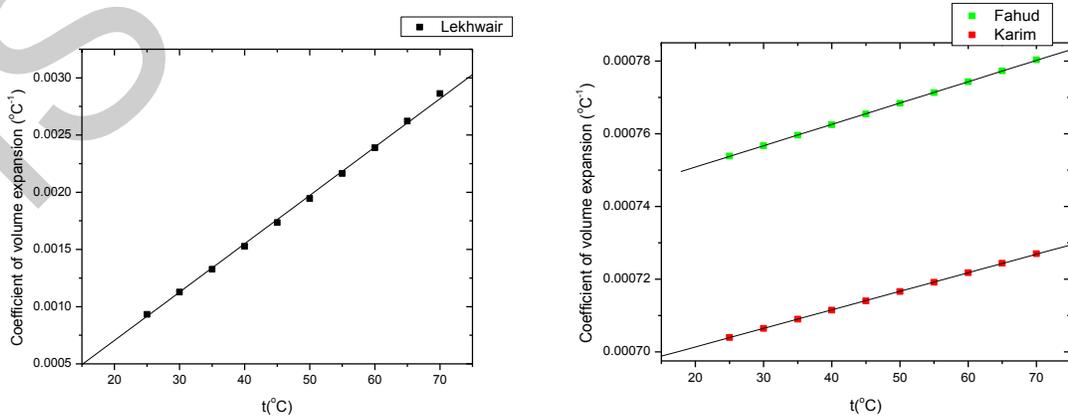


Fig. 4: Variation of the coefficient of volume expansion with temperature for the oil samples

The volume expansion of Lekhwair sample is about 24% and 33% higher than that of Fahud and Karim samples respectively.  $(d\beta/dt)_p$  for Lekhwair, i.e.  $(4.23 \times 10^{-5})^\circ\text{C}^{-2}$ , is significantly higher than that of Fahud, i.e.  $(5.87 \times 10^{-7})^\circ\text{C}^{-2}$  and Karim, i.e.  $(5.1 \times 10^{-7})^\circ\text{C}^{-2}$  respectively.  $\beta$  is an important thermal function which reveals the expanding property of the substance on heating in microscopic level (Ashcroft and Mermin, 1976). When the atoms vibrate along a line connecting the pair, the asymmetry in the potential causes an increase in the mean distance between the atoms as the temperature increases. This picture does indeed reveal the most important mechanism for positive thermal expansion and indicates that atomic vibrations give rise to thermal expansion only because of anharmonicity. But it can not account for negative  $\beta$  found in many materials (Barrera et al, 2005). In such system non-vibrational contributions should be responsible for negative  $\beta$ .

### 3.4 Acoustic Impedance

The value of the acoustic impedance  $Z$  of hydrocarbon liquids is an important parameter useful for the seismic exploration. The acoustic impedance is defined as,

$$Z(t) = v(t)\rho(t) \tag{7}$$

where  $v(t)$  and  $\rho(t)$  are respectively the velocity of ultrasound and the density. The variation of  $Z(t)$  as a function of temperature is highly affected by the density and velocity. A plot of  $Z(t)$  as a function of temperature is given in Fig. 5.

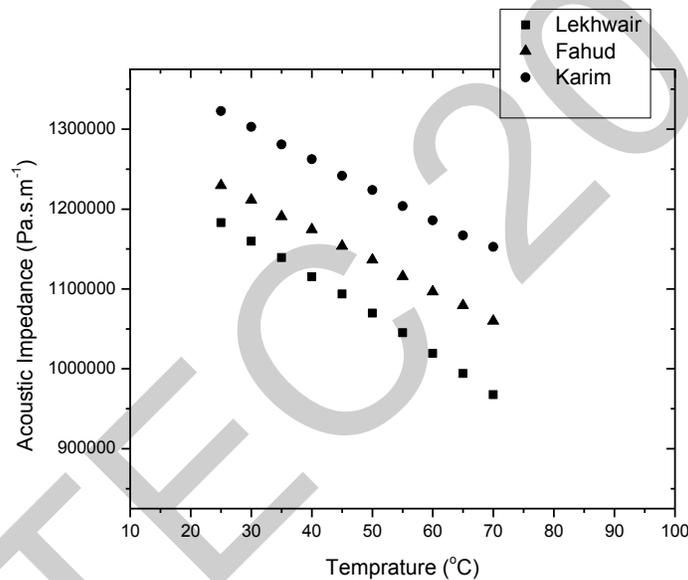


Fig. 5: Variation of acoustic impedance with temperature for the crude oil samples

Due to the complexities of reservoirs, a direct determination of the impedance in situ conditions is very difficult and hence the measurement of  $Z$  from  $v$  and  $\rho$  is of considerable significance (Arafin et al 2006). The acoustic impedance of the samples are found to decrease linearly with increasing temperature. The data are found to follow the equations below,

$$\text{Lekhwair} : Z(t) = 1.30E6 - 4.7 \times 10^3 t \tag{8a}$$

$$\text{Fahud} : Z(t) = 1.32E6 - 3.7 \times 10^3 t \tag{8b}$$

$$\text{Karim} : Z(t) = 1.42E6 - 3.9 \times 10^3 t \tag{8c}$$

where  $t$  is the temperature measured in ( $^\circ\text{C}$ ) and  $Z$  is in ( $\text{Pa s m}^{-1}$ ).

The acoustic impedance of a liquid is analogous to the electric impedance of an electrical circuit. In liquids the motion of a fluid particle is equivalent to the behavior of electrical current in an electrical circuit having elements of inductance, capacitance and resistance. The electrical analogue of the pressure difference across an acoustic element of a fluid is the voltage across the corresponding part of the electrical circuit. It is useful to analyze the transmission and reflection of elastic waves. In particular, it becomes quite significant when elastic waves cross the interface between the layers of hydrocarbon fluids and brines.  $(dZ/dt)_p$  is found to be  $4.7 \times 10^3 \text{ Pa s m}^{-1}^\circ\text{C}^{-1}$ ,  $3.7 \times 10^3 \text{ Pa s m}^{-1}^\circ\text{C}^{-1}$  and  $3.9 \times 10^3 \text{ Pa s m}^{-1}^\circ\text{C}^{-1}$  for Lekhwair, Fahud and Karim samples respectively. By increasing the temperature of the samples from  $25^\circ\text{C}$

to 70°C, Z decreases by 18.2%, 13.8% and 12.9% for Lekhwair, Fahud and Karim respectively. The value of Z can be used to analyze the transmission and reflection of pressure waves across the interface between the layers of adjoining fluids, such as the crude oil - water interface or crude oil - gas interface. The maximum transmission of a pressure wave across the two adjoining liquids occurs when their impedances,  $Z_1$  and  $Z_2$  are equal. The pressure transmission ( $t_p$ ) and the reflection coefficient ( $r_p$ ) at the interface can be evaluated as

$$t_p = \frac{2Z_2}{Z_1 + Z_2} \quad (9)$$

$$r_p = \frac{Z_2 - Z_1}{Z_2 + Z_1} \quad (10)$$

For a large acoustic impedance mismatch ( i.e.,  $Z_1 \gg Z_2$ ), let us take an example of the interface of Karim oil ( $Z_1 = 1.3 \times 10^6$  Pa s m<sup>-1</sup>) and air ( $Z_2 = 429$  Pa s m<sup>-1</sup>) at 20°C, one gets  $r_p \rightarrow -1$  and  $t_p \rightarrow 0$ , i.e. nearly all of the pressure wave is reflected. At such interfaces there is a phase change of 180°C for the pressure. For  $Z_1 \approx Z_2$ , one has  $r_p \rightarrow 0$  and  $t_p \rightarrow 1$ , as if there were one uniform medium and there is no reflection. For a typical water - crude oil interface at 20°C, we find  $t_p = 0.89$  and  $r_p = -.11$ .

For such an interface, the transmitted acoustic intensity,  $\frac{I_t}{I_i} = \left( \frac{Z_t}{Z_p} \right) |t_p|^2$ , ( $I_t$  and  $I_i$  are transmitted and incident intensities ) is very high, about 98% of the incident intensity.

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# TİPİTOP VE ARKADAŞLARI İLE TOPRAĞI TANIYORUZ 3: KÜÇÜK ÇOCUKLAR İÇİN BİR TOPRAK EĞİTİMİ PROJESİ<sup>1</sup>

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## Özet

Araştırmanın amacı, TÜBİTAK 4004 Doğa ve Bilim Okulları proje grubunda yer alan 111B004 numaralı Tipitop ve Arkadaşları ile Toprağı Tanıyoruz 3 isimli projenin, 1. ve 2. gruplarda yer alan çocukların toprakla ilgili bilgi düzeyleri üzerindeki etkisini incelemektir. Bu projenin ilki ve ikincisi (Tipitop ve Arkadaşları ile Toprağı Tanıyoruz 1 ve 2) son iki yıl içinde Denizli’de uygulanmıştır. Önceki projelerin çocukların toprakla ilgili bilgi düzeylerini arttırdığı belirlenmiştir. Bu araştırmada toprak eğitiminin 5-6 yaş çocukları üzerindeki etkisinin incelenmesi amacıyla yapılan çalışmada deneysel yöntem kullanılmıştır. Dokuz günlük uygulamalarda 5-6 yaş grubundan 52 çocuk, anne-babaları ve iki anasınıflı öğretmeni yer almıştır. Araştırmada programın etkisini ortaya koymak için, 5-6 yaş grubu 48 çocuğun oluşturduğu bir kontrol grubu da yer almıştır. Projenin etkililiğini ortaya koymak için çocuklara ön, son ve tekrar-son test uygulanmıştır. 1. ve 2. grupların proje öncesi ve sonrası ön-son test ve tekrar son test uygulamaları arasındaki ilişkiyi belirlemek amacıyla Wilcoxon İşaretili Sıralar Testi, deney ve kontrol grupları arasındaki farklı ortaya koymak için de Mann Whitney U Testi yapılmıştır.

**Anahtar kelimeler:** Çevre eğitimi, toprak eğitimi, 5-6 yaş çocuklar.

## WE ARE LEARNING ABOUT THE SOIL WITH TIPITOP AND HIS FRIENDS 3: A SOIL EDUCATION PROJECT FOR YOUNG CHILDREN

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## Abstract

The aim of this research is to assess the effect of the project no. 111B004 entitled “We are Learning about the Soil with Tipitop and His Friends 3” included in the project group of TUBITAK 4004 Nature and Science Schools on the levels of knowledge about soil among children in the 1<sup>st</sup> and 2<sup>nd</sup> groups. The first and second projects (We are Learning about the Soil with Tipitop and His Friends 1 and 2) was applied in Denizli in the last two years. These projects were determined to increase the level of children’s knowledge about soil. In the research, the experimental method was used in order to examine the effect of soil education on 5-6 years old children. 52 children from the age group of 5-6 years old, their parents, and two kindergarten teachers participated in the applications which lasted nine days. A control group consisting of 52 children from 5-6 years age group was also included in the research in order to determine the effect of the program. Pretest, posttest and repeated posttest will be applied to children to establish the efficacy of the project. Wilcoxon Signed Rank Test was conducted to determine the relationship between the pre-post test and delayed posttest applications before and after the project in the 1<sup>st</sup> and 2<sup>nd</sup> group children, and Mann Whitney U Test was conducted to demonstrate the difference between the experiment and control groups.

**Key Words:** Environment education, soil education, 5-6 years old children.

## Giriş

### Tipitop ve Arkadaşları İle Toprağı Tanıyoruz 3 Projesi

Okul öncesi dönemde gerçekleştirilen çevre eğitiminin kısa ve uzun süreli etkileri göz önünde bulundurularak hazırlanan Tipitop ve Arkadaşları ile Toprağı Tanıyoruz 3 isimli projenin amacı, okul öncesi eğitime devam eden 5-6 yaş çocuklarına toprağı ve toprakla ilgili kavramları tanıtmaktır. Bu amaç doğrultusunda, 5-6 yaş çocuklarını, toprağın özellikleri, toprağın altında/üstünde yaşayan canlılar, toprağın önemi, erozyonun ne olduğu, sebepleri, sonuçları konularında bilgilendirmek ve bu bağlamda çevrelerini tanımalarını sağlamak, duyarlılıklarını arttırmak hedeflenmiştir.

Proje, belirlenen konularda (toprağın özellikleri, toprağın altında/üstünde yaşayan canlılar, toprağın önemi, toprağı koruma, erozyonun ne olduğu, sebepleri, sonuçları) hazırlanan çeşitli etkinliklerden oluşan 9 günlük bir programın dört farklı anasınıflı grubuna uygulanmasını kapsamaktadır. Projenin hedef kitlesini, Denizli il merkezindeki Kayhan Mehmet Atmaca ve Kayhan Zehra Nihat Moraloğlu İlköğretim Okullarının anasınıflarına devam eden 5-6 yaş grubu çocuklar, anne-babaları ve öğretmenleri oluşturmuştur. Bu araştırmada projede yer alan birinci ve ikinci gruplarına ilişkin sonuçlar yer almaktadır. Hedef kitlenin seçiminde iki kriter temel alınmıştır. Bunlardan ilki, çocukların düşük sosyo-ekonomik düzeydeki ailelerden gelmeleri, diğeri de çocukların daha önce toprak, erozyon, çevre gibi konularda herhangi bir eğitim almamış, herhangi bir etkinliğe katılmamış olmalarıdır. Belirtilen kriterlerle, zengin içerikli, farklı eğitim uygulamaları gerçekleştirilmemiş çocuklar için

<sup>1</sup> <http://topragitaniyoruz.pau.edu.tr>

olumlu, farklı, zengin öğrenme yaşantıları sağlamak amaçlanmıştır. Projede, çocukların yaparak-yaşayarak ve eğlenerek öğrenmelerini sağlamak amacıyla, çocukların gelişim özelliklerine yönelik hazırlanmış etkinlikler, (sanat, Türkçe dil, fen ve doğa) farklı öğretim yöntemleri (drama, oyun, gezi-gözlem, deney, soru-cevap) yer almaktadır. Çok yönlü gelişimi desteklemek için farklı etkinlik türlerinden yararlanılmıştır. Etkinliklerin dikkat çekici olmasına, çocukları soru sormaya teşvik etmesine önem verilmiştir. Projede eğitimin devamlılığının sağlanması açısından yapılan çeşitli düzenlemeler bulunmaktadır. Bunlardan ilki, eğitim ortamlarındaki etkinliklere paralel aile katılımı çalışmalarıdır. Ailenin çocukların davranışlarını geliştirmede önemli etkisinden dolayı, aileler de proje de yer almıştır. Bilindiği gibi, okul öncesi dönemde, davranışlar anne-babaların davranışlarının model alınması ve onlarla gerçekleştirilen etkileşimlerle şekillenmektedir (Başal, 2003; Musser & Diamond, 1999). Programda da aile katılımı etkinlikleri ile eğitimin sürekliliğini sağlamak, ailelerin de konu ile ilgili bilgilerini, duyarlılıklarını arttırmak, çocuk-anne-baba arasındaki etkileşimi geliştirmek, okul-aile işbirliğini geliştirmek amaçlanmıştır. Eğitimin devamlılığını sağlamak için yapılan diğer çalışma ise projenin uygulandığı anasınıflarında oluşturulan toprak köşesidir.

Bunların yanı sıra proje kapsamında bu yıl iki sergi ve iki konferans da gerçekleştirilmiştir. Birinci ve ikinci grupların proje boyunca yaptıkları çalışmalar, Pamukkale Üniversitesi Eğitim Fakültesi ve Kayhan Zehra Nihat Moraloğlu İlköğretim Okulu'nun toplantı salonunda sergilenmiştir. Çevre Eğitiminin Önemi konulu konferansların da ilki Pamukkale Üniversitesi Eğitim Fakültesi'nde, diğeri de Halk Eğitim Merkezi'nde gerçekleştirilmiştir.

Pamukkale Üniversitesi Eğitim Fakültesi Okul Öncesi Eğitimi ABD. tarafından yürütülen projede Pamukkale Üniversitesi ve Marmara Üniversitesi'nden öğretim üyeleri, Adana Bilim ve Sanat Merkezi'nden bir uzman biyoloji öğretmeni ve Denizli Orman Bölge Müdürlüğü'nden bir yönetici, proje grubunun anasınıfı öğretmenleri ve Pamukkale Üniversitesi Hastahanesi'nden bir hemşire yer almıştır.

Yaşları dikkate alındığında, projenin hedef kitesinin hızlı bir öğrenme potansiyeline sahip oldukları görülmektedir. Dolayısıyla bu dönemde çocukların dikkatlerini yaşadıkları çevreye ait önemli konulara çekmek, bu konularla ilgili duyarlılıklarını arttırmak önem taşımaktadır. Okul öncesi dönem çocuklarının yaşadıkları coğrafyayı farklı bir boyuttan ve yakından tanımalarını sağlamak, güncel bir çevre sorunu hakkında bilgilendirmek, farkındalıklarını arttırmak, bu amaçlara ulaşırken öğretmenlerin yanı sıra ailelere de yer vermek eğitimin kalıcılığını, sürekliliğini sağlamak adına da önem taşımaktadır. Bu bağlamda, küçük çocukların, ailelerinin toprağı tanımaları, önemli bir çevre sorununa yönelik bilinçlendirilmelerini de sağlayacaktır. Okul öncesi dönem çocuklarına yönelik çevre eğitimi ile ilgili çalışmaların yeterli olmaması, hedef kitlenin gelişim özellikleri projenin önemini arttıran faktörlerdendir.

## Yöntem

Toprak eğitiminin 5-6 yaş çocukları üzerindeki etkisinin incelenmesi amacıyla yapılan araştırmada, deney ve kontrol gruplu deneysel yöntem kullanılmıştır. Birinci ve ikinci grup uygulamaları 2011-2012 eğitim öğretim yılının güz döneminde gerçekleştirilmiştir. Her grup için proje çalışması, ön test, pilot etkinlikler, programın uygulanması, son test-tekrar son test uygulamalarıyla on altı gün sürmüştür. Proje etkinliklerinden önce anne-babalara ve öğretmenlere projenin amacı, içeriği ve etkinlikler hakkında bilgi verilmiştir. Konu ile ilgili bilgi düzeylerini belirlemek için çocuklara ön testler uygulanmıştır. Proje çalışmalarından önce çocuklara projenin ana karakteri Tipitop'u ve dolayısıyla projeyi ve eğitimcileri tanıtmak amacıyla pilot etkinlikler (sohbet, kukla gösterisi ve drama) uygulanmıştır. Proje ile ilgili hazırlanan etkinlikler, rehberlerin yardımıyla eğitimciler tarafından 9 gün boyunca uygulanmıştır. Her gün 2-3 etkinlik gerçekleştirilmiştir. Etkinlikler, çocukların devam ettikleri okulların anasınıflarında, Pamukkale Üniversitesi Biyoloji Labortuarı'nda, Pamukkale Üniversitesi Bitki Serası'nda, Çamlık Orman ve Mesire Yeri'nde gerçekleştirilmiştir. Proje, toprakla ilgili konu başlıklarına yönelik hazırlanmış çeşitli etkinliklerle (hikaye, oyun, drama, şarkı, bilmece, gezi-gözlem, deney, sanat) gerçekleştirilmiştir. Projenin sonunda anasınıfında toprak köşesi oluşturulmuştur. Projedeki etkinlikler tamamlandıktan sonra çocuklara, anne-baba ve öğretmenlere son testler uygulanmıştır. Bilgilerin kalıcılığını belirlemek amacıyla çocuklara son testten iki hafta sonra tekrar-son test uygulanmıştır.

Projenin etkiliğini ortaya koymak amacıyla 1. ve 2 deney gruplarıyla aynı okullarda, projeye katılmayan diğer anasınıflarından kontrol grupları seçilmiştir. Bu gruplara proje ile ilgili herhangi bir bilgi verilmemiş, etkinlik yaptırılmamıştır. Kontrol gruplarına yalnızca deney grupları ile eş zamanlı olarak ön, son ve tekrar-son testler uygulanmıştır. Çocuklar tüm deney ve kontrol gruplarına random olarak atanmışlardır.

## Örneklem grupları

Tipitop ve Arkadaşları ile Toprağı Tanıyoruz 3 isimli projenin birinci deney grubunda, Kayhan Mehmet Atmaca İlköğretim Okulu'nun sabahçı anasınıfına devam eden 8 kız (% 47 ), 9 erkek (% 53 ) çocuğı yer almıştır. Çocukların yaş ortalaması; 5 yaş, 7 ay, 20 gündür (en az, 4 yaş, 6 ay, 5 gün; en çok, 6 yıl, 4 ay, 6 gün). Birinci proje grubu için seçilmiş kontrol grubunda Kayhan Mehmet Atmaca İlköğretim Okulu'nun öğlenci anasınıfına devam eden 8 kız (% 47 ), 9 erkek (% 53) çocuğı yer almıştır. Kontrol grubunun yaş ortalaması; 5 yaş, 1 ay, 1 gündür (en az, 4 yaş, 1 ay, 10 gün; en çok, 6 yıl, 1 ay, 9 gün). Projenin ikinci deney grubunda Kayhan Zehra Nihat Moraloğlu Okulu'nun sabahçı anasınıfına devam eden 11 kız (% 31.4 ), 24 erkek (%68.6 ) çocuğı yer almıştır. Çocukların yaş ortalaması; 5 yaş, 6 ay, 5 gündür (en az, 4 yaş, 8 ay, 6 gün; en çok, 6 yıl, 3 gün). İkinci proje grubu için seçilmiş kontrol grubunda Kayhan Zehra Nihat Moraloğlu Okulu'nun öğlenci anasınıfına devam eden 11 kız (% 31.4 ), 24 erkek (%68.6 ) çocuğı yer almıştır. Kontrol grubunun yaş ortalaması; 5 yaş, 5 aydır (en az, 4 yaş, 6 ay, 8 gün; en çok, 6 yıl, 4 ay, 10 gün).

## Veri Toplama Aracı

Projede veri toplama araçları olarak çocuklar için hazırlanan kişisel bilgi formu ve ön-son test olarak kullanılan bilgi ölçmeye yönelik başarı testi kullanılmıştır. Çocukların kişisel bilgi formlarında, kendilerinin ve ailelerinin demografik bilgilerini ortaya çıkartacak sorular yer almaktadır. On üç sorudan oluşan formlar anne-babalar tarafından doldurulmuştur. Veri toplama

araçlarının ikincisi, proje konusu ile ilgili ön ve son test olarak kullanılan başarı (bilgi) testidir. Proje konusu ile ilgili ön-son testlerde, çocukların proje konusu ile ilgili var olan bilgi düzeylerinin ve projenin çocukların bilgi düzeylerine etkisinin ortaya çıkartılması amaçlanmıştır. Ön ve son test olarak kullanılan başarı testi bilgisayarın elektronik ortamında cevaplandırılacak sorulardan oluşmaktadır. Çocukların okuma-yazma bilmemeleri nedeniyle fotoğraflardan, resimlerden oluşan testte, on iki soru yer almaktadır. Sorular, projede yer alan konu alt başlıklarına (toprağın biçimsel özellikleri, toprağın altında ve üstünde yaşayan canlılar, toprağın yararları, işlevleri, toprağı koruma, erozyon) göre hazırlanmıştır. Ön ve son test, proje başlamadan önce ve proje uygulamasının sonunda çocuklara bireysel olarak anasınıfı ortamında, uzman personeller tarafından uygulanmıştır. Uzman personel çocuklara slaytları gösterip, soruları yöneltmiştir. Çocuklar bilgisayar faresini kullanarak cevap vermiştir. Yanlış ve doğru cevaplar karşısında gelen sesli uyarılarla test tamamlanmaktadır. Testteki 12 sorudan 7 tanesi üç şıklı sorulardan oluşmaktadır. Kalan sorulardan bir tanesi açık uçlu, bir tanesi farklılıkları bulma, bir tanesi olayları sıralama, iki tanesi olayları anlatmayı içermektedir. Her soru bir slaytta yer almaktadır. Her bir sorunun puan değerleri 0 ile 6 puan arasında farklılık göstermektedir. Testin toplam puanı, her bir sorunun puan değeri toplanarak elde edilmektedir. Testten alınabilecek en düşük puan 0, en yüksek puan ise 41dir. Şıklı olmayan soruların slaytında çocuklara sorular sorulmuş ve cevapları ses kayıt cihazına kaydedilmiştir. Çocukların ön-son test soruları, cevap şıkları proje yürütücüsü tarafından hazırlanmış, test uzman personel tarafından da elektronik ortamda oluşturulmuştur. Çocukların öğrendiklerinin kalıcılığını kontrol etmek amacıyla son testten iki hafta sonra son test tekrarlanmıştır.

### Verilerin analizi

Çocukların ön-son test, tekrar son test bulguları SPSS 15.0 paket programında analiz edilmiştir. Deney ve kontrol gruplarının proje öncesi ve sonrası ön-son test ve tekrar son test uygulamaları arasındaki ilişkiyi belirlemek amacıyla Wilcoxon İşaretli Sıralar Testi yapılmıştır. Deney ve kontrol gruplarının ön, son ve tekrar son test sonuçlarını karşılaştırmak amacıyla Mann Whitney U Testi yapılmıştır.

### Bulgular

Tablo 1. Birinci Grup Çocuklarının (Deney grubu) Proje Öncesi ve Sonrası Ön Test-Son Test /Tekrar Son Test-Son Test ve Tekrar Son Test-Ön Test Puan Ortalamalarına İlişkin Wilcoxon İşaretli Sıralar Testi Sonuçları

Son Test- Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	0	.00	.00	3.62	.000
Pozitif Sıra	17	9.00	153.00		
Eşit	0				
Tekrar Son Test- Son Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	10	7.95	79.50	1.70	.088
Pozitif Sıra	4	6.38	25.50		
Eşit	3				
Tekrar Son Test -Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	2	2.25	4.50	3.42	.001
Pozitif Sıra	15	9.90	148.00		
Eşit	0				

1. grup çocuklarının (deney grubu) proje öncesinde ve sonrasında aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olduğu tespit edilmiştir ( $z = 3.62$   $p < .001$ ). Program sonrasındaki son test puan ortalaması, ön test puan ortalamasından yüksektir. 1. grup çocuklarının (deney grubu) proje sonrasında son ve tekrar son testten aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olmadığı tespit edilmiştir ( $z = 1.70$   $p > .05$ ). 1. grup çocuklarının (deney grubu) proje sonrasında ön ve tekrar son testten aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olduğu tespit edilmiştir ( $z = 3.42$   $p < .001$ ). Program sonrasındaki son test puan ortalaması, tekrar son test puan ortalamasından yüksektir.

Tablo 2. Birinci Grup Çocuklarının (Kontrol grubu) Proje Öncesi ve Sonrası Ön Test-Son Test /Tekrar Son Test-Son Test ve Tekrar Son Test-Ön Test Puan Ortalamalarına İlişkin Wilcoxon İşaretli Sıralar Testi Sonuçları

Son Test- Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	3	2.00	4.00	1.37	.168
Pozitif Sıra	4	4.25	17.00		
Eşit	11				
Tekrar Son Test- Son Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	4	4.00	16.00	.345	.730
Pozitif Sıra	3	4.00	12.00		
Eşit	10				
Tekrar Son Test -Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	2	2.50	5.00	1.160	.246
Pozitif Sıra	4	4.00	16.00		
Eşit	11				

1. grup çocuklarının (kontrol grubu) proje öncesinde ve sonrasında aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olmadığı tespit edilmiştir ( $z = 1.37$   $p > .05$ ). 1. grup çocuklarının (kontrol grubu) proje sonrasında son ve tekrar son testten aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olmadığı tespit edilmiştir ( $z = .345$   $p > .05$ ). 1. grup çocuklarının (kontrol grubu) proje sonrasında ön ve tekrar son testten aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olmadığı tespit edilmiştir ( $z = 1.160$   $p > .05$ ).

Tablo 3. Birinci Gruptaki Deney ve Kontrol Grubundaki Çocukların Proje Öncesinde Ön-Son ve Tekrar Son Test Puan Ortalamalarına ait Mann Whitney U Testi Sonuçları

Ön test	n	Sıra Ortalaması	Sıra Toplamı	U	p
Deney	17	18.18	309.00	133.000	.691
Kontrol	17	16.82	286.00		
Son test	n	Sıra Ortalaması	Sıra Toplamı	U	p
Deney	17	23.65	402.00	40.000	.000
Kontrol	17	11.35	193.00		
Tekrar son test	n	Sıra Ortalaması	Sıra Toplamı	U	p
Deney	17	22.74	386.50	55.500	.002
Kontrol	17	12.26	208.50		

Deney ve kontrol grubundaki çocukların, proje öncesinde ön test puan ortalamalarına ilişkin Mann Whitney U Testi sonucuna göre iki grup arasında (deney ve kontrol) anlamlı fark olmadığı belirlenmiştir ( $U = 133.000$   $p > .05$ ). Deney ve kontrol grubundaki çocukların, proje sonrasında son test puan ortalamalarına ilişkin Mann Whitney U Testi sonucuna göre iki grup arasında (deney ve kontrol) anlamlı fark olduğu belirlenmiştir ( $U = 40.000$   $p < .001$ ). Deney grubu ortalaması, kontrol grubu ortalamasından anlamlı derecede yüksek bulunmuştur. Deney ve kontrol grubundaki çocukların, proje sonrasında tekrar son test puan ortalamalarına ilişkin Mann Whitney U Testi sonucuna göre iki grup arasında (deney ve kontrol) anlamlı fark olduğu belirlenmiştir ( $U = 55.500$   $p < .001$ ). Deney grubu ortalaması, kontrol grubu ortalamasından anlamlı derecede yüksek bulunmuştur.

Tablo 4. İkinci Grup Çocuklarının (Deney grubu) Proje Öncesi ve Sonrası Ön Test-Son Test Puan Ortalamalarına İlişkin Wilcoxon İşaretli Sıralar Testi Sonuçları

Son Test- Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	0	.00	.00	5.16	.000
Pozitif Sıra	35	18.00	630.00		
Eşit	0				

İkinci grup çocuklarının (deney grubu) proje öncesinde ve sonrasında aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olduğu tespit edilmiştir ( $z = 5.16$   $p < .001$ ). Program sonrasındaki son test puan ortalaması, ön test puan ortalamasından yüksektir.

Tablo 5. İkinci Grup Çocuklarının (Kontrol grubu) Proje Öncesi ve Sonrası Ön Test-Son Test / Puan Ortalamalarına İlişkin Wilcoxon İşaretli Sıralar Testi Sonuçları

Son Test- Ön Test	n	Sıra Ortalaması	Sıra Toplamı	z	p
Negatif Sıra	7	8.21	57.50	1.787	.074
Pozitif Sıra	13	11.73	152.50		
Eşit	15				

2. grup çocuklarının (kontrol grubu) proje öncesinde ve sonrasında aldıkları puanların Wilcoxon İşaretli Sıralar Testi sonucuna göre toprak konusu ile ilgili bilgi puan ortalamaları arasında anlamlı fark olduğu tespit edilmiştir ( $z = 1.787$   $p < .05$ ).

Tablo 6. İkinci Gruptaki Deney ve Kontrol Grubundaki Çocukların Proje Öncesinde Ön-Son ve Tekrar Son Test Puan Ortalamalarına ait Mann Whitney U Testi Sonuçları

Ön test	n	Sıra Ortalaması	Sıra Toplamı	U	p
Deney	35	38.20	1337.00	518.000	.265
Kontrol	35	32.80	1148.00		
Son test	n	Sıra Ortalaması	Sıra Toplamı	U	p
Deney	35	35	50.16	99.500	.000
Kontrol	35	35	20.84		

Deney ve kontrol grubundaki çocukların, proje öncesinde ön test puan ortalamalarına ilişkin Mann Whitney U Testi sonucuna göre iki grup arasında (deney ve kontrol) anlamlı fark olmadığı belirlenmiştir ( $U = 518.000$   $p > .05$ ). Deney ve kontrol grubundaki çocukların, proje sonrasında son test puan ortalamalarına ilişkin Mann Whitney U Testi sonucuna göre iki grup arasında (deney ve kontrol) anlamlı fark olduğu belirlenmiştir ( $U = 99.500$   $p < .001$ ). Deney grubu ortalaması, kontrol grubu ortalamasından anlamlı derecede yüksek bulunmuştur.

### Sonuç

Araştırmanın sonuçlarına göre okul öncesi dönem çocuklarına toprağı tanıtmak ve toprağı koruma doğrultusunda çevre bilincini kazandırmayı amaçlayan toprak eğitiminin, deney grubundaki 1. ve 2. grup çocuklarının toprakla ilgili (özellikleri, yararı, üstünde ve altında yaşayan canlılar, işlevleri, toprağı koruma, erozyon konularında) bilgi puanlarını kontrol gruplarına göre istatistiksel açıdan anlamlı biçimde arttırdığı belirlenmiştir. Ayrıca deney gruplarının toprakla ilgili bilgi puanları proje sonrasında artış göstermiştir. Sonuçlar projenin etkililiğini ortaya koymaktadır.

Proje üçüncü kez Denizli’de uygulanmaktadır. İlki, 2009-2010 eğitim-öğretim yılında 5-6 yaş çocuklarına ve ailelerine uygulanmıştır. İkincisi ise 2010 yılında Denizli Sosyal Hizmetler Müdürlüğü Çocuk Yuvası’nda kalan 7-12 yaş grubundaki korunmaya muhtaç çocuklara uygulanmıştır. İki proje uygulamasının sonuçları, gerek okul öncesi dönem çocuklarının gerekse korunmaya muhtaç çocukların proje sonunda bilgi puanlarında artış olduğunu göstermektedir (Gülay, Önder, Turan-Güllaç, & Yılmaz, 2011; Gülay, Yılmaz, Turan Güllaç, & Önder, 2010).

Türkiye’de ve yurt dışında 5-6 yaş çocukları için hazırlanmış bir toprak eğitimi projeleri oldukça az sayıdadır. Ancak Türkiye’de genel olarak okul öncesi dönem çocuklarının çevre algısını etkileyen değişkenlere yönelik betimsel çalışmalara rastlamak mümkündür (Kesicioğlu & Alisinanoğlu, 2009; Taşkın & Şahin, 2008). Uygulamalı çalışmalar içerisinde de Bursa’da 2000-2001 eğitim öğretim yılında ilköğretim ve anaokullarında gerçekleştirilen Uygulamalı Çevre Eğitimi Projesi ile müzik çalışmaları ağırlıklı olmak üzere çeşitli etkinliklerle ile çevre ile ilgili konular ele alınmıştır (Sungurtekin, 2001). Yurt dışındaki örneklere bakıldığında ise İngiltere’de 2003 yılında başlayan Orman Okulları (Forest Schools) Projesi’ne 6-8 yaş arasındaki çocuklar katılmıştır. Çocukların gelişim düzeylerine göre oluşturulan oyunlar, problem çözme, yaratıcı düşünme, etkinliklerinden meydana gelen projenin sonunda çocuklarda çevre bilincinin artmasının yanı sıra sosyal ilişkilerinin ve kendilik değeri algılarının geliştiği belirlenmiştir (Swarbrick, Eastwood, & Tutton, 2004). Wilson (1996) da çeşitli ülkelerdeki (Amerika, İngiltere, Kanada, Hindistan) okul öncesi çocuklarına yönelik 9 çevre eğitimi programını incelediği çalışmasında, çevre eğitimi programlarının etkili hale getiren ortak noktalar belirlenmiştir. Bu ortak noktalar, yaşanan çevrede ön plana çıkan yakın çevre sorunlarına odaklanılması, doğal ortamlarda gerçekleştirilen etkinliklerin ön planda olması, empati gelişiminin desteklenerek, doğal çevreye yönelik duyarlılığın artırılması, programların çocukların gelişim özelliklerine göre hazırlanması, 2-3 saatlik, yarım günlük sürelerden oluşmaları ve ailelere yönelik çalışmaların da yer almasıdır. Görüldüğü gibi gerek bu çalışmada gerek konu ile ilgili benzer çalışmalarda, okul öncesi dönemde çevre eğitiminin çocukların çevre duyarlılığını arttırmasının yanı sıra diğer gelişim alanlarını da geliştirdiği belirlenmiştir. Özellikle son 30 yıldır çevre sorunlarındaki artış, çevre eğitiminin okul öncesi eğitimden başlayarak tüm eğitim kademelerinde sistematik biçimde yer almasını bir zorunluluk haline gelmiştir. Bu noktada küçük çocuklar için hazırlanacak çevre eğitimi programlarının sayı, çeşit ve nitelik olarak arttırılması önem taşımaktadır. Ayrıca eğitim programlarına öğretmenlerin ve anne babaların da daha aktif olarak katılımı sağlanmalıdır.

Proje ile ilgili bazı sınırlılıklar da bulunmaktadır. Proje, belirtilen hedef kitleyle ve dokuz günlük bir eğitim programı ile sınırlıdır. Sonraki çalışmalarda, daha uzun süreli ve daha geniş hedef kitleleri kapsayan projeler gerçekleştirilebilir. Bu projede son tekrar testler proje takvimi nedeniyle en geç iki hafta sonra gerçekleştirilmektedir. Gelecekte yapılacak çalışmalarda tekrar test sayısı arttırılarak, projenin uzun süreli etkileri de incelenebilir. Proje toprak konusu ile sınırlıdır. Ancak geliştirilecek diğer projelerde daha farklı konular ya da daha çok sayıda konu proje kapsamına alınabilir. Proje düşük sosyo-ekonomik düzeyden gelen çocuklar ve aileleri ile sınırlıdır. Sonraki çalışmalarda farklı sosyo-ekonomik düzeyden gelen ailelerle de çalışılabilir.

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# TOWARDS HOP-COUNT MAPPING IN A RANDOM WIRELESS SENSOR NETWORK

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## ABSTRACT

Networks composed of a large number of tiny sensors, also known as “smart dust”, can provide long range observation of phenomena that can only be detected at short range or contact. Mapping is necessary so that information arriving from a particular sensor can be linked to a location within the network. Previously we determined that distances can be accurately measured by counting the number of hops or rebroadcasts that are necessary to transmit a message between two sensors. In the present paper we investigate whether it is also possible to determine angles which may be combined with distances to determine relative position

## INTRODUCTION

The function of a sensor is to detect and if possible locate objects or events. Long range systems such as radar, sonar or imaging can achieve this with a single sensitive element. However, some phenomena such as vibration or temperature can only be detected at short range or even contact. It may therefore be helpful to extend the detection range by using several sensors or even a network.

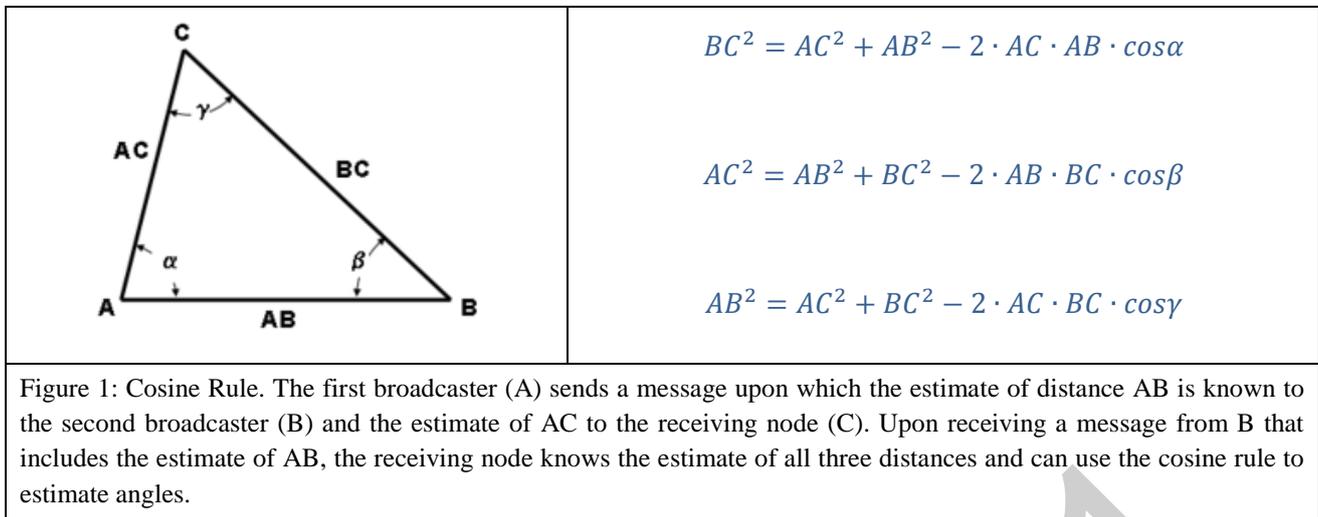
We are interested in a network that would contain a large (~10<sup>4</sup>) number of tiny sensors. Sensors of millimeter size have indeed been developed including energy generation and storage, sensory element and communication [7]. A large number of such sensors, distributed over a large area, can detect objects and events in their neighborhood and broadcast the information to a user located somewhere in the network. This type of network could be described as smart dust and has been proposed to secure military terrain [6], at home [5] in vineyards [4] or to detect forest fire [3].

Mapping is an important aspect of a sensor network. Information obtained from a sensor within the network is of limited use if the location of that sensor is unknown. Mapping is relatively simple if the sensors are equipped with navigation aid such as GPS. However, if the sensors need to be tiny or cheap this may not be possible. Alternatively the communication aid can be used also to determine distances [1] or angles [2].

An interesting possibility is to use the fact that a tiny sensor is likely to be equipped with a weak communication aid so that it can only contact a limited number of sensors in the immediate neighborhood. In order to broadcast a message across the network the neighboring sensor nodes need to rebroadcast it to their neighbors. This step has to be repeated a number of times until the message has reached its destination. The number of rebroadcasts or hops that is necessary to transmit a message between two sensor nodes may be used to estimate the distance between them.

Previously we have carried out simulations to investigate the effectiveness of hop-counting as a distance measure [6]. The message does not usually travel in a straight line and the distance is initially overestimated. However, we found that for a given actual (geometric) distance, the fluctuation of the hop-count (estimated distance) between many simulated network realizations is small and that a linear relationship between actual and estimated distance so that the accuracy can be increased by calibration. When a node communicates with 5-10 neighbors, sufficiently large distances could be estimated with 1% accuracy or better in a homogeneous network [6].

In the present paper we consider angle measurement as a next step towards determining positions of the sensors within the network. For this it is not sufficient to determine distances with respect to one broadcasting node. Therefore, we propose a protocol where randomly selected nodes broadcast a message across the network at random intervals. When distances are known towards two or more broadcasting nodes it becomes possible to estimate angles between the lines of sight towards those sensors. We present a number of simulations to determine the accuracy of these estimates and the possibility to use them to obtain relative positions within the network.



### BACKGROUND INFORMATION

The concept of hop-counting has been explained previously [6]. Briefly, two nodes are neighbors when they are within a hop-range from each other. A hop-route is a series of nodes where each is a neighbor to the next. The hop-count or hop-distance between two nodes is defined by the shortest possible hop-route that connects them. In an actual network this distance can be obtained by broadcasting a message that includes the number of re-broadcasts. A node may receive the message more than once but will re-broadcast only the one with the lowest re-broadcast number. This number is also its hop-distance from the origin.

In a simulation we perform a global search to find the shortest hop-route between two nodes. This is most efficiently done with a similar procedure. We first determine which nodes are neighbors to each other. Once an origin has been selected we determine first the nodes that are located at a distance of one hop, then the ones located at two hops, etc. until the network has been covered. This provides the hop-distance to all nodes within the network.

Angles can be estimated when a message is received from two distinct nodes. The geometric angle is simply the angle between the lines of sight that connect the receiving node to the two broadcasters. In the aforementioned scenario, when a node has received a message from two broadcasters, the estimated distance to those broadcasters is also known. Together, the three nodes form a triangle. But, in order for the receiving node to estimate the angles within that triangle it also needs to know the distance between the two broadcasters. This was obtained by the second broadcaster when it received the message from the first. An obvious solution is that the second broadcaster includes this information in the message that it sends across the network. With this information the receiving node can use triangulation to estimate its position with respect to the two broadcasters. The mathematics to do this is rather simple: just use the cosine rule as can be seen in figure 1.

In some exceptional cases, a triangulation result will not be obtained, i.e. when the summed distance of a node to two broadcasters is less than the presumed distance between the broadcasters. Also when the nodes involved are nearly on a straight line, the position estimate will not be accurate. The individual nodes will observe this and the position estimation algorithm should be accommodated for such exceptions.

### SIMULATION RESULTS

Figure 2 illustrates our approach. We have simulated a network of 7600 nodes randomly scattered in an square area of size 1000 x 1000 m. The hop-range (i.e. the range at which neighbors can contact each other) was set to 25 m so that on average a node is able to contact 15 neighbors. Two broadcasting steps are shown. The positions of all nodes are plotted and those of the broadcasters are marked. The colored rings illustrate the rebroadcasting process (number of hops). The straight lines mark the lines of sight between the two broadcasting nodes and the receiver and the lines curling around them mark a shortest hop-route that was found between them. These routes do not exactly follow the lines of sight and the distance estimated from them overestimates the actual distance. The extent of this deviation depends on hop-range, node density and the length of the route.

The two images of figure 2 show the two steps of the angle determination process. For each step a random node was selected as the broadcaster (A and B). A third node was selected to be displayed as a receiver (C). In fact all nodes receive the messages and can use triangulation to determine their position with respect to the broadcasters. In the first step distances are determined with respect to the first broadcaster. In the second step the distance from the second broadcaster to the receiver is determined. Since we assumed that this message also includes the distance between the two broadcasters, all three distances are then known to the receiver upon which it can estimate the angles as described above and its position with respect to the two broadcasters.

Figure 3 illustrates the position estimate obtained by the receiver. The dotted lines represent the actual distances. The solid lines represent the estimated distances. The two triangles are overlaid by placing the first broadcaster in the origin and the second one on the positive X-axis. One can clearly see that, the calculated estimated angles correspond well to the real angles. The size of the triangle is overestimated, but the fact that the angles are not, agrees with our previously obtained result that distances are overestimated by a constant factor which can be corrected for by calibration [6].

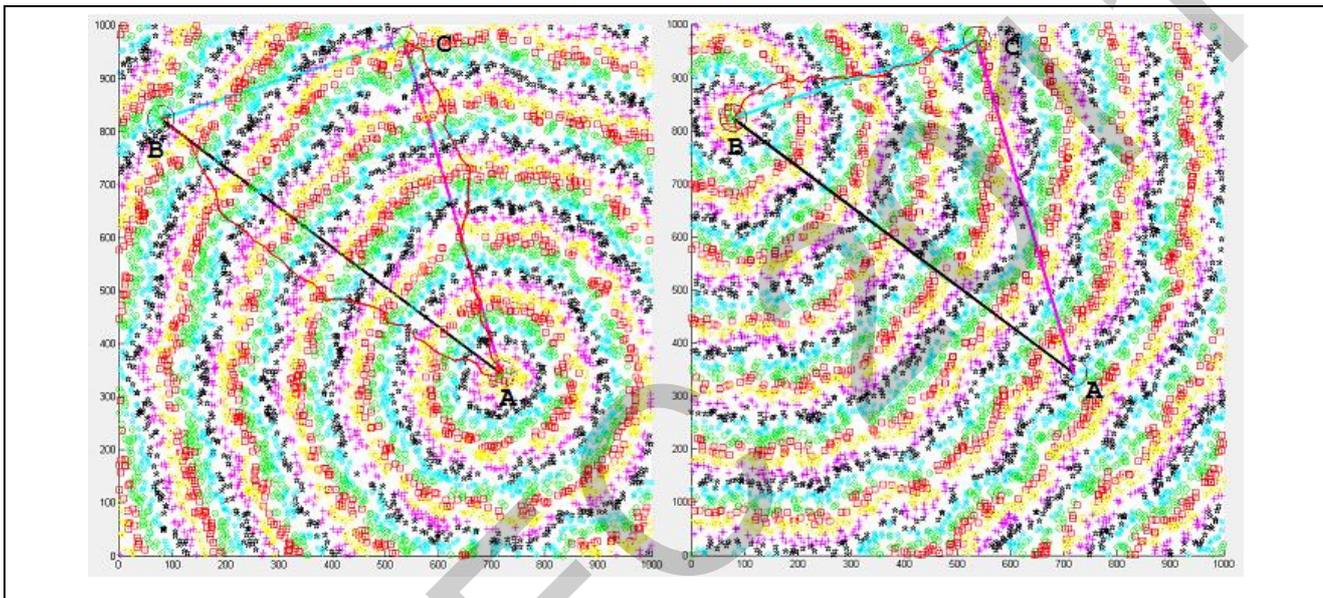


Figure 2: Three reference nodes. Node A which lies in the center of the broadcast circles (left drawing) broadcasts a message “I’m the first”. This message along with the number of hops is received by nodes B and C (the red lines indicate a possible route). In the right upper drawing node B broadcasts his message “ I’m number two and my distance to node A is ... hops”. This message is received by reference node C which now can calculate its position relative to the first two reference nodes.

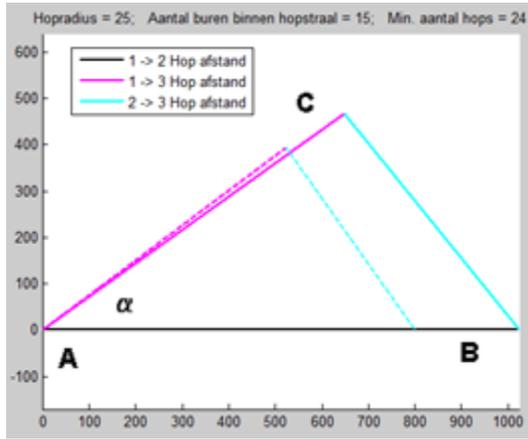


Figure 3: Local coordinate system. The dotted lines represent the 'real' distances between the reference nodes, while the solid lines symbolize the 'hop' distances. The two triangles were superimposed. Reference node A is positioned in the origin and node B lies on the positive X-axis (black line). Reference node C is positioned in the positive XY-plane. This coordinate system, however, can be translated and rotated at will without effecting the relative position. Compared with figure 2 this particular system is also mirrored with respect to the X-axis.

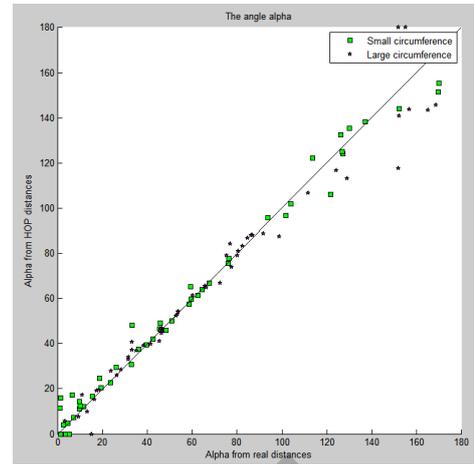


Figure 4: Results of a 101 runs simulation. In this figure the 'real' angle is plotted against the 'hop' angle. Ideally all the data points should lay on the solid line (hop angle = real angle). It is however clear that at angles smaller than 20° or larger than 120° degrees errors occur.

Also the calculated coordinate system is rotated and mirrored with respect to the original map. While relative positions can be obtained and produce an actual map, which may be refined by including more nodes, the orientation of the map is impossible to obtain using only distance estimates. Without the calibration constant, also the scale of the map is unknown. However, for many applications this is not a problem. Otherwise, association with an actual geographic map is necessary.

So far we have only considered one node network. To get a more general view about the accuracy of the angle measurements we have performed a series of simulations. With the same parameters as used in the example above, we constructed random networks in which we selected random reference nodes (A, B and C) and determined the angle ( $\alpha$ ) between the lines AB and AC. The results are shown in figures 4 and 5. From figure 4 one can conclude that hop distances between the reference position can be used to estimate this so called 'hop' angle. With this angle and the distances one can determine the relative position of the nodes. Most of the hop angles are situated near the 'real' angle, especially between 20° and 120°.

In the other cases the hop angle does not appear to be so accurate. This could be expected because as can be seen in figure 5a and b reference node C is near to the line through A and B. In such cases a small error in the distance measurements has a large impact on the estimated angle. In reality, however, more reference nodes will be available with which better results will be obtained.

We also investigated the relationship between the circumference of the triangle and the calculated angle alpha. In figure 4 the green squares represent results found with ‘small’ triangles while the purple stars represent the ‘large’ triangles. A triangle is called ‘small’ if its circumference is less than the median of the circumferences in the series. It was expected that the large triangles (in which high hop distances occur) would result to more accurate hop angles. From figure 4 however such a relationship is not quite obvious. There are of course more parameters to be considered. For example the situation sketched in figure 5d where A and B are near each other. In this case,  $\alpha$  is not extreme and the triangle is not ‘small’ but still the found result is not accurate. This case can also be dealt with when more reference nodes are available. This requires more detailed research.

### DISCUSSION

We propose a protocol by which sensor nodes can use triangulation to determine their position within a wireless network. This protocol is especially useful for so called smart dust, i.e. networks composed of a very large number of tiny sensors with limited communication range. The number of re-broadcasts that is necessary to transmit a message between two nodes forms a measure for the distance between them. Here we have shown that, by measuring distances with respect to several nodes, angles can also be estimated yielding to relative positioning.

For our simulation it was sufficient to randomly select sensors within the network but in an actual case the network should figure this out by itself. This may be done as follows. After startup each node selects a random delay after which it will declare itself ‘first’ broadcaster and transmit a message. The sensor that has selected the shortest time will actually send the message. When the other nodes receive this message they will cancel theirs and select a new random delay.

Since a finite time is necessary to broadcast a message across the network it is possible that a sensor transmits a message without realizing that one is already being broadcasted. This is a collision and means that the entire broadcast needs to be cancelled. If too many collisions occur the time period is too short (for the size of the network) and the sensors should decide to lengthen it.

After some initialization a proper delay period will have been established and broadcasts will take place at more or less regular intervals using random sensors that have selected themselves. The broadcasters will function as temporary reference nodes for the rest of the network. When the process continues more and more reference nodes will be available for the triangulation. This removes ambiguity since a position determined by triangulation is not always unique. But, more importantly, it provides

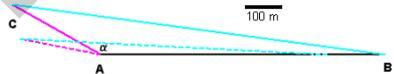
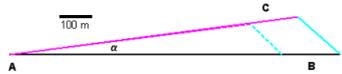
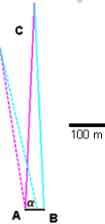
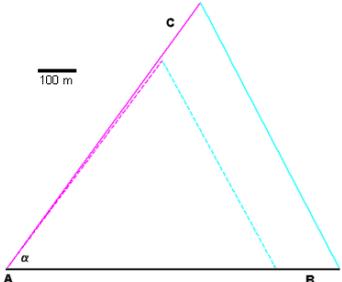
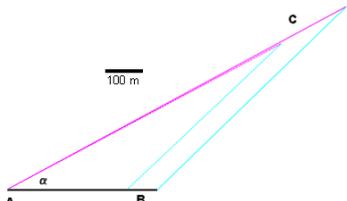
		
<p>a. Very small angle (<math>&lt;20^\circ</math>)</p>	<p>b. Very large angle (<math>&gt;120^\circ</math>)</p>	<p>c. Small angle (<math>\approx 20^\circ</math>)</p>
		
<p>d. A near to B</p>	<p>e. Ideal situation (<math>20^\circ &lt; \alpha &lt; 120^\circ</math>)</p>	<p>f. Ideal situation (<math>20^\circ &lt; \alpha &lt; 120^\circ</math>)</p>

Figure 5. Typical local coordinate systems from the simulation series from figure 4. Cases c, e and f give accurate results while a, b and d require additional reference nodes (see text).

redundancy which will significantly increase the accuracy of the triangulation result.

In our paper we have only discussed two broadcasts since this is the minimum number after which triangulation is possible. The receiver then perceives itself in a triangle with the two broadcasters. When this was superimposed with the actual triangle the results matched rather well although, as expected, the size was overestimated. When comparing a large number of estimated and actual angles, we found a good agreement. In some cases the results are less accurate, for example when the angle is near to its extreme.

In some cases the positions of the randomly selected reference nodes are unsuitable leading to very inaccurate angle estimates. This is the case when two or more reference nodes are very near to each other or when three or more are located near to a straight line. Some of these cases also occurred in our simulations. However, this should not be a major problem since these cases occur only with a small probability and the receiving sensor will notice this and therefore know that the estimate is inaccurate. When a larger number of reference nodes is used sufficient suitably located reference nodes will be available for accurate triangulation. In fact the selection method proposed above may be adapted so that sensors in suitable locations are more likely to select themselves as the next broadcaster.

Finally, we conclude that that accurate angle estimates can be derived from hop-distance measurements and can be used to determine the positions of sensors within a wireless network by triangulation. This requires regular broadcasts from a random sensor within the network which will act as a temporary reference node. So far we have only considered two broadcasters, but this can be extended to provide redundancy and prevent inaccurate triangulation from ill positioned reference nodes. In the future we hope to determine actual maps with this procedure and determine their accuracy

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# TRAFFIC POLLUTANTS LEVELS AT DIFFERENT DESIGNS OF KING FAHD ROAD, SAUDI ARABIA: COMPARATIVE STUDY

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## ABSTRACT

Dammam and Khobar governorates constructed tunnels and bridges on King Fahd road. This study aimed at comparing traffic pollutants' levels on normally designed parts and at about 50m from the portals of tunnels and bridges. This study was conducted during March to August 2009. Particulate matter; traffic vapors and gases; and noise were measured at roadside level at the three designs of King Fahd Road in the two governorates. Levels of particulate matter, total volatile organic compounds, sulfur dioxide, carbon monoxide, and noise at the normally designed parts of King Fahd road [687(25.4) $\mu\text{g}/\text{m}^3$ , 1.0(1.0) 0.1(0.2), 4.0(5.0) ppm and 76.5(6.3)dB] were higher than that at tunneled [359.1(231.0), 1.0(1.0), ND(0.1), 2.0(2.0) and 72.8(5.3)] and bridged parts [420.4(259.8), ND(1.0), ND(0.0), 1.0(2.0) and 72.2(5.3)] respectively. Therefore, it can be concluded that traffic pollutants at tunneled and bridged parts of King Fahd road were lower than that at normally designed parts.

Key Words: Carbon monoxide, particulate matter, road re-design, sulfur dioxide, total volatile organic compounds, traffic gases, traffic pollution, traffic vapors.

## 1. INTRODUCTION

In the past, the major sources of poor air pollution were industrial activities and domestic heating. Nowadays; traffic pollution is predominant and significantly contributes in the urban air quality problems especially in roads of condensed traffic. Traffic congestion contributes to traffic pollution, and hence affects public health, and may cause annoyance particularly for those live, or work in heavy traffic roads. Traffic emissions and noise levels are higher in congested, stop-and-go and idling traffic than they are when traffic is moving at a steady speed (Balbus et al., 2010; Ingle, Wagh, Pachpande, Patel, & Attarde, 2005; Kassomenos, Karakitsios, & Papaloukas, 2006; Potoglou & Kanaroglou, 2005).

Traffic pollution is a drastic public health problem in both developed and developing nations (Issever et al., 2005). It is usually associated with human health hazards including asthma exacerbations and other cardiovascular illness (de Kok, Driece, Hogervorst, & Briede, 2006; Linn & Gong, 1999). Moreover, traffic pollutants, of which particulate matter (PM), total volatile organic compounds (VOCs) sulfur dioxide ( $\text{SO}_2$ ), and carbon monoxide (CO), have significant effects on emergency department visits for asthma among children less than 2 years and elderly of more than 75 years (Villeneuve, Chen, Rowe, & Coates, 2007). According to World Health Organization, 2004 atmospheric pollution is the cause of 2.4 million deaths per year worldwide (Chimonasa & Gessner, 2007). In addition to their adverse effects on public health, traffic pollutants have also great impact on the environment that causes public health problems. These environmental impacts include depletion of ozone layer, generation of tropospheric ozone, greenhouse effects and acid deposition phenomenon (EPA, 2004; Fenger, 2009).

Dammam is the capital of the Eastern Province of Saudi Arabia. It is about 400 km away from Riyadh. It is the major seaport of the region. Khobar is another large city in the Eastern Province. It is one of the main commercial centers. In addition, there is increase in the migration of people to Dammam and Khobar governorates for getting job and studying. King Fahd Road is one of the heavy traffic roads that connects the two governorates Dammam and Khobar and penetrates them deeply. The two fractions of the road penetrate Dammam and Khobar are characterized by length, multiple activities, and heavy traffic. There are industries, universities and different governmental and commercial centers in the King Fahd Road. Hence, air pollution abatement will remain a challenge because of increasing demands for transportation (Potoglou & Kanaroglou, 2005). Recently, increasing traffic flow on Dammam and Khobar roads leads to traffic congestion that necessitates developing and implementing transportation control strategies, of which road redesign is one of the important strategies (NG, 2000; Orubu, 2004).

So, the two governorates implemented projects of re-designing King Fahd Road. Their objectives were to ease and speed up the transportation and reduce travelling time and time wasted at intersections (UNITED NATIONS, 2002). This took place by considering the two fractions in the road penetrate Dammam and Khobar governorates. Then, each road fraction was divided into three parts. The first part was left with normal design (normally designed parts). The second and third parts were re-designed by construction of tunnels and bridges (tunneled and bridged parts). On each of the tunneled and bridged parts the road was divided into two alternative pathways, one of which was the tunnel or bridge (below or above the roadside level) and the other was the normal road (at the roadside level). Hence, vehicles at the modified parts of King Fahd road were distributed between the two alternative pathways. Consequently, traffic congestion and idling traffic was greatly reduced and traffic flow was increased.

The research questions were whether the traffic pollutants at the roadside level on normally designed parts and at re-designed parts at about 50 m from the portals of tunnels or bridges are similar or not? And which road design is the best from air pollution and public health points of view? So this study aims at comparing traffic pollutants' levels on normally designed parts of King Fahd road and at about 50 m from the portals tunnels and bridges at the roadside level and thus recommending the best design from air pollution and public health points of view.

## 2. MATERIAL AND METHODS

The study was conducted during March to August 2009 (after nearly one year of completing construction of tunnels and bridges under study) at the fractions of King Fahd road penetrate deeply in Dammam and Khobar governorates.

The sampling stations were located on the Curbside at the roadside level on the normally parts and at 50 m from the portals of both tunnels and bridges to be away from intersections and the portals of tunnels and bridges. The first parts in each fraction represented normally designed parts of road in both Dammam and Khobar (two sampling stations). The second and third parts represented parts of road modified by constructing tunnels and bridges in the two governorates (four sampling stations). Therefore, six sampling stations were included in the two governorates. Sampling occurred during the morning rush hours (6 am – 8 am) at the working days (Saturday – Wednesday).

Four traffic pollutants were measured during the present study including: particulate matter (PM) which was measured in micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ); total volatile organic compounds (VOCs), sulfur dioxide ( $\text{SO}_2$ ), and carbon monoxide (CO) which were measured in parts per million (ppm); in addition to noise levels in decibel (dB). The EntryRAE (PGM-3000) Multi-Gas Monitor was used for measurement of VOCs and the VRAE Hand Held 5 Gas Surveyor (Model 7800 Monitor) was used for measurement of  $\text{SO}_2$  and CO. For Quality Assurance purposes, data of the two gas monitors were calibrated against known concentrations of these gases. Noise levels were measured using Sound Level Meter Model CA832 calibrated at 114 dB. At each sampling station, 25 readings (over two-hour period) were directly recorded on the basis of 5 minutes averages for each gaseous pollutant and noise levels. Therefore, in the present study, there were 6000 records for each of the VOCs,  $\text{SO}_2$ , CO and noise levels. Half of the 6000 records were taken from Dammam and the other half from Khobar.

Particulate Matters were sampled on 60 mm diameter glass fiber filters by the pre-calibrated Hand Held Battery Portable air sampler on the basis of two- hour samples. After sampling, the filters were transferred to the Occupational Health and Air Pollution Research Unit Laboratories in High Institute of Public Health, Alexandria University, for further gravimetric determination and calculation of PM concentrations in  $\mu\text{g}/\text{m}^3$ . Therefore, there were 600 PM records, 300 of which from Dammam and the other 300 from Khobar.

### Statistical Analysis

Data entry, statistical analysis and graphical presentation of data were done at High Institute of Public Health, Alexandria University using SPSS-16 package (Chicago, Illinois, 2007). The used statistical analysis were: Kolmogorov-Smirnov and Shapiro- Wilk tests of normality, descriptive statistics (median and interquartile range), Kruskal Wallis test as a significance test of more than two independent samples and Mann Whitney Test as a significance test of two independent samples.

## 3. RESULTS AND DISCUSSION

Traffic pollutants levels at roadside on normally designed parts of King Fahd Road were higher than that at 50 m from the portals of tunnels and bridges. The total volatile organic compounds (VOCs), sulfur dioxide ( $\text{SO}_2$ ) and carbon monoxide (CO) showed highly significant Kolmogorov-Smirnov and Shapiro-Wilk tests of normality ( $p < 0.05$  at 95% C.I). Therefore, VOCs,  $\text{SO}_2$  and CO were non-parametric variables (did not follow normal distribution). Particulate matter (PM) and noise levels proved non-significant Kolmogorov-Smirnov and Shapiro-Wilk tests ( $p > 0.05$  at 95% C.I). Hence, they were parametric variables (follow normal distribution). For simplification, all numeric variables were assumed to be non-parametric (Glasser, 2005). Therefore, the data were expressed as [median (Inter-quartile range IQR)] and the tests of significance used were the non-parametric tests (Kruskal-Wallis and Mann Whitney tests).

### 3.1. Traffic Pollutants at the Two Governorates

The levels of PM [545.2(210.6)  $\mu\text{g}/\text{m}^3$ ], VOCs [1.0(2.0) ppm],  $\text{SO}_2$  [0.1(0.1) ppm], CO [3.0(3.0) ppm], and noise [74.5(5.9)dB] on King Fahd road in Dammam were higher than that in Khobar [287.9(428.6)  $\mu\text{g}/\text{m}^3$ ], [Non-detected ND (1.0) ppm], [ND(0.1) ppm], [2.0(2.8) ppm], and [73.1(6.4) dB] respectively (table 1). This may be attributed to higher traffic volume as a result of higher commercial activities and presence of educational institutions on King Fahd road in Dammam. Mann-Whitney test revealed the highly significant differences of the five traffic pollutants' levels between the two governorates. This means that differences of traffic pollutants' levels between the two governorates were not due to chance.

### 3.2. Traffic Pollutants at Normally Designed and Modified Parts of the Road

The levels of PM, VOCs,  $\text{SO}_2$ , CO, , and noise levels at the normally designed parts of road [687(25.4)  $\mu\text{g}/\text{m}^3$ , 1.0(1.0) 0.1(0.2), 4.0(5.0), ppm and 76.5(6.3)dB respectively] were higher than that at tunneled [359.1(231.0)  $\mu\text{g}/\text{m}^3$ , 1.0(1.0), ND(0.1), 2.0(2.0) ppm, and 72.8(5.3) dB] and bridged parts [420.4(259.8)  $\mu\text{g}/\text{m}^3$ , ND(1.0), ND(0.0), 1.0(2.0) ppm and 72.2(5.3) dB respectively] (figures.1, 2, 3, 4, 5). This may be due to different designs of King Fahd road in which the vehicles on tunneled or bridged parts were distributed between the two alternative pathways. This may reduce both traffic congestion, and idling and increase traffic flow. Hence, traffic pollutants at tunneled and bridged parts were consequently reduced <sup>(4)</sup>. These findings were supported by two studies in Trento (Heimann et al., 2007 ), and Sydney(NSW, 2010) <sup>(18)</sup>. which concluded that emissions released from bridges and tunnels respectively reduce surface traffic congestion and improve roadside air quality(LightHouse, 2007).

It is also clear from figure 1 that at the roadside level, PM at tunneled parts of road [359.1(231.0)  $\mu\text{g}/\text{m}^3$ ] were lower than that at bridged parts [420.4(259.8)  $\mu\text{g}/\text{m}^3$ ] (NSW, 2010) <sup>(18)</sup>. In addition, PM levels at tunneled and bridged parts were 52% and 61% of that at normally designed parts respectively. This may be attributed to the aerodynamic diameter and collision of PM with walls and ceilings of the tunnels that may enhance settling at tunneled parts and consequently, reduce PM concentrations at the roadside level. In addition, PM excitation and dispersion at bridged parts of road reduce the settling velocity and enhance suspension in the atmosphere consequently increase PM concentrations at the roadside level(EPA, 2010). Kruskal Wallis test indicated the highly significant variation of PM among the three designs ( $p < 0.05$ , at 95% C.I). Mann Whitney test showed

significant differences between PM concentrations at the roadside levels of normal and tunneled, normal and bridged and tunneled and bridged parts of King Fahd Road ( $p < 0.05$ , at 95% C.I.). This indicated that the observed differences of PM concentrations at different road designs were realistic and were not due to chance.

Considering traffic vapors (VOCs), figure 2 indicates the same VOCs levels at the roadside of tunneled and bridged parts. At bridged parts, the better vertical and horizontal diffusion and dilution of VOCs as a result of higher sources' heights reduce VOCs concentrations at roadside level while at tunneled parts the ceilings and walls of tunnels may absorb VOCs and hence, reduce their concentrations at roadside level (Heimann, et al., 2007 ; TAN, Vergel, & Camagay, 2006). Kruskal Wallis test indicated the highly significant variation in VOCs levels among the three road designs ( $p < 0.05$ , at 95% C.I.). Further analysis using Mann Whitney test revealed highly significant differences of VOCs at the roadside level between normal and tunneled and normal and bridged parts ( $p < 0.05$ , at 95% C.I.) and non-significant difference between tunneled and bridged parts ( $p > 0.05$ ). This means that the observed variations were not due to chance.

Regarding traffic gases,  $SO_2$  at the roadside level confirmed higher levels at tunneled [ND (0.1) ppm] than at bridged parts [ND (0.0) ppm] (figure 3). This may be due to the lower vertical and horizontal diffusion and hence lower dilution at tunneled than that at bridged parts. Kruskal Wallis test, indicated the highly significant variation of  $SO_2$  levels among the three road designs ( $p < 0.05$ , at 95% C.I.). Further analysis using Mann Whitney test revealed highly significant differences of  $SO_2$  levels between normal and tunneled, normal and bridged and tunneled and bridged parts ( $p < 0.05$ , at 95% C.I.). Therefore, the observed differences were realistic and were not due to chance.

The lower levels of CO at bridged [2.0(2.0ppm)] than at tunneled parts [1.0(2.0)] of road were owing to higher diffusion that increased by increasing heights of emission sources (figure-4). Kruskal Wallis test revealed the highly significant variation of CO at the roadside among the three road designs ( $p < 0.05$ , at 95% C.I.). Further analysis using Mann Whitney test revealed highly significant differences of CO between normal and tunneled, normal and bridged and tunneled and bridged parts ( $p < 0.05$ , at 95% C.I.). Hence, the observed differences were not due to chance.

Considering noise levels, figure 5 indicates that noise levels at the roadside of the bridged parts [72.8(5.3) dB] were slightly lower than that at tunneled parts [72.2(5.3) dB]. This ensures that traffic is the main source of noise in King Fahd road. Kruskal Wallis test revealed the highly significant variation of noise among the three road designs ( $p < 0.05$ , at 95% C.I.). Further analysis by Mann Whitney test revealed highly significant differences of noise levels between normal and tunneled, normal and bridged and tunneled and bridged parts ( $p < 0.05$ , at 95% C.I.). Therefore, the observed differences were realistic and were not due to chance.

All of the above results indicate the positive impact of the alternative roads on reducing traffic congestion and traffic pollutants levels. Both tunnels and bridges improve air quality at roadside level. The choice between tunnels and bridges depends mainly on the nature of traffic pollutants. That is to say, in case of higher PM concentrations, tunnels are more recommended while in case of higher traffic gases and noise levels bridges are more recommended.

### 3.3. Conclusions and Recommendations

Traffic pollutants at the roadside level of tunneled and bridged parts of King Fahd road were lower than that at normally designed parts. Particulate matters (PM) at tunneled parts were lower than that at bridged parts. Traffic gases ( $SO_2$ , CO), and noise levels were lower at bridged than at tunneled parts. Traffic vapors (VOCs) levels were similar at both tunneled and bridged parts.

It is recommended to design and implement tunnels and/or bridges as one of the transportation control strategies in heavy traffic roads to reduce traffic congestion and mitigate traffic pollution. This mainly has positive impacts on the public health.

Further studies are recommended to assess the importance and effect of using other emission control technologies (catalytic converter, and electric transport; continuous maintenance of vehicles and transformation into cleaner fuel) on reduction of traffic pollutants on roads. In addition, improvement of public transportation and encouragement of their use may also lead to reduction of traffic density and traffic pollutants.

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Table 1: Comparison of medians of PM, vocs, SO<sub>2</sub>, CO and noise at fractions of King Fahd Road in Dammam and Khobar Governorates during the period from during March to August 2009

	Dammam					Khobar					Mann-Whitney Test
	N <sub>0</sub>	Median	Q1	Q3	IQR	N <sub>0</sub>	Median	Q1	Q3	IQR	
PM	30	545.2	476.86	687.4775	210.6	30	287.9	245.2	673.9	428.6	<0.05
VOCs	300	1.0	ND	2.0	2.0	300	ND	ND	1.0	1.0	<0.05
SO <sub>2</sub>	300	0.10	ND	0.1	0.1	300	ND	ND	0.1	0.1	<0.05
CO	300	3.0	1.0	4.0	3.0	300	2.0	1.0	3.8	2.8	<0.05
Noise	300	74.5	71.8	77.7	5.9	300	73.1	69.6	76.0	6.4	<0.05
PM	Concentration of particulate matter (µg/m <sup>3</sup> )					CO	Concentration of carbon monoxide (ppm)				
VOCs	Concentration of total volatile organic compounds (ppm)					Noise	Noise level (dB)				
SO <sub>2</sub>	Concentration of sulfur dioxide (ppm)					IQR	Inter-quartile range = Q3 – Q1				
ND	Non-detected										

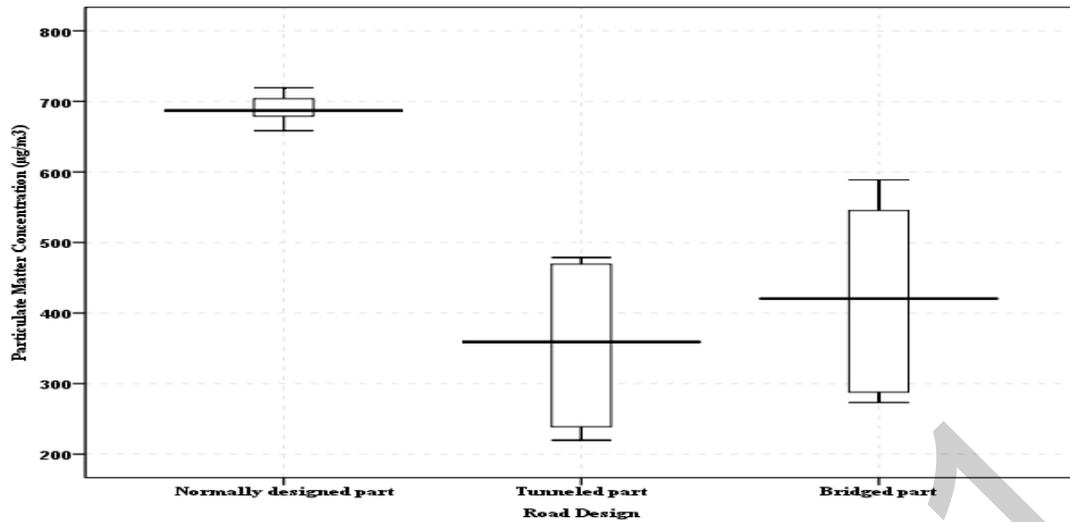


Figure (1): Particulate matter levels at normally designed parts and at 50m from the portals of tunnels and bridges on King Fahd Road in Dammam and Khobar Governorates during the period from March to August 2009

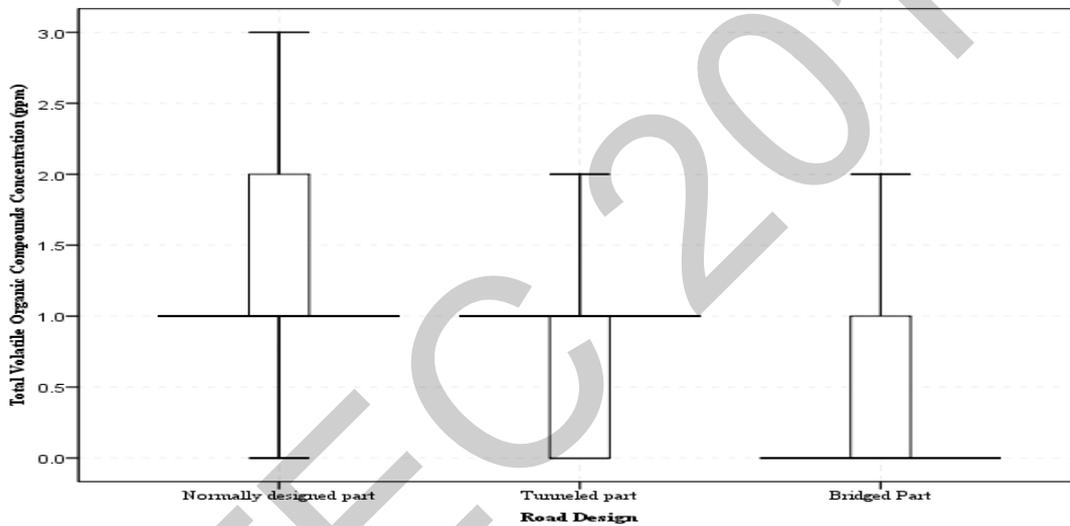


Figure (2): Total volatile organic compounds levels at normally designed parts and at 50m from the portals of tunnels and bridges on King Fahd Road in Dammam and Khobar Governorates during the period from March to August 2009

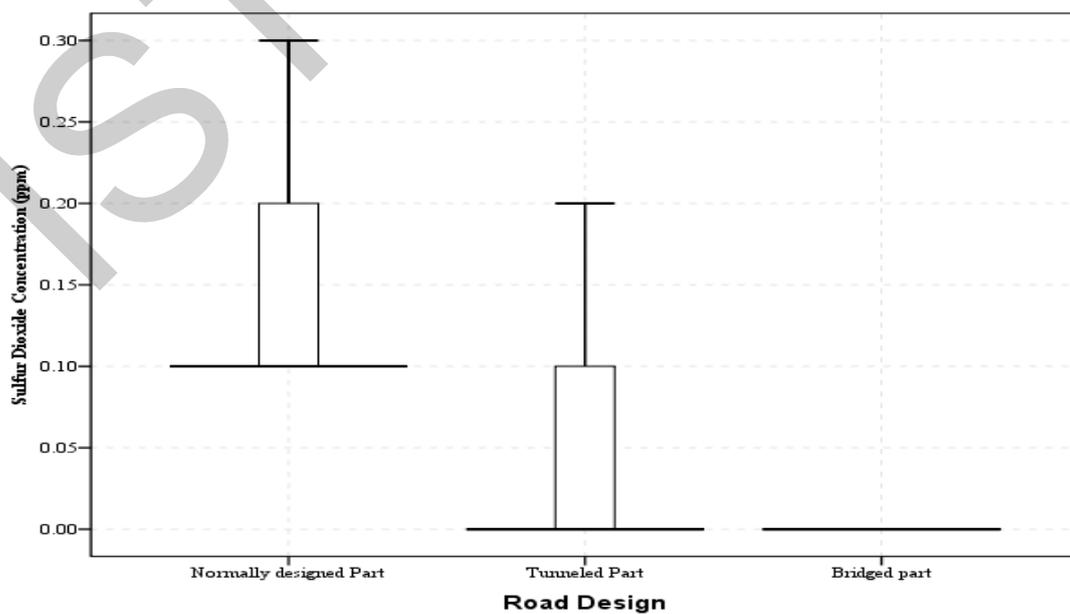


Figure (3): Sulfur dioxide levels at normally designed parts and at 50m from the portals of tunnels and bridges on King Fahd Road in Dammam and Khobar Governorates during the period from March to August 2009

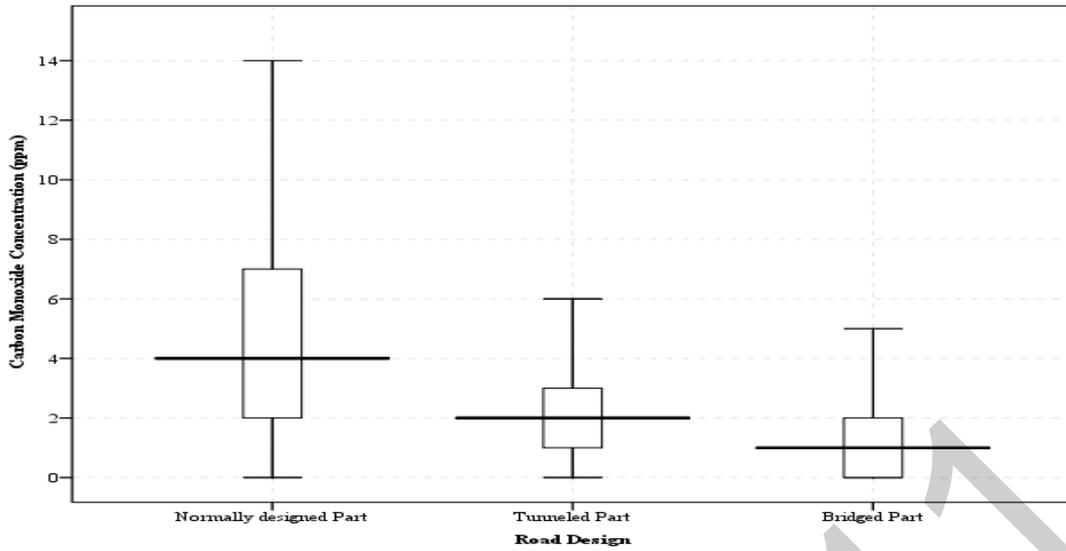


Figure (4): Carbon monoxide levels at normally designed parts and at 50m from the portals of tunnels and bridges on King Fahd Road in Dammam and Khobar Governorates during the period from March to August 2009

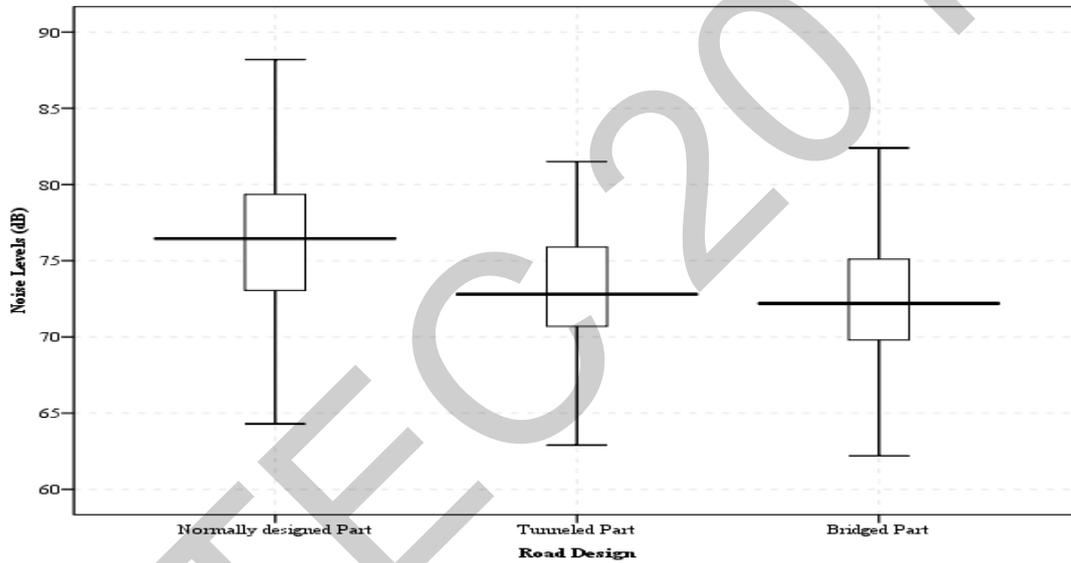


Figure (5): Noise levels at normally designed parts and at 50m from the portals of tunnels and bridges on King Fahd Road in Dammam and Khobar Governorates during the period from March to August 2009

# TREATMENT OF 2,4,5-TRICHLOROPHENOL BY MgAl-SDBS ORGANO-LAYERED DOUBLE HYDROXIDES: KINETIC AND EQUILIBRIUM STUDIES

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## ABSTRACT

Clay-based adsorbents were synthesized by incorporating anionic surfactants sodium dodecylbenzenesulfonate (SDBS), into LDH (MgAl-C) via ion exchange. The sample has been characterized by powder X-ray diffraction, FT-IR spectroscopy and B.E.T measurement. The result shows that SDBS adsorption on the calcined phase is enhanced by reconstruction of a matrix LDH with basal spacing of 30 Å. The product is an organo-LDH (MgAl-SDBS). The adsorption of 2,4,5-trichlorophenol (TCP) from solutions by MgAl-SDBS was investigated in a batch mode. The influence of pH, TCP concentration and temperature has been tested. The results showed that the kinetic adsorption could be described by a pseudo-second order model. The equilibrium isotherm was fitted to the Langmuir model with  $R^2$  of 0.992. Its maximum adsorption amount is 240.5 mg/g from this model at 298K and pH = 4. The negative value of  $\Delta G^0$  and the positive value of  $\Delta H^0$  indicate the spontaneous and endothermic nature of the process.

**Keywords:** Adsorption; MgAl-SDBS; 2, 4, 5-trichlorophenol; kinetics; thermodynamic.

## 1. INTRODUCTION

Water purification is of extreme importance in many parts of the world. Many of the world's water ways and water sources are polluted or contaminated with a range of chemicals including pesticides, herbicides and chlorophenols. In this work, we have used 2,4,5-trichlorophenol (TCP) to test an organo-hydrotalcite clay for the removal of TCP from an aqueous medium.

Recently, layered double hydroxides (LDHs) have received considerable attention due to their potential technological applications: catalysis, photochemistry, electrochemistry, polymerization, magnetization, biomedical science, and environmental applications (Cavani et al, 1991; Newman and Jones, 1998; Carriazo et al., 2007). LDHs are host-guest materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. LDHs can be represented by the general formula: written as  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2] (A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations respectively and occupy the center of  $[M^{2+}/M^{3+}] (\text{OH})_6$  octahedral units.  $A^{n-}$  is the gallery anions and  $x$  is defined as the  $M^{2+}/M^{2+}+M^{3+}$  ratio (You et al., 2002 (1); Khenifi et al., 2010). Hydrotalcite-like compounds possess exchange capabilities for organic and inorganic anions, due to their structural positive charge. Hydrotalcite containing carbonates as the interlayer anion is decomposed into oxide solid solution when heated at 500°C. The calcined product can rehydrate and incorporate anions, to rebuild the initial hydrotalcite structure. Although hydrotalcite shows anion exchange properties, it cannot readily be used for this purpose. The carbonate is preferentially sorbed and prevents significant anion exchange. Only the thermally treated hydrotalcite can re-adsorb water and anions as it return to its original structure (Lazaridis and Asouhidou, 2003). The incorporation of organic species in LDHs yields modified it with hydrophobic and organophilic surface properties (Anbarasan et al., 2005).

The objectives of this study were to characterize the surface modification of MgAl-CO<sub>3</sub>, MgAl-C and MgAl-SDBS samples and apply these solids for removing 2,4,5-TCP from aqueous solutions.

## 2. SAMPLE PREPARATION: NON CALCINED, CALCINED AND ORGANO HYDROTALCITE

The layered double hydroxide MgAl-CO<sub>3</sub> with [Mg]/[Al] ratio equal to 2 was synthesized by co-precipitation at a constant pH of 10 following the method described by Reichle (Reichle, 1986). A mixed solution of 0.66 mol of MgCl<sub>2</sub>·6H<sub>2</sub>O and 0.33 mol of AlCl<sub>3</sub>·6H<sub>2</sub>O in 500 mL of distilled water were added drop wise under vigorous stirring to 500 mL of an aqueous solution containing 2 mol of NaOH and 1 mol of Na<sub>2</sub>CO<sub>3</sub>. During the co-precipitation process, the pH was maintained at a constant value (10) by addition of 1 N HNO<sub>3</sub> solution. The obtained gel was stirred for 18 h at 70 °C until crystallization. The solid was filtered and washed with distilled water until obtaining a Cl<sup>-</sup> free MgAl-CO<sub>3</sub> (AgNO<sub>3</sub> test). This material was dried at 80 °C for 24 h, ground and finally stored in plastic bottles. A fraction of the resulting material was calcined at 500 °C for 4 h. The solid obtained was noted MgAl-C. The surfactant of sodium dodecyl benzene sulfonate was intercalated by the calcined hydrotalcite by rehydration method which was used in the literature for the insertion of several types of organic molecules (You et al., 2002 (2)). The synthesized MgAl-C was added to 0.1 mol/L surfactant solution with solid/solution ratio of 1 g per 50 mL. The LDH anionic exchange capacity (AEC) is 5 mmol/g and 50 mL of surfactant solution represent 100% of the AEC (Reichle, 1986). The suspension was shaken at low speed on a reciprocal shaker for 16 h, centrifuged and the supernatant solution decanted. The solid material was washed several times using distilled water and oven dried at 65 °C for 24 h, crushed and passed through a 0.250 mm sieve. The obtained material was noted MgAl-SDBS dodecyl benzene sulfonate-hydrotalcite.

### 3. CHARACTERIZATION OF PREPARED SAMPLES

The basal spacing  $d_{003}$  of samples was determined by X-ray diffraction analysis using a Bruker D8 advance diffractometer operating at 40 kV and 30 mA with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15406$  nm). Nitrogen gas adsorption-desorption isotherms were measured using a Quanta Chrome Autosorb-1 instrument at 77 K. The specific surface area (S.B.E.T) was calculated by the B.E.T method (Brunauer et al., 1938) and the pore size was calculated by the B.J.H method (Barrett et al., 1951) using the adsorption and desorption isotherms, respectively. The total pore volume was calculated from the maximum amount of nitrogen gas adsorption at partial pressure ( $P/P_0$ ) = 0.999. FT-IR study was carried out using FTIR 8400S Shimadzu having a standard mid-IR DTGS detector. FT-IR spectra were recorded, in the range of 400–4000  $\text{cm}^{-1}$  with KBr pellets technique.

### 4. KINETIC STUDIES

Adsorption experiments were carried out in a batch equilibrium mode. An amount of MgAl-SDBS (20 mg) was dispersed in 50 mL of TCP solution and stirred with an agitation speed of 100 rpm. After each time of contact, a sample was removed. The TCP concentrations were determined using a UV-1700 UVspectrophotometer at 290 nm for dispersions at acidic pH and 310 nm at basic pH. The amount of TCP adsorbed was calculated as:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad \text{Eq. 1}$$

where  $q_t$  is the amount of adsorbed TCP at time  $t$  (mg/g);  $V$  the volume of solution (L),  $C_0$  and  $C_t$  are the initial and at time  $t$  TCP concentration respectively (mg/L) and  $m$  is the mass of adsorbent (g).

## 5. RESULTS AND DISCUSSION

### 5.1 Characterization of samples

The X-ray powder diffraction pattern of MgAl- $\text{CO}_3$ , MgAl-C and MgAl-SDBS are represented in Fig. 1. MgAl- $\text{CO}_3$  formed a typical, well-crystallized diffraction pattern that corresponds to a hydrotalcite phase, with sharp and symmetric reflections 7.61 Å ( $d_{003}$ ); 3.82 Å ( $d_{006}$ ); 2.58 Å ( $d_{012}$ ); 2.31 Å ( $d_{015}$ ); 1.97 Å ( $d_{018}$ ); 1.53 Å ( $d_{110}$ ); 1.51 Å ( $d_{113}$ ). The similar results are founded by other authors (Pesic et al., 1992; Bouraada et al., 2008). MgAl-C shows that LDH structure was destroyed and converted to an amorphous material after calcination and formation of oxide metals as MgO and  $\text{Al}_2\text{O}_3$ .

The infrared spectrum of MgAl- $\text{CO}_3$  shows the characteristic absorption bands of an hydrotalcite, particularly a broad band at 3421  $\text{cm}^{-1}$  (due to the interlayer water molecules) with a shoulder near 3200  $\text{cm}^{-1}$  (due to the H-bonded stretching vibration). The weak peak at 1637  $\text{cm}^{-1}$  can be assigned to the  $\text{H}_2\text{O}$  bending vibration of interlayer water. The strong peak at 1359  $\text{cm}^{-1}$  can be assigned to the vibration of carbonate species. The bands in the range of 500–700  $\text{cm}^{-1}$  are attributed to metal-oxygen-metal stretching. The surfactant SDBS intercalation in the hydrotalcite interlayer is confirmed by the infrared spectra. The presence of dodecylsulfate ions in the sample is evidenced by the C-H stretching vibration bands at 2955, 2919 and 2821  $\text{cm}^{-1}$ , C-H bending vibration band at 1467  $\text{cm}^{-1}$  and  $\text{CH}_3$  stretching vibration at 1375. MgAl-SDBS spectrum shows also the characteristic vibration bands of the sulfonate group at 1183, 1130, 1039, 1011 and 832  $\text{cm}^{-1}$ . The spectra of Fig. 2 are similar to those reported in the literature for the same materials (Zhao and Nagy, 2004; Wang et al., 2005).

The specific surface area of the MgAl- $\text{CO}_3$  increased from 59 to 132  $\text{m}^2/\text{g}$  by heating at 500°C. The increase in porosity in MgAl-C arises from the loss of  $\text{CO}_3^{2-}$  after calcinations of the MgAl- $\text{CO}_3$  at 500°C. The pores and empty spaces are accessible to the nitrogen molecules. We notice a decrease in BET specific surface area by modifying the MgAl-C with a surfactant. The decrease of surface area can be explained by the aggregation of organo-LDHs (You et al., 2002 (2)).

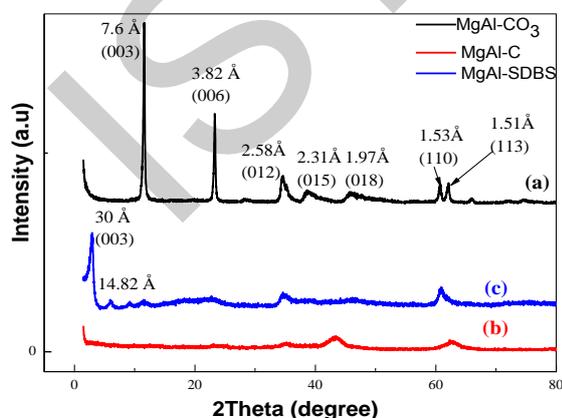


Fig.1: X-ray powder diffraction patterns of samples

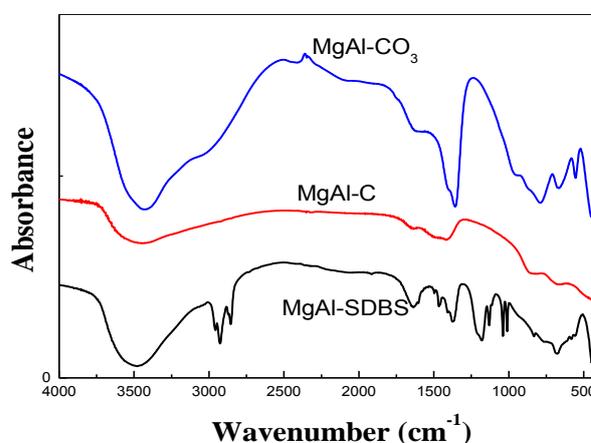


Fig. 2: FTIR spectra of LDHs

5. 2 Kinetics of adsorption

5. 2. 1 Effect of contact time and initial concentration

The plots in Fig. 3 show that the adsorption of TCP increases with an increase in agitation time and attains equilibrium earlier for solutions with lower initial concentrations. The maximum adsorption of TCP was sequestered within 30-40 min after the beginning for the low concentrations and 40-60 min for the high concentrations. The rapid adsorption at the initial contact time is due to the availability of physisorbed molecules of SDBS on MgAl-SDBS surface. Hydrophobic attractions between adsorbent and adsorbate are strong. The later slow rate of TCP adsorption is probably due to the electrostatic hindrance as well as the slow pore diffusion of the solute into the bulk of the adsorbent. It can be said that the TCP is adsorbed by the exterior surface of the adsorbent and when the adsorption of exterior surface of the adsorbent reacted saturation, the TCP entered into the adsorbent pores and adsorbed by the interior surface of the particles (Hameed, 2007). In this way, the contact time is very long. Fig. 3 showed also that the adsorption capacity at the equilibrium increased from 52 to 155 mg/g with an increase in the initial TCP concentrations from 50 to 250 mg/L indicating that increasing initial TCP concentrations would increase the mass transfer driving force and therefore the rate at which the TCP molecules pass the bulk solution to the particle surface. This would result in a higher TCP adsorption (Hameed, 2007).

In order to study the various mechanisms involved during the adsorption of TCP, three kinetic models were tested: the pseudo-first-order, the pseudo-second order and intra-particle diffusion kinetic models. The experimental conditions calculated models parameters and correlation coefficient  $R^2$  parameters are listed in Table 1 for all the experimental runs. As can be seen from Table 1, the two models give a reasonably good fit to the experimental data, but comparison of the  $R^2$  values, indicates that the pseudo-second order model (Ho, 2006) gives the best overall fit. Furthermore, the calculated value  $q_{ecal}$  using this model is also good agreement with the experimental value  $q_{exp}$ .

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport process, which is often the rate-limiting step in many adsorption processes, especially in a rapidly stirred batch reactor (McKay, 1983). Models of intraparticle mass diffusion model have been extensively studied and in this work the model adopted is based on theories developed by Weber and Morris (Weber and Morris, 1962) which is expressed by the following equation:

$$q_t = k_i t^{0.5} + C \tag{Eq. 2}$$

where  $k_i$  ( $\text{mg/g min}^{0.5}$ ) is the rate constant and obtained from the slope of the straight line of  $q_t$  versus  $t^{0.5}$  (Figure not showed).  $C$  is the intercept which gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect (Kavitha and Namasivayam, 2007). The values of intercept  $C$  and the rate constant  $k_i$  are in Table 2. The constant  $C$  and  $k_i$  increase with increase of TCP concentration. These results indicate that increasing the TCP concentration of the solution seems to reduce the rate of diffusion of TCP in the boundary layer and to enhance the diffusion in the solid (Lazaridis et al., 2004).

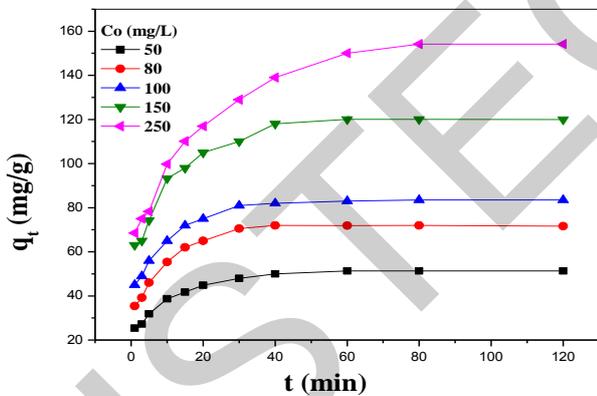


Fig. 3: Effect of initial TCP concentration and contact time on the adsorption

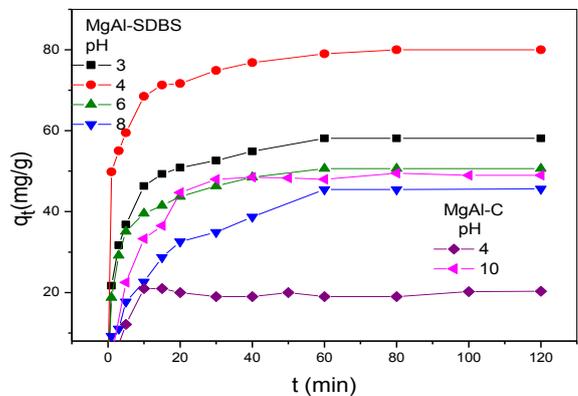


Fig. 4: Effect of pH solution on the adsorption

5. 2. 2 Effect of temperature

The study of the temperature effect on adsorption of TCP by MgAl-SDBS enabled us to determine the thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  of the adsorption reaction by using the following equation:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{Eq. 3}$$

$$K_D = \frac{q_e}{C_e} \tag{Eq. 4}$$

where  $R$  is the ideal gas constant,  $T$  the temperature (K) and  $K_D$  the distribution coefficient. The plot of  $\ln K_D$  against  $1/T$  (Figure not showed) gives a straight line, the slope and the intercept correspond to  $\Delta H^\circ/R$  and  $\Delta S^\circ/R$ , respectively.  $\Delta G^\circ$  values at three temperatures are calculated using the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

Eq. 5

The thermodynamic parameters calculated from the values of the slope and the intercept are reported in Table 3. The negative values of  $\Delta G^{\circ}$  indicate that the adsorption process is more spontaneous when increased temperature. The positive value of  $\Delta H^{\circ}$  shows that the process is endothermic. The positive value of  $\Delta S^{\circ}$  suggests the increased randomness at the solid/solution interface during the adsorption of TCP on MgAl-SDBS.

Table 1

Kinetic models parameters obtained in adsorption of 2,4,5-TCP on MgAl-SDBS

pH	C <sub>0</sub>	m	T	q <sub>e,exp</sub>	Pseudo-first-order			Pseudo-second-order		
					q <sub>e,cal</sub>	k <sub>1</sub> (10 <sup>-2</sup> )	R <sup>2</sup>	q <sub>e,cal</sub>	k <sub>2</sub> (10 <sup>-2</sup> )	R <sup>2</sup>
3	100	20	298	58.1	43.5	8.89	0.953	59.7	0.58	0.999
4	100	20	298	83.5	38.5	7.73	0.983	85.4	0.54	0.999
6	100	20	298	50.6	40.0	9.57	0.960	52.0	0.68	0.999
8	100	20	298	45.6	51.7	7.72	0.916	50.0	0.21	0.995
4	100	20	288	77.6	64.5	9.35	0.963	80.3	0.35	0.999
4	100	20	308	85.5	24.7	7.58	0.920	86.0	0.92	0.999
4	100	30	298	67.60	42.80	7.20	0.983	69.70	0.40	0.999
4	100	40	298	57.40	36.50	6.50	0.979	59.40	0.40	0.999
4	100	50	298	48.40	24.00	6.00	0.797	50.30	0.50	0.999
4	50	20	298	51.4	32.1	8.61	0.972	52.8	0.66	0.999
4	80	20	298	71.6	48.1	11.68	0.970	73.5	0.63	0.999
4	150	20	298	120.0	68.1	8.00	0.957	123.0	0.38	0.999
4	250	20	298	154.0	95.3	5.00	0.989	161.0	0.12	0.998

C<sub>0</sub> (mg/L), m (mg), T (K), q<sub>e</sub> (mg.g<sup>-1</sup>), k<sub>1</sub> (min<sup>-1</sup>), k<sub>2</sub> (g (mg min)<sup>-1</sup>)

### 5. 2. 3 Effect of the solution pH

The pH is an important variable affecting adsorption at water-adsorbent interface. The pH affects TCP speciation and metal dissolution from sorbent; hence, it has a significant impact on the adsorption of TCP on MgAl-C and MgAl-SDBS. To study the influence of the pH solution, experiments were investigated using the pH varying from 3 to 8. Fig. 4 showed that the uptake of TCP increased with increasing the pH from 3 to 4 and decreased with increasing the pH from 4 to 8 for system MgAl-SDBS/2,4,5-TCP. The dissociation (pK<sub>a</sub>) of 2,4,5-TCP is 6.8, in this case the 2,4,5-TCP can be presented as a phenolate when the pH is > 6.8, and as molecular when the pH is < 6.8. Almost 75% was the anionic type of 2,4,5-TCP at pH 7, and a similar percentage was molecular type at pH 6. This percentage can be 95% or more anionic when the pH is > 8 and ≥ 95% molecular when the pH is < 6. The pH also affects Mg and Al dissolution from MgAl-C and MgAl-SDBS. Mg dissolves at pH < 10 and Al at pH < 4 and >10 (Bardossy, 1959). Thus, in the MgAl-C and MgAl-SDBS systems, the percentage of Mg that dissolves increases as pH decreases, whereas Al is only slightly dissolved within the pH range of 5-10. Consequently, because Mg dissolves at a low pH, the MgAl-C and MgAl-SDBS structure can be destroyed, and the resultant positive position and SDBS-intercalated LDH contents can diminish. For the MgAl-C, TCP was not adsorbed at pH 3 because there are no attractions between hydrophilic surface of MgAl-C and molecules of TCP. At pH 4 and 6, the quantity adsorbed onto MgAl-C is very low due to the low ionisation of TCP. At pH 10, all TCP is in ionic form and it is intercalated into layers of the MgAl-C and the uptake of adsorption is high at pH 10 because there is no (or slowly) competing anions. In the MgAl-SDBS/2,4,5-TCP system (Fig. 4), the decreasing adsorption capacity when the solution pH increases from 4 to 8 is due to the dissociation of the 2,4,5-TCP which is increases when pH increases. The lowest sorption capacity at pH 8 is due to the electrostatic repulsions between chlorophenolate-chlorophenolate anions in the solution (Hamdaoui and Naffrechoux, 2007 (1)) and interaction between 2,4,5-TCP ions and hydrophobic MgAl-SDBS surface is very low. There was 95 % anionic type of 2,4,5-TCP that could interfere with the sorption of the 5 % slightly polar molecular type of 2,4,5-TCP on MgAl-SDBS. Figure 4 showed that the adsorption capacity increases when the solution pH increases from 3 to 4. This effect is due to the partial dissolution of MgAl-SDBS at pH 3 which is higher than at pH 4. SDBS-intercalated LDH contents can diminish more at pH 3 than at pH 4 which gave low adsorption capacity at pH 3. Consequently, MgAl-SDBS exhibits its best sorption capacity for molecular type of 2,4,5-TCP at pH 4. The hydrophobic-hydrophobic partition interactions of MgAl-SDBS is more vital and MgAl-SDBS can adsorb molecular type of 2,4,5-TCP by partition in the free intermolecular space.

### 3. 3 Equilibrium isotherms

Equilibrium studies were carried out in order to determine the optimum conditions for maximum TCP adsorption on MgAl-C and MgAl-SDBS. Fig. 5 shows the equilibrium isotherm which indicates that the amount of adsorbed TCP at equilibrium increases with increasing the equilibrium concentration of TCP. The curve in Fig. 5 shows that isotherm of adsorption of 2,4,5-TCP on MgAl-C has very low affinity toward MgAl-C hydrophilic surface. The upward isotherms suggest cooperative sorption in which weak MgAl-C interactions are presumed to occur at low aqueous concentrations, while at higher aqueous concentrations the sorbed TCP promotes further sorption due possibly to the creation of additional sorptive sites. It is possible that after the intercalation of the low anionic fraction of TCP at pH 4, the MgAl-C surface becomes hydrophobic

which enhanced adsorption of TCP by hydrophobic interactions. As shown in Fig. 5, there exists an obvious inflexion point in sorption isotherm, indicating a changing sorption mechanism with TCP equilibrium concentration during the sorption.

Fig. 5 shows that organic compound adsorption results, clearly demonstrate that the adsorptive properties of MgAl-C can be greatly enhanced by intercalation of anionic surfactants into LDH for the low initial concentrations. In this part the adsorption capacity of MgAl-SDBS is five times greater than that of MgAl-C which is an advantage for purification of drinking water. The curve tended toward a constant value of  $q_e$ , indicating the formation of a complete monolayer of TCP molecules covering the surface of the sorbent.

The experimental adsorption isotherms for low concentrations were fitted to the classic Langmuir (Hamdaoui and Naffrechoux, 2007 (2)) model (Eq.6).

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{Eq. 6}$$

where  $q_m$  and  $K_L$  are constants related to the loading capacity and the free energy of adsorption;  $C_e$  is the equilibrium concentration (mg/L) and  $q_e$  is the amount adsorbed TCP at equilibrium (mg/g) with correlation coefficient are 0.999 for system MgAl-SDBS/TCP and 0.998 for system MgAl-C/TCP

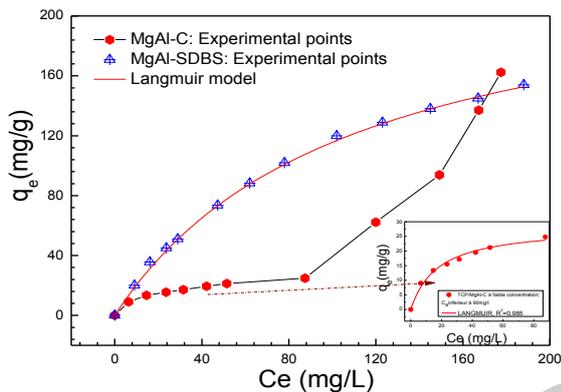


Fig. 5. Equilibrium isotherms for adsorption of TCP on MgAl-C and MgAl-SDBS.

Table 2: Intraparticle diffusion model constants for adsorption

$C_0$ (mg/L)	$k_i$ ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ),	$C$ ( $\text{mg g}^{-1}$ )	$R^2$
50	5.53	19.40	0.966
80	8.37	27.51	0.970
100	8.52	36.60	0.974
150	12.22	48.20	0.940
250	15.20	49.00	0.981

Table 3  
Values of thermodynamic parameters for adsorption of TCP on MgAl-SDBS

Temp. (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)
288	-0.31		
298	-0.50	5.3	19.6
308	-0.70		

#### 4. Conclusion

The efficiency of an organo-LDH, as adsorbent to remove 2,4,5-trichlorophenol from aqueous solution, has been studied. The organo-LDH with an Mg/Al ratio of 2 has a marked ability to adsorb organic compounds. The result provides clear evidence that the intercalation of surfactant in the interlayer of LDH influence greatly the adsorption capacity of LDH for low concentrations. The adsorption loading is higher and it was found that TCP are removed much at low pH than at high pH. The adsorption rates decrease at high adsorbate concentration and hence more time is needed to reach equilibrium. The rate of adsorption increases with the temperature of aqueous solution. Adsorption kinetics was found to follow pseudo-second-order with correlation coefficient  $R^2$  of 0.999. The negative values of  $\Delta G^\circ$  and positive value of  $\Delta H^\circ$  suggested that the processes of adsorption was spontaneous and endothermic. It may be concluded that this organo-LDH may have environmental applications in treating water for the removal of organic pollutants.

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# TURKISH AND ENGLISH LANGUAGE TEACHER CANDIDATES' ATTITUDES TOWARD COMPUTER AND PERCEIVED COMPUTER SELF- EFFICACY

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## ABSTRACT

The aim of this study is to address the Turkish and English language teacher candidates' attitudes toward computer and perceived computer self-efficacy with respect to social demographic characteristics. The population of the study consists of the teacher candidates in the Turkish and English language departments at the universities in Cyprus. The sample consists of 136 teacher candidates who were selected according to purposeful sampling in Faculty of Education at Cyprus International University. In this study, the "Attitude Toward Computer" scale developed by Aşkar and Orçan and the "Perceived Computer Self-Efficacy" scale developed by Aşkar and Umay were used for collecting data. Considering the purposes of the study percentage documentation average, t-test, ANOVA, Mann-Whitney U, Kruskal Wallis, Scheffe test and Pearson product-moment correlation coefficient were figured out in data analysis. The statistical significance level was accepted as 0.05 in the study. The result of this study shows that there is a differentiation in teacher candidates' department, age, English proficiency level and socioeconomic parameters according to the perceived computer self-efficacy whilst according to the attitude toward computer there is only a differentiation in English proficiency level. Also, there is a positive relation between teacher candidates' perceived information literacy self-efficacy and perceived computer self-efficacy.

**Keywords:** Attitudes toward computer, perceived computer self-efficacy, Turkish teacher candidates, English teacher candidates

## INTRODUCTION

Motivation, incentives, sense organs, intelligence, age, attention, preparedness, lack of motivation, physical conditions, psychological medium and perceived self-efficacy are among the factors affecting learning. Perceived self-efficacy is a concept taking place within the scope of social learning theory. According to the social learning theory, the most basic motivating structure behind the behaviors of the individuals is perceived self-efficacy. The societies of nowadays require individuals who possess life-long learning talents; in other words, individuals who can continuously renew their knowledge, comply with transformation, follow developments and can produce conscious knowledge. The basic outcome expected from the education institutes is to educate self-learning individuals equipped with knowledge and talents, who can utilize technology (Akkoyunlu, Orhan, 2003).

Perceived self-efficacy is defined as people's beliefs about their capabilities to produce designated levels of performance that exercise influence over events that affect their lives. Self-efficacy beliefs determine how people feel, think, motivate themselves and behave. Such beliefs produce these diverse effects through four major processes. These include cognitive, motivational, affective and selection processes. A strong sense of efficacy enhances human accomplishment and personal well-being in many ways. People with high assurance in their capabilities approach difficult tasks as challenges to be mastered rather than as threats to be avoided. Such an efficacious outlook fosters intrinsic interest and deep engrossment in activities. They set themselves challenging goals and maintain strong commitment to them. They heighten and sustain their efforts in the face of failure. They quickly recover their sense of efficacy after failures or setbacks. They attribute failure to insufficient effort or deficient knowledge and skills which are acquirable. They approach threatening situations with assurance that they can exercise control over them. Such an efficacious outlook produces personal accomplishments, reduces stress and lowers vulnerability to depression (Bandura, 1994).

Perceived self-efficacy plays a significant role in displaying the students' behaviours and in keeping their motivation high. Perceived self-efficacy explains success as follows: it is dependent on the interactions between behaviours, personal factors and surrounding conditions. Perceived self-efficacy affects the individual's task selection, effort, patience and success (Schunk, 1984).

In contrast, people who doubt their capabilities escape from difficult tasks which they view as personal threats. They have low aspirations and weak commitment to the goals they choose to pursue. When faced with difficult tasks, they dwell on their personal deficiencies, on the obstacles they will encounter, and all kinds of adverse outcomes rather than concentrate on how to perform successfully. They slacken their efforts and give up quickly in the face of difficulties. They are slow to recover their sense of efficacy following failure or setbacks. Because they view insufficient performance as deficient aptitude it does not require much failure for them to lose faith in their capabilities. They fall easy victims to stress and depression (Bandura, 1994).

Perceived computer self-efficacy is defined as “self-judgement of individual regarding computer literacy”. The relevant studies on this topic clearly show that those individuals with high rates of perceived computer self-efficacy are more motivated for participating at computer-related activities in addition to the high level of their expectations from such events. Also, these individuals can much more easily cope with the difficulties they encounter regarding computers (Akkoyunlu, Orhan, 2003).

Within the scope of relevant scientific studies, it is mentioned that perceived computer self-efficacy is a significant parameter in using computers (Aşkar, 2001; Işıksal, 2003; Işman, Çelikli, 2009) and thus perceived computer self-efficacy is tried to be measured by adopting various scales (Harrison, Kelly, 1992; Torkzadeh, Koufteros 1994; Akkoyunlu, Orhan, Umay, 2005).

Another important variable affecting computer usage is the attitudes toward the computer itself. Attitude, on the other hand, together with its formation, transformation, causing transformation or their measurement, is a topic relevant to social psychology. In general, attitudes can be defined as a learned predisposition to respond in a consistently favorable or unfavorable manner with respect to a given object. (Fishbein, Ajzen, 1975). They are relatively less stable than personality traits and can be changed both across time and across situations in virtue of individual’s interaction with the environment (Robinson, Simpson, Huefner, 1991). From years of prior research in the psychological sciences we know that both positive and negative reactions are reflected in attitudes, which are a key component in predicting behavior (Ajzen, 2001). Thus, to more fully understand computer usage, reactions to computers, and the psychological outcomes associated with computer use it is necessary to assess computer attitudes (Morris, Gullekson, Morse, 2009). The learner attitude towards computer measures his capabilities in effective learning. Computer attitude has been defined as a person’s general evaluation or feeling of antipathy towards computer technology and specific computer related activities (Smith, Caputi, Rawstone, 2000).

Equipping teacher candidates with adequate computer literacy is a significant variable in enhancing the quality of education. Many researchers stated that the attitudes of teacher candidates toward computer are closely related with the effectiveness and efficiency of the education process (Altun, 2003; Atıcı, 2000). Within the scope of the studies executed, it was found out that a positive attitude is formed toward computer usage with increased computer literacy (Deniz, 2000), whereas a negative attitude is formed toward computer usage in case of lack of computer literacy (Hashim, Mustapha, 2004). The utilization of computer as a tool of education ought to be an inevitable characteristic of teachers in the current contemporary education approaches. Çavuş and Gökdaş (2006) have also stressed the importance of basic computer skills and education related to internet usage of the teachers and especially the teacher candidates from the viewpoint of their success in their professions and has as well claimed that this will also lead to effective utilization of computer and Internet.

The aim of this study is to address the Turkish and English language teacher candidates’ attitudes toward computer and perceived computer self-efficacy according to their socio-demographic characteristics.

### 1.1. Problem Statements of the Study

The main problem statement: Is there a relation between teacher candidates’ “Attitudes Toward Computer” and “Perceived Computer Self-Efficacy” according to their social demographic characteristics.

#### 1.1.1. Sub Problems

The following sub questions were answered in order to reach at a solution to the main problem.

1. Is there any statistical difference teacher candidates’ “Attitudes Toward Computer” and “Perceived Computer Self-Efficacy”?
  - a) according to the department?
  - b) according to the gender?
  - c) according to the age?
  - d) according to the English proficiency level (self-perception)?
  - e) according to the level of socio-economic parameters (SEP)?
2. Is there any statistical meaningful relation between teacher candidates’ “Attitudes Toward Computer” and “Perceived Computer Self-Efficacy”?

## 2. Research Methodology

The research was carried out via the descriptive type and is in accordance with the associational research model. The associational research models are the research models aiming presence and degree of difference between two or more variables (Karasar, 1998).

### 2.1. The Universe and Sample of the Study

The universe of the study consists of the teacher candidates at the universities in North Cyprus. The sample consists of 136 [57.40% (n=78) female, and 42.60% (n=58) male] Turkish and English teacher candidates who were selected according to convenience sampling in Faculty of Education at Cyprus International University.

This number comprises 65 % of the entire students registered to the programs. The information regarding the distribution of the demographic characteristics of the teacher candidates participating at the research is presented in Table 1.

Table 1. Teacher Candidates' Demographic Properties

Independent Variables		n	%
Department	English	54	39.7
	Turkish	82	60.3
	Total	136	100
Gender	Female	78	57.4
	Male	58	42.6
	Total	136	100
Age	18	7	5.1
	19	10	7.4
	20	32	23.5
	21+	87	64.0
	Total	136	100
	Total	136	100
English proficiency level	Very Bad	4	2.9
	Bad	42	30.9
	Average	33	24.3
	Good	33	24.3
	Very Good	24	17.6
Level of socio-economic parameters	Total	136	100.0
	Less than 1000 TL	20	14.7
	1000-1500 TL	37	27.2
	1501-2000 TL	34	25.0
	2001-2500 TL	18	13.2
	More than 2501 TL	27	19.9
Total	136	100.0	

## 2.2. Research Instruments

### 2.2.1. Demographic Information Form

This 5-question form is prepared by the researchers to collect data about department, gender, age, English proficiency level and socio-economic parameters of teacher candidates.

### 2.2.2. Perceived Computer Self-Efficacy Scale

The scale for Perceived Computer Self Efficacy was an 18-item and 5-point Likert scale developed by Aşkar and Umay (2001) to define participants' self-efficacy level toward for computers. The participants were asked to rate each item on a scale ranging from 1 to 5. The maximum score which could be received from the scale was 90. The Cronbach's alpha reliability coefficient of the scale was calculated to be 0.71. The degree of differentiation of the items of the scale was found out to be high (Aşkar, Orçan, 2001).

### 2.2.3. Attitude Toward Computer Scale

The scale for Attitude Toward Computer Scale was a 24-item and 5-point Likert scale developed by Aşkar and Orçan (1987) to define participants' attitudes toward computer.

The minimum and the maximum score which could be received from the scale were 24 and 120 respectively. High scores indicate a positive attitude toward computers. The alpha reliability coefficient of the scale was calculated to be 0.87.

## 2.3. Data Analysis

In the statistical evaluation of the research all analysis are performed by using SPSS 15.0 for windows. Since it is recommended to take Kolmogorov-Smirnov test results into consideration in case the number of individuals included within the scope of the research exceeds 50, Kolmogorov-Smirnov test is utilized for testing whether or not the data obtained from the attitude scales display a normal distribution (Coakes, Steed, 1997; Tabachnick, Fidell, 2000). In the Kolmogorov-Smirnov test, since the statistical null hypothesis establishes that "the distribution of the grades does not display a meaningful difference from the normal distribution", the fact that the calculated "p" value exceeds 0.05 has led to the acceptance that the grades do not display a meaningful deviation from the normal distribution (Büyüköztürk, 2006).

When the Kolmogorov-Smirnov test results are considered, t test and uni-directional variance analysis (ANOVA) tests were applied for the data showing a normal distribution; while for the data not showing a normal distribution, the non-parametric tests Mann-Whitney U test and Kruskal Wallis test were applied. The relation between the dependent variables were calculated by utilizing Pearson moments multiplication correlation coefficient. Within the scope of the research, the level of statistical meaningfulness was accepted as 0.05.

## 3. Findings

The data obtained from the research were taken into consideration under convenient subtitles in accordance with the sub problems under evaluation and are interpreted accordingly.

With the objective of comparing the scores obtained from the dependent variables “Attitudes toward Computer” and “Perceived Computer Self-Efficacy”, they are examined via Kolmogorov-Smirnov test to check the convenience of the variables with respect to normal distribution. The results of the analysis are presented in Table 2.

Table 2. Analysis Result Regarding Normal Distribution Test of Dependent Variables

Dependent Variables	Kolmogorov-Smirnov		
	Statistic	df	P
Perceived Computer Self-Efficacy	0.075	136	0.060
Attitude Toward Computer	0.105	136	0.001*

\*  $p < 0.05$  (Non-parametric)

As a result of the analysis, it was found that  $\text{Kolmogorov-Smirnov}_{\text{Perceived Computer Self Efficacy}} = 0.075$  S.d.=136  $p=0.060$ ;  $\text{Kolmogorov-Smirnov}_{\text{Attitude Toward Computer}} = 0.105$  S.d.=136  $p=0.001$ . It was also observed that the data regarding perceived computer self-efficacy indicated a normal distribution, whereas the data regarding attitude toward computers did not indicate a normal distribution.

### Findings of the First sub-question of the Research

The first sub-question of the research was expressed as “Is there any statistical difference teacher candidates’ Attitudes Toward Computer and Perceived Computer Self-Efficacy according to the department, gender, age, the level of English language and level of socioeconomic parameters?”

As can be observed from Table 3, t-test is applied to the data with the objective of designating whether or not the average scores for the dependent variables according to department and gender yielding meaningful differentiation. As a result of the analysis, it was observed that the average scores for the perceived computer self-efficacy of the teacher candidates differentiated meaningfully according to departments and whereas there is no a meaningful differentiation for the case of gender. As can be observed from Table 3, the perceived computer self-efficacy of the English Department teacher candidates is better than those of the Turkish Department teacher candidates. When the averages regarding gender are evaluated, although it was found out that the perceived computer self-efficacy of the male teacher candidates was better than those of the female teacher candidates, this difference was not statistically meaningful.

Table 3. t-Test Results of the Teacher Candidates’ Perceived Computer Self-Efficacy According to the Department and Gender.

Independent Variables	n	Mean	Std.Dev.	t	P	Meaningful Difference	
Department	English	54	64.037	11.386	2.112	0.037	$p < 0.05$
	Turkish	82	59.914	10.973			
Gender	Female	78	60.448	9.952	1.278	0.204	$p > 0.05$
	Male	58	63.034	12.793			

With the objective of designating whether or not the perceived computer self-efficacy scores of the teacher candidates differentiate with respect to age, English proficiency and socio-economic level, single sided variance analysis (ANOVA) was applied to the data. As a result of the variance analysis, it was found out that perceived computer self-efficacy was indeed affected by the independent variables age, English proficiency level and socio-economic level and the findings were indeed statistically meaningful. The descriptive statistics regarding age, English proficiency level and socio-economic level and the ANOVA results are presented in Tables 4 and 5.

With the objective of designating the source groups of differentiation with regard to the variables gender, English proficiency level and socio-economic level, LSD test is applied to the data. As can also be seen from Table 5, the differentiation arose from the student groups of ages 20, 21 and above. This differentiation is in favor of the ages 21 and above. It was observed that the differentiation with respect to English proficiency level arose from the groups a-b\*, a-c\*, a-d\*, a-e\*. On the other hand, it was observed that the differentiation with respect to socio-economic level was indicative for less than 1000 TL and between 2001-2500 TL.

Table 4. Descriptive Statistics of Perceived Computer Self-Efficacy of the Teacher Candidates with respect to Age, English Proficiency Level and Socio-Economic Level

Independent Variables	n	Mean	Std.Dev	SE	
Age	18 (a)	7	56.857	10.761	4.067
	19 (b)	10	63.900	9.480	2.997
	20 (c)	32	57.250	9.672	1.709
	21 and 21+ (d)	87	63.241	11.676	1.251
	Total	136	61.551	11.280	0.967
English proficiency level	Very Bad (a)	4	49.000	6.377	3.189
	Bad (b)	42	60.238	9.307	1.436
	Average (c)	33	59.576	11.393	1.983
	Good (d)	33	63.515	11.311	1.969
	Very Good (e)	24	65.958	12.909	2.635
	Total	136	61.552	11.281	.967
Level of socio-economic parameters	Less than 1000 TL (a)	20	56.550	8.134	1.819
	1000-1500 TL (b)	37	61.703	10.556	1.735
	1501-2000 TL (c)	34	59.000	10.759	1.845
	2001-2500 TL (d)	18	68.778	10.669	2.515
	More than 2501 TL (e)	27	63.444	13.004	2.503
	Total	136	61.552	11.281	.967

Table 5. ANOVA Test Result of Perceived Computer Self-Efficacy of the Teacher Candidates with respect to Age, English Proficiency Level and Socio-Economic Level

Independent Variable	Source of Variance	Sum of Squares	df	Mean Square	F	p	Meaningful Difference
Age	Between Groups	1049.952	3	349.984	2.864	0.039	p<0.05 c-d*
	Within Groups	16129.688	132	122.195			
	Total	17179.640	135				
English proficiency level	Between Groups	1424.759	4	356.190	2.962	0.022	p<0.05 a-d* a-e* b-e* c-e* d-e*
	Within Groups	15754.880	131	120.266			
	Total	17179.640	135				
Level of socio-economic parameters	Between Groups	1759.182	4	439.796	3.736	0.007	p<0.05 a-d*
	Within Groups	15420.458	131	117.713			
	Total	17179.640	135				

\* Indicates that the difference in favor of the group.

As can be understood from Table 6, whether or not the differentiation between attitude toward computer scores with respect to departments is meaningful was controlled by Mann Whitney U test and it was observed that there existed no meaningful differentiation among the attitude scores of the two groups (Mann-Whitney U=1951.000 WilcoxonW=5354.000 z=-1.170 p>0.05).

Table 6. U-Test Result of Attitude Toward Computer Scores According to Department and Gender

Independent Variable		n	Mean Rank	Sum of Ranks	U	p	Meaningful Difference
Department	English	54	73.37	3962.00	1951.000	0.242	p>0.05
	Turkish	82	65.29	5354.00			
Gender	Female	78	64.47	5028.50	1947.500	0.166	p>0.05
	Male	58	73.92	4287.50			

Whether or not the differentiation between attitude toward computer scores with respect to gender is meaningful was again controlled by Mann Whitney U test. As a result of the analysis, it was observed that there existed no statistically meaningful differentiation among the attitude scores of the teacher candidates with respect to gender. (Mann-Whitney U=1947.500 WilcoxonW=5028.500 z=-1.385 p>0.05).

Table 7. Kruskal Wallis Test Result of Attitude toward Computer of the Teacher Candidates with respect to Age, English Proficiency Level and Socio-Economic Level

Independent Variables		n	Mean Rank	df	X <sup>2</sup>	p	Meaningful Difference
Age	18	7	73.36	3	1.325	0.723	p>0.05
	19	10	81.35				
	20	32	67.75				
	21 and 21+	87	66.91				
English proficiency level	Very bad	4	18.50	4	9.771	0.044	p<0.05
	Bad)	42	63.12				a-b*
	Average	33	70.32				a-c*
	Good	33	70.58				a-d*
Level of socio-economic parameters	Very good	24	80.90	4	9.042	0.060	a-e*
	Less than1000 TL (a)	20	51.60				p>0.05
	1000-1500 TL (b)	37	70.54				
	1501-2000 TL (c)	34	61.81				
	2001-2500 TL (d)	18	85.97				
More than 2501 T'L (e)	27	75.00					

\* Indicates that the difference is in favor of the group.

Whether or not the differentiation between attitude toward computer scores with respect to age and socio-economic level is meaningful was controlled by Kruskal Wallis test. As a result of the analysis, it was observed that there existed no statistically meaningful differentiation among the attitude scores (X<sup>2</sup><sub>age</sub>=1.325 p>0.05; X<sup>2</sup><sub>SEP</sub>=9.042 p>0.05).

Whether or not the differentiation between attitude toward computer scores of the English Department and Turkish Department teacher candidates with respect to English proficiency level is meaningful was controlled by applying Kruskal Wallis test to the data. As a result of the analysis, it was observed that there existed statistically meaningful differentiation with respect to English proficiency level (X<sup>2</sup><sub>English proficiency level</sub>=9.771 p<0.05). With the objective of designating the source groups of differentiation, the dual comparisons of each of the items of the independent variable regarding English proficiency level were realized by Mann-Whitney U test. As a result of the Mann-Whitney U test, it was observed that the differentiation arose from the a-b\*, a-c\*, a-d\*, a-e\* groups. This differentiation is against the teacher candidates perceiving English proficiency level as very bad.

**Findings of the Second sub-question of the Research**

The second sub-problem of the research is indicated as “Is there a statistically meaningful differentiation among the attitudes toward computer and perceived computer self-efficacy of the teacher candidates?”.

The relation between the dependent variables of the research “Attitudes Toward Computer” and “Perceived Computer Self-Efficacy” is calculated by the Pearson Moments Multiplication Correlation Coefficient. The result of the analysis is given in Table 8.

Table 8. Pearson Moments Multiplication Correlation Coefficient between Attitudes Toward Computer and Perceived Computer Self-Efficacy

		Attitudes Toward Computer
Perceived Computer Self-Efficacy	R	0.535(**)
	P	0.000
	N	136

\*\*p<0,001

It was observed that there existed an average positive statistically meaningful relation between attitude toward computer and perceived computer self-efficacy at the medium level. When the analysis result of the second sub problem is taken into consideration, it can be concluded that in case the attitudes toward computer or the perceived computer self-efficacy scores of the Turkish Department teacher candidates increase, an increase will also be observed in the same scores of the English Department teacher candidates. Similarly, in case of observation of a decrease in the attitudes toward computer or the perceived computer self-efficacy scores of the Turkish Department teacher candidates, a parallel decrease will also be observed in the same scores of the English Department teacher candidates.

## DISCUSSION

Within the scope of this study aiming to designate whether or not there exists a differentiation between the attitudes toward computer and perceived computer self-efficacy of the Turkish Department and English Department teacher candidates with respect to department, age, English proficiency level and socio-economic level, the observed findings were discussed comprehensively.

It was observed that there exist a meaningful differentiation between the perceived computer self-efficacy of the teacher candidates with respect to department, age, English proficiency level and socio-economic level, whereas there exist no meaningful differentiation with respect to gender.

When the perceived computer self-efficacy of the teacher candidates are evaluated according to their departments, it was observed that the perceived computer self-efficacy of the English department teacher candidates were better than those of the Turkish department teacher candidates. This can be explained by the fact that the majority of the computer commands and information technologies are in English and this leads to self confidence and motivation of English department teacher candidates.

When perceived computer self-efficacy is examined with respect to age, it was observed that the perceived computer self-efficacy of the teacher candidates show an increase with increasing age. This situation can be explained by the fact that the experiences of the teacher candidates increase as they get older. However, since self-efficacy is a variable representing a psychological structure, the result obtained cannot be generalized as it is. For this reason, in case the variables other than the perceived computer self-efficacy which develop with age (experience, improved technological structuring, etc.) are included within the research model and a new study is carried out, different results can be obtained (Akkoyunlu, Orhan, 2003).

On the other hand, when perceived computer self-efficacy was evaluated with respect to gender, it was observed that there existed no statistically meaningful differentiation. The designations of both Gerçek and Soran (2006) and Akkoyunlu (2003) indicating no meaningful difference in the perceived computer self-efficacy scores of the teacher candidates support this result.

It was observed that there existed a meaningful difference in the teacher candidates' perceived computer self-efficacy with respect to their English proficiency level. The reason for this can be explained by the fact that the teacher candidates with high English proficiency levels feel themselves confident regarding information technologies and terminology and this must have affected their perceived computer self-efficacy.

It was observed that there existed a meaningful difference in the teacher candidates' perceived computer self-efficacy with respect to their socio-economic level. The research study of Çetin (2008) related with the perceived computer self-efficacy of Marmara University teacher candidates support the findings of this study. The high socio-economic level of the individual increases the chance to possess or access the computer. This situation prepares the grounds for the teacher candidate to increase the perceived computer self-efficacy via increasing the computer literacy.

It was observed that the teacher candidates' attitudes toward computers differentiate meaningfully with respect to English proficiency level, whereas there existed no meaningful difference regarding the attitudes toward computers with respect to department, age, gender and socio-economic level.

It was observed that the teacher candidates' attitudes toward computers did not show any differentiation with respect to department. When Table 6 is examined, it was found out that the English Department teacher candidates' attitudes toward computers were comparatively higher than those of the Turkish Department teacher candidates' attitudes toward computers but however that this difference was not statistically meaningful. As it can be observed from the study, the differentiation with respect to department arose from the teacher candidates' perceived computer self-efficacy, not from their attitudes toward computers.

It was observed that the teacher candidates' attitudes toward computers indicated no meaningful differentiation with respect to gender. The research studies carried out support the fact that the attitudes toward computers do not indicate any meaningful differentiation with respect to gender (Güler, Sağlam, 2002; Deniz, 2000; Hunt, Bohlin, 1993).

There was no meaningful differentiation in the teacher candidates' attitudes toward computers with respect to their age. Gerçek (2006)'s research studies carried out on teacher candidates' attitudes toward computers also support this result.

It was observed that there was meaningful differentiation in the teacher candidates' attitudes toward computers with respect to English proficiency level. The reason for this is the same with that of the reason for the differentiation in perceived computer self-efficacy with respect to English proficiency level.

There was no meaningful differentiation in the teacher candidates' attitudes toward computers with respect to their socio-economic levels. Atay (2008)'s research study on the comparison of Engineering and Education Faculty teacher candidates' attitudes toward computers also support this finding.

It has been found out that there exists a positive and medium level meaningful correlation among the perceived computer self-efficacy and the attitudes toward the computer. Busch (1995)'s study examining the relation between the perceived computer self-efficacy and attitudes of university students toward computers also supports this finding. It is necessary to take this relation into consideration while organizing the education medium. Since cause and effect relation could not be established in the correlation studies, it cannot be discriminated whether attitudes increases self-efficacy or self-efficacy increases attitudes. In order to render this possible, detailed causative comparisons and experimental studies should be implemented.

## CONCLUSION AND RECOMMENDATION

It was observed that there existed meaningful differentiation in the perceived computer self-efficacy of the teacher candidates with respect to department, age, English proficiency level and socio-economic level, whereas there was no meaningful differentiation with respect to gender.

It was observed that there existed meaningful differentiation in the teacher candidates' attitudes toward computer with respect to English proficiency level, whereas there existed no meaningful differentiation with respect to department, gender, age, English proficiency level and socio-economic level.

It was determined that there existed a medium level positive statistical meaningfulness between perceived computer self-efficacy and attitudes toward computers.

For the purpose of disseminating the use of computers as a tool of education by the teachers, it is necessary for the teachers, to whichever branch they belong to, to improve their skills related with information and computer literacy as well as in learning softwares developed for computer aided language education and to utilize them in various courses.

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# TÜRKİYE VE SEÇİLMİŞ AB ÜYE ÜLKELERİNİN TURİZM GELİRLERİNİN ÇOK BOYUTLU ÖLÇEKLEME (MDS) ANALİZİ İLE DEĞERLENDİRİLMESİ

## EVALUATION OF TOURISM REVENUES OF TURKEY AND SELECTED EU COUNTRIES WITH MULTI-DIMENSIONAL SCALING (MDS)

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### Özet

Günümüzde turizmin neden olduğu sosyal, kültürel, politik ve ekonomik etkiler ve uluslararası ilişkilerde oynadığı rol gittikçe önem kazanmaktadır. Avrupa'daki geleneklerin ve kültürlerin çeşitliliği ve zenginliği, Avrupa Birliği'ni oluşturan ülkeleri pazarın en büyük payını alan bölgeler yapmaktadır. Turizmin geçmişteki tarihsel gelişimine bakıldığında, AB üye ülkelerinin dünya turizminin gelişiminde önemli bir yere sahip olduğu görülmektedir. Türkiye'nin dünya turizmi içindeki pazar payını artırması, ancak AB ülkeleri ile rekabet edebilirliğine bağlıdır. Dolayısıyla turizm gelirlerinin, ekonomik buhranların aşılmasında; yatırım ve gelir yaratarak istihdam hacmini artırması, ülkelerin bu ekonomik olgu üzerinde daha fazla yoğunlaşmalarına neden olmuştur.

Bu çalışmada 2000-2009 yıllık verileriyle seçilmiş 12 adet AB üye ülkeleri ve bazı gelişmiş ülkeler ile Türkiye turizm gelirlerinin benzerlik ve farklılıklarını çok boyutlu olarak karşılaştırmak ve Türk turizminin dünyadaki yeri ve önemi hakkında bilgi edinmek amaçlanmıştır. Uygulamada istatistiksel yöntem olarak çok boyutlu ölçekleme tekniği kullanılmıştır. Bu tekniği tercih etmekteki amaç, nesnel arasındaki ilişkileri dikkate alarak bunların daha küçük bir uzayda görsel olarak değerlendirilmesini sağlamasıdır.

**Anahtar kelimeler:** Çok boyutlu ölçekleme analizi, turizm gelirleri, Çok Değişkenli İstatistik

### Abstract

Today, social, cultural, political and economic effects caused by tourism and its role in the international relations have increasingly gained importance. Diversity and abundance of the traditions and cultures in Europe causes the countries constituting the EU to be the regions having the biggest share of the market. With respect to the historical development of tourism in the past, it is observed that EU member countries have a significant place in the development of global tourism. That Turkey might increase its market share in the global tourism depends on its competitiveness with the EU countries. Accordingly, tourism revenues has increased the employment volume by creating investment and income for overwhelming economic depressions and this situating caused countries to further focus on this economic phenomenon.

In this study, it was aimed to compare similarities and differences multi-dimensionally between the tourism revenues of 12 EU member countries and some developed countries as well as Turkey which were selected with the data for the years 2000-2009, and to have an idea as to the place and importance of Turkish tourism in the world. As a statistical method, multi-dimensional scaling was used in the study. The aim for choosing this method is that the method enables to visually evaluate the relationship between the items in a smaller space.

**Keywords:** Multi-dimensional Scaling analysis, Tourism Revenues, Multivariate Statistics

### 1.1 GİRİŞ

1980'li yıllardan sonra küreselleşme olgusu ile birlikte turizm sektörü, gerek Avrupa Birliği için, gerekse Türkiye için gittikçe artan en büyük sektör olma yolunda gelişim göstermektedir. Diğer tüm alanlarda olduğu gibi turizm sektörü de sürekli değişim içindedir. AB üye ülkeleri ve Türkiye'nin karşılaştırmalı değerlendirilmesi turizm pazar payları ve üyelik sürecinde Türkiye'nin turizmle ilgili alınacak tedbirleri belirlemek açısından oldukça önemlidir. Türkiye, başta rakipleri olan Yunanistan, Portekiz, Fransa, İtalya, İspanya gibi AB üye ülkelerinin turizm politikalarını takip etmekte, bu ülkelerde uygulanan turizm politikaları da Türkiye'yi çok yakından ilgilendirmektedir. Avrupa Birliği politikalarını çok yakından izleyen Türkiye, turizm sektörünün gelişmesinin önemini üzerinde yoğunlaşmaktadır.

Avrupa Birliği ülkelerinin turizmde başarılı olmalarından en önemli etken marka olmalarından kaynaklanmaktadır. Turizmde marka olan ülkeler, farklı özelliklerini ön plana çıkarmak suretiyle turist çekmeye devam etmektedir. Örneğin, İtalya dendiğinde Pizza Kulesi ve Venedik, Fransa dendiğinde Eiffel Kulesi ve Disneyland ve Cannes'ı, İspanya dendiğinde ise Mayorka hemen akla gelmektedir. Türkiye dendiğinde ise turizmde marka olabilecek bir çok tarihi güzellik ve mirasa sahip olmamıza rağmen, deniz-kum ve güneş dışında akla gelen bir ülke imajımız ne yazık ki yoktur (Kozak vd, 2001), (Kazancı, 2004:75). Buradan hareketle, Türkiye'nin AB ülkeleri ve diğer büyük ekonomiler içindeki turizm gelirleri bakımından konumunu araştırmak ve bu konudaki yapılan çalışmalara katkı sağlamak amaçlanmıştır. Yöntem olarak, çok boyutlu ölçekleme analizi tercih edilmiştir.

Çok boyutlu ölçekleme analizi (Multidimensional scaling, MDS), n nesne yada birim arasındaki p değişkene göre belirlenen uzaklıklara dayalı olarak nesnelere k boyutlu bir uzayda gösterimini amaçlayan istatistiksel bir yöntemdir. MDS ,

kişisel tercihler, tutum ve beklentiler gibi bireysel davranışların analizi için geliştirilmiş çok değişkenli analiz tekniğidir (Hair vd., 1998). Örneğin psikolojide birbirleriyle benzer yada farklı olan bireylerin açıkça ortaya konmadığı durumlarda birbirleriyle benzer olguların benzerliklerine göre sıralanmalarını sağlamak için kullanıldığı gibi Pazarlama alanında değişik araba türlerinin ve markalarının bireylerce seçilmelerinde birbirlerine göre benzerliklerini ortaya koymak amacıyla da yararlanılır.

MDS boyut indirgeme yöntemi olarak da kullanılan bir yöntemdir. MDS aynı zamanda n nesne yada birim arasındaki subjektif bir sıralamaya tabi tutmak için de kullanılır. Bu yöntem aynı zamanda, n nesne ile ilgili bilgilerin farklı kaynaklardan elde edilmesi (anketörler, anket formları, ...vb) halinde bu kaynaklardan elde edilen farklılıklar yada uyumluluğu ortaya koymak için de kullanılan bir yöntemdir (Özdamar, 2002: 488).

Elde edilen verilerin analizinde SPSS 16.0 paket programından yararlanılmıştır. Veriler SPSS ALSCAL algoritmasında, gözlemler arasında uzaklık matrisine dönüştürülerek analiz edilmiştir. Çok boyutlu ölçekleme analizlerinde kullanılan algoritmalar, nesnelere arasındaki benzerlikleri ikili, üçlü veya çoklu gruplar halinde karşılaştırırlar. İkili karşılaştırmalar genellikle, Takane, Young ve De Leeuw (1977) tarafından ortaya atılan ve dalgalı en küçük kareler ölçeği (Takane, Young ve De Leeuw, 1977: 7-67). Alternating Least Square SCALing) olarak bilinen Alscal algoritması kullanılarak elde edilmektedir (Cox ve Cox, 2001:217). Bu algoritma, nesnelere ya da birimler arasında fark gözetmeden karşılaştırmalar yaparak grupları belirlemektedir (Chou vd., 2007:717-728), (Kalaycı vd., 2005:379), (Yenidoğan, 2008:139). Bu çalışmada herhangi bir ağırlık söz konusu olmadığı için SPSS Alscal algoritması ile ikili karşılaştırmalar yapılarak gruplandırılmıştır.

Literatürde çalışmanın konusunu oluşturan turizm ile ilgili bazı ampirik çalışmalar dikkati çekmektedir. Bu çalışmalarda turizm gelirlerinin ekonomik büyümeye etkisi ölçülmeye çalışılmıştır. Emsen ve Değer (2004) çalışmasında, Türkiye'deki terör olayları sayısı ile turizm gelirlerine etkisini 1984-2001 verileriyle araştırmış, söz konusu dönemde giderek artan terör olaylarının turizm gelirlerine olumsuz etkisi olduğu sonucuna ulaşmıştır. Bahar (2006), 1963-2004 yılları arasındaki turizm gelirleri ile GSMH değişkenleri için VAR modeli oluşturularak incelemiş, her iki değişken arasında uzun dönemli karşılıklı ilişkinin olduğunu göstermiştir. Alper (2008), Türkiye'nin ekonomik gelişiminde turizmin rolünü 1992:1-2007:2 dönemi için Johansen eşbütünleşme ve Granger nedensellik testleriyle araştırmış, turizmin ekonomik büyümeyi desteklediği sonucuna varmıştır. Çetintaş ve Bektaş (2008), 1964-2006 dönemi verileriyle Türkiye'de turizm ve ekonomik büyüme arasındaki ilişkiyi ARDL yaklaşımıyla analiz etmiş, turizm sektörünün Türkiye'nin önemli büyüme kaynaklarından biri olduğunu göstermişlerdir. Dritsakis (2004) Yunanistan verileriyle turizmin ekonomik büyümeye etkisini VAR modeller ile araştırmış, ekonomik büyüme ve turizm gelirleri arasında güçlü bir nedensellik olduğu bulgusuna ulaşmıştır. Kırbaş- Kasman ve Kasman (2004) ekonomik büyüme ve turizm gelirleri arasındaki ilişkiyi koentegrasyon ve nedensellik testleri ile araştırmış turizm ve ekonomik büyüme arasında ilişki olduğunu tespit etmiştir. Karacaer ve Kapusuzoğlu (2010), İmkb'de işlem gören turizm firmalarının benzerlik ve farklılıklarını çok boyutlu ölçekleme analizi ile değerlendirmiş, çalışma sonucunda, entellektüel sermaye bileşenlerinin firma değeri üzerinde etkisi olduğu sonucuna ulaşmışlardır.

Bu çalışmadaki amaç ise diğer çalışmalardan farklı olarak; Türkiye'nin Avrupa Birliğine uyum amacıyla yapması gerekenler olduğu varsayımı ile Türkiye'nin turizm gelirleri bakımından dünya pazarındaki yeri konusunda fikir edinebilmektir.

## 2.METODOLOJİ

### 2.1.Çok Boyutlu Ölçeklemede Varsayımlar

MDS yöntemi, veriler ile ilgili dağılım varsayımı gerektirmeyen bir yöntemdir. Yöntem, değişkenlerin tipine bağlı olarak hesaplanan nesnelere arasındaki uzaklıkları en az data ile temsil edecek bir MDS gösterim uzaklıklarını herhangi bir regresyon yöntemi ile belirlemeyi sağlar.

N nesne yada birim arasındaki uzaklıklara uygun ve daha az boyutlu bir geometrik gösterim elde etmek için orjinal uzaklıklara oldukça çok yakın bir koordinat sistemi elde etmeye çalışılır. Orjinal uzaklıklarla gösterim uzaklıkları arasındaki uygunluğu ölçen ölçüye stres ölçüsü adı verilir (Tatlıdil, 2002: 353).

MDS ,verilerin tipine bağlı olarak metrik MDS ve metrik olmayan MDS olarak iki biçimde uygulanır. Metrik ölçekleme tekniğinin uygulanmasında temel bileşenler analizine benzer bir yaklaşım kullanılmaktadır. MDS yaklaşımının belirlenmesinde veri tipinin önemi büyüktür.

MDS bir veri indirgeme yöntemi olarak kullanıldığında veriler özellikle nicel veriler ise alternatif yöntem faktör analizidir.

### 2.2. Çok Boyutlu Ölçekleme Analizinin Uygulama Aşamaları

Çok boyutlu ölçekleme yönteminin uygulanması temel olarak 6 aşamada özetlenebilir.

**1. aşama:** Problemin tanımlanmasına bağlı olarak verilerin elde edilmesi.

Veri matrisinde yer alacak verilerin ölçek türlerinin standart hale getirilmesi gerekmektedir. Yani verilerin arasında farklı ölçek kullanılmışsa, verilerin için uygun olan bir ölçeğe dönüştürülmelidir. Veri matrisi aşağıdaki gibi  $X_{ij}$  şeklinde ifade edilebilir (Kalaycı vd., 2005: 380).

$$X_{ij} = \begin{bmatrix} x_{11} & x_{12} & \dots & x_{1n} \\ x_{21} & x_{22} & \dots & x_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ x_{k1} & x_{k2} & \dots & x_{kn} \end{bmatrix}$$

**2. aşama:** Veri tipine bağlı olarak uygun uzaklıklar matrisinin hesaplanması.

Uzaklıklar matrisi K boyutlu bir uzayda nesnelere temsil eden noktalar  $X_i$  olarak tanımlanırsa,  $d_{ij}$  öklit uzaklığı şu formülle elde edilir (Hair vd., 1998:537), (Kruskal ve Wish, 1983);

$$d_{ij} = \sqrt{\sum_{k=1}^K (x_{iK} - x_{jK})^2}$$

**3.aşama:** n nesne yada birimin kaç boyutlu bir uzayda gösterilebileceğine karar verilir. Genellikle uygulamada 2,3,4, ... gibi boyutlar seçilir ve boyutların MDS çözümleri elde edilir. Ayrıca herbir k elde edilen çözümlerin orjinal uzaklık matrisine uygunluğu yani stress ölçüsü hesaplanır. Bütün stress istatistiklerinden en küçük boyutu veren çözümde kullanılacak boyut sayısıdır.

**4.aşama:** Tahmini uzaklık matrisi verinin tipine göre hesaplanır. Regresyon yöntemi veri tipine bağlı olarak doğrusal, polinominal yada monotonik regresyon yöntemlerinden uygun olan biri olarak seçilir. Belirlenen regresyon denklemi aracılığı ile tahmini konfigürasyon uzaklıkları belirlenir.

**5.aşama:** Gerçek uzaklıklar ile tahmini uzaklıklar arasındaki uygunluğu belirlemek amacıyla stress istatistiği hesaplanır. Stress istatistiği değişik biçimlerde hesaplanmaktadır. (Kruskal stress Statistic, young Stress statistic). Kruskal stress 1 istatistiği aşağıdaki gibi hesaplanmaktadır (Özdamar, 2004:506).

$$\text{Stress1} = [\sum \sum (d_{ij} - td_{ij})^2 / \sum \sum (td_{ij})^2]^{1/2}$$

Kruskal stress istatistiği; konfigürasyon ölçüleri ile tahmini konfigürasyon ölçüleri arasındaki farkların tahmini konfigürasyon uzaklıklarına oranının karekökü alınarak hesaplanır ve veri uzaklıkları ile konfigürasyon uzaklıkları arasındaki uygunluğu ifade eder.

**6.aşama:** k boyutuna göre birim yada nesnelere koordinatları elde edilir. Arzu edilen çözüm, üç yada daha az boyuttaki bir çözümdür. Boyut sayısı arttıkça grafiksel gösterimler kolay anlaşılır olmaktan uzaklaşır.

MDS çözümlerinde istenen stress istatistiğinin sıfıra yakın olarak belirlenmesidir. Sıfıra yakın olan stress değeri veren boyut çözümleri uygun olarak nitelendirilebilecek çözümdür (Jobson, 1992: 570).

Stress değerlerinin büyüklüklerine göre konfigürasyon uzaklıklarının orjinal uzaklıklara uyumluluğu aşağıdaki gibi değerlendirilir (Özdamar, 2002: 492)

≤0.20 .....ise uyumsuz gösterim

0.10-<0.20.....ise düşük uyum

0.05-<0.10.....ise iyi uyum

0.025-<0.05 .....ise mükemmel uyum

0.00-<0.025.....ise tam uyum

Metrik MDS ile metrik olmayan MDS arasında stress değerlerinin irdelenmesinde bazı farklılıklar vardır.

Metrik olmayan MDS, metrik MDS ye göre daha az varsayım gerektirmekte ve çözümlemelerde tercih edilen bir yöntem olmaktadır (Mead, 1992: 28). Metrik yöntem, veriler eşit aralıklı veya oransal ölçek ile elde edildiğinde kullanılmaktadır. Metrik olmayan yöntem ise veriler sıralayıcı veya sıralı ölçek ile elde edildiğinde kullanılmaktadır (Aytaç ve Bayram, 2001).

Stress değeriyle birlikte uyum indeksi  $R^2$  de modelin uyumluluk derecesinin belirlenmesi için incelenen değerlerden biridir. Stress değeri uyumsuzluğu ölçerken,  $R^2$  uyum iyiliğini ölçer.  $R^2$ 'nin değerinin iyi uyumu gösterebilmesi için en az 0.60 olması gerekir (Malhotra, 2004:617).

### 3.AMPIRİK BULGULAR

Çok boyutlu ölçekleme analizinin etkinliği Kruskal stress istatistiği ile değerlendirilir. Tablo.1'de görüldüğü gibi Kruskal stress istatistiğinin değeri 0.005000'den küçük olduğu değere kadar iterasyona devam edilmiştir. Stress istatistiği 0.00908 bulunmuş ve uyumluluk düzeyi "iyi uyum" olarak bulunmuştur. Stress değeri Kruskal Stress formülüne göre 0.99988 olarak hesaplanmıştır. Bu bağlamda k=2 boyut için stress değeri, verileri 0,99 oranında açıklamaktadır.

**Tablo.1.Uyum ve Güvenilirlik**

Stress(uyum)	0.00908
$R^2$ (güvenilirlik)	0.99988

\*Stress değeri Kruskal Stress 1 formülü ile hesaplanmıştır.

Stress değerinin 0,00908 elde edilmiş olması (0,00908<0,025) uyumun tam olduğunu göstermektedir. Verinin değişiminin ne kadar açıklandığını gösteren  $R^2$  değeri ise kabul edilebilecek en az düzey olan 0,60 değerinden büyüktür (0,60< 0,99985).

**Tablo.2.Analizde Kullanılan Seçilmiş AB Üye Ülkeler ve Diğer Gelişmiş Ekonomiler**

VAR1	Almanya-Germany
VAR2	Avusturya- Aust
VAR3	Belçika-Belgium
VAR4	Fransa-France
VAR5	Hollanda-Nether
VAR6	İngiltere-UK
VAR7	İrlanda-Ireland
VAR8	İspanya-Spain
VAR9	İsveç-Sweden

- VAR10 İtalya-Italy  
 VAR11 Portekiz-Portug  
 VAR12 Yunanistan-Gree  
 VAR13 ABD-USA  
 VAR14 Japonya-Japan  
 VAR15 Kanada-Canada  
 VAR16 Avustralya-Aust  
 VAR17 G. Kore- S. Kor  
 VAR18 TÜRKİYE-TURKEY

Tablo.3.Uyarıcı Koordinatlar

Uyarıcı Sayısı	Uyarıcı İsmi	1.Boyut	2.Boyut
1	Almanya-Germany	,4924	,1078
2	Avusturya- Aust	-,4453	,0022
3	Belçika-Belgium	-,8827	-,0776
4	Fransa-France	1,1663	,4067
5	Hollanda-Nether	-,7554	-,1373
6	İngiltere-UK	,5373	,0271
7	İrlanda-Ireland	-1,1581	-,1384
8	İspanya-Spain	1,5071	,3876
9	İsveç-Sweden	-,9599	-,0316
10	İtalya-Italy	,7817	,1980
11	Portekiz-Portug	-,9605	-,0985
12	Yunanistan-Gree	-,6735	-,0229
13	ABD-USA	4,7669	-,4241
14	Japonya-Japan	-,9167	-,1193
15	Kanada-Canada	-,6024	-,1106
16	Avustralya-Aust	-,3716	,0901
17	G. Kore- S. Kor	-1,0031	-,1981
18	TÜRKİYE-TURKEY	-,5224	,1389

Tablo.3’de verilen uyarıcı koordinat tablosuna göre, birincil boyutta Fransa, İspanya, Amerika, pozitif yüklü ve 1’in üzerinde değerlere sahiptir. Dolayısıyla birincil boyutta bu ülkelerin 2000-2009 döneminde benzer algılandıkları görülmektedir. Bu ülkelerin aldıkları değerler diğer ülkelere kıyasla daha yüksek olduğundan birincil boyutta en önemli ayrıştırıcılarıdır. İrlanda ve Güney Kore ise negative yüklü ve 1’in üzerinde bir değerle diğer ülkelerden önemli derecede farklılık göstermektedirler. Aynı şekilde birincil boyutta, Almanya, Avusturya, Belçika, Hollanda, İngiltere, İsveç, İtalya, Portekiz, Yunanistan, Japonya, Kanada, Avustralya, Türkiye ise değerleri sıfıra yakın ve negatiftir.

İkincil boyutta, bütün ülkeler sıfıra yakın bir değerle görülmektedir. Yani ikincil boyutta ülkeler arasında önemli bir ayrım bulunmamaktadır. Ayrıca hangi ülkelerin birbirlerine yakın olarak algılandıklarını, hangi ülkelerin birbirinden farklı algılandıklarını göstermek için farklılıklar matrisi oluşturulmuştur. 18 ülkenin birbirine göre farklılıklarını gösteren bu matris aşağıda Tablo.4’de verilmiştir.

Tablo 4.Farklılıklar matrisi

Almanya Avusturya Belçika Fransa Hollanda İngiltere İrlanda İspanya .....

Almanya	,000									
Avusturya	,940	,000								
Belçika	1,385	,444	,000							
Fransa	,743	1,662	2,104	,000						
Hollanda	1,272	<b>,350</b>	<b>,156</b>	1,994	,000					
İngiltere	,180	,993	1,425	,754	1,310	,000				
İrlanda	1,666	,723	<b>,278</b>	2,386	<b>,405</b>	1,704	,000			
İspanya	1,049	1,987	2,432	,364	2,322	1,039	2,714	,000		
İsveç	1,457	,517	<b>,123</b>	2,168	<b>,230</b>	1,506	<b>,233</b>	2,502	,000	
İtalya	,304	1,239	1,684	,447	1,572	<b>,328</b>	1,965	,747	1,755	,000
Portekiz	1,464	,522	<b>,089</b>	2,184	<b>,214</b>	1,506	<b>,198</b>	2,513	<b>,080</b>	1,764

<b>Yunanistan</b>	1,171	<b>,235</b>	<b>,213</b>	1,887	<b>,147</b>	1,216	<b>,494</b>	2,217	<b>,289</b>	1,469
<b>ABD</b>	4,307	5,229	5,660	3,694	5,530	4,256	5,932	3,358	5,740	4,032
<b>Japonya</b>	1,426	<b>,491</b>	<b>,137</b>	2,155	<b>,243</b>	1,467	<b>,264</b>	2,475	<b>,183</b>	1,727
<b>Kanada</b>	1,116	<b>,209</b>	<b>,279</b>	1,841	<b>,166</b>	1,149	,553	2,166	<b>,373</b>	1,416
<b>Avustralya</b>	,867	<b>,153</b>	,552	1,570	,456	,938	,825	1,905	,601	1,160
<b>Güney Kore</b>	1,524	,590	<b>,181</b>	2,250	<b>,260</b>	1,565	<b>,176</b>	2,576	<b>,176</b>	1,826
<b>Türkiye</b>	1,014	<b>,162</b>	<b>,423</b>	1,709	<b>,373</b>	1,078	,694	2,044	<b>,474</b>	1,304

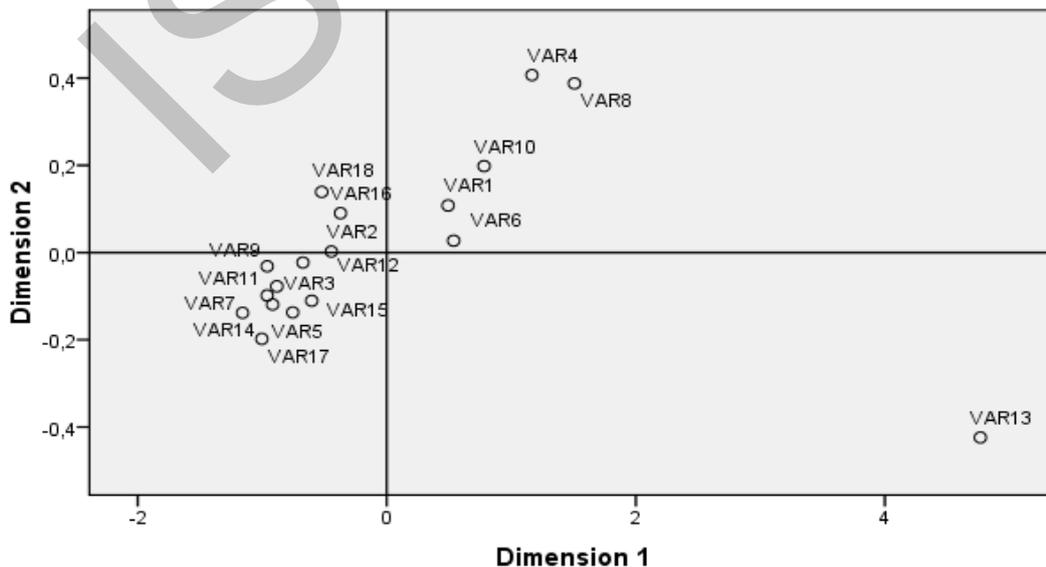
<b>Portekiz</b>	,000									
<b>Yunanistan</b>	,294	,000								
<b>ABD</b>	5,737	5,455	,000							
<b>Japonya</b>	,131	,297	5,693	,000						
<b>Kanada</b>	,358	,112	5,379	,346	,000					
<b>Avustralya</b>	,623	,341	5,164	,604	,337	,000				
<b>Güney Kore</b>	,118	,372	5,774	,186	,414	,694	,000			
<b>Türkiye</b>	,500	,229	5,319	,485	,274	,180	,584	,000		

Tablo.4'e bakıldığında değişkenlerin birbirine en benzer ve en benzemez olarak algılananlar görülmektedir. Sıfıra yakın değerlere sahip olan ülkelerin benzer olarak algılandıkları, 1'in üzerindeki değerlere sahip olan ülkelerin ise en benzemez oldukları yorumu yapılabilir. Buna göre, Hollanda ile Avusturya, Hollanda ile Belçika, İrlanda ile Belçika, İrlanda ile Hollanda, İsveç ile Belçika, İsveç ile Hollanda, İsveç ile İngiltere, İtalya ile İngiltere, Portekiz ile Belçika, Portekiz ile Hollanda, Portekiz ile İrlanda, Portekiz ile İsveç, Yunanistan ile Avusturya, Yunanistan ile Belçika, Yunanistan ile Hollanda, Yunanistan ile İrlanda, Yunanistan ile İsveç, Japonya ile Avusturya, Japonya ile Belçika, Japonya ile Hollanda, Japonya ile İrlanda, Japonya ile İsveç, Kanada ile Avusturya, Kanada ile Belçika, Kanada ile Hollanda, Kanada ile İsveç, Avustralya ile Avusturya, Güney Kore ile Belçika, Güney Kore ile Hollanda, Güney Kore ile İrlanda, Güney Kore ile İsveç, Türkiye ile Avusturya, Türkiye ile Belçika, Türkiye Hollanda, Türkiye ile İsveç, Türkiye ile Kanada, Türkiye ile Avustralya, Japonya ile Portekiz, Güney Kore ile Portekiz, Japonya ile Yunanistan, Kanada ile Yunanistan, Kanada ile Japonya, Avustralya ile Yunanistan, Avustralya ile Güney Kore, Türkiye ile Yunanistan 0'a yakın değerler aldıkları için birbirine en benzer ülkeler konumundadır.

Farklılıklar matrisinde 1 ve 2'nin üzerinde değerlere sahip olan ülkelerin ise birbirlerinden oldukça farklı olarak algılandıkları söylenebilir. Burada özellikle ABD'nin turizm gelirleri bakımından 4 ve 4'ün üzerinde değerlerle diğer ülkelerden oldukça farklı olduğu özellikle dikkati çekmektedir.

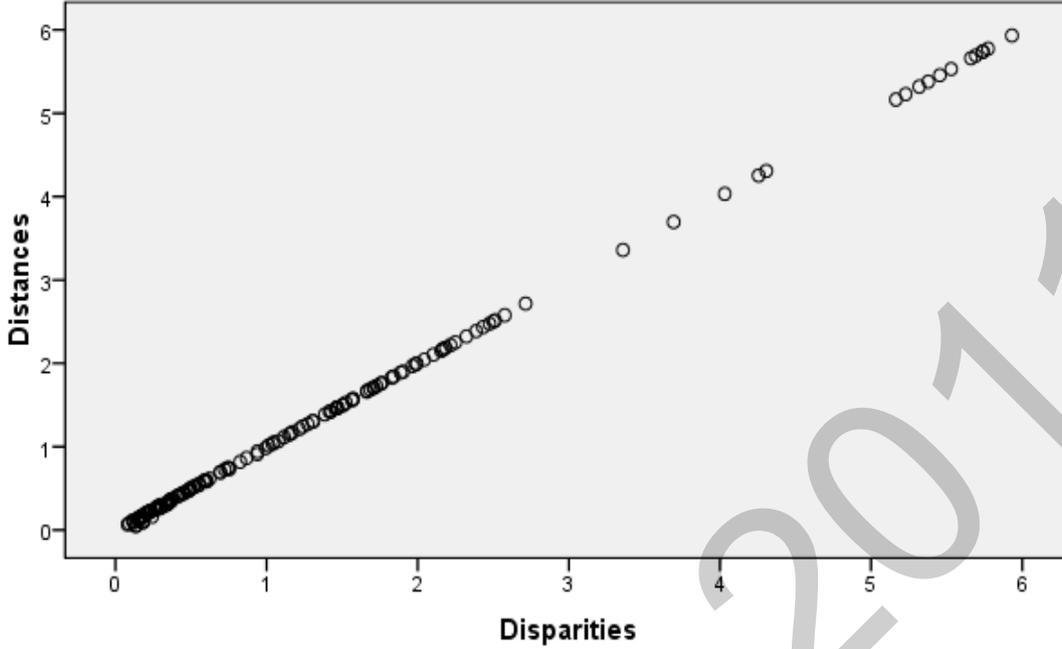
Koordinatlar tablosunda iki boyutlu uzayda koordinatlara göre düzenlenen grafiksel gösterim elde edilmiştir. Analizde kullanılan değişkenler aralıklı veya oransal ölçekle ölçüldüğünden Şekil.1'deki gibi öklid mesafesi modeli kullanılmıştır. Grafiksel düzenlemede de birbirine benzer olarak algılanan ülkelerin bir arada toplandıkları, birbirlerine benzemeyenlerin ise birbirinden uzak oldukları görülmektedir. Grafik ayrıntılı olarak değerlendirildiğinde turizm gelirlerine göre ülkelerin iki boyutlu uzayda dört farklı grup oluşturduğu söylenebilir. Buna göre, ABD bir alt grup, Almanya, Fransa, İspanya, İngiltere, İtalya benzer bir alt grup, Avusturya, Avustralya, Türkiye bir başka benzer grup, İsveç, Portekiz, Yunanistan, Belçika, İrlanda, Japonya, Hollanda, Kanada, Güney Kore ise bir grup oluşturmaktadır. ABD'nin genel eğilimden oldukça farklı olduğu dikkati çekmektedir.

Şekil.1.Öklit Mesafesi Modeli



Gözlenen uzaklıklar (distances) ile farklılıkların (disparities) dağılımını gösteren Serpilme diyagramı Şekil 2’de verilmektedir. Buna göre, uzaklıkların gerçek değerler ile uyum içinde olduğunu, yani uzaklıklar ile farklılıklar arasında doğrusal bir ilişki bulunduğunu göstermektedir.

**Şekil.2.Öklid Uzaklık Modeli Doğrusal Serpilme Diyagramı**



#### 4.SONUÇ VE DEĞERLENDİRME

Türkiye’yi ziyaret eden turistlerin büyük bölümünü AB üye ülkelerden gelmektedir. Öte yandan turizm hareketleri keyfi harcamalardan oluştuğu için turizm gelirlerinin yapısı iniş-çıkışlarla dolu kırılğan bir yapıdadır. Bu bağlamda, turizm sektöründe hükümetler tarafından hayata geçirilen bir turizm politikası veya verilen destekler bir ülkenin turizm endüstrisinde farklı etkilere sebep olabilmektedir.

Bu çalışmada ülkemizin sahip olduğu turizm potansiyelini Avrupa Birliği ülkeleri ile bazı gelişmiş ekonomilerle karşılaştırmak hedeflenmiştir. Seçilmiş AB üye ülkeleri ve bazı gelişmiş ülkelerin turizm gelirleri bakımından birbirlerine göre benzerliklerinin veya farklılıklarının ortaya konulması ve bu sayede iki yada daha fazla grup halinde bölünmesi amaçlanmıştır. Yapılan çok boyutlu analiz sonucunda, ABD bir alt grup, Almanya, Fransa, İspanya, İngiltere, İtalya benzer bir alt grup, Avusturya, Avustralya, Türkiye bir başka benzer grup, İsveç, Portekiz, Yunanistan, Belçika, İrlanda, Japonya, Hollanda, Kanada, Güney Kore ise bir grup oluşturmaktadır. ABD’nin genel eğilimden oldukça farklı olduğu dikkati çekmektedir. Türkiye’nin Avustralya ve Avusturya ile aynı grupta yer alması çok farklı şekillerde yorumlanabilir. Dünyada pek çok turistik bölge birbirlerine rekabet halindedir. Sözkonusu rekabet; sadece turizm potansiyeli olan şehirler veya bölgeler değil, işletmeler, oteller, tatil köyleri, doğa güzellikleri ve bunların farklı biçimlerde sunumları ile olabilir. Elde edilen bulgulara göre, Türkiye’nin turizm gelirleri bakımından genel görünümü, Avustralya gibi uzak ülkeler gibi düşünülmektedir. Yani bir akdeniz ülkesi olarak görülememektedir. Tunus, Cezayir ve Türkiye gibi ülkelerin, İspanya, İtalya, Yunanistan gibi bölgenin diğer ülkelerine karşı fiyat avantajları olmasına rağmen; bu durum, alt yapı ve turizm tesislerinde büyük gelişmeler kaydeden ülkemiz için önemli sorunun tanıtım ve organizasyon yetersizliği ile açıklanabilir.

Uyarıcı koordinat tablosu sonuçlarına göre; birincil boyutta Fransa, İspanya, Amerika, pozitif yüklü ve 1’in üzerinde değerlere sahiptir. Dolayısıyla birincil boyutta bu ülkelerin 2000-2009 döneminde benzer algılandıkları görülmektedir. Bu ülkelerin aldıkları değerler diğer ülkelere kıyasla daha yüksek olduğundan birincil boyutta en önemli ayrıştırıcılarıdır. İrlanda ve Güney Kore ise negative yüklü ve 1’in üzerinde bir değerle diğer ülkelere önemli derecede farklılık göstermektedirler. Aynı şekilde birincil boyutta, Almanya, Avusturya, Belçika, Hollanda, İngiltere, İsveç, İtalya, Portekiz, Yunanistan, Japonya, Kanada, Avustralya, Türkiye ise değerleri sıfıra yakın ve negatiftir. İkincil boyutta, bütün ülkeler sıfıra yakın bir değerle görülmekte, ülkeler arasında önemli bir ayrım bulunmamaktadır.

Farklılıklar matrisi değerlendirildiğinde, 1 ve 2’nin üzerinde değerlere sahip olan ülkeler ise birbirlerinden oldukça farklı olarak algılandıklarının göstergesidir. Özellikle ABD’nin turizm gelirleri bakımından 4 ve 4’ün üzerinde değerlerle diğer ülkelere oldukça farklı olduğu dikkati çekmektedir. Yani ABD’nin turizm gelirleri bakımından diğer ülkelere oldukça farklı bir yapısı olduğu görülmektedir.

Bütün bu sayısal sonuçlardan hareketle; Türkiye’nin turizm sektöründeki geleceği, dünyadaki trendleri iyi izlemesine, turist taleplerindeki eğilimleri doğru analiz etmesine, dünyanın temel ilke olarak benimsediği çevre duyarlılığı, toplam kalite kavramlarına önem vermesine bağlıdır yorumu yapılabilir. Ülkemizde 1980’li yıllardan itibaren, hızla gelişen turizm sektörü, günümüzde ülke ekonomisi için önemli bir konuma ulaşmıştır. Ülkenin turizm potansiyelinin dünya pazarına sunulabilmesi ve ciddi anlamda kazanç sağlanabilmesi için turizm kaynaklarının etkin şekilde pazarlanmasını gerektirmektedir. Söz konusu

rekabet ortamında dünya turizm gelirinden Türkiye'nin aldığı payı büyütme ve ülke turizm potansiyelini geliştirebilmek için Türkiye'nin uluslararası turizm pazarındaki rekabet gücünü artırıcı stratejilerin, dünya pazarındaki diğer ülkeleri de dikkate alarak belirlenmesi gerekmektedir. Sayısal sonuçlardan da ayrıca, uluslararası pazarda Türkiye'nin en önemli rakipleri, İspanya, İtalya, Fransa, Portekiz ve Yunanistan'dır. Kıtalararası pazarlarda ABD ve Uzakdoğu'nunda önemli bir rakip olduğu göz önünde bulundurulmalıdır. Öte yandan, çalışmanın kapsamına alınmayan Fas, Tunus, Cezayir hatta Mısır gibi ülkelerde rakip olarak değerlendirilmelidir.

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# TÜRKİYE’DE TRAFİK KAZALARIYLA İLGİLİ YASAL DÜZENLEMELER VE MÜHENDİSLİK ÖNERİLERİ

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## Özet

Türkiye'nin coğrafi bakımdan Asya ve Avrupa arasında yer alması ve üç tarafının denizlerle çevrili olmasından dolayı, konum itibarıyla ulaşımın yoğun olduğu bir güzergâh üzerinde yer almaktadır. Nüfusun yoğun olması, sanayileşme ve ticaretle birlikte ulaşım ihtiyacını arttırmış, yurtiçi ve yurtdışı ticari yük ve yolcu taşımacılığının büyük kısmı karayolları tarafından karşılanmıştır. Karayollarında mevcut taşıt ve yol miktarının artması ile birlikte trafik kazalarında da artışlar görülmekte, bu durum bir takım trafik güvenliği tedbirlerinin alınmasını zaruri kılmaktadır. Trafik kazaları, beraberinde ekonomik, sosyal ve çevresel etkiler olarak çeşitli sorunlar doğurmakta ve telafisi zor sıkıntılara yol açmaktadır. Trafik ile ilgili önlemler alınırken, bu önlemlere yönelik yasal düzenlemelerin gerçekleştirilmesi, kazalarda caydırıcı rol alması bakımından önem arz etmektedir. Bu çalışmada, trafik kazalarıyla ilgili yasal düzenlemelere, denetimlere değinilmiş ve alınan önlemlerde yaşanan sorunlar belirtilmiştir. Ayrıca şehir içi ve şehirlerarası yollardaki alt yapı mühendislik hizmetlerinde alınması gereken tedbirler tespit edilmiştir. Sonuç olarak, ülkemizde her yıl yaşanan trafik kazalarında meydana gelen can ve mal kayıplarının ülke ekonomisinde yol açtığı zararların azaltılması ve can kayıplarının önüne geçilmesi için kalıcı çözüm önerileri getirilerek sorunların ortadan kaldırılmasına yönelik çözüm önerileri sunulmuştur.

**Anahtar kelimeler:** Trafik kazaları, Yasal düzenleme, Mühendislik önerileri

## LEGAL ARRANGEMENTS AND ENGINEERING RECOMMENDATIONS REGARDING TRAFFIC ACCIDENTS IN TURKEY

### Abstract

Turkey, located between Asia and Europe in terms of geographical and surrounded by seas on three sides, is located on a route of transportation is intense as the location. The population dense, industrialization and trade, along with increased transportation need, domestic and international commercial cargo and passenger transport are met by most of the highways in Turkey. In highways, along with the existing transport and increase the amount of road traffic accidents also seen increases, this situation has made a number of essential safety measures are taken. Traffic accidents, along with economic, social and environmental effects and make-up gives rise to a variety of difficult problems leading to difficulties. When the measures related to traffic, the legal arrangements for the implementation of these measures, in terms of accidents, it is important to take deterrent role. In this study, the legal regulations regarding traffic accidents, the problems experienced in the controls are addressed and measures are taken. In addition, city and intercity roads infrastructure engineering services have been identified measures to be taken. As a result, in our country that occur each year in traffic accidents in the casualties and property losses and damages caused by the reduction of the national economy and to avoid loss of life, permanent solution proposals for the elimination of the problems presented.

**Keywords :** Traffic accidents, Legal regulation, Engineering recommendations

## 1. GİRİŞ

Türkiye’de ulaşım sektöründe karayollarının payı büyüktür. Yük ve yolcu taşımacılığının büyük payı karayolları ulaşımı ile sağlanmaktadır. Ulaştırımda yoğunluğun karayollarında olması beraberinde trafik kazalarına da yol açmaktadır. Özellikle karayollarında yolcu taşımacılığı amaçlı, otomobil, otobüs ve yük taşımacılığında kullanılan kamyon sayısı birçok Avrupa ülkesiyle kıyaslanmayacak şekilde artmıştır (Şekil 1). Bu durum beraberinde bir takım sorunlara yol açmakta her yıl trafik kazalarında binlerce insan yaşamını yitirmekte, yaralanmakta ve sakat kalmaktadır. Türkiye’de 2001-2010 yılları dönemlerinde yüzbin nüfusa düşen ölü ve yaralı sayısında 2003-2007 yıllarında ciddi artışlar olmuş, 2007 yılından sonra ölü sayısında azalma olmasına rağmen yaralı sayısında artışlar devam etmiştir. Bu sayı her geçen yıl artmakta ve alınan trafik güvenlik hizmetlerinin yetersiz kaldığı sonucunu ortaya çıkarmaktadır. Bununla birlikte trafik kazalarının ülke ekonomisine yol açtığı yıllık maliyet milyarlarca lirayı aşmaktadır (Şekil 2). Trafik güvenliği olarak stratejik bir yaklaşımla gerekli önlemler alınarak kalıcı çözüm yolları geliştirilmezse bu sorunun yol açtığı zararlar ileriki dönemlerde daha fazla geniş bir kitleyi etkileyecektir. Trafik kazalarının azaltılmasında yönünde yalnızca yasal düzenlemeler ve günlük alınan önlemlerle yetinilmesi sorunun çözümünde kısır döngüdür. Uzun vadede ve planlı yapılacak yasal düzenlemeler, mühendislik ve eğitim amaçlı çalışmalar sorunların azaltılmasına zemin oluşturacaktır.

Karayolları Trafik Kanunu’nda 1984 yılından bu yana tam 11 defa değişiklik gerçekleşmiş fakat bu durum trafik güvenliğinde sorunların çözümüne tam anlamıyla bir katkı sunmamıştır.

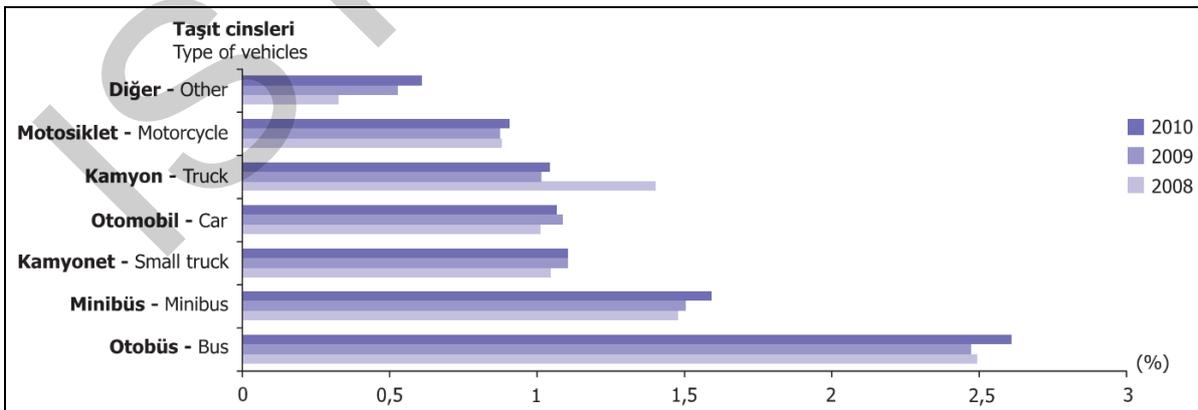
Trafik kazalarının azaltılmasında hem kamuoyu hem de karar vericilerin yapmış olduğu çalışmalarda stratejilere dayalı bütüncül eylem planı yerine kısa vadeli yasal değişikliklerle sorunun çözümünü sağlama prensibi halen süregelmektedir. Oysa yasa değişiklikleri bütüncül çalışmanın küçük bir unsuru olduğu gibi, yasaların yeterince etkili uygulanamaması, yaşama geçirilememesi sorunları da göz ardı edilmektedir.

Kamuoyunda komisyon çalışmalarından özellikle yeni yasa düzenlemelerine ilişkin öneriler ortaya çıkarılması beklentisi bulunmaktadır. Komisyon çalışmalarının temel gayesi sorunların tüm yönlerini ortaya koymak ve kapsamlı çözüm önerileri hazırlamak olmuştur. Yeni yasa değişiklikleriyle, kural ihlallerinde caydırıcılık unsurunu ortaya çıkarmak, ihlallerin cezalandırılmasına yönelik yasa değişiklikleri kapsamında şekillenmiştir.

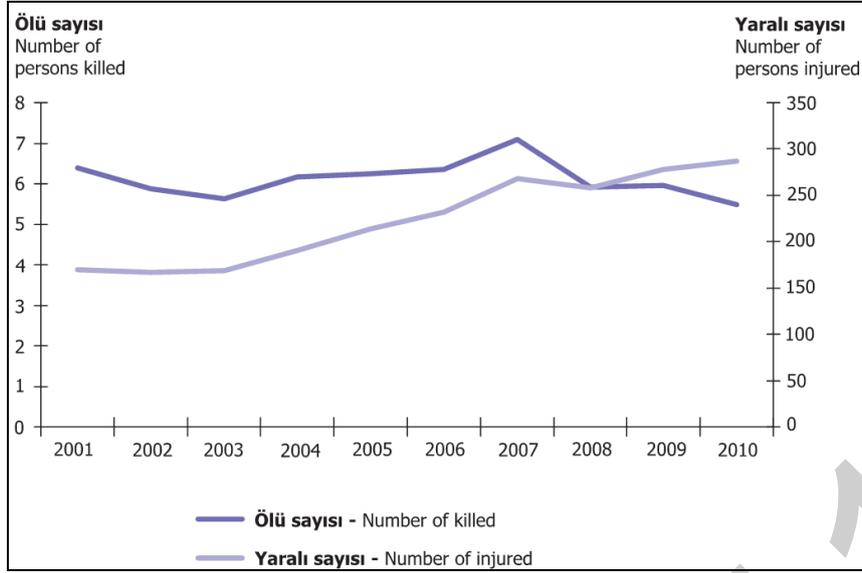
Mühendislik hizmetleri olarak altyapıya ilişkin düzenlemeler trafik güvenliğinin sağlanmasında kalıcı ve uzun vadeli değişimlerin gerçekleşmesi olanağını yaratmaktadır. Proje kapsamında ve uygulama safhasında yaşanan mühendislik eksiklikleri giderilerek, teknolojik gelişmelerden de faydalanarak yetişmiş kalifiye elemanlarla uygulama çalışmaları yürütülmelidir.

Son yıllarda güvenli bir trafik ortamının sağlanabilmesi için sorumlu kuruluşların çabaları yanında basın ve yayın kuruluşlarının katkıları, toplumdaki sürücü, yolcu, yay ve kurumsal bilinçlenmeyi belirli bir düzeye getirmiş, buna rağmen trafik kazaları ülkemizdeki öncelikli problemler arasında yerini korumaktadır.

Trafik güvenliğinin sağlanmasına yönelik yapılacak yatırımlar açısından önemli bir belirleyici olarak kaza istatistik verilerine ihtiyaç kaçınılmaz olup, bu çalışmalarla ilgili Emniyet Genel Müdürlüğü ve Jandarma Genel Komutanlığı bölgelerindeki kaza istatistik bilgilerinden faydalanılmaktadır. Alınan istatistik verilerinden kazaya yol açan etmenler belirlenerek olay kendi içinde bir bütün olarak değerlendirilmelidir [1-4].



Şekil 1. Trafik Kazalarına Karışan Taşıtların Kayıtlı Taşıt İçindeki Oranı [4]

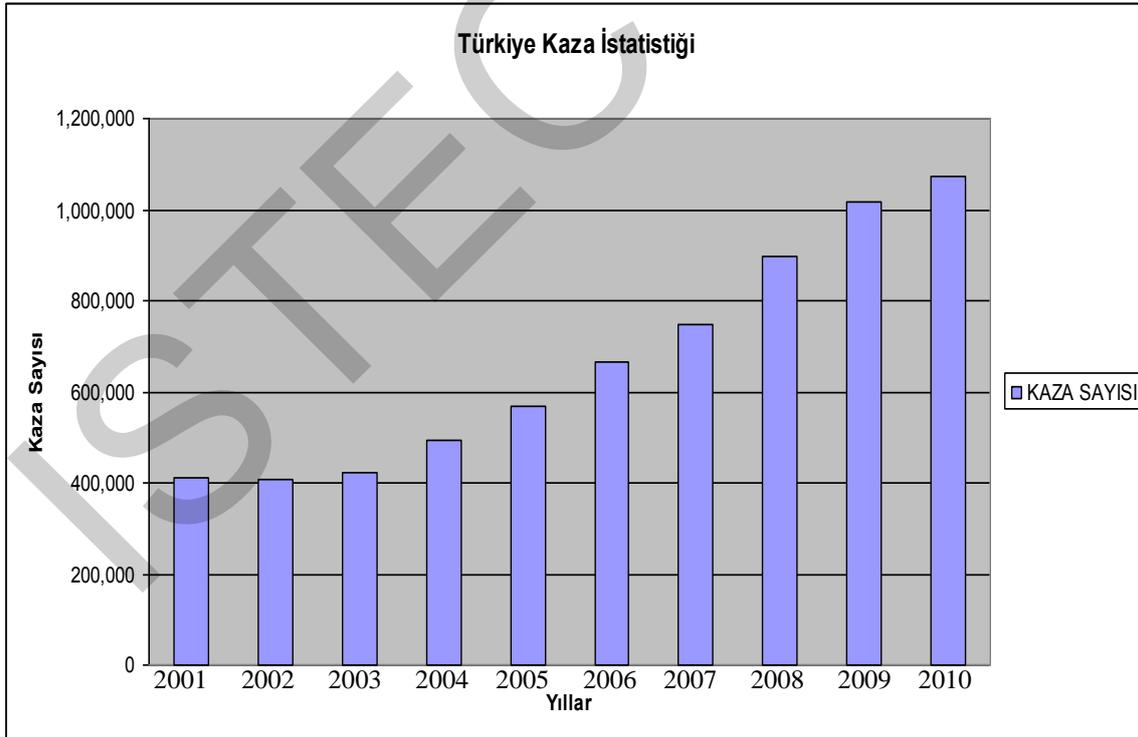


Şekil 2. Türkiye’de Trafik Kazalarında Yüz bin Nüfusa Düşen Ortalama Ölü ve Yaralı Sayısı [4]

## 2. AB ÜLKELERİ ve TÜRKİYE’DEKİ TRAFİK KAZA İSTATİSTİKLERİ

Türkiye’de 2001-2010 yılları döneminde trafik kazalarına bakıldığında ciddi artışlar yaşanmış 2001 yılından 2010 yılına yaklaşık %76 artış olmuş, bu durum alınan tedbirlerin ve düzenlemelerin yetersiz kaldığı sonucunu doğurmuştur (Tablo 1). Bu duruma trafiğe çıkan taşıt sayısındaki artışlarda etkenlerden biri olmuştur.

Tablo 1. Türkiye Trafik Kazası İstatistikleri [4-9]



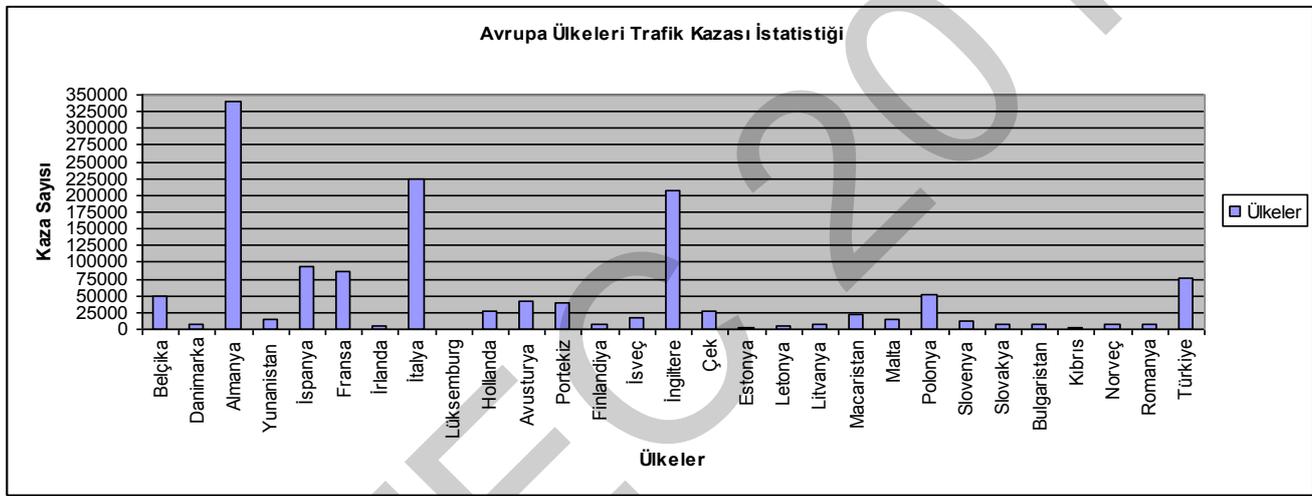
Türkiye’de her yıl trafik kazasına bağlı birçok insan ölmekte, yaralanmakta ve yaralanmaya bağlı sakat kalmaktadır. Bu durum ülke ekonomisine maliyet bakımından ciddi anlamda sorun yaratmaktadır.

2001-2010 yılları döneminde Karayolu Trafik İstatistik Verilerinde jandarma ve trafik polisi sorumluluk bölgesinde meydana gelen kazalar Tablo 2’de gösterilmiştir. Tablo 2’den anlaşılacağı üzere yıllara göre trafik kazaları sayısında artışlar olmakta trafik kazası başına ortalama ölü sayısında zamanla azalmasına rağmen yaralı sayısında artışlar görülmektedir.

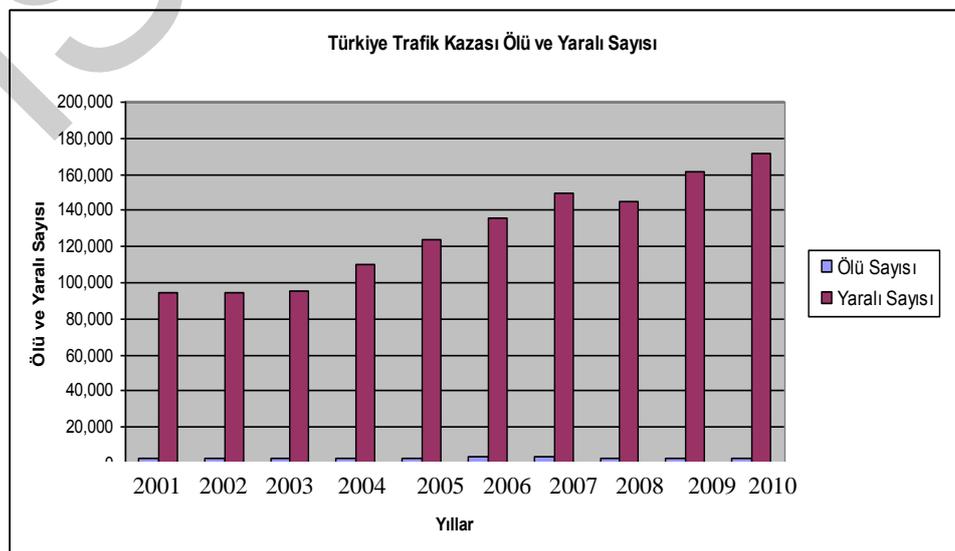
**Tablo 2.** Trafik Kazası Başına Ortalama Ölü ve Yaralı Sayısı [4]

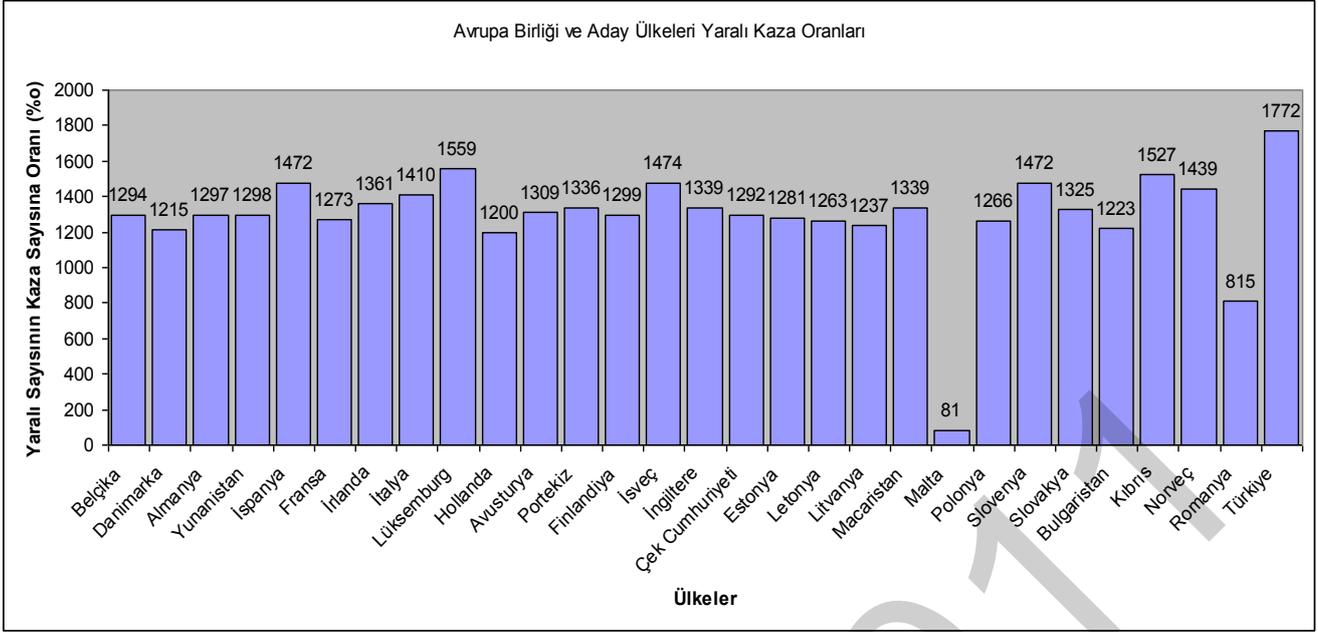
Yıllar	Trafik Kazası Sayısı	Ölü Sayısı	Ölü Sayısı (%)	Yaralı Sayısı	Yaralı Sayısı (%)
2001	66243	4386	66,21	116203	1754,19
2002	65748	4093	62,25	116412	1770,58
2003	67031	3946	58,87	118214	1763,57
2004	77008	4427	57,49	136437	1771,73
2005	87273	4505	51,62	154086	1765,56
2006	96128	4633	48,20	169080	1758,90
2007	106994	5007	46,80	189057	1766,99
2008	104212	4236	40,65	184468	1770,12
2009	111121	4324	38,91	201380	1812,26
2010	116804	4045	34,63	211496	1810,69

Trafik kazaları sadece Türkiye’de değil Avrupa Birliği ülkelerinde de sorun teşkil etmekte özellikle Almanya, İngiltere, İtalya gibi nüfus yoğunluğu fazla olan ülkelerde 2001-2010 yılları dönemlerinde ciddi boyutta artmıştır (Tablo 3).

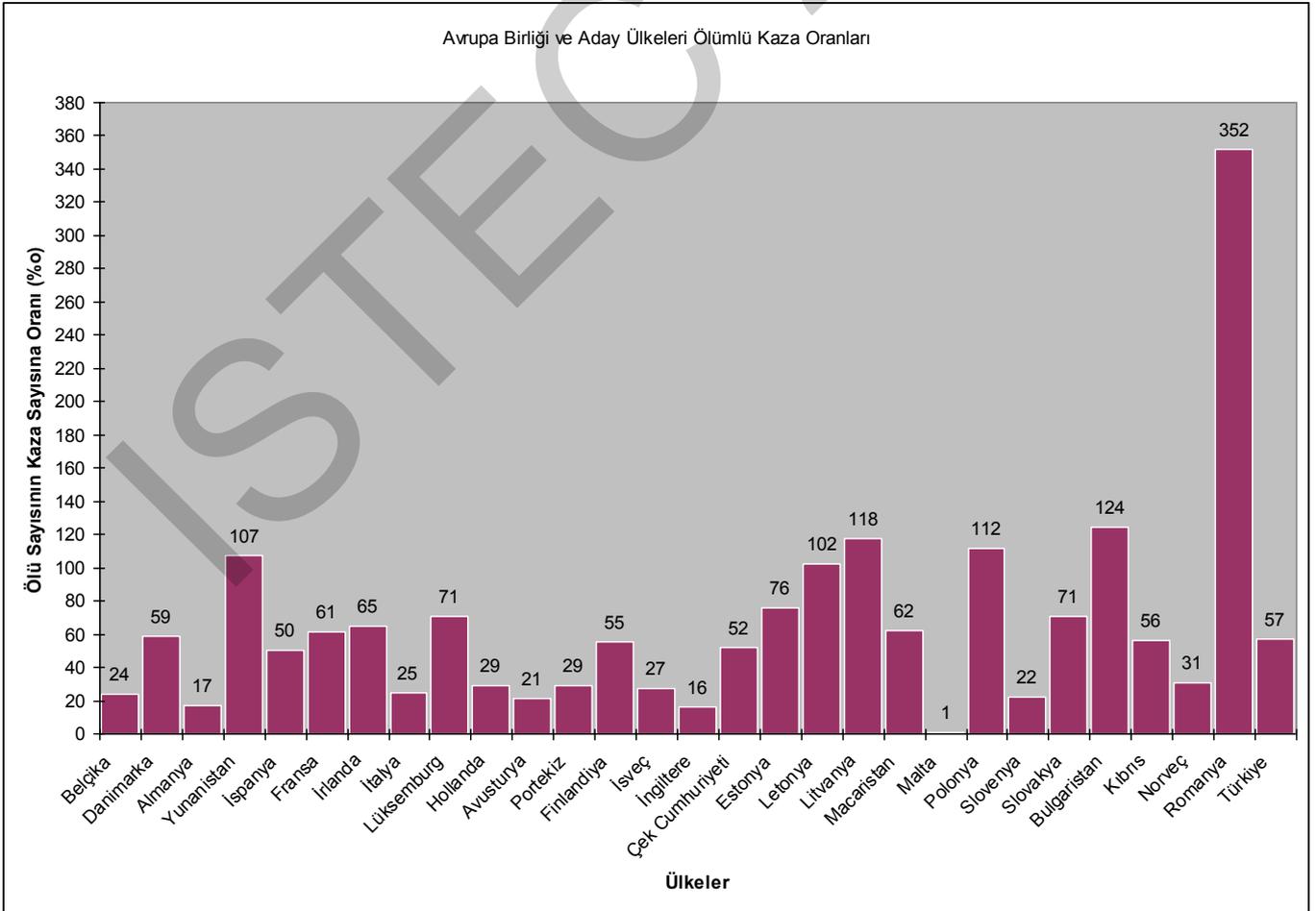
**Tablo 3.** Avrupa Ülkeleri Kaza İstatistikleri [4]

Özellikle trafiğin yoğun olduğu kesimlerdeki trafik kazalarına bağlı çok sayıda ölüm ve yaralanma vakaları görülmektedir (Tablo 3). AB ülkelerinde 2001-2010 yılları dönemlerinde meydana gelen trafik kaza sayıları birbirine yakın olup, kaza sayısı ortalamaları yaklaşık 47705’tir. Yaralanma sayısı ortalaması yaklaşık 1338 olup, Türkiye ile karşılaştırıldığında 1772 trafik kazası yaralanma sayısı bakımından Türkiye’de trafik kazalarına bağlı yoğunluk fazladır (Tablo 4-5).

**Tablo 4.** Türkiye Trafik Kazası Ölü ve Yaralı Sayısı [4-9]

**Tablo 5.** Avrupa Birliği ve Aday Ülke Yaralı Kaza Sayısı Oranları [4]

Avrupa Birliği ülkeleri ve Türkiye ölümlü trafik kazaları bakımından karşılaştırıldığında Türkiye bu ülkeler içinde değerlendirildiğinde orta sıralarda yer almakta Romanya 352 ölümlü kaza oranıyla en fazla malta ise 1 ölümlü kaza sayısı oranıyla en az bu tür kazaların yaşandığı ülke konumunda yer almaktadır (Tablo 6).

**Tablo 6.** Avrupa Birliği ve Aday Ülke Ölümlü Kaza Oranları [4]

## 2. TRAFİK KAZALARINA AİT YASAL DÜZENLEME DEĞERLENDİRMESİ

Trafik kazaları ile ilgili yasal düzenlemelerin etkin bir şekilde uygulanması bakımından bazı olumsuzluklar yaşanmaktadır. Bu olumsuzluklar etkileyen faktörler şu şekilde sıralanabilir.

- Cezalandırmaların kısıtlı yapılması ve caydırıcılığının yetersiz kalması
- Trafik kuralı ihlallerinin tümünün yakalanamaması
- Trafik kural ihlali yapanların cezalandırılmaması
- Alkollü araç kullanma ve aşırı hız gibi kural ihlallerinde özel değerlendirmelerin yetersiz kalması
- Bazı kural ihlallerindeki maddi ceza miktarlarının düşük olması
- Hapis cezası ve ehliyete el koyma gibi uygulamalar parasal cezalara göre daha efektif uygulanamama
- Trafik kazası yapan sorumlular hakkında uygulanan yaptırımların kazanın sonuçları bakımından mağdurlarda ve kamuoyunda yeterli bulunamaması şeklindedir.

Ölümlü ve yaralanmalı trafik kazalarında, Türk Ceza Kanunu'nun 455. ve 459. maddeleri uygulanmaktadır. Bu maddeler sadece trafik kazaları için hazırlanmış özel maddeler olmayıp her türlü taksirli yaralanma ya da ölüme sebebiyet verme suçlarında kullanılan genel maddedir. Bu maddelerin son fıkralarında verilecek cezalar kusurun derecesine göre sekizde birine indirilebilir. Bu hükmün pratikte uygulanması 2918 sayılı Karayolu Trafik Kanunu'nun 84 maddesinde belirtilen Karayolları Trafik Yönetmeliği'nin 173.maddesinin "b" bendinde düzenlenerek olaylar bir bütün olarak değerlendirilmektedir. Bu düzenlemeye göre, kazaya karışan araçların sürücülerinin ve yayaların kusuru 8/8 üzerinden yapılmaktadır. Olay bir bütün olarak değerlendirilip kusur tayini yoluna gidilmektedir. Olayların bu şekilde değerlendirilmesi ile sanıklar ceza hukukunun temel prensiplerine aykırı olarak daha düşük bir ceza almaktadırlar.

2918 sayılı Karayolu Trafik Kanunu'nun 84.maddesine göre birden fazla failin kazaya sebep olması halinde olay bir bütün olarak ele alınıp kusur tayini yapıldığı için, faillerden her birinin kusur oranı paylaşırma sonucu düştüğü için, faillerin birden fazla olması cezada adeta hafifletirici sebep olmaktadır. Bu bakımdan olay değerlendirilirken kazaya karışın sürücü ve yayaların kusurlu hareketlerinin kendi içinde bütün olarak değerlendirilmesi uygun olacaktır [1,2,3,5].

## 3. TRAFİK KAZALARIYLA İLGİLİ MÜHENDİSLİK ÖNERİLERİ

Şehir içi ve şehirler arası yollarda kalıcı ve uzun vadeli değişimler için çeşitli önlemler alınarak kazaların azalmasına yönelik çalışmalar yürütülmelidir. Yolla ilgili alınması gereken tedbirler şu şekilde sıralanabilir.

- Yol kenarlarında sürücülerin dikkatini dağıtacak trafik işareti dışındaki ilan ve reklamlardan kaçınılmalı
- Karayollarına ait trafik levha sayısı, ışıklandırma ve bakım onarım çalışmalarında yol işaretleri eksikliği giderimi
- Kazaların yoğunlaştığı yerlerdeki kara noktalar ortadan kaldırılmalı
- Yolla ilgili hazırlanan projelerde tasarım hususlarına dikkat edilmeli
- Yol kenarlarında ihtiyaç duyulan bariyerlerin sağlanması
- Teknik ve çalışan personelin Trafik mühendisliği eğitimi verilmesi
- Trafığın yoğun olduğu alanlarda kavşak düzenlenmesi çalışmalarının titizlikle yürütülmesi
- Otopark çalışmalarına önem verilmesi ve yol kenarlarında trafiğe engel olan taşıtların parklarının engellenmesi
- Şehir planlamalarında uzun yıllar ihtiyacı karşılayacak yol ağı planının uzman heyetler tarafından gerçekleştirilmesi gibi çeşitli alanlarda çalışmalar tamamlanmalıdır.

Zeeger'e göre şerit genişliği arttıkça yaralı ve hasarlı kaza oranları düşerken ölümcül kaza oranlarında büyük bir değişim olmamaktadır. Bu duruma bakılırsa yollardaki şerit genişlemeleri araçların süratlerinde artışlara yol açarak, taşıt sürücülerinin dikkatlerinin dağılması ve manevra kabiliyetlerinin yavaşlamasıyla kaza riskini çoğaltmaktadır (Şekil 3). Smeed yaptığı çalışmada değişik ülkelerden elde ettiği trafik verileriyle ölümcül kaza sorunlarını nüfus ve taşıt sayısı oranlarına göre belirlemiş ve kendi modelini geliştirmiştir. [5-8].



Şekil 3. Zincirleme Trafik Kazası

#### 4. SONUÇ

Trafik kazalarında meydana gelen kazaların yol açtığı maddi ve manevi unsurların yol açtığı zararların önüne geçilmesinde hem yasal düzenlemelerin hem de mühendislik hizmetlerinin beraber ele alınması, tek başına değerlendirilmemesi gerekmektedir. Kalıcı çözümler üretilmesi bakımından ayrıca sürücü, yaya ve yolcuların insani davranışlarının geliştirilmesi yönelik çabaların yoğunlaştırılması önem arz etmektedir. Kamuoyunda çeşitli bilgilendirmeler ve kampanyalar hazırlanarak eğitim amaçlı programlar hazırlanmalı, vatandaş bilgilendirilmeli, eğitim kurumlarında bu konuda uzman eğitimciler tarafından öğrencilere gerekli bilgi akışı sağlanmalıdır. Yasalarda çeşitli düzenlemeler yapılarak alkollü araç kullanımı, hız limitlerinin aşımı, ehliyetsiz araç kullanımı gibi kural dışı davranışların önüne geçmede cezalarda caydırıcılığın sağlanması gerekmektedir. Kazalarda insan faktörü daha çok olduğundan alınacak önlemler yasa bazında arttırılmalı her kaza kendi içinde bir bütün olarak değerlendirilmelidir. Sürücü kursları kurumsallaştırılarak hizmetin daha etkin sağlanması sağlanmalıdır. İlk yardım, trafik ve araçların teknik özellikleri bakımından kullanıcılar daha etkin bir şekilde bilgilendirilmelidir. Mühendislik olarak yol alt yapı ve üst yapı hizmetlerinde ihtiyaçların karşılanması ve ihtiyaç duyulan onarım çalışmalarının ve eksikliklerinin zaman kaybetmeden giderilmesi gerekmektedir.

Trafik kazaları sadece ülkemizin değil bir çok ülkenin önemli sorunlarından biridir. Bir anlık dikkatsizlik kazaların olmasına davetiye çıkarmaktadır. Bu bakımdan alınan tedbirlerin dikkatsizliğin ve mühendislik hizmetlerinin eksikliklerinin önüne geçecek şekilde geniş kapsamda ele alınarak çözüm yoluna gidilmelidir.

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# USE OF DMA TO STUDY RIGID AND PLASTICIZED PVC/PMMA BLENDS

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## ABSTRACT

The dynamical mechanical properties of rigid and plasticized PVC/PMMA blends were investigated. Blends of variable composition from 0 to 100 wt% were prepared in the presence (15, 30 and 50 wt %) and in the presence of di-2-(ethyl hexyl) phthalate or DEHP as plasticizer.

The tang peak, width, the  $\tan \delta_{\max}$  area under the tang curve were used to understand the miscibility and damping properties of the blends. The dynamic mechanical properties as a function of temperature for various concentration of PMMA and different content of DEHP vary. The loss tangent ( $\tan \delta$ ) varies with the concentration of the plasticizer. For a given content of DEHP, the  $T_g$  of blends increases with the increase of PMMA. It can be observed that the magnitude of  $\tan \delta$  reduces as the concentration of PMMA decreases. The increase in height of  $\tan \delta$  peak and the decrease in the  $T_g$  indicate greater molecular mobility. The damping property of the blend increases with an increase in frequency. An increase in frequency shifts the  $\tan \delta$  curve to higher temperatures.

## INTRODUCTION

The study of polymer blends is at the present time of capital importance for the development of new polymeric materials [1]. The polymer blends often exhibit properties that are superior to any individual component polymer. However, the manifestation of superior properties depends upon the miscibility of homo polymer on the molecule scale [2]. The type of interaction between polymer and their products depend on the level of the distribution or mutual miscibility of the components in blend. Despite extensive literature available, the miscibility issue in PVC/PMMA blends, however, is still controversial. The first study on PVC was done by Schurer et al. [3] who concluded that PVC was partially miscible with atactic and syndiotactic PMMA but almost completely immiscible with isotactic PMMA. The PMMA/PVC blend is a well-known system in which a hydrogen bonding type of specific interaction involving the  $\alpha$ -hydrogen of PVC and the carbonyl group of PMMA is expected [4]. In previous works, the thermal [5, 6] and thermo-oxidative [7] dehydrochlorination of rigid and plasticized PVC/PMMA blends were studied by measuring the amount of HCl released from PVC by a continuous potentiometric method. In both cases, it was found that PMMA exerted a stabilizing effect on the thermal degradation of PVC by reducing the zip dehydrochlorination and by leading to the formation of short polyenes. In the present work, miscibility for different composition of blends have been studied using mechanical thermal analysis (DMTA).

## MATERIALS AND PROCEDURE

Commercial grades of PVC, PMMA and additives listed in Table 1 were used as received. The K value of PVC is 67 according to the DIN 53-726;  $\rho$  (PVC) = 1.54 g/cm<sup>3</sup>;  $\rho$  (PMMA) = 1.18 g/cm<sup>3</sup>; Mn(PVC) = 89,700; Mn(PMMA) = 57,900. Blends of PVC and PMMA of variable compositions from 0 to 100wt% were prepared in the presence of 0, 15, 30 and 50 wt% of DEHP, 1wt% of lubricant and 3wt% of heat stabilizer. The amounts of the three additives were added according to the amount of PVC in the blend. Melt mixing was performed at 175°C for 8 min in a two-roll mill.

**Table 1.** Compounds used

Compound	Commercial name	Source
PVC	4000 M	ENIP SKIKDA (Algeria)
PMMA	Vedril 09	BASF (Germany)
Complex Ba/Cd/Zn (heat stabilizer)	Palatinol AH-L	Ackros Chemicals (USA)
Stearic acid (lubricant)	Loxiol G 20	HENKEL (Germany)
Di(ethyl-2-hexyl)phthalate (plasticiser)	Palatinol AH-L	BASF (Germany)

Investigation of the  $\alpha$ -relaxation process associated with the glass transition and the  $\beta$ -transition were performed by dynamic mechanical thermal analysis (DMTA) on a DMTA 2980 from TA instruments. Specimens were excited using 20  $\mu$ m dynamic displacement, and a small preload (0,2N) to insure that the specimens were always in tension. The runs were conducted at a heating rate of 2°C/min between -50°C and 150°C using different frequencies 1, 3 and 5 Hz. The aim of these runs was to locate the glass transition region for each sample and see the effect of plasticizer content on the  $\beta$ -transition of the polymer. The viscoelastic properties were characterized versus temperature, namely, the storage modulus ( $E'$ ), the loss modulus ( $E''$ ), and the mechanical loss factor  $\tan \delta = E''/E'$ .

RESULTS AND DISCUSSIONS

Dynamic Mechanical Thermal Properties Dynamic mechanical thermal analysis is a reliable approach to examine the relaxation behavior of materials. In order to evaluate the effects of PMMA and DEHP addition into the PVC matrix, thermo mechanical properties were measured.

The variations of storage modulus, loss modulus, and tan d with temperature for pure PVC and pure PMMA at frequencies of 1, 5, and 10 Hz are shown in Figs. 1 and 2, respectively. Figures 1a and 2a show the variation of tan d as a function of temperature. A peak in tan d associated with a-relaxation, in correspondence with the glass transition, can be observed for PVC at 91.1°C and PMMA at 127°C. Strictly speaking, the dynamic mechanical thermal analysis (DMTA) Tg should be referred to as T $\alpha$ , since one observes by DMTA the a-relaxation peak. However, for simplicity, Tg will be used in this article. The pure polymers PVC (Fig. 1b) and PMMA (Fig.2b) have, respectively, the values of storage modulus 2.74 and 3.43 GPa at 250°C. This temperature was chosen because flexible samples were studied, especially those containing 50 wt% of DEHP. The region (II) is the region where the storage modulus decreased rapidly. This region is the transition where the blend changes from glassy (I) to the rubbery state (III). Loss modulus (E'') plots versus temperature for pure PVC and PMMA are shown in Figs. 1c and 2c, respectively. The loss modulus (E'') for the pure polymers PVC and PMMA shows two peaks. One is associated with the a-transition, in correspondence with the glass transition, at 91.1°C for PVC and 127°C for PMMA. The other peak is a broad secondary b-transition centered at 250°C for PVC and 20°C for PMMA [15]. The damping property of the blends increases with an increase in frequency. An increase in frequency shifts the tan d curve to higher temperatures (see table 2).

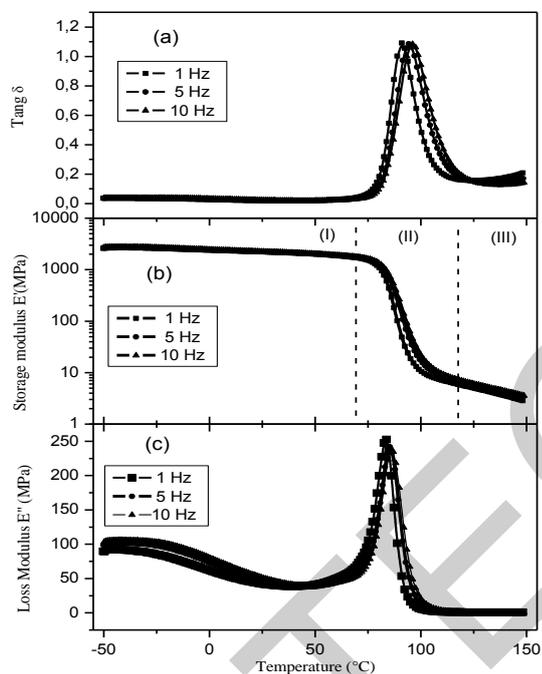


Fig.1. Effect of various frequencies on the DMA parameters of PVC

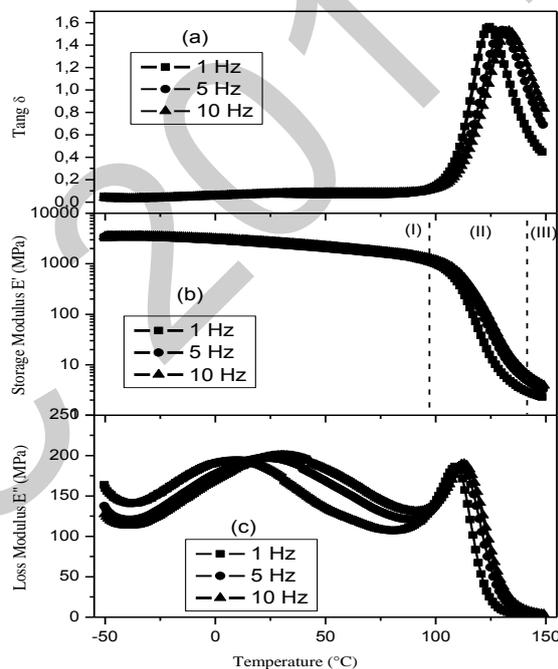


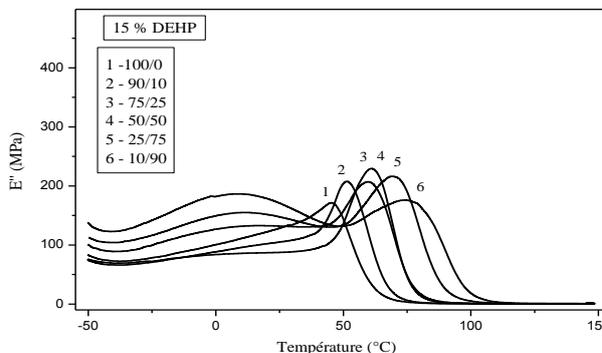
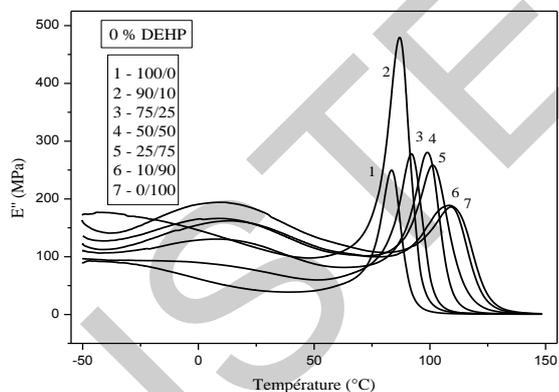
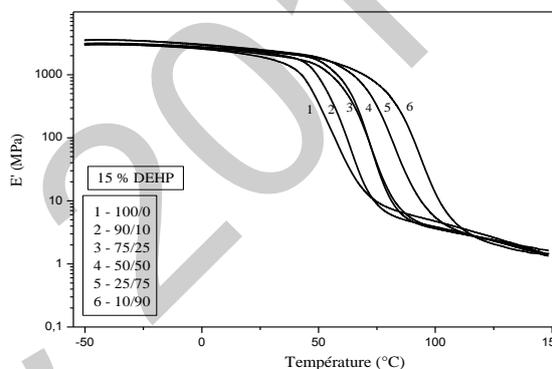
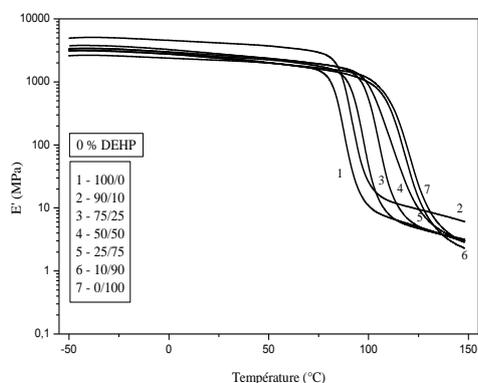
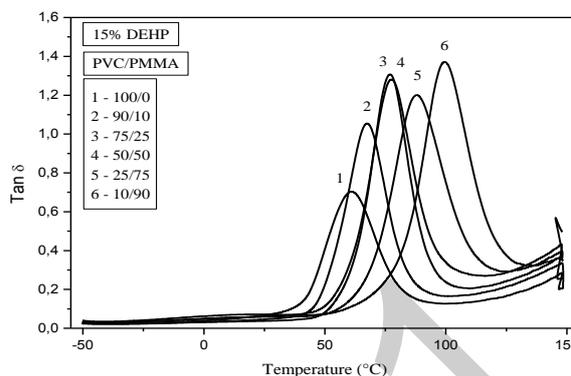
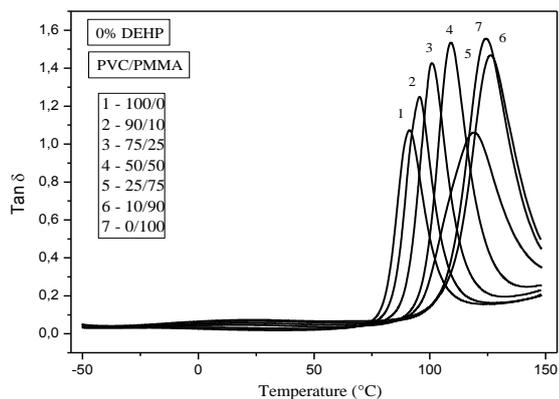
Fig. 2. Effect of various frequencies on the DMA parameters of PMMA.

Table 2. Glass transition temperature of rigid PVC/PMMA blends at various frequencies.

PVC/PMMA blends	Glass transition temperature (Tg) (°C)		
	1 Hz	5 Hz	10 Hz
100/0	91,1	94,3	96,0
90/10	95,5	98,4	100,2
75/25	100,7	105,0	106,6
50/50	109,0	113,5	115,5
25/75	119,3	123,6	125,8
10/90	126,1	131,8	134,9
0/100	127,0	132,8	135,7

Figure 3 and 4 show the variation of tang  $\delta$  in function of temperature of various concentration of PMMA and different content of DEHP. The region where the tan  $\delta$  curve reaches the maximum value is close to the glass transition temperature of the material. The measurement of Tg as a function of the composition give an idea about miscibility of the system. The presence of a single loss peak for each blend composition is a clear symptom of the miscibility of PVC/PMMA blends, since this is assimilated to a single Tg located between the corresponding Tg's of pure components. The Tg transition of the PVC/PMMA blends is higher than the Tg of PVC because of the presence of PMMA with a higher molecular weight. However, the Tg of

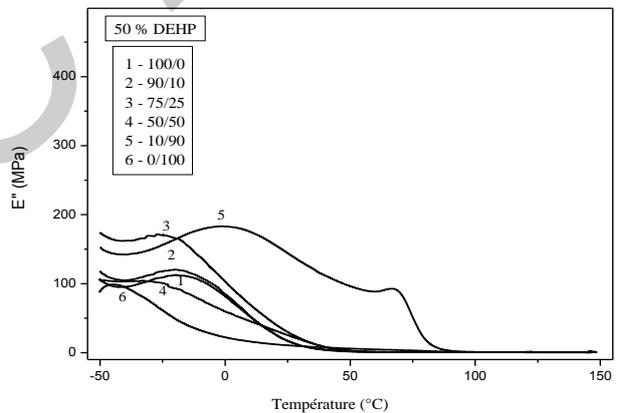
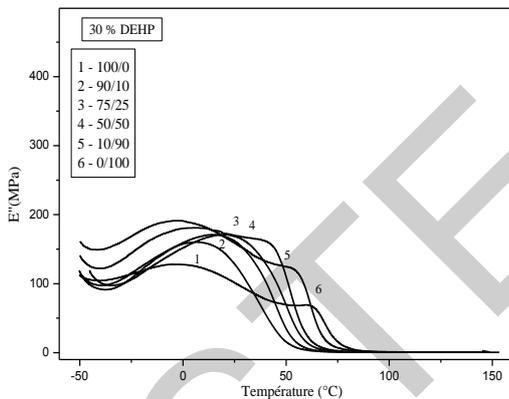
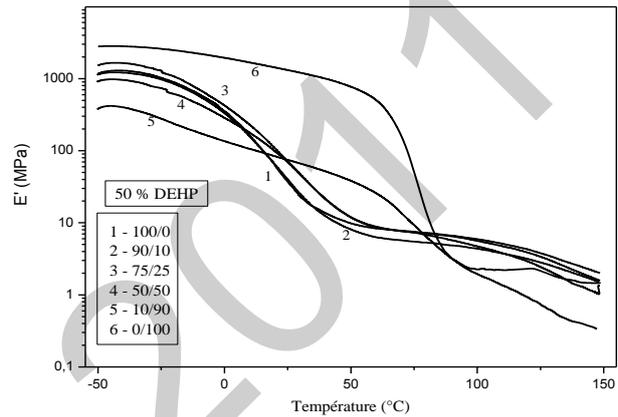
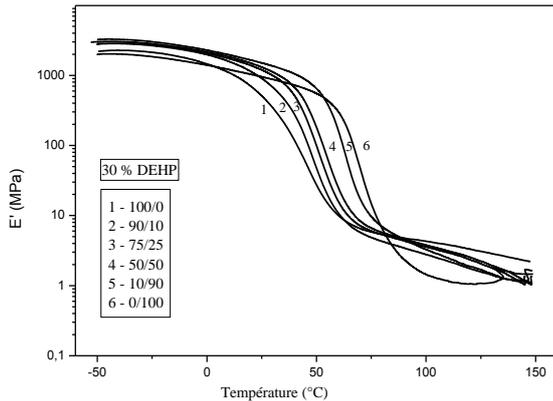
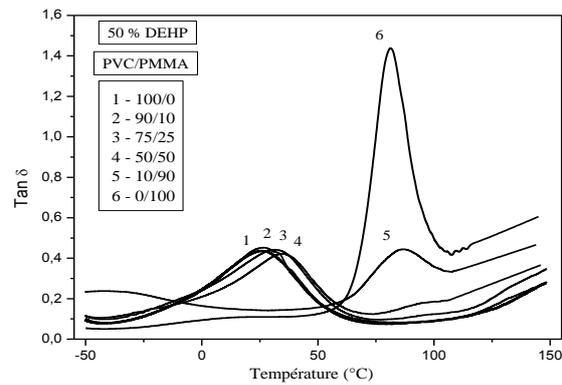
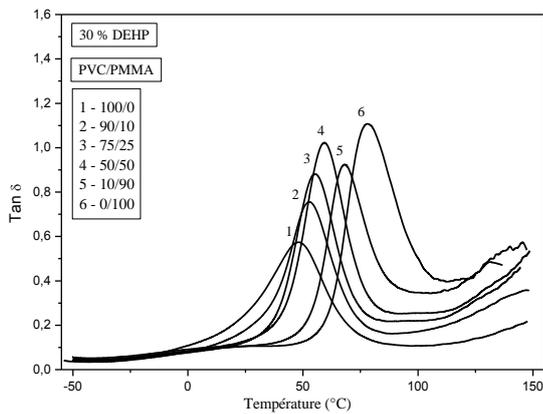
the PVC/PMMA blends is lower than of the PMMA Tg. Plasticized samples show a shift to lower temperature for the glass transition temperature at different level of plasticizer. These shifts are associated with the esters that may interact with the polymer molecules, and are able to fill the free volume in the polymer matrix, increasing chain mobility of PMMA and allowing the long-range motion [13-17].



**Fig. 3.** Loss  $\tan \delta$ , Storage modulus and Loss modulus of rigid PVC/PMMA blends.

**Fig. 4.** Loss  $\tan \delta$ , Storage modulus and Loss modulus of plasticized PVC/PMMA blends with 15% DEHP.

The glass transition temperatures ( $T_g$ ) of rigid and plasticized PVC/PMMA blends are reported in table 2 at 1, 5 and 10 Hz. It is known that the presence of a plasticizer decreases the  $T_g$  value. In our case and for same blend composition, all the plasticized blends showed lower  $T_g$  in comparison with the rigid blends. Furthermore, for a same blend composition, the values of  $T_g$  decreased with the amount of plasticizer. The damping propriety of the blends increases with an increase in frequency. An increase in frequency shifts the  $\tan \delta$  curve to higher temperature. The loss modulus shows two peaks, one is associated with the  $\alpha$ -transition, in correspondence with the glass transition, and the other a broad secondary  $\beta$ -relaxation. The  $\beta$ -relaxation of the blends seems to result from the combination of secondary relaxation of PVC and PMMA. The plasticizing character of DEHP shows up by a decrease of  $T_g$ .



**Fig. 4.** Loss  $\tan \delta$ , Storage modulus and Loss modulus of plasticized PVC/PMMA blends with 30% DEHP.

**Fig. 5.** Loss  $\tan \delta$ , Storage modulus and Loss modulus of plasticized PVC/PMMA blends with 50% DEHP.

The glass transition temperatures of rigid and plasticized PVC/PMMA blends at 1, 5, and 10 Hz are reported, respectively, in Tables 3 and 4. It is known that the presence of a plasticizer decreases the  $T_g$  value. In our case and for the same blend composition, all the plasticized blends showed a lower  $T_g$  in comparison with the rigid blends. Furthermore, for the same blend composition, the value of  $T_g$  decreased with the amount of plasticizer. The damping property of the blends increases with an increase in frequency. An increase in frequency shifts the  $\tan \delta$  curve to higher temperature. Figure 4 shows the variation of storage modulus with temperature for rigid and plasticized PVC/PMMA blends. The results demonstrate that the values of storage modulus decreased slightly while raising the temperature in a range lower than 75°C or higher than 120°C for the rigid blends and lower than 50°C or higher than 100°C for the blends plasticized with 15 and 30% of DEHP. However, within the ranges of 75–120°C and 50–100°C, the storage modulus decreased rapidly. This region is the transition one, where the blend changes from glassy to the rubbery state. This behavior was attributed to the segmental mobility of polymer chains in that region. The increase of plasticizer content decreases the storage modulus. The DMTA traces are likely to yield some extra information regarding the distribution of interaction within the plasticized systems. As the  $\alpha$  peaks continuously broaden with increasing the amount of DEHP; it turns out that the specific interactions responsible for both miscibility and plasticization are more and more distributed. The  $\beta$ -relaxations have little shifts from the maximum temperature value, apparently unaffected by the presence of plasticizer even up to 30 wt %. Thus, the presence of 50 wt % of DEHP is sufficient to provoke the quasi-disappearance of the  $\beta$ -relaxation [9,10].

**Table 3.** Glass transition temperature of plasticized PVC/PMMA with 15, 30 and 50% of DEHP and at various frequencies.

Frequency	Glass transition temperature (T <sub>g</sub> ) (°C)								
	1 Hz			5 Hz			10 Hz		
PVC/PMMA	15%	30%	50%	15%	30%	50%	15%	30%	50%
100/0	61.1	47.5	26.1	64.95	51.9	30.5	67.07	53.6	32.2
90/10	67.49	52.5	26.3	71.44	56.6	29.8	73.70	58.2	32.0
75/25	76.94	101.1	31.5	81.46	104.8	35.7	83.46	107.1	38.0
50/50	77.55	59.4	34.6	82.59	63.6	38.5	84.56	66.0	40.5
25/75	87.81	68.1	86.5	93.59	71.4	90.8	96.27	73.3	92.9
10/90	99.52	77.8	81.2	105.4	83.0	85.0	108.4	85.1	86.9

Dynamic mechanical thermal analysis (DMTA) is a reliable approach to examine the relaxation behavior of the materials. In order to evaluate the effect of the PMMA and the DEHP into the PVC matrix, thermomechanical properties were measured. The variation of storage modulus, loss modulus, and  $\tan \delta$  with temperature for pure PVC and pure PMMA at frequency 1, 3 and 5 Hz is shown in figure 1 and 2 respectively. In figure (1-b), (2-b) the pure polymers PVC and PMMA have the value of storage modulus 2735.5 MPa and 3422.8 MPa, respectively, at  $-50^{\circ}\text{C}$ . Figure (1-a), (2-a) show the variation of  $\tan \delta$  in the function of the temperature. A peak in  $\tan \delta$  is associated with  $\alpha$ -relaxation, in correspondence with the glass transition can be observed both for the PVC at  $91.1^{\circ}\text{C}$  and for the PMMA at  $127^{\circ}\text{C}$ .

(Strictly speaking, the DMTA T<sub>g</sub> should be referred to as T<sub>a</sub> since one observes by DMTA the  $\alpha$ -relaxation peak; however, for simplicity, T<sub>g</sub> will be used). Loss modulus (E''), versus temperature, for pure PVC and PMMA are shown in figure (1-c), (2-c). The loss modulus (E'') for the pure polymer PVC and PMMA show two peaks, one is associated with the  $\alpha$ -transition, in correspondence with the glass transition at  $91.1^{\circ}\text{C}$  for PVC and  $127^{\circ}\text{C}$  for PMMA, and the other a broad secondary  $\beta$ -transition centered at  $-50^{\circ}\text{C}$  for PVC and  $20^{\circ}\text{C}$  for PMMA [8]. The damping propriety of the blends increases with an increase in frequency. An increase in frequency shifts the  $\tan \delta$  curve to higher temperature.

The variations of loss modulus (E'') for rigid and plasticized PVC/PMMA blends are shown in Fig. 5. The loss modulus shows two peaks. One is associated with the  $\alpha$ -transition, in correspondence with the glass transition, and the other denotes a broad secondary  $\beta$ -relaxation. The  $\beta$ -relaxation of the blends seems to result from the combination of the secondary relaxations of PVC and PMMA. The plasticizing character of DEHP is shown by a decrease of T<sub>g</sub>. The DMTA traces are likely to yield some extra information regarding the distribution of interactions within the plasticized systems. As the  $\alpha$  peaks continuously broaden with increasing amounts of DEHP, the specific interactions responsible for both miscibility and plasticization are more and more distributed. The  $\beta$  relaxations have minimal shifts from the maximum temperature value, and are apparently unaffected by the presence of plasticizer even up to 30 wt%. Thus, the presence of 50 wt% of DEHP was sufficient to provoke the quasi-disappearance of the  $\beta$ -relaxation [16, 17] or shift it to a temperature below which measurements were made.

## CONCLUSION

The DMTA analysis of rigid and plasticized PVC/PMMA blends showed polymer miscibility. This is seen from the presence of single T<sub>g</sub> which changes with the composition of the blends.

Regarding DMTA analysis, plasticizers cause the glass transition to shift markedly lower temperature, the typical effect of plasticizers, however, the temperatures and peak heights of the  $\beta$ -relaxation are unchanged even up to 30 wt % DEHP.

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# UZAKTAN EĞİTİM PROJELERİNİN DEĞERLENDİRİLMESİ

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## ÖZET

Uzaktan eğitim veren kuruluşların sayıları her geçen gün artmaktadır. Ösym'nin 2011 YGS klavuzuna göre 28 üniversite önlisans uzaktan eğitim programı açmıştır. Yine aynı klavuzda göre 13 üniversite lisans programı açmıştır. Bunun dışında yüksek lisans programlarını uzaktan eğitimle veren üniversiteler de bulunmaktadır. Her geçen gün daha zor derslerin verilebildiği uzaktan eğitim projelerinde, 2011 Ösym tercih klavuzuna göre 10 adet mühendislik eğitimi veren uzaktan eğitim programı eğitimlerine devam etmektedir.

Ayrıca bazı özel kurumlar da eğitimlerini uzaktan eğitim kullanarak vermeyi tercih etmeye başlamıştır. Her gün karşımıza çıkan yeni bir bilgi ve iletişim teknolojisi aracı ve yeni yazılımlar uzaktan eğitimin ilerlemesinde ve gelişmesinde önayak olmaktadır. Web sitelerinin bant genişliğinin artması ve saniyedeki veri aktarım hızının yükselmesi uzaktan eğitimdeki faaliyetleri ve etkileşimi arttırmaktadır.

Bu büyük resme bakarak uzaktan eğitimin gün geçtikçe çok daha hızlı büyüyeceğini görebiliriz. Bu kadar çok paydaşın 1.dereceden etkilendiği bir sistemin işleyişinin sağlıklı olabilmesi için gereken en önemli unsurlardan biri uzaktan eğitim projelerinin değerlendirilmesidir.

## GİRİŞ

Uzaktan eğitim, öğrencilerin nasıl, nerede öğreneceğini ve öğretmenlerin ne çeşit öğretim yapacağını açıklayan bir kavramdır. Geçmişte uzaktan eğitim öğrencilerinin eğitimi için iyi bir fırsat sunulmuştur. Günümüzde ise uzaktan eğitimle ilkökul, ortaokul, lise ve üniversite düzeyinde eğitim verilmektedir. Bir çok üniversite lisans eğitimini uzaktan eğitim ile vermeye başlamıştır (İşman, 2011).



Uzaktan eğitim belli başlı ana kavramlar üzerinde hızla büyüyen ve gelişen bir sistemdir. Tablo-1 (İşman, 2011- 5. madde tarafımızdan eklenmiştir.)

Ceylan (2011)'a göre Türkiye genelinde yaklaşık 2 milyona yakın kişi uzaktan eğitim alıyor. 10 yıl içerisinde bu sayının 10 milyona ulaşacağı tahmin ediliyor. Soncul (2010) ise 2008 yılında İngiltere'de uzaktan eğitim alan öğrenci sayısının 180 bine ulaştığını, dünyada ise bu sayının yaklaşık 90 milyon olduğunu tahmin edildiğini belirtmiştir. Amerika'da uzaktan eğitim alan öğrenci sayısı 2002 yılında 1.6 milyon öğrenciyi aşarken (Allen ve Seaman, 2003, akt. Keçik, 2011), bu rakam 2005 yılında 3.18 milyon öğrenciye ulaşmıştır ve bu rakamın yaklaşık yüzde 25'i eğitim alanındaki uzaktan öğretim öğrencilerinden oluşmaktadır (Allen, Seaman ve Garret, 2007, akt. Keçik, 2011)

Eğitsel bağlamda, değerlendirme çalışmaları, programların, politikaların, personelin, işleyişin, ürünlerin/çıktıların ve organizasyonun geçerliliğini geliştirme, inceleme ve bunları raporlama uygulamalarıdır (American Evaluation Association, akt. Saba, 2000).

Değerlendirme beklenen ve beklenmeyen olayların her ikisini de kapsar ve değeri ve bedeli hakkında yapılan yargılamaları içerir (Chambers, 1995; Institute for Higher Education Policy, 1999; Rowntree, 1992; Stufflebeam, 1999; Thorpe, 1996, akt. ). Bu nedenle değerlendirmenin odağı her zaman programlanan grup ya da grupların paydaşlarının –toplum, kurum, öğrenci, işveren vs.- önemi üzerinedir (Thompson ve Irele, 2003). Diğer taraftan değerlendirme, bazı önemli değişkenlerin-test puanı, etkileşim seviyesi, tepki süresi ve vb.- nesnel zeminin belirleme girişimidir (Joint Committee on Standards for Educational Evaluation, 1994).

Değerlendirme ile ölçme odağının “what is – ne olduğu” değer tahmininin alt kollarıdır (Rowntree, 1992). Önceki odak noktalarının sahip olduğu belirleme standartlarının soruları –“What should be?-Ne olmalı”- geniş değerlendirme

faaliyetinde önemli bir araçtır. Değerlendirme “How much?-Ne kadar?” sorusunu sorar. Değer biçilirken “Is it good enough? – Yeterince iyi mi?” ve “If not, why not? – Eğer değilse, neden değil?” soruları sorulur. (Thompson ve Irele,2003).

Değerlendirme çalışmaları paydaşları ilgilendiren soruları cevaplandırmak için yapılır. Bu nedenle bir değerlendirmenin odağı, paydaşların veya paydaş gruplarının bilgi ihtiyacına göre değişebilir. Buna rağmen birçok değerlendirme faaliyetinin birden daha fazla amacı vardır. Ortak amaçlar, haklı yatırım kaynaklarını, kalitesinin ve geçerliliğinin incelenmesini, program hedefleri doğrultusunda ölçme işlemlerini, program süreçlerinin ve çıktılarının temel gelişiminin saptanmasını ve stratejik kararlar vermek için bir temel saptamayı kapsar(Thompson ve Irele,2003).

Bir değerlendirici bir değerlendirme projesinin planlamasında ve uygulamasında bazı tercihlerle karşı karşıyadır. Değerlendirici;

1. Paydaşların bilgi ihtiyaçlarını açığa çıkarmalı,
2. Özellikle neyin değerlendirileceğine karar vermeli,
3. En uygun veri toplama metodlarını ve araçlarını seçmeli ve
4. Kendisine doğru yollardan doğru bilgiyi verecek uygun raporlama biçimine karar vermelidir(Thompson ve Irele,2003).

### Değerlendirmedeki Amaç ve Odak

Güvenilir ve geçerli değerlendirme bilgisini elde etmek için değerlendiriciler değerlendirmenin amacını ve odağını net bir şekilde anlayarak başlamalıdır. Şu gibi sorularla değerlendirmeye başlamalıdır:

- Paydaşlar kimlerdir? Who are the stakeholders?
- Ne bilmeye ihtiyaç duyarlar? What do they need to know?
- Bilgi/veri nasıl kullanılacak? How will the data be used? (Cyrus, 2001)

Muhtemelen değerlendiriciler tarafından en çok yapılan ortak hata bir değerlendirme faaliyeti için çok fazla soruya cevap vermeye çalışmak ya da çok genel sorulara cevap vermeye çalışmaktır (Thompson and Irele, 2003). Ehrmann(1997a), şunu öne sürer: ”yapılan bir çalışma hakkındaki en zor sorun, ne çalışılacağını bulma sürecidir.”

Yıllar içinde, deneyimli birkaç uzaktan eğitimci özellikle uzaktan eğitime odaklanan değerlendirme yaklaşımları geliştirdiler. Bu alanda yapılan çalışmalar Flagg(1990, akt. Saba,2000), Duning et al.(1993), Ehrmann(1997b; 1999a; 2001), Bates(2000) ve Cyrus(2001) tarafından temsil edildi.

### FLAGG(1990)'a Göre;

Flagg (1990, akt. Saba,2000), özellikle formative(geliştirilebilir) değerlendirmeye odaklandı ve bunu dersleri değerlendirmede bir araç olarak kullandı. Geliştirilebilir değerlendirmenin planlaması ve uygulaması için 7 basamak önerdi:

- Açıklığa Kavuşturma; değerlendirme çalışmalarının amaçlarını saptayın
- Değerlendirme bilgisinin alıcılarını açıkça belirtin ve seçin
- Değerlendirme sorularını listeleyin
- Değerlendirmenin genel şemasını ya da paradigmasını (egemen düşüncesini) gösterin
- Veri toplama stratejisini ve ölçüm araçlarını seçin
- Cevap niteliğindeki örnekleri belirleyin
- Değerlendirme ayarlarını ve prosedürü seçin

Saba(2000), yöneticilerin, Flagg tarafından önerilen yedi basamağın tamamı ile ilgilenmesine rağmen, son beş basamağını “technical in nature” olarak adlandırdı ve deneyimli değerlendiriciler tarafından en iyi başarıya ulaşılabilecek adımlar olduğunu belirtti.

### **DUNİNG ve Arkadaşları. (1993)'na Göre**

Duning ve arkadaşları uzaktan eğitimin değerlendirilmesine, “değerlendirme ve sürdürülebilir kalite” perspektifinden yaklaşmışlardır. Onlar tartışmalarına “efsane ve onun yararlı gerçekleri” ile başlamışlardır.

Myth(Efsane): Telekomunikasyon tabanlı eğitimin kalitesi, geleneksel eğitim standartları ile teknik erişilebilirlik, güvenilirlik ve etkileşimin değerlendirilmesi önemli bir mesele-husus- olacaktır.

Reality(Gerçeklik): Eğitsel telekomunikasyon sistemlerinin potansiyel ulaşımı ve öğrenimsel etkisi öğrencilerle yeni ilişkiler temelinde yatan değerleri konuşma kalitesinin tedbirlerini gerektirecektir.

Bu nedenle yazarlar, uzaktan eğitimde, bu kavramları düzgün bir şekilde entegre edecek yeni ve iyi ifade edilmiş standartlara ihtiyaç duymuşlardır. Duning ve arkadaşları uzaktan öğrenme sistemlerinin 3 aşamada değerlendirilebileceğine değinmişlerdir. Bu adımlar:

- The Functional – Fonksiyonel olması
- The Managerial – Yönetilebilir olması
- The Instructional Or Ethical – Öğretici veya etik olması

Teknik tasarım faaliyetleri ile fonksiyonel olma aşaması, donanım ihtiyaçlarını ve teknik olarak iyi donanımlı personeli içerir. Yönetilebilir olma aşaması, programın organizasyon yapısı içindeki ve dışındaki gerekli ilişkilerin teşvik edilmesi ve yönetilmesindeki başarının boyutu üzerine odaklanır. Bu ilişkiler diğer örgütsel birimler ile ilgili veya öğretim üyeleri, öğrenciler ve programın uygulanması için gerekli olan diğer önemli-kritik- noktalar hakkında olabilir. Son olarak etik olma aşaması programın çıktıları üzerine odaklanmaktadır. Bu aşamanın etik boyutu ne ölçüleceği ve kurumun değerleri hakkında ne kararlar verileceği seçimlerini yansıtmaktadır.

### **EHRMANN (1997a, 1997b, 1999a, 2001)'e Göre**

Ehrmann kendi değerlendirme yaklaşımını uzaktan eğitimin sahip olduğu ve imkanı kıldığı izole edilebilen ve yakından incelenebilen genel hedefler fikri etrafında inşa etmiştir.

- Etkinleştirilebilecek şekilde düşünülmüş önemli yeni içerik
- Kimin öğrenebileceğini değiştirme
- Öğrenme ve öğretme etkinliklerini geliştirme
- Öğrenme ve öğretme etkinliklerinin ücretlendirmesinin düşürülmesi veya kontrol altına alınması

Küçük bir bölgeyi ışıl ışıl aydınlatan bir el fenerinin metaforunu kullanmayı önerir. Değerlendiriciler, genel ilkeler hakkında, genellikle “neredeyse tutarsız-anlamsız” bir soru ile sorularına başlar, ardından, şekilsiz bir “damla”yı, odaklanmış bir değerlendirme “üçlü”süne dönüştürür. Ehrmann “üçlü” kelimesini incelenmek için hazırlanmış soruların yerine kullanmayı tercih etmiştir. Bu sorular:

- Belirli bir teknoloji veya yöntem (e-mail gibi) ile ilgili
- Denenmiş etkin kılınabilecek belirli bir teknoloji veya metod ile ilgili
- Arzulanan bir program çıktısıyla ilgili

Süreçteki bir sonraki adım soruları ilgili beş alan hakkında sormaktır:

- Her kimseye-kullanıcıya teknoloji
- Teknolojinin faaliyetler için kullanımı
- Her kimseye-kullanıcıya faaliyet
- Faaliyetin istenen sonuca nasıl katkıda bulunduğu ya da bulunup bulunmadığı
- Her kimseye-kullanıcıya çıktı(outcome)

Bu El feneri projesi (The Flashlight Project) değerlendiricilerin kendi değerlendirme projelerinde odaklanabilmelerine yardımcı olan bazı hizmetler ve araçlar geliştirmiştir. 500 maddelik geçerli öğrenci envanteri, örneğin, 1,3 ve 5 adet sorudan daha fazla öğrenme ve öğretmen alanları ile ilgili bir dizi soru doğurmaktadır:

<b>Bu sorular ile ilgili alanlar</b>	
Aktif öğrenme	Bilişsel ve yaratıcı sonuçlar
İşbirlikçi öğrenme	Erişilebilirlik
Verimli zaman kullanma	Pozitif teknoloji bağımlılığı
Zengin ve hızlı geri dönüt	Teknoloji kullanımı için önkoşullar
Öğrenmedeki sorumluluk	Görev süresi (Time on task)
Fakülte-öğrenci etkileşimi	Çeşitliliğe saygı
Öğrenme stili ne olursa olsun tüm öğrenciler için yüksek beklentiler	Gerçek dünyaya uygulanması

### **BATES (2000)'e Göre**

Bates'in ACTIONS-Eylemler Modeli "teknolojinin sınıfta öğrenmedeki yeteneğini arttırmaktan daha çok etkenlerin daha geniş bir alanı kapsamasına" dikkatle odaklanır. Kısaca Eylem Modeli farklı öğretim teknolojilerinin etkinliğini değerlendirirken dikkate alınması gereken 7 faktörü temsil eder:

- Erişim ve esneklik
- Maliyet
- Öğretmen ve öğrenme
- Etkileşimliliği ve kullanıcı dostluğu
- Örgütsel konular
- Yenilik
- Hız

Bu faktörlerin her biri için Bates, uygun değerlendirme ve araştırma soruları önerir. Teknolojilerin öğrenme etkinliğine odaklanmasının yanı sıra; Bates,

- yazılım uygulamalarına ilişkin değerlendirme konularını,
- öğrenen etkisini(öğrenme çıktılarının haricinde),
- akademik teknoloji organizasyonu ve yönetimini ve
- fayda-maliyet analizlerini inceler.

Bates tüm bu kategorilerdeki soruların cevaplarına odaklanmış özenle tasarlanmış değerlendirme çalışmalarına olan ihtiyacı göz önüne serer ve her birinin çalışılması gerekli önemli alanlar olduğunu belirtir.

### **CYRS (2001)'a Göre**

Cyrs, değerlendiricilere uzaktan eğitim programı geliştirmek ve uygulamak için kurallar ve ses, görüntü, veri ve çıktı programları için ders değerlendirmeleri önerir. Cyrs uzaktan eğitimdeki değerlendirme biçimleri arasından değerlendirme kuraları olarak 10 alana odaklanır:

- Değerlendirmenin amaçları
- Cevap verilecek sorular
- Biçimlendirici ve özetleyici değerlendirme
- Değerlendirme araçlarının çeşitleri
- Ders tasarımı
- Ders yönetimi
- Öğrenme Çıktıları
- Teknolojinin verimi
- Öğreticinin sunum becerileri
- Öğrenme ortamı
- Örnek değerlendirme kriterleri ve değerlendirme ölçekleri
- Farklı öğretme (iletişim) stratejilerinin kullanılması

Cyrs, her alan içinde, ders programındaki değerlendirmenin özel elementlerine odaklanan yararlı ve uygun soruları sormayı önerir. Cyrs, aynı zamanda, derslere uygun ek değerlendirme kriterlerini ve WWW üzerinden programın verimli olmasını şart koşar. Bunun dışında olan özel hususlar;

- sınıf mevcudunu,
- senkron ve asenkron etkinliklerin dengesini,
- öğretmenin yanıt süresini,
- site navigasyonunun kolaylığını ve
- ekranları ve eğitmeni ile etkileşim için sunulan fırsatları içerir.

## SONUÇ

Uzaktan Eğitim Projelerini Değerlendirme Modelleri projelerin verimliliği açısından çok önemlidir. Projedeki tüm paydaşların deneyimlerini arttırmak için, projeye uygun değerlendirme modeli seçilmeli ve titizlikle değerlendirme yapılmalıdır. Kaliteli bir değerlendirme sonucu hem öğrenenleri hem eğitimcileri hem de yöneticileri memnun edecektir ve projelerin amaçlarına ulaşmasını sağlayacaktır.

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## UZAKTAN EĞİTİM SORUNLARI

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### ÖZET

Bu çalışmanın amacı, gelişen teknoloji ve artan ihtiyaçlar doğrultusunda hayatımızın bir parçası olan uzaktan eğitimde karşılaşılan sorunların incelenmesi üzerinedir. Bu doğrultuda uzaktan eğitim sorunları incelenirken, uzaktan eğitimde karşılaşılan idari yapı, organizasyon değişiklikleri, teknik uzmanlık, destek ve altyapı, sosyal etkileşim, maaş ve zaman, teknoloji tehdidi, telif hakkı, değerlendirme, etkililik, erişim, öğrenci destekleme servisi, iletişim, öğretmen ve öğrenci gibi sorunlar genel bir çerçevede incelenmiştir. Buna ilave olarak uzaktan eğitimin uygulanma modellerine göre (tek yönlü, çift yönlü iletişim) karşılaşılabilecek sorunlara değinilmiş, son olarak da günümüzde en çok kullanılan ve geleceğin uzaktan eğitim anlayışı olarak görülen bilgisayar, internet ve mobil teknolojilerle uygulanan uzaktan eğitim anlayışlarına özgü (web based learning, e-learning, online learning) bazı sorunlara değinilmiş ve bu şekilde sonlandırılmıştır.

**Anahtar Kelimeler:** Uzaktan Eğitim, E-Öğrenme, Web Tabanlı Öğrenme, Uzaktan Eğitim Sorunları.

### ABSTRACT

In this study, issues of distance education which is a part of our daily life due to increasing needs and technology were investigated. Accordingly, the issues are faced in distance education like administration, organisational changes, technical speciality, support and substructure, social interaction, wages and time, technological threat, copyright, evaluation, efficiency, reach, student support service, communication, teacher and student were investigated in a general perspective. In addition to this, possible issues which according to enforcement of distance education models (one way, two way communication) were expressed. Finally, native to issues of these distance education models which the most common distance education models which are seen the most promising in the future and are applied via internet and mobile technologies were expressed.

**Keywords:** Distance Education, E-Learning, Web-Based Learning, Distance Learning Issues

### GİRİŞ

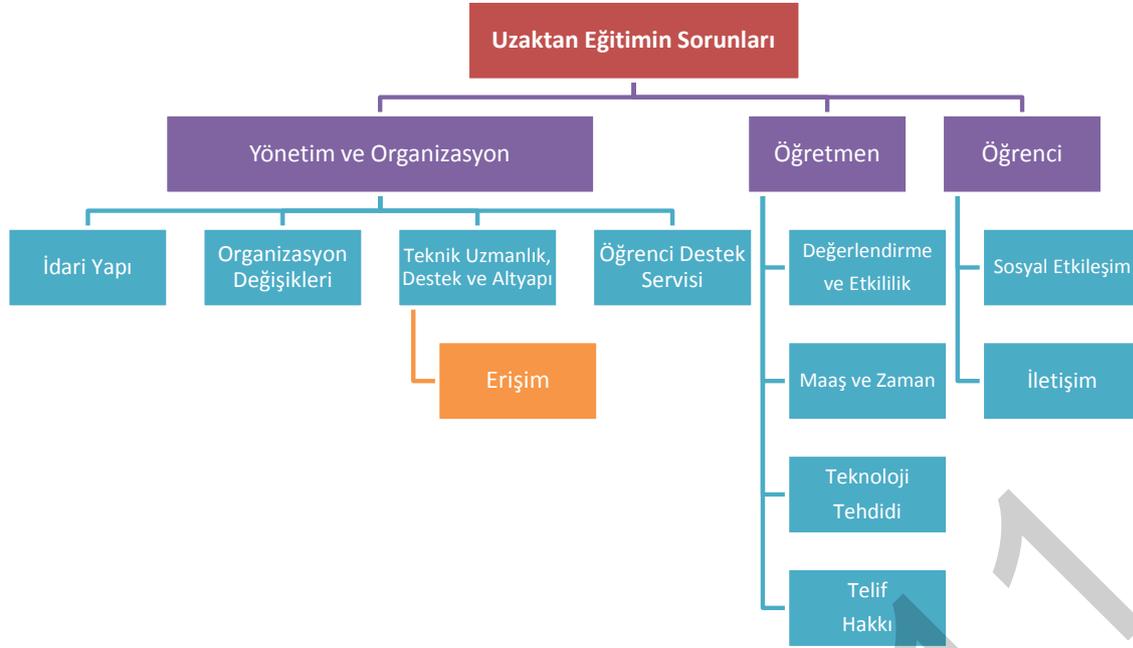
Uzaktan eğitim ile gelişmekte olan bilgisayar teknolojileri etkileşimi, eğitimin her alanında öğretmen ve öğrenciye bir çok yenilik, toplumsal açıdansa yüksek bir eğitim oranı yakalama şansı vaat etmektedir. Ancak teorikte kulağa hoş gelen bu etkileşimin, pratikte bir çok giderilmesi gereken sorunu da beraberinde getirdiği görülmektedir. Bu makalede teknolojik altyapıyla ilgili sorunları, uzaktan eğitimin öğretim yöntemlerinin geleneksel eğitimden farklı olmasının sebeplerini, yer ve/veya zamandan bağımsız yapısı itibariyle yüksek öğrenci motivasyonuna ihtiyaç duymasının yarattığı sorunları, telif hakkı problemlerini ve öğretmen-öğrenci iletişiminde yaşanan sorunlar ele alınmıştır.

"Uzaktan Eğitimdeki Engeller" isimli araştırmalarında analitik faktör kullanan Muilenberg and Berge (2001) uzaktan eğitimde en sık görülen sorunları idari yapı, organizasyon değişiklikleri, teknik uzmanlık, destek ve altyapı, sosyal etkileşim, maaş ve zaman, teknoloji tehdidi, telif hakkı, değerlendirme/etkililik, erişim ve öğrenci destekleme servisi başlıkları altında ifade etmiş, bu on soruna ise İsmail (2011), iletişim, öğretmen ve öğrenciden kaynaklanan sorunları ilave ederek on üç başlık altında toplamıştır. Bu çalışmada ise Muilenberg and Berge (2001) ve İsmail (2011) tarafından belirtilen on üç başlığı bir hiyerarşi içinde alt başlıklara bölüp Şekil 1'deki gibi yorumlanabilir.

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Şekil 1. Uzaktan Eğitim Sorunları Hiyerarşik Grafiği

## 1. Yönetim ve Organizasyon

Uzaktan eğitim sistemlerinin yönetimi geleneksel eğitim sistemlerinin yönetiminden metodolojik açıdan farklılıklar gösterse de, iki eğitim sisteminde de ham madde bilgi ve bilginin aktarılması gereken grup öğrenci olduğu için yaşanan sorunlar benzerlikler göstermektedir. Her iki sistemde de çarkın dönmelerini sağlayan tüm dinamiklerle organize çalışılması ve bu organizasyonun muhafazası önemlidir. Yönetimsel eksiklikler nedeniyle ortaya çıkacak sorunlar, tüm sisteme olumsuz yansıtacaktır.

### 1.1 İdari Yapı

Uzaktan eğitim organizasyonunda, tutarlılık, etkililik, güvenilirlik ve yeterlilik programı yönetmek için en gerekli niteliklerin başında gelmektedir. Sistemin idaresinde ise başarı, merkezi bir yönetim politikası oluşturabilmek ve bu politikadan ödün vermemekten geçer.

Cho ve Berge (2002) uzaktan eğitimde idari yapı ile ilgili sorunları ve bunlara sundukları çözüm önerilerinden şöyle bahsetmişlerdir;

- Organizasyonun yapısında çıkan sorunların giderilmesi için merkezi yapıya uyum sağlamak ve uzaktan eğitim programının yönetimini tutarlı bir tasarım şeklinde geliştirmek gerekmektedir.
- Mali yönetim eksiklikleri neticesinde oluşan sorunların çözümü için periyodik maliyet analizlerini ihmal etmemek ve yönetim kademesini sık sık bilgilendirmek gerekmektedir.
- Personel ve takım yapısı bazında sorunlarla karşılaşmamak için, deneyimli ve işinin ehli profesyonellerle çalışılması ve bu kriterin tüm personel için uygulanması önemlidir. İçinde bir profesyonelin olduğu uzaktan eğitim takımı oluşturulmalıdır.
- Uzaktan eğitimin pazarlanamaması da sistemin işleyişi ve mali disiplin programlarına uyulması açısından sıkıntılı bir durumdur. Bu sorunun meydana gelmemesi ya da düzeltilmesi için bir pazarlama ve reklam stratejisi oluşturulmalı, bunlarla ilave olarak yüksek kalitede kataloglar, bilgi, kaynak ve görseller içeren web sitesi oluşturmak akılcı bir çözüm olabilir.

### 1.2 Organizasyon Değişikliği

Toplumun ihtiyaçlarına göre değişim gösteremeyen kurumlar varlıklarını uzun süre sürdüremezler. Aynı şekilde uzaktan eğitim kurumlarının da başarılı olmak için yeniliğe ve değişime açık olmaları gerekmektedir. Aksi takdirde uzaktan eğitimde organizasyon sorunları ortaya çıkar, eğitim programının yavaş ve zor bir süreç olmasına sebep olur (İsman, 2011).

Uzaktan eğitim programının planlanması kadar planlanan programın kısa aralıklarla ve keyfe keder değiştirilmemesi de önemlidir. Farkında olmadan öğrenmeye karşı direnci kırılma eğilimi gösteren öğrenciler, verimini az bularak değiştirdiğiniz yeni programla bu direnci tekrar kazanabilirler.

### 1.3 Teknik Uzmanlık, Destek ve Altyapı

Uzaktan eğitimin altyapısını kuran, yöneten ve içinde bulunan herkesin konusunda uzmanlaşmış, yetkin kişilerden seçilmeleri gerekmektedir. Gerekli şartları sağlamayan teknik personelin işe alınmasıyla, sistemin geleceği, devam eden eğitim-öğretim dönemi ve kurumun prestiji büyük risk altına girer.

Cho ve Berge (2002) e göre teknik destek sorunları yaşamamak adına öğretmenin kullanması için moderasyon panelleri, teknik personel için kurulum aşamasında operasyonel paneller ve yedek plan hazırlanmalıdır.

#### 1.3.1 Erişim

Erişim, “bilimsel literatürün Internet aracıyla finansal, yasal ve teknik bariyerler olmaksızın, erişilebilir, okunabilir, kaydedilebilir, kopyalanabilir, yazdırılabilir, taranabilir, tam metne bağlantı verilebilir, yazılıma veri olarak aktarılabilir ve her türlü yasal amaç için kullanılabilir biçimde kamuya ücretsiz açık olmasıdır” şeklinde tanımlanmaktadır (Anadolu Üniversite Kütüphaneleri Konsorsiyumu [AÜKK], 2006).

Erişim kaynağa ulaşmadır. Ulaşım ne kadar kolay bir şekilde gerçekleşiyorsa, eğitim de o kadar kolay gerçekleşecektir. Bundan dolayı basit bir teknoloji seçilmelidir. Seçilen teknoloji herkese hitap etmelidir. Sadece yazılım olarak değil, donanım olarak da güçlü bir altyapı gereklidir.

### 1.4 Öğrenci Destek Servisi

Uzaktan eğitimde öğrenci ve öğretmenler farklı mekânlarda olduğu için, öğrencilerin eğitimden kopuk kalmaması ve dirik bir şekilde derse katılması için öğrenci destek sistemleri sunulmalıdır.

Öğrenci destek hizmetleri öğrenciler tarafından uzaktan eğitim programlarında aranan ve tercihlerini etkileyen özelliklerden birisidir. Bu nedenle uzaktan eğitim kurumları da öğrencilerine öğrenci destek hizmetlerini sunmak için çaba harcamalıdır. İyi organize olmuş bir idari yapı en etkili öğrenci desteği için çözümler önerir (Cho ve Berge, 2002).

## 2. Öğretmen

Uzaktan eğitimde öğretmenin öğrenciyle iletişim kurmaktan çekinmesi yada öğrencinin yazdığı sorulara geç cevap yazmasından dolayı öğrencinin derse ilgisi azalır ve tekrar geri dönmesi zorlaşır (İşman, 2011).

### 2.1 Değerlendirme / Etkililik

Bilindiği gibi uzaktan eğitim senkron ve asenkron biçimlerde gerçekleştirilmektedir. Durum böyle olunca da örgün eğitimden farklı olarak, değerlendirme konusunda sıkıntılar yaşanmaktadır. Öğretmen ve öğrenci farklı mekânlarda olduğu için birbirini yeterince tanıma fırsatı bulamamaktadır. Değerlendirmenin sistem tarafından belirli ölçeklerle yapılması her ne kadar avantaj olsa da, kendini sistem üzerinde yeterince ifade edemeyen öğrenciler, bilgi düzeyleri her ne kadar iyi olsa da öğreticinin gözünden kaçacaktır.

Bazı öğretmenler öğrencilere değerlendirme faaliyetlerinde adaletsiz davranmaktadırlar. Bu da öğrencilerin derse bakış açısını değiştirmekte ve olağan motivasyonlarını düşürmektedir. Bu tür sorunların çözümünde öğretmenlerin değerlendirme metotlarını gözden geçirmeleri ve adaletli davranmaları gerekmektedir.

### 2.2 Maaş ve Zaman

Uzaktan eğitimde de geleneksel eğitimde olduğu gibi öğretmenin kendi hayatını idame ettirebilmesi için zaman harcadığı mesleğinden tatmin seviyesinde gelir elde etmesi gerekmektedir.

Tatmin seviyesinde gelir elde edemezse uzaktan eğitime karşı direnci yükselir ve performansı düşer. Bunun giderilmesi için Cho ve Berge (2002) e göre, uzaktan eğitim programı için çalışan herkese yeteri kadar teşvik ve ödül verilmelidir, öğretmenler için detaylı bir rehber hazırlanmalıdır sürekli eğitim seminerleri düzenlemelidir ve öğretmenlerin normal çalışma sürelerine ilave çalışma saatleri belirlenirken fikirleri alınmalıdır.

### 2.3 Teknoloji Tehdidi

Uzaktan eğitimde teknoloji korkusu olan öğretmen ve öğrenciye bu korkunun üstesinden gelmesi için teknolojik araçları nasıl daha rahat kullanabileceği öğretilmelidir.

Öğretmenlerin uzaktan eğitimle öğrenmenin gerçeklemeyeceğine dair tabularının olması sorununu ise uzaktan eğitim konusunda öğretmene kapsamlı bir eğitim verilerek ve uzaktan eğitimde nasıl istedik davranışlar elde edebileceğine dair yöntemler kazandırılarak aşılabılır.

### 2.4 Telif hakkı

Kelime anlamı orijinal ya da özgün diyebileceğimiz bir fikrin veya eserin (düşünce ürününün) yasalarla sahiplenilmesini ve korunmasını sağlayan hak olarak tanımlanabilir. Bu hak sayesinde ortaya konan eser, ancak sahibinin izni ile kullanılabilir ve yayılabilir. Sembolü © şeklindedir ve bu sembolün bir eser üzerinde mevcut olması, o eserin telif hakkı tesciliyle sahiplenildiğini ve korunduğunu gösterir. Sembol İngilizce copyright sözcüğünden türetilmiştir.

İnternet uzaktan eğitim kullanıcıları için sınırsız olanaklar sunar. Birçok kişi kolaylıkla istediği bilgiye ulaşabilir. Durum böyle olunca da bilginin asıl sahibi ve onu ortaya koyan kişinin zamanla, bilginin kopyalanarak çoğalması ve başka kişiler tarafından sahiplenilmesi ile belirsizleşir.

Yalın (2008)'a göre uzaktan eğitim dersinin içerdiği bilgilerin sahiplik, içerik ve kaynak ile ilgili kontrolü yapılmamış birbiriyle ilişkisiz olması, bilginin kime ait olduğu ve telif hakkı konusunda uzaktan eğitim de önemli problemlerdendir.

## 3. Öğrenci

Öğrenci zaman ilerledikçe derse olan ilgisini kaybedebilir ve bu durum o öğrencinin derste başarısız olmasına neden olur. Uzaktan eğitimde öğrenciyi geri döndürmek ve tekrar motivasyonunu yükseltmek oldukça zordur. Bu sorunla karşılaşmamak için eğitimde motivasyon unsurları aktif bir şekilde öğretici tarafından uygulanmalıdır.

### 3.1 Sosyal Etkileşim

Genelde uzaktan eğitim derslerinde, eğitsel ve sosyal kazanımlarda önemli bir yeri olan yüz yüze eğitim ve iletişim hiç olmamakta ya da eksik kalmaktadır. Eğer uzaktan eğitimde öğrenciler ile diğer öğrenciler arasında bir iletişim gerçekleşmezse öğrenciler kendini dışlanmış hissederler. Çoğu zaman bu durum eğitimi bırakmakla son bulur. Bunun giderilmesi yada hiç yaşanmaması için, öğrenciler derse katılmaları için cesaretlendirilmeli ve aralarındaki etkileşim artırılmalıdır.

Öğrencilerin bireysel farklılıklarına önem verilmeli ve grup çalışmaları yaptırılmalıdır (Cho ve Berge, 2002).

### 3.2 İletişim

Uzaktan eğitim uygulanırken iletişimin kalitesi için bazı önemli noktalara dikkat edilmesi gerekmektedir. Bu noktalar şu şekilde sıralanabilir (Teknotürk, 2001):

1. Öğrenim materyallerinin kalitesi,
2. Materyallerin kullanılabilirliği,
3. Öğrencilerin eğiticiler tarafından desteklenmesi,

4. Sistemin yönetimi,
5. Erişim kolaylığı,
6. Görüntüleme ve geri besleme mekanizmaları.

Uzaktan ve çevrimiçi eğitimde, sanal sınıfın yetersiz kaldığı alanlardan biri iletişimdir. Gerçek sınıf ortamında öğrenci, öğretim üyesi ve diğer sınıf arkadaşları ile rahatlıkla iletişim kurabilmektedir. Sanal sınıfta ise bu ortamın sağlanabilmesi için İnternet teknolojisi içinde yer alan bileşenlerin etkin ve yeterli düzeyde kullanılması gerekir. Otomasyona ait iletişim modülü iyi bir şekilde tasarlanırsa, gerçek sınıf ortamından daha geniş bir iletişim imkânı oluşur. Çünkü eğitimin en önemli parçası olan iletişim e-posta, forum, sohbet odaları gibi özellikler sayesinde eşzamanlı veya eşzamansız olabilecek ve günün her saatinde gerçekleştirilebilir.

Genel olarak uzaktan eğitim iletişim engelleri şunlardır:

**İletişimin yapıcı engelleri:** Her ne kadar engel olarak anılmasalar da iletişim için konulmuş bir dizi protokol zinciridir. Yapıcı bir biçimde sınırlandırır.

**İletişimin bozucu engelleri:** bunlar genel olarak çok çeşitlidir ve genelde çevresel kaynaklıdır. Ses, gürültü, statü farklılığı, cinsel farklılık, aşırı bilgi veya az bilgi, yetersizlik gibi faktörlerdir.

**İletişimin kişisel engelleri:** kişiler bir yaşantı ve deneyim dünyasıdır. İletişimde farklı dünyalar birbirine açılır ve bağlantı kurmaya çalışır. Bundan dolayı mesajın doğru bir şekilde karşı tarafa aktarılması önemlidir.

**İletişimin kanal engelleri:** iletişim bilindiği gibi kaynaktan alıcıya bir kanal yoluyla iletim şeklinde gerçekleşmektedir. Sorun bazen sadece iletimde olabilir. Kaynak ve alıcı hazır olmasına rağmen aktarım konusundaki sıkıntı iletişimi engelleyecektir.

**İletişimde psikolojik engeller:** Kaynağın ve alıcının değer yargıları ve inançları iletişimi etkiler. Alıcı kendi inançlarına göre kaynaktan gelen mesajları yorumlar. Yanlış yargılar yanlış iletişime yol açar.

**İletişimin teknik engelleri:** Bunlar daha çok kurulum ve alt yapıdan kaynaklanan engellerdir. Şifreleme, filtreleme, mesajı iletme, kullanılan kanal, deşifre problemleri ve geri besleme karşılaşılan teknik problemler olabilir.

**Fiziksel uzaklık:** Bilindiği gibi uzaktan eğitimde öğretmen ve öğrenci farklı mekânlarda olduğu için, fiziksel olarak birbirlerine uzaktadırlar. Bu da iletişimde kopukluğa neden olur.

**Zaman baskısı:** Daha çok yeterli zaman oluşturamama problemi söz konusudur. Bazen altyapıdan kaynaklanan sorunlarda iletişimin süresinin uzamasına sebebiyet verdiği için, öğrencilerin dersten kopmasına sebebiyet verebilir.

**Kesintiler:** iletişim aktif bir şekilde gerçekleştirilirken, araya başka bir şeyin de dâhil olmasıdır. Örneğin; öğretmen ve öğrenci etkileşim sürecinde başka bir öğrencinin söz alarak iletişimi koparması.

### **Uzaktan Eğitim Sorunlarının Tek Yönlü ve Çift Yönlü Modellere Göre İncelenmesi**

Uzaktan eğitim sorunları uzaktan eğitimin tek yönlü ve çift yönlü uygulama modellerine göre sınıflandırılabilir (İşman, 2011). Tek yönlü iletişimin bulunduğu uzaktan eğitim modelleri ve bunlarda karşılaşılan sorunlar kısaca şunlardır (İşman, 2011):

Tek yönlü uygulama modelleri mektup ile uygulama modeli, tek yönlü radyo ile uygulama modeli, televizyon ile uygulama modeli, tek yönlü bilgisayar ile uygulama modeli ve tek yönlü karma uygulama modelleridir. Televizyonun görsel olması öğrenenler boyutunda radyo ile öğretim modeline göre önemli bir dezavantajdır. Tek yönlü bilgisayar ile uygulama modelinde de eğitim hizmetleri öğrencilere CD ve DVD ler aracılığıyla ulaştırılır. Bu nedenle iletişim tek yönlüdür. Tek yönlü karma

model ise tüm bu modellerde kullanılan medyaların birlikte kullanıldığı modellerdir. Bu modellerde karşılaşılan problemler büyük ölçüde benzerdir. Tüm bu modellerde karşılaşılabilecek genel sorunlar organizasyon, idari ve teknik sorunlardır. Ayrıca sosyal etkileşim yetersizliği, teknoloji kullanımına karşı direnç gösterilmesi, telif hakkı, ölçme-değerlendirme, danışma-kütüphane servis sorunları gibi sorunlardır. Çift yönlü uygulama modellerinde öğrenen ve öğreticiler çift yönlü iletişim kurabilmektedir. Bu modeller çift yönlü radyo ile uygulama modeli, çift yönlü televizyon ile uygulama modeli, çift yönlü etkileşimli bilgisayar ile uygulama modeli, çift yönlü karma uygulama modelidir. Çift yönlü radyo ile uygulama modelinde öğretim radyo konferansları ile çift yönlü televizyonla uygulama modelinde ile video konferanslarla yapılır ancak öğrenenler dersleri daha önce kendilerine gönderilen öğretim materyallerinden takip ederler. Tek yönlü modellerde olduğu gibi bu modellerde de en önemli sorunlar organizasyon, idari ve sosyal etkileşim, teknik sorunlar, teknoloji kullanımına karşı direnç gösterilmesi, telif hakkı, ölçme-değerlendirme gibi sorunlardır. Çift yönlü etkileşimli bilgisayar ile uygulama modeli günümüzde en çok kullanılan modeldir. Genellikle iki şekilde kullanılmaktadır; birincisi: sanal ileti, chat ve bilgisayarlar arası iletim sistemleriyle gerçekleştirilir. İkincisi ise, internet üzerinden telekonferans şeklinde gerçekleştirilmektedir. Bu model e-öğrenme (e-learning), çevrimiçi öğrenme (online learning), internet tabanlı öğrenme (web-based learning) gibi uzaktan eğitim uygulamalarını kapsar. Bu uygulamalar günümüzde en çok kullanılan uygulamalar olmakla beraber geleceğin uzaktan eğitim uygulamaları olarak görülmektedir. Çift yönlü etkileşimli bilgisayar ile uygulama modelinde tüm modellerde olduğu gibi organizasyon ve idari yapı iyi hazırlanmırsa önemli problemlere neden olabilir niteliktedir. Bunun yanında öğrencilerden, öğretmenlerden, teknik konulardan, telif hakkı ve ölçme değerlendirme gibi konulardan kaynaklanan sorunlar bulunmaktadır. Çift yönlü karma uygulama modeli ise bütün çift yönlü modellerde kullanılan bilgi iletişim teknolojilerinin aynı anda kullanılmasını ifade eder.

Günümüzde en çok kullanılan ve geleceğin uzaktan eğitim uygulamaları olarak görülen bilgisayar, mobil cihazlar ve internet teknolojilerinin uygulamaları sonucu ortaya çıkan çevrimiçi öğrenme (online learning), e-öğrenme (e-learning), internet tabanlı öğrenme (web-based learning), sanal kampüs (virtual campus) gibi uzaktan eğitim yöntemleri hakkında birçok araştırma yapılmıştır. Bu teknolojiler büyük kolaylıklar sağladığı gibi yeni sorunları da beraberinde getirmektedir (Gülbahar, 2009). Mungania (2003)'e göre, e-öğrenme sorunlarını yedi başlık altında toplamıştır, bunlar: bireysel sorunlar, öğrenme stili sorunları, öğretim veya sunuş sorunları, organizasyon sorunları, durumsal sorunlar, içerik uygunluğu sorunları, teknolojik sorunlardır. Ayrıca e-öğrenme sorunlarını için dört önemli öngörü önermiştir; organizasyon türü, özyeterlilik, bilgisayar eğitimi, bilgisayar okur-yazarlığı yeterliliği. Bunlarla beraber yaş, cinsiyet, etnik köken, medeni durum, eğitim düzeyi, meslek pozisyonu, bilgisayar sahipliği, çalışma alanı, e-öğrenme ile ilgili daha önceki tecrübelerinin önemli olduğunu belirtmiştir. Mungania (2003) tüm bunların birleşimi ile e-öğrenmede karşılaşılabilecek engelleri sınıflandırmıştır. Kışla, Sarsar, Arıkan, Meşhur, Şahin ve Kokoç (2010)'a göre internet tabanlı sistemlerde ortaya çıkabilecek sorunlar kullanılan öğretim yönetim sistemi (learning management system-LMS) ve içerik yönetim sisteminden (content management system-CMS) kaynaklanabilecek sorunlar, medya olarak kullanılan akışkan videolar (streaming video) ve sohbet ortamlarında oluşan sorunlar, çoklu ortam teknolojileri sorunları, sunucu ve bağlantı çeşidi sorunları, kurumsal, fiziksel ve dijital güvenlikle, destek hizmetlerinin yetersizliği gibi sorunlardır. Stansfield, Connolly, Cartelli, Jimoyiannis, Magalhaes ve Maillat (2009), uzun vadeli e-öğrenme ve sanal kampüs geliştirme girişimlerinde karşılaşılan muhtemel ana sorunları organizasyon sorunları, teknolojik sorunlar, pedagojik sorunlar, öğrenci/kullanıcı sorunları, finansal sorunlar ve devam ettirilebilirlik sorunları olmak üzere 6 ana grupta toplamışlardır. Claus (2006), uzaktan eğitimdeki sorunları belirlemek amacıyla yaptığı bir araştırmada kurumsal, öğrenci ve fakülteden kaynaklanabilecek sorunlar ve endişelerin yanında, klasik öğrenimdeki öğrencilerin okullara gidip ders görmelerini kapsayan sosyal etkileşimlerin uzaktan eğitim anlayışı ile kurumların öğrencilere öğretimi getirerek ters çevrildiğini ve bu nedenle de kurumların bu nedenle yönetim, fakülte, öğretmenler bazında sorunlar yaşadığını ifade etmektedir. Bununla beraber internet yardımıyla sunulan uzaktan eğitimde halen kalitenin ne olduğunun tartışılmasının önemli bir sorun olduğunu da ifade etmiştir. Chen (2009) teknoloji aracılığıyla sunulan uzaktan eğitimin kabullenilmesi yönünde yaptığı bir çalışmada, kurumların teknoloji yardımıyla sunulan uzaktan eğitim içeriklerinin hazırlanmasında çalışanlarına büyük bir iş yükü getirdiği, kuruma maliyetinin yüksek olduğu ve başarılı çalışmalara gösterilen ödüllendirmelerin azlığının gibi sorunların önemli olduğunu belirtmiştir. Anetta, Folta ve Klesath (2010) uzaktan eğitimin maliyetlerinin iyi analiz edilmesi gerektiğini ve uzaktan eğitimin görünmeyen maliyetleri olabileceğini belirtmiştir. Bununla beraber uzaktan eğitimde en önemli sorunlardan biri olarak anlamlı öğrenmelerin gerçekleşebilmesi olarak nitelendirmişlerdir.

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# UZAKTAN EĞİTİM YENİ MODEL ÖNERİSİ

## DISTANCE LEARNING PROPOSAL FOR A NEW MODEL

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### ÖZET

Uzaktan eğitim öğretim faaliyetlerinden süreklilik ve eğitim öğretim maliyetlerinin azalması gibi amaçlarla kullanılmaktadır. Günümüzde uzaktan eğitim yoluyla binlerce insan eğitim almakta ve kendilerini geliştirmektedir.

Uzaktan eğitim aynı zamanda bireyler zaman para ve iş tasarrufu sağlamıştır. Birey işinden ayrılmadan derslerini iletişim teknolojileri sayesinde takip etmekte ve istediği diplomaya kavuşabilmektedir. Uzaktan eğitim iletişim teknolojilerinin gelişmesi ile paralel olarak yaşamın her aşamasında gerekli olan yaşam boyu öğrenme ve hizmeti içi eğitim ihtiyaçlarının karşılanması için bir çözüm olarak görülmektedir.

Günümüz iletişim teknolojileri hızlı bir gelişim göstermektedir. Bu hızlı gelişim toplumsal yaşamın her alanını etkilemektedir. Bu alandan toplumsal değişmeyi olumlu yönden etkileyecek ve yönlendirecek olan eğitimidir. İletişim teknolojilerinin eğitim sistemine olan etkilerinin istenilen yönde olabilmesi için eğitimcilerin gerekli olan çalışmaları yapması gerekmektedir.

### ABSTARCT

Communication technologies are improving fast. This effects all area of social life. The one that will effect and direct is the education. Communication technologies in the desired direction of the effects of the education system needs to the work that needed to be educators.

Continuous education and distance learning activities are used for purposes such as education and training costs will decrease. Today, distance education through the thousands of people receiving training and developing themselves. Distance education at the same time when people saved more money and work.

The individual lessons of leaving his job and wants to follow through and communication technologies kavuşabilmektedir diploma. In parallel with the development of communication technologies in distance education that is required at every stage of life, lifelong learning and service training is seen as a solution to meet the needs.

### GİRİŞ

Uzaktan eğitim insanların eğitim ihtiyaçlarının artması sonucu klasik eğitim sisteminin kapasitesinin yetersiz olmaya başladığı zamanlarda ortaya çıkmıştır. Devletler kendi uzaktan eğitim sistemlerini geliştirirken devalı olarak var olan iletişim teknolojilerini kullanmışlardır. Bunun nedeni uzaktan eğitim gelişim aşamalarının iletişim teknolojilerini gelişimine paralel gitmesidir.(Garrison, 1989; Nipper, 1989).

Yapılan araştırmalar uzaktan eğitimin aşağıdaki beş aşamadan geliştiğini ortaya çıkarmıştır.

- 1.Mektup
- 2.Radyo ve televizyon
- 3.Telekonferans
- 4.Bilgisayar ve internet
5. Bilişim teknolojileri

### MODEL YAPISI

İletişim teknolojilerinde görülen hızlı gelişmeler eğitim sisteminin de yapısını etkilemiş ve değiştirmiştir. Bu nedenle önerilen bu modelin temelini hızla gelen iletişim teknolojileri yazılım ve eğitim öğretim ortamlarının tasarımı oluşturmaktadır. (İşman, A. 2011).



## I. DONANIM

İletişim teknolojileri temeli olan bu model iki ana yapıda bulunmaktadır. Bunlar

Transmisyon sistemi:

Telekonferans sistemi

Çağdaş uzaktan eğitim sistemi oluşturabilmek için her iki sistemin aynı anda işe koşulması gerekmektedir. Bunun nedeni çift yönlü telekonferansın geliştirilebilmesi için mutlaka transmisyon sisteminin kullanılması gerekliliğidir.

Uydu Sistemi

Bilgi transferi için kullanılacak sistemlerden biri uydudur. Uydunun avantajı, dünyanın her yerinde ulaşılabilir olmasıdır. Hız da önemli bir etkidir. Bilgi transferi uydu sistemlerinde hızlıdır.

Türkler tarafından uzaya gönderilen ilk uydu Türksat 1/A uydusudur. Fakat teknik arıza nedeniyle görevini yerine getirememiştir. Bunun yerine Türksat 1/C uydusu gönderilmiştir.

Uydu sistemlerinin uzaktan eğitimde kullanılması 1980'li yıllara dayanmaktadır. İlk olarak uydu sistemleri üzerinden basılı materyaller gönderilmiştir.

Bunun yanında Türkiye Cumhuriyeti sahip olduğu uydularda eğitim-öğretim için gerekli olan bant ayarlaması yapmıştır.

Uydu sisteminin faydaları şu şekilde özetlenebilir:

1. Fiber optik kabloların ulaşamadığı yerlere rahatlıkla ulaşabilir. Eğitim-öğretim hizmetinin tam olarak
2. Etki alanı çok geniştir. Mekan ve zaman sınırlaması olmadığı için, bir öğretmen çok daha fazla öğrenciye ulaşabilir.

Uydu sistemleri akılcı bir çözümdür, fakat fiber optik kablolarına göre çok daha maliyetli olduğu için, ödenek ayrılması gerekmektedir.

Tele-Konferans Sistemi

Teknolojinin ilerlemesiyle birlikte, eğitim yolundaki engeller birer birer kalkmaktadır. Mesela eğitim için artık dört duvar, kara tahta gibi zorunluluklar ortadan kalkmıştır. Tele-Konferans sisteminde öğretmen ve öğrenci buluşmak için bir mekana ihtiyaç duymamaktadır. Bunlarla ilgili ihtiyaç duyulan şey ise, uydu ya da fiber optik kablo yardımıyla sesin, resmin, video görüntüsünün aktarımının yapılmasıdır. İki farklı yöntem ile gerçekleştirilebilir:

a) Çift Yönlü Video Konferans

Öğretmen ve öğrencilerin, tele-konferans yöntemiyle yüzyüze etkileşime geçmesidir. Gerekli araç-gereçler şunlardır:

- Öğretmen-öğrenci kamerası
- Büyük bir televizyon ekranı

- Ses düzeni
  - Bilgisayar ve ders notlarını gösteren kamera
  - Transmisyon sistem bağlantısı
- b) Masaüstü Konferans
- Pekçok katılımcının birbiriyle etkileşimde bulunabildiği konferans sistemidir.
- Gerekli araçlar şunlardır:
- Transmisyon sistemine bağlantı
  - Kamera, bilgisayar
  - PCB kartları
  - Yazılım programı
  - Ses sistemi
  - Mikrofon
  - Ekran
  - Fare
  - Klavye

## YAZILIM

**Yazılım**, değişik ve çeşitli görevler yapma amaçlı tasarlanmış elektronik araçların birbirleriyle haberleşebilmesini ve uyumunu sağlayarak görevlerini ya da kullanılabilirliklerini geliştirmeye yarayan makine komutlarıdır.

**Uzaktan Eğitim Yazılım**, eğitim için gerekli donanımlar alındıktan sonra tasarlanan hedefleri gerçekleştirmek için satın alınan paket programlar veya geliştirilen programlardır.

Uzaktan eğitim yazılımı için izlenilmesi gereken yol; ilk önce kurumun ihtiyaç ve hedefleri göz önünde bulundurulur. Sonra gerekli donanımlar alınır. En son tasarlanan ihtiyaçlar ve hedefler doğrultusunda programlar seçilir.

Yazılım ihtiyacı sırası; ilk önce İletişim ihtiyacını karşılayan yazılımlar bulunur sonra sanal öğrenme ortamları sağlayacak olan yazılımlar bulunur ve en son ölçme ve değerlendirmeyi yapacak yazılımlar edinilir.

### Scorm

1997'de ABD ordusu tarafından geliştirilmiştir. Çeşitli ülkelerdeki Amerikan orduların eğitimi için ortaya atılmıştır. Başta İngiltere olmak üzere çeşitli ülkelerden ve akademisyenlerden gelen desteğin ardından ADL(Advanced Distributed Learning) adlı şirket ortaya çıkmıştır. ADL'nin çalışmaları doğrultusunda e-öğrenme alanında geliştirilmiş birçok standart ve tanımlamalar tek bir başvuru modeli çatısı altında toplanmaya başlamış ve oluşturulan bu modele SCORM(Sharable Courseware Object Reference Model) adı verilmiştir. En son sürümünü Ocak 2004'de sunmuşlardır.

## UZAKTAN EĞİTİM İÇİN YAZILIM ÖRNEKLERİ

### 5m Firması - Fullearn Lms Programı

5M'in bir Ar-Ge ürünü olarak ilk sürümünü 2004 yılında çıkarttığı FullearnLMS(Eğitim Yönetim Sistemi)'in SCORM 2004 uyumlu 3.0 versiyonu 2008 Mart ayında çıkmıştır.

FullearnLMS, yüz yüze eğitim ile yapılabilecek eğitim aktivitelerinin bir çoğunu web üzerinde yapmaya yarayan bir eğitim sistemidir.

Bu yazılımı kullanan kurumlardan bazıları; Watener ( Online Su ve Enerji Akademisi ) , Fatih Üniversitesi Uzaktan Eğitim Sistemi ve Deep (Doğalgaz Eğitim Programı)

### Milli Eğitim Bakanlığı

Milli Eğitim Bakanlığı'nın uzaktan eğitim için çalışmaları vardır. Bu çalışmalardan bazıları; MEB Uzaktan Eğitim, Kursiyernet.Meb , Yenilik ve Eğitim Teknolojileri Genel Müdürlüğü ve Adobe Connect – e-Toplantı Randevu Yönetim Sistemi'dir.

## EĞİTİM-ÖĞRETİM ORTAMLARININ TASARIMI

Eğitim-öğretim ortamlarının tasarımı için sadece donanım ve yazılım almak sistemin etkili bir şekilde çalışmasını sağlamaz. Uzaktan eğitimin etkili olarak işleyebilmesi için en son yapılması gereken, eğitim-öğretim ortamlarının tasarlanmasıdır.

Tasarım faaliyetleri 7 ana noktada yapılmalıdır. Bu noktalar; öğrencilere kazandırılması gereken hedef ve davranışların tek tek belirlenmesi, öğrencilerin daha önceden var olan geçmiş bilgilerinin yoklanması ve tekrar işlem yapılması, hedeflere uygun olan eğitim-öğretim yöntemlerinin seçilmesi ve etkililiğinin belirlenmesi, hedef ve yöntemlere

uygun eğitim teknolojilerinin kullanılması, uygulama yapılması, uygulama sonrasında elde edilen ürün ile hedeflerin gözden geçirilmesi ve ortaya çıkan hataların düzeltilmesi için dönüt işleminin yapılmasıdır.

## UZAKTAN EĞİTİM MODEL YAPISI

- Model yapısında üç ana nokta bulunmaktadır. Bu noktalar;

### **Proje Grubunun Oluşturulması**

Uzaktan eğitim başlamadan önce projeyi yürütecek grup oluşturulmalıdır. Bu kişiler; bilgisayar uzmanı, eğitimci, elektronik mühendisi, yazılımcı, tasarımcı ve konu alanında uzmanlardır.

### **Sistemin Kurulması**

Grup, kurumun bilişim alt yapısını inceleyip, uzaktan eğitim için gerekli ihtiyaçlar ve hedefler belirlenir. Daha sonra gerekli donanım ve yazılımlar alınır.

### **Yönetim Modelinin Geliştirilmesi**

Uzaktan eğitim sisteminin etkili olarak işleyebilmesi için yeni bir yönetim modeli geliştirilmelidir.

- Uzaktan eğitim merkezi kurulmalıdır. Bu merkeze bağlı 4 ana birim vardır. Bu birimler;

### **Eğitim Programları Birimi'nin Görevleri;**

Ekibin eğitim amaçlarını belirler. Eğitim-öğretimde ulaşılmak istenilen, hedef ve davranışları belirlerler. Eğitim-öğretim ortamında kullanılacak materyalleri tasarlarlar ve Eğitim-öğretim ortamında kullanılacak öğrenme-öğretme yöntemi belirlerler.

### **Yönetim ve Finans Birimi'nin Görevleri;**

Uzaktan eğitim merkezinde çalışacak olan personelin görevlerini belirlerler. Kurum içi ve kurumlar arası iletişimi sağlarlar. Eğitim-öğretim için gerekli olan malzeme alım-satımını yaparlar ve Uzaktan eğitim merkezinin bütçesini hazırlar.

### **Öğrenci Hizmetleri Birimi'nin Görevleri;**

Öğrencilerin kayıt işlemlerini yaparlar. Müfredatı hazırlayıp öğrencilere öğretilmesini planlar. Yapılacak olan sınavları belirler ve öğrencileri bilgilendirirler.

### **Bilişim Birimi'nin Görevleri;**

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# UZAKTAN EĞİTİMDE ÖĞRENCİ ROLLERİ

## STUDENT ROLES IN DISTANCE LEARNING

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### Özet

Bilişim ve iletişim alanında meydana gelen hızlı gelişmelere paralel olarak uzaktan eğitim sistemi de kendi içinde gelişme göstermektedir. Uzaktan eğitim sisteminin alt yapısını oluşturan bilişim ve iletişim araçları sayesinde uzaktan eğitimde içerik sunumunun kalitesi de artan yönde bir ivme kazanmıştır. Artan bu ivme ile öğretmen ve öğrenci rollerinde de birtakım değişiklikler söz konusu olmuştur. Geleneksel eğitim anlayışının tersine bilginin akış yönü öğreticiden öğrenene olmaktan çıkıp; öğrenci merkezli eğitim anlayışı gelişme göstermiştir. Öğrenme-öğretme sürecinin merkezinde olan öğrenci profili; bilgiye özgür bir şekilde istediği zaman ulaşabilen öğrencilerden oluşmaktadır. Uzaktan Eğitim sürecinde de öğrenciler, bu eğitimin temel bileşeni olduklarından bir takım roller yüklenmektedir. Bu roller öğrencilerden eğitim süreci boyunca beklenen davranışları içermektedir. Bu davranışların uzaktan eğitimde uygulama modellerinde de değişmesi kaçınılmazdır. Bu çalışmada, literatür desteğinde uzaktan eğitim uygulama modellerinde öğrenci rolleri açıklanmaya çalışılmıştır.

**Anahtar Kelimeler:** Uzaktan Eğitim, Uzaktan Eğitim Uygulama Modelleri, Öğrenci, Rol.

### Abstract

In parallel to the rapid advances in the fields of informatics and communication, distance learning system has also been advancing on its own. Thanks to the informatics and communication tools which form the infrastructure of the distance learning system, the quality of content presentation in distance learning has become increasingly prominent. As a result of this, several changes in the teacher and student roles have been under discussion. Contrary to the traditional approaches, the information is no more transmitted from teacher to the learner, but a learner-centered approach is adopted. The student profile, in the center of learning process, consists of those who are free to reach the information whenever they would like. As they are one of the basic components of this kind of education, those learners have to take up several roles in distance learning process. Those roles incorporate the ones that the learners are expected to establish through learning process. It is inevitable that those roles also change in distance learning application models, too. In this study, student roles in distance learning application models have been explained through literature support.

**Key Words:** Distance Learning, Distance Learning Application Models, Student, Role.

## GİRİŞ

21. yy eğitim-öğretimini duvarlardan dışarıya taşıma fikri uzaktan eğitim kavramının önem kazanmasına neden olmuştur. Bilişim ve iletişim teknolojilerinde meydana gelen hızlı gelişmeler ise bu kavramın desteklenmesine altyapı oluşturmuştur. Geleneksel eğitim anlayışının tersine, aktaranın öğretici olduğu ortamlardan uzaklaşıp öğrenciye bir takım yeni roller ve sorumluluklar yüklenmektedir. Bu roller ve sorumluluklar uzaktan eğitim uygulama modellerine göre şekillenmektedir. Öğrenenin merkezde olduğu eğitim öğretim sürecinde etkileşim kavramı önemli bir yere sahiptir.

Uzaktan eğitimde üç türlü etkileşim söz konusudur: Öğrenci – içerik, öğrenci – öğretmen, öğrenci – öğrenci (İşman ve diğerleri, 2004). Öğrenci – öğrenci, öğrenci - öğretmen etkileşimi geleneksel eğitim anlayışının yaygın olduğu sınıflarda kullandığımız kavramlardır. Fakat uzaktan eğitimde bir diğer etkileşim türü olan öğrenci içerik etkileşimi diğer etkileşim türlerinden farklı ve önemli bir yere sahiptir. Çünkü, uzaktan eğitim öğrencisinin hatalı öğrenmelerine anında dönüt verecek bir uzmanın bulunmaması öğrenci – içerik etkileşiminin kalitesinin önemini ortaya koymaktadır. İçeriğin kapsamlı ve kaliteli olması uzaktan eğitim öğrencisinin bağımsız öğrenme ve doğruya ulaşma becerisini arttıracaktır. Ayrıca içinde bulunduğumuz çağa paralel olarak öğrenci profillerinin oluşmasında etkili olacaktır.

Uzaktan eğitim öğrenci profili denildiğinde kendi kendine, bağımsız öğrenen ve hatalı öğrenmelerini içerikte gezinerek düzeltebilen, ne öğreneceğini bilen, ne zaman öğreneceğinin farkında olan öğrenenler aklı gelmektedir.

Schrump ve Hong (2002) , uzaktan eğitimde öğrenci rollerini şu şekilde ele almaktadır:

- Öğrenim araçlarına erişebilen,
- Teknolojiyi kullanabilen,
- Çalışma şekil ve alışkanlıkları kazanabilen,
- Öğrenenin amaç ve hedeflerini uygulayabilen,
- Yaşam tarzı olan,
- Kişisel özellik ve karakter temaları bulunan,
- Görevlerinde sorumluluk bilincine sahip olan,
- Kullanılacak erişim yöntemleri açısından danışmanları yönlendiren,
- Bireysel öğrenebilen,
- Öğretmenlerle klasik öğrenmedeki gibi etkin etkileşim kurabilen,
- Kendi performansını değerlendirip muhakeme edebilen,
- İletişim engellerine yol açan ruhsal ön yargılardan kurtulabilen şeklindedir.

Vonderwell ve Savery (2004), uzaktan eğitimde öğrencilerin öz düzenleme becerisine sahip olmalarını, kısaca nasıl öğreneceğini, öğrendiklerini nasıl kullanacağını ve zaman yönetimi becerilerini etkili bir şekilde nasıl kullanacağını bilen bireyler olmalarını söylemektedir. Zimmerman (2000)'e göre öz düzenleme öğrencilerin biliş üstü, güdü ve davranış açısından kendi öğrenme süreçlerine aktif olarak katılma becerisidir. Pintrich (2000)'e göre, öz düzenleme yapabilen öğrenciler kendi çabaları ile öğrenirler ve belli amaçlara ulaşmak için belli stratejiler kullanırlar. Öz düzenlemeye dayalı öğrenme, öğrencilerin çeşitli öz düzenleyici süreçlerden geçtikten sonra, aktif bir şekilde bilişlerini, davranışlarını düzenledikleri öğrenme sürecidir.

Sorgulayan, araştıran, temel teknolojik yeterlilikleri yerine getirebilen, karşılaştığı fiziksel ve ruhsal sorunlar ile başa çıkabilen, arkadaşları ile etkileşim halinde kalıp eksiklerini tamamlayabilen, öğrendiklerini kullanmak ve uygulamak için fırsatları değerlendiren, teknik sorunlar ile baş edebilen ve öğrenme sürecinin her aşamasına etkin bir biçimde katılan bireyler uzaktan eğitimdeki öğrenci kimliğini ifade etmektedir.

İşman (2011)'e göre uzaktan eğitimde öğrenci rolleri tek yönlü uygulama modellerinde öğrenci rolleri ve çift yönlü uygulama modellerinde öğrenci rolleri olmak üzere ikiye ayrılmaktadır. Uzaktan eğitim tek yönlü ve çift yönlü uygulama modellerinde öğrencinin 12 tane rolü bulunmaktadır. Bunlar psikolog, öğretici, teknoloji uzmanı, teknisyen, site eğitmeni, sosyalleşme uzmanı, araştırmacı, lider, sistem uzmanı, uzaktan eğitim uzmanı

ve motivasyon sağlayıcı şeklindedir. Bu roller uygulama modellerinde öğrencinin etkileşimde bulunduğu ortamın niteliğine göre değişiklik göstermektedir. Bu rolleri şu şekilde sıralanmaktadır:

### **Psikolog**

Tek yönlü uzaktan eğitim uygulama modellerinde öğrenci, psikolog rolünü kullanarak eğitim esnasında karşılaşılabilecek psikolojik sıkıntı ve sorunlarına çözümler üretebilmelidir. Bunun nedeni uzaktan eğitimin tek yönlü modelinde öğrenci, sıkıntı ve sorunlarını eş zamanlı olarak öğretici ile paylaşarak, çözüm önerisi getirme avantajından yoksundur ve kendi ihtiyaçlarına psikolog rolünü üstlenerek çözüm üretmekle sorumludur. Ancak bunun yanı sıra öğrenciler kendi aralarında etkileşim sağlayarak genel olarak karşılaşılan sorunlara ortak bir zeminde çözüm üretebilmeye olanağına sahiptir. Bu çözüm ortaklığı sayesinde öğrenciler eksik olduklarını düşündükleri noktalarda daha çabuk psikolojik destek sağlayabilmektedirler.

### **Öğretici**

Öğretici rolünü üstlenen öğrenci uzaktan eğitimde aynı konuları gören diğer arkadaşlarına konuyla ilgili eksik öğrenmelerini giderme amaçlı yardım etmeli, birbirlerinin öğrenmelerini destekleyici konumda bulunmaları gerekmektedir. Tek yönlü uzaktan eğitim uygulama modellerinde konuların anlaşılmayan kısımları öğretici ile eş zamanlı etkileşim kurulmaması nedeniyle öğrenciler arası yardımlaşma ile anlaşılır hale getirilebilir. Öğrenciler kendi aralarında etkileşim sağlayarak, genel olarak konuların anlaşılması güç kısımlarına ortak bir zeminde açıklık getirip, birbirlerine anlamadıkları kısımlarda yardımcı olmalıdırlar. Bu çözüm ortaklığı sayesinde öğrenciler eksik olduklarını düşündükleri noktalarda daha çabuk öğretimsel destek bulabilirler. Öğretici rolü de bu noktada devreye girmesiyle anlamadığı kısım hakkında yardım isteyen öğrenci arkadaşına konuyu güzel bir şekilde öğretebilme açısından öneme sahiptir.

### **Teknoloji Uzmanı**

Uzaktan eğitim sisteminde adı geçen belli başlı yazılım ve donanımın öğrenci tarafından teknoloji uzmanı rolü sayesinde bilinçli ve etkili kullanımı söz konusudur. Teknoloji uzmanı rolündeki öğrenci hem mevcut yazılım ve donanımı etkili bir şekilde kullanır hem de yeni gelecek teknolojileri yakından takip edip hazır bulunuşluğunu artırır. Teknoloji uzmanı rolünün en önemli kullanım alanlarından bir tanesi de öğrencilerin tek yönlü uzaktan eğitim uygulama modelinde diğer öğrenciler ile iletişimini sağlayabilecek teknolojilerin farkında olmalarını sağlamasıdır. Bu teknolojileri kullanmaları sayesinde 'Psikolog' rolleri ile diğer arkadaşlarına psikolojik destek, 'Öğretici' rolleri ile de diğer arkadaşlarının konuyu anlamadıkları kısımlarda öğretici olma imkânına sahiptirler.

### **Teknisyen**

Tek yönlü uzaktan eğitim uygulama modellerinde öğrenci, öğretim esnasında çıkan teknik sıkıntılara çözüm üretecek, çıkabilecek teknik sorunları önceden sezinleyip gerekli önlemleri alabilecek bilgiler ile teknisyen rolüne sahip olmalıdır. Özellikle TV ve radyo ile tek yönlü uzaktan eğitim uygulama modellerinde öğretim esnasında çıkan teknik sorunların hızlı bir şekilde çözülememesi durumunda eğitimin aksaması durumu ile karşı karşıya gelmektedir. Eğitimin uzaktan yapılması nedeniyle, öğrencilerin veya teknik servisin çıkabilecek sorunlara müdahale etme şansı çok zordur. Bu durumda herhangi bir aksama ile karşılaşmamak için öğrenciden teknisyen olma rolünü yerine getirmesi beklenmektedir.

### **Site Eğitmeni**

Dünyada ve ülkemizde teknolojiyle birlikte paralel gelişen internet teknolojisi sayesinde bilgisayar kullanıcıları daha hızlı makineler ile daha hızlı internet kullanımı imkânına sahip olmaktadır. İnternete ulaşımın yaygınlaşması ve kolaylaşması ise diğer alanlar gibi uzaktan eğitim alanının da faaliyetlerini internet üzerinden sürdürmesini ortaya çıkarmaktadır. Öğrenciler uzaktan eğitim sistemlerini etkili bir şekilde internet siteleri üzerinden kullanabilmek ve kullanmakta problem ile karşılaşan arkadaşlarına yardımcı olabilmek için site eğitmeni rolüne sahip olmalıdırlar. Özellikler çift yönlü uzaktan eğitim uygulama modellerinden internet üzerinden etkileşimli eğitim alan öğrencilerin sahip olması gereken site eğitmeni rolü, tek yönlü uzaktan eğitimde de göz ardı edilmemelidir.

### **Sosyalleşme Uzmanı**

Sosyal yapı, teknolojik değişimlerle birlikte, hızlı bir değişim içindedir. Bu yapının sağlanması ve sürdürülmesi, başka bir deyişle mevcut kültürün tüm sosyal tabakalara ve yeni nesillere aktarılması, kendine has eğitim tekniklerini de zorunlu kılmaktadır. Böylece yeni ihtiyaçlara uygun olan eğitim teknolojileri

üretilmektedir. Uzaktan eğitim teknolojisi, sosyal realitenin tam bir yansıması olarak ele alınmalıdır (Birkök, 1998). Uzaktan eğitimde yer alan öğrencilerin, düzenli olarak sınıfta arkadaşları ile birlikte ders gören kişilere göre daha az sosyal çevre ile yetinmek zorunda kalmaları, kendi sosyalleşme uzmanları olmalarını ve kendilerine yeni ortamlar seçip arkadaşları ile daha sıkı iletişim sağlamalarını gerektirmektedir.

### **Araştırmacı**

Tek yönlü uzaktan eğitim uygulama modellerinde öğrenci, edindiği bilgilerin doğruluğu hakkında detaylı araştırma yapabilmeli, bu sayede yeni bilgiler edinip daha kalıcı öğrenme sağlayabilmelidir. Çift yönlü uzaktan eğitim uygulama modellerine nazaran tek yönlü modellerde öğrenci öğretici ile eş zamanlı etkileşim içerisinde bulunmadığı için kendisine gerekli bilgi ve dokümanlara araştırmacı kimliği ile ulaşip diğer arkadaşları ile de ulaştığı bu bilgileri paylaşabilmelidir. Öğreticilerin uzaktan eğitim sistemi dâhilinde öğrencilerden araştırmalarını istedikleri konular dışında, öğrencilerin yıl boyunca ellerindeki kitap veya sanal ortamdaki içeriklere destek amaçlı kaynaklara ulaşmaları daha iyi öğrenmelerin kapısını açacaktır.

### **Lider**

İşman (2011), uzaktan eğitimde liderlik rolünü şöyle tanımlıyor; uzaktan eğitimde öğrencinin lider rolünde ise, öğrenci liderlik özelliği göstererek diğer arkadaşlarının motivasyonunu artırmalı, grup çalışmalarında sorumlulukları paylaşırabilmeli ve arkadaşlarını cesaretlendirmelidir. Bu sayede öğrencinin uzaktan eğitimde daha etkin olması sağlanacaktır. Yine uzaktan eğitimde lider rolünde öğrenciler beklenmedik durumlara karşı alacağı kararlarla liderlik örneği göstermelidir.

### **Sistem Uzmanı**

Uzaktan eğitimde kullanılan sistemlerin çeşitliliği her geçen gün artarak devam etmektedir. Öğrenci, öğrenim gördüğü uzaktan eğitim sisteminin çalışma şeklini, oluşabilecek sorunlarda nasıl çözüm önerileri getirebileceğini, sistem içerisindeki içerik yönetimi, değerlendirme yöntemleri, kayıt işlemleri gibi sistem hakkındaki detaylı bilgilere sahip olmalı bu sayede öğretimini sorunsuz devam ettirebilmelidir. Tek yönlü uzaktan eğitim uygulama modellerinde öğrencinin sistem uzmanı rolü, çift yönlü uzaktan eğitim uygulama modellerine göre daha büyük öneme sahiptir. Sistemle ilgili bir sorunla karşılaşan öğrenci öğretiminin aksamaması için kendi bilgileri ışığında soruna çözüm getirmeli ve öğretimine devam edebilmelidir.

### **İletişim Uzmanı**

Uzaktan eğitimde öğrenci ve öğretmenlerin aynı ortamda bulunmaması iletişimin önemini en üst düzeye taşımaktadır. Öğretmen ve öğrenciler arasındaki iletişim esnasında yaşanacak olası sorunları giderebilecek iletişim uzmanı rolüne sahip öğrenciler, öğretmenleri ve diğer öğrenci arkadaşları ile sağlıklı iletişim kurarak bilimsel, teknik, sosyal alanlarda birbirleri ile temas halinde kalabilmektedir. Aksi takdirde öğretmen- öğrenci ve öğrenci-öğrenci arasında doğru iletişim yöntemlerinin kullanılmaması durumunda mesaj yerine ulaşmayıp öğretimin aksaması söz konusu olacaktır. Tek yönlü uzaktan eğitim uygulama modellerinde böyle bir durumla karşılaşılması durumunda öğretim süresi uzayacak ve öğrencide motivasyon eksikliği artacaktır. Bu tür durumlar ile karşılaşılması için öğrenci bir iletişim uzmanı kimliği ile uzaktan eğitim sisteminde yerini almalıdır.

### **Motivasyon Sağlayıcı**

Motivasyon sağlayıcı rolünü üstlenen öğrenci, uzaktan eğitimin yüz yüze eğitim ile arasındaki farklardan; dikkat dağılımı, isteksizlik, derslerden uzaklaşma, aidiyet duymama gibi sorunlar ile başa çıkarak derslerine yoğunlaşmakta zorluk çekmemektedir. Motivasyon sağlayıcı kimliği ile öğrenciler hem kendi motivasyonlarını hem de birbirlerinin derslere ve uzaktan eğitim sistemine olan ilgilerini üst düzeyde tutabilmektedir. Tek yönlü uzaktan eğitim uygulama modellerinde öğrenci ile öğretici arasında eş zamanlı etkileşim eksikliğinden doğabilecek motivasyon düşüklüğü bu rol sayesinde gerekli seviyeye çekilerek öğrenimin sağlıklı yürütülebilmesine katkı sağlayacaktır. Sonuçta öz-yeterlik inancı yüksek olan bireyler bir işi başarmak için büyük çaba harcarlar, karşılaştıkları sorunlar karşısında yılmıyarak göstermezler, kolayca vazgeçmezler başarılı bir sonuç elde etmek için ısrarlı ve sabırlı davranırlar (Akkoyunlu ve Orhan, 2003).

### **Uzaktan Eğitim Uzmanı**

Uzaktan eğitimde kullanılan öğretim yöntem ve tekniklerinin çeşitliliği öğrencilerin uzaktan eğitim uzmanı kimlikleri ile belirlenen hedeflerin gerçekleştirilmesinde etkin rol oynayacaktır. Öğrenci, öğrenim gördüğü uzaktan eğitim sisteminin çalışma şeklini, oluşabilecek sorunlarda nasıl çözüm önerileri

getirebileceğini, sistem içerisindeki içerik yönetimi, değerlendirme yöntemleri, kayıt işlemleri gibi sistem hakkındaki detaylı bilgilere sahip olarak bu sayede öğretimini sorunsuz devam ettirebilecektir. Tek yönlü uzaktan eğitim uygulama modellerinde öğrencinin uzaktan eğitim uzmanı rolü, çift yönlü uzaktan eğitim uygulama modellerine göre daha büyük öneme sahiptir. Uzaktan eğitim sistemi ile ilgili bir soruyla karşılaşan öğrenci öğretiminin aksamaması için kendi bilgileri ışığında soruna çözüm getirmeli ve öğretimine devam edebilmelidir.

## SONUÇ

Sonuçta değişen ve ilerleyen çağın gerekliliklerinden olan rollerin uzaktan eğitim sistemi içerisinde de uygulanması gerekmektedir. Yapılandırmacı yaklaşımın etkisiyle şekillenen bu rollerde, öğrenciler kendilerini daha özgür bir biçimde ifade edebilmekte ve sorumluluklarının bilincinde bireyler olarak topluma kazandırılmaktadır.

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### Özet

Günümüzde, özellikle teknoloji ve teknolojiyle birlikte iletişim sistemlerinin gelişmesiyle uzaktan eğitimin yaygınlığı ve etkinliği Türkiye’ de ve tüm dünyada artmıştır. Örgün eğitim ve giderek yaygınlaşan uzaktan eğitimin farklılıklar göstermesi dolayısıyla, her iki eğitim sisteminin öğretmenlerinin rolleri de farklılıklar göstermektedir ( İşman, 2011 ). Uzaktan eğitim ortamındaki öğretmen, öğretici olmaktan çok öğrencinin kendi kendine öğrenmesini sağlayacak ortamın profesyonel düzenleyicisi, öğrencinin gerektiğinde başvuracağı bir danışmandır ( Büyükkaragöz, 1997 ). Buradan da anlaşılacağı üzere, öğretmen, örgün eğitimdeki rollerinin yanı sıra, uzaktan eğitimde yeni roller de üstlenmektedir. Uzaktan eğitimde istenilen başarı ve kaliteyi yakalayabilmek, uzaktan eğitim öğretmenlerinin, sistem içerisinde kendisine yüklenen rollerini iyi anlaması ve hakkıyla yerine getirebilmesiyle yakından alakalı olduğundan, bu rollerin incelenmesi gerekmektedir. Bu çalışmada uzaktan eğitim öğretmenlerinin üstlendiği roller incelenecek, tek ve çift yönlü iletişime dayalı uzaktan eğitim modellerine göre gruplandırılacaktır.

**Anahtar kelimeler:** Uzaktan Eğitim, Öğretmen Roller, Eğitim Teknolojileri

### Giriş

Ülkemizde ve tüm dünyada hızla yaygınlaşan ve birçok açıdan büyük öneme sahip olan uzaktan eğitim, örgün eğitimden farklılıklar göstermektedir. Uzaktan eğitim, eğitimciye çok ciddi ve büyük sorumluluklar yükler. Geleneksel bir sınıfta, öğretmenin sorumluluğu ders içeriğini aktarmak ve öğrencinin ihtiyaçlarını göz önünde bulundurmakla sınırlıdır. Oysa uzaktan öğretimde baş edilmesi gereken yeni durumlar ortaya çıkar. Mesela öğretmen uzaktaki öğrencilerin özelliklerini ve ihtiyaçlarını anlamayı başarmalıdır; öğretme metodlarını öğretim verdiği kişilerin ihtiyaç ve beklentilerine uydurmalıdır; öğretme rolünü arka plana atmadan, iletişim teknolojilerini öğrenmelidir ( Halis, 2001: 78 ). Dolayısıyla uzaktan eğitim öğretmenlerinin görevleri de hem artmış hem de yeni bir çehre kazanmıştır.

### Uzaktan Eğitimde Öğretmen Roller

İncelemenin ilerleyen bölümlerinden de anlaşılacağı üzere uzaktan eğitim öğretmen rolleri, örgün eğitim öğretmen rollerinden daha kapsamlıdır. Uzaktan eğitimde öğretmen rollerini incelemeye önce, bir öğretmenin temel niteliklerine değinmek faydalı olacaktır. Ülkemizde 1739 sayılı Milli Eğitim Temel Kanunu’nun 43. maddesinde “ öğretmenlik mesleğine hazırlık genel kültür, özel alan eğitimi ve pedagojik formasyon ile sağlanır. “ denilmiştir. Bir öğretmen, içinde yaşadığı toplumu iyi tanımalı ve toplumunun kendisinden beklediği görev ve sorumlulukları yerine getirmelidir. Ayrıca alan ve meslek bilgilerine hakim olmalıdır.

Ders vermek, öğretmekten daha fazla bir anlama sahiptir. Ders veren bir okul sınıfının öğretmeni, çocukları dikkate almayan bir öğreticiden daha fazla ve daha başka hususlar ister. Öğrenci yalnız öğretmekle, yalnız bilen hale getirilmekle, yalnız okullandırılmakla kalmamalıdır ( Hesapçioğlu, 1994: 34 ). Günümüzde öğrenciye eskisine nazaran daha çok görev ve sorumluluk yüklenmektedir. Uzaktan eğitim ortamında öğretmen, öğretici olmaktan çok öğrencinin kendi kendine öğrenmesini sağlayacak ortamın profesyonel düzenleyicisi, öğrencinin gerektiğinde başvuracağı bir danışmandır ( Büyükkaragöz, Çivi, 1997 ). Öğrenciye bu açıdan bakıldığında ve öğrencinin bu durumundaki öğretmenin pozisyonu göz önünde bulundurulduğunda, öğretmene yeni görevlerin düştüğünü, öğrencinin öğrenme sürecini yönetme ve öğrenciye rehberlik etme görevlerinin ön plana çıktığını görüyoruz. Bütün bunların yanında uzaktan eğitimde, öğretmen ve öğrencinin fiziksel olarak aynı ortamlarda bulunmadıklarını yada nadiren bir araya gelebildiklerini düşünürsek, öğretmenin, eğitimdeki konumunun ne kadar önemli olduğunu çıkarabiliriz. Aşağıdaki tabloda uzaktan eğitimde görev alan öğretmenler gösterilmiştir.

Sıra No	Öğretmenler
1	Kitap ve not yazarı öğretmenler
2	Ödev düzeltici ve değerlendirici öğretmenler
3	Uygulamacı öğretmenler
4	Koordinatör öğretmenler
5	Danışman
6	Belletici ( monitör ) öğretmenler
7	Televizyon ve radyo öğretmenleri
8	Gezici öğretmenler
9	Tele ( telefonlu ) öğretmenler
10	Eğitim teknolojileri

( Kaynak: Hızal, 1983: 37, Akt: Büyükkaragöz, Çivi, 1997 )

Tablodaki öğretmenlerin uzaktan eğitim sistemindeki görev ve sorumlulukları Büyükkaragöz ve Çivi ( 1997 )' ye göre şu şekilde açıklanmıştır.

**Kitap ve Not Yazarı Öğretmenler:** Bu gruptaki öğretmenler, yazılı gereçleri hazırlayan ve geliştiren öğretmenlerdir.

**Ödev Düzeltici ve Değerlendirici Öğretmenler:** Öğrencilerden gelen ödevleri zamanında düzeltip değerlendiren ve uzaktan eğitim kurumunun ilgili servislerine ulaştıran öğretmenlerdir. Ayrıca ders kitabı ve not yazımını da görev almaktadır.

**Uygulamacı Öğretmenler:** Bu öğretmenlerin temel görevi, yazılı ve diğer kaynaklarda yapılan öğretimi tanımlamak, bu kaynaklarda verilmeyen bilgileri öğrencilere kazandırmak, daha çok laboratuvar, atölye ve diğer uygulamalı çalışmalarını yürütmektir.

**Koordinatör Öğretmenler:** Kurum yönetimi – öğrenci ve diğer öğretmenler arasında bağlantı sağlayan temel elemanlardır.

**Danışman Öğretmenler:** Genellikle uzaktan eğitim kurumuna bağlı “ eğitim merkezi “ inde görev yapmaktadırlar. Tüm eğitsel problemlerde öğrencilere yardımcı olmaktadır.

**Belletici ( monitör ) Öğretmenler:** Radyo ve televizyon yayınlarının izlenmesine yardımcı olan ve yayının izlenmesi sırasında öğrencilerin yayınları sessiz olarak dinlemelerini ve izlemelerini, gerekiyorsa not almalarını sağlayan öğretmenlerdir.

**Radyo ve Televizyon Öğretmenleri:** Uzaktan eğitim öğrencilerine yönelik radyo ve televizyon programlarını başta gelen canlı kaynağını oluşturmaktadırlar. Bu gruptaki öğretmenlerin ders kitabı ve not yazarı veya ödev düzeltici öğretmenlerle yakın işbirliği içinde olmaları gerekmektedir.

**Gezici Öğretmenler:** Yüz yüze eğitime katılamayan, eğitim merkezlerinden çok uzakta oturan öğrencilerin oturdukları yere kadar gidip onlara yardımcı olurlar. Ziyaret ettikleri öğrencilerin eğitsel problemlerinin çözümüne yardımcı olmakta ve onlara yeni ders kitabı ve notlarının yanında, okumaları gereken kaynakların listelerini de götürmektedirler.

**Tele Öğretmenler:** Bazı uzaktan eğitim sitemleri , öğrencilerin telefonla başvurup belirli konularda bilgi alış verişinde bulunabilecekleri öğretmenler görevlendirilmektedirler. Öğrencilere hangi gün ve saatte telefonlu öğretmenlerden yararlanabilecekleri bildirilmektedir.

**Eğitim Teknolojileri:** uzaktan öğretim sistemlerinde eğitim programları hazırlama ve geliştirme ekipleri içerisinde yer alan uzmanlardır. Amaçlara ulaşmak için hangi yöntem ve araç – gereçlerden yararlanılması gerektiğini belirlemede görev almaktadırlar.

Uzaktan eğitimde görev alacak öğretmenlerin geleneksel eğitim kurumlarında görev yapanlar gibi öğretmenlik formasyonu kazanmış olmalarının yanında, uzaktan öğretim konusunda yetişmiş, yetişkinler eğitimi ve bireysel öğretim konularında da uzmanlaşmış olmaları gerekmektedir ( Büyükkaragöz, Çivi, 1997 ). Son yıllarda uzaktan eğitimin teknolojiye paralel bir şekilde gelişmesi yukarıda sıralanan öğretmen rollerine yenilerini eklemiştir. Günümüze daha yakın zamanda yapılmış araştırma sonuçlarına bakacak olursak, daha geniş kapsamlı, teknolojiyle daha barışık ve özellikle internetin gelişimi sonucu çevrim içi öğrenmenin öneminin arttığı uzaktan eğitim sistemlerindeki öğretmen rollerine rastlamak mümkündür.

Her arařtırmacı uzaktan eđitim retmenlerinin rollerini belirlemiřtir. Ařađıdaki tabloda bu arařtırmacılar ve belirttikleri roller verilmiřtir ( Bawane, Spector, 2009, Akt: Iřman, 2011 )

<b>Uzaktan Eđitimde retmen Rollerini</b> ( Bawane, Spector, 2009 )	
<b>Arařtırmacı</b>	<b>Roller</b>
Thach and Murphy ( 1995 )	Eđitmen, retim tasarımıcsısı, teknoloji uzmanı, teknisyen, ynetici, site eđitmeni, editr, ktphaneci, deđerlendirme uzmanı, grafik tasarımıcsısı
Wiesenberg and Hutton ( 1996 )	Moderatr, pedagojik, sosyal, teknik ve ynetimsel
Gold ( 2001 )	Ynetimsel, sosyal ve entelektel
Goodyear et al ( 2001 )	Sre eđitmeni, danıřman, arařtırmacı, ierik eđitmeni, teknoloji uzmanı, tasarımıcsı ve ynetici
Williams ( 2003 )	Ynetici, eđitmen, retim tasarımıcsısı, teknoloji uzmanı, site eđitmeni, teknisyen, deđerlendirme uzmanı, ktphaneci, grafik tasarımıcsısı, medya yayıncısı, editr ve lider
Dennis et al ( 2004 )	İerik eđitmeni, sre eđitmeni, danıřman, teknisyen, ynetici, tasarımıcsı, kaynak sađlayıcı, arařtırmacı
Aydin ( 2005 )	İerik uzmanı, sre eđitmeni, retim tasarımıcsısı, tanıřman, teknisyen, ynetici, materyal retici
Egan and Akdere ( 2005 )	İdari ynetici, eđitmen, teknisyen, retim tasarımıcsısı, teknoloji uzmanı, site eđitmeni, deđerlendirme uzmanı, grafik tasarımıcsısı, lider, sistem uzmanı
Richey et al ( 2005 )	Analist, e – renme uzmanı, proje yneticisi
Varvel ( 2007 )	Ynetici, teknisyen, retim tasarımıcsısı, pedagojik , deđerlendirme ve sosyal roller

Yapılan bu arařtırmalar, Iřman ( 2011 )' da deđerlendirilmiř ve uzaktan eđitimde 21 tane retmen rolnden bahsedilmiřtir. Bu roller ve aıklamaları Iřman ( 2011 )' a gre ařađıdaki gibidir:

<b>Uzaktan Eđitimde retmen Rollerini</b>		
1. Psikolog	8. Editr	15. lme – Deđerlendirme Uzmanı
2. retici	9. Grafik Tasarımcısı	16. Sistem Uzmanı
3. retim Tasarımcısı	10. Sosyalleřme Uzmanı	17. Proje Yneticisi
4. Teknoloji Uzmanı	11. Danıřman	18. İletiřim Uzmanı
5. Teknisyen	12. Arařtırmacı	19. Motivasyon Sađlayıcı
6. Ynetici	13. Lider	20. Uzaktan Eđitim Uzmanı
7. Site Eđitmeni	14. Materyal retici	21. İerik Tasarımcısı

**1. Psikolog:** Uzaktan eđitim retmeni, rencilerinin her trl psikolojik sorunlarıyla ilgilenmek durumundadır.

**2. retici:** rencilerin bireysel farklılıklarını ve renme stillerini gz nnde bulundurarak rencide kalıcı izli deđiřiklik meydana getirmek ile sorumludur. Uzaktan eđitim iin gerekli zel yntem ve teknikleri de kullanmak durumundadır.

**3. retim Tasarımcısı:** rencilerin kolay renebilmeleri iin gereken ortamı hazırlayan, dersin hedeflerini belirleyen ve ders ieriđini uzaktan eđitime uygun olarak tasarlayan uzmandır.

**4. Teknoloji Uzmanı:** Teknolojiyi yakından takip etmeli ve yeni teknolojileri uzaktan eđitime uygulamalıdır. Ayrıca, Kaya ( 2006 )' da, retmenler teknoloji ve materyal kullanımı konusunda ilgisiz yada yetersizse, eđitim programının rencilerin renmesini sađlamada bařarılı olamayacağı sylenbilir denilmektedir.

**5. Teknisyen:** Oluřan herhangi bir teknik probleme mdahale edebilmelidir.

**6. Ynetici:** retmen liderlik vasfına sahip olmalı, kuralları belirlemeli ve dzeni sađlamalıdır. Ayrıca zellikle uzaktan eđitimde iletiřim kaynaklı sorunları gidermek iin arabuluculuk ve hakemlik de yapılmalıdır.

- 7. Site Eğitmeni:** Öğretmen web sayfasının içeriğiyle ilgili gereken bilgiyi öğrenciye sağlamalı ve öğrenciyi motive ederek düzenli olarak sisteme giriş yapmasını sağlamalıdır.
- 8. Editör:** Materyallerin uzaktan eğitimde kullanılabilecek özelliklere sahip olup olmadığını ve hedef kitleye uygunluğunu denetlemelidir.
- 9. Grafik Tasarımcısı:** Görsel öğretim materyallerinin seçimini ve tasarımını yapar. Telif haklarıyla ilgilenir. Seçilen materyallerin hedef kitleye uygunluğunu kontrol eder.
- 10. Sosyalleşme Uzmanı:** Öğrencilerin birbirleriyle iletişimlerini sağlamalı ve organize etmelidir.
- 11. Danışman:** Öğrenciye yol göstermeli ve rehberlik etmelidir. Öğrencilerin sorunlarına çözüm bulmalarına yardımcı olmalıdır.
- 12. Araştırmacı:** Yıl içerisinde gereken kaynakları araştırmalı ve bu kaynakları bir kütüphaneci rolü üstlenerek öğrencilere sağlamalıdır.
- 13. Lider:** Öğrencinin motivasyonunu arttırmalı, öğrenciye sorumluluk vermeli ve onları cesaretlendirmelidir. Bu sayede öğrencinin uzaktan eğitimde daha etkin olması sağlanacak aynı zamanda öğretmenin yöneticilik rolü pekiştirilecektir.
- 14. Materyal Üretici:** Öğrenmeyi sağlayabilmek için gerekli her türlü materyali öğrencilere sağlamalıdır. Öğretmen bu amaçla öğrencilere yazılı materyaller hazırlayabileceği gibi uygulanan uzaktan eğitim modeline göre radyo programı, televizyon programı, bilgisayar programı yada internet destekli öğretim materyali hazırlayabilir.
- 15. Ölçme – Değerlendirme Uzmanı:** uzaktan eğitim kapsamında öğrencilerden beklenen öğrenmelerin gerçekleşip gerçekleşmediğini ölçme – değerlendirme faaliyetleri ile ortaya çıkarmalıdır.
- 16. Sistem Uzmanı:** Uzaktan eğitim sisteminde oluşabilecek sorunları önceden kestirip bunlara çözüm önerileri üretebilmelidir. Öğretmenin uzaktan eğitim sistemini tanıması bu sistemdeki görev ve sorumluluklarını bilmesini sağlar dolayısıyla sistemde oluşan veya oluşabilecek sorunlara ve sorunlara daha kapsamlı bir şekilde bakıp çözüm önerileri getirebilecektir.
- 17. Proje Yöneticisi:** Derslerin zamanında ve istenilen bütçede hazırlanması proje yöneticisinin sorumluluğundadır. Proje yönetimi uzaktan eğitim sisteminin maliyet ve etkililik boyutunda istenilen hedeflere ulaşmasının sağlanması açısından önemlidir.
- 18. İletişim Uzmanı:** Öğretmen ve öğrencilerin etkili bir iletişim içinde olmasını sağlamalıdır. Uzaktan eğitim sisteminde kullanılan iletişim sistemlerini iyi bir şekilde kavramalı ve bu iletişim sistemlerini etkin biçimde kullanarak iletilmesi gereken tüm mesajları ilgili kişi ve birimlere doğru bir şekilde göndermelidir. Ayrıca açık ve uzaktan eğitim derslerinde öğretmen üniversite ve öğrenciler arasında aracı rolü oynamalıdır ( Oral, 2007 ).
- 19. Motivasyon Sağlayıcı:** Uzaktan eğitimde öğrencilerin motivasyonlarının düşük olmasının öğrenmeyi yakından ve negatif yönde etkileyeceği göz önünde bulundurularak öğrenci motivasyonu olabilecek en yüksek düzeyde tutulmalıdır. Öğretmen, gerektiğinde aidiyet duygusunun gelişmesini sağlayacak yöntemler kullanarak öğrencileri güdülemelidir. Ayrıca öğrencileri kubaşık öğrenme gibi öğretim teknikleri kullanarak derse olan motivasyonunu arttırmalıdır.
- 20. Uzaktan Eğitim Uzmanı:** öğretmen uzaktan eğitimin nasıl olması gerektiğini ve oluşabilecek teknik problemleri önceden bilir ve çözüm önerileri üretir.
- 21. İçerik Tasarımcısı:** Öğretim materyallerini tasarlar ve içeriğin nasıl olması gerektiğini belirler. Bunun için öğretmenin alan bilgisinin iyi olması gerekmektedir.

Yukarıda açıklanan rollere baktığımızda, uzaktan eğitim öğretmenin oldukça fazla sorumluluğunun oluştuğunu açıkça görebiliriz. Öğretmenin sorumluluğunun artması daha fazla özveri gerektirecektir. İşman ( 2011 )' a göre uzaktan eğitimde öğretmenin aldığı bu denli fazla görevi, tek öğretmenin yürütmesi oldukça zor olacaktır. Buradan hareketle, öğretmen normal olarak bazı rollerini elinde olmadan aksatmak durumunda kalacak ve dolayısıyla gerçekleştirilen eğitimin bazı yönlerinin aksayacağı söz konusu olacaktır. Bu olumsuz durum ise, uzaktan eğitim sistemi içindeki öğretmenlerin işbirliği içinde hareket etmesiyle aşılabılır. Bu roller, işlev açısından gösterdiği benzerlikler açısından gruplandırılabilir ve uzaktan eğitim öğretmeni kendisine uygun olan gruptaki rolleri üstlenebilir. Böylelikle hem öğretmenin aldığı görevler azalmış olacak hem de öğretmen belirli alanlarda daha uzman hale gelecektir. İş yükü hafifleyen ve rollerinde daha da uzmanlaşmış öğretmenin,

uzaktan eğitimde iş yükü orantısızlığından kaynaklanan oluşması muhtemel bu olumsuz etkileri kaldırmasının yanında, eğitime olumlu yönde katkılar sağlaması söz konusu olacaktır.

### Uzaktan Eğitim Uygulama Modellerinde Öğretmen Rollerini

Uzaktan eğitimin, uygulama modellerine ve uygulama modellerine ilişkin iletişim şekline bağlı olarak farklı türleri mevcuttur ( Mektupla tek yönlü, radyoyla tek ve çift yönlü, televizyonla tek ve çift yönlü, bilgisayarla tek ve çift yönlü, karma tek ve çift yönlü ). Öğretmen rolleri, örgün eğitim ve uzaktan eğitimde farklılıklar gösterdiği gibi, uzaktan eğitim içinde, uzaktan eğitim modellerine göre de farklılıklar göstermektedir. Yukarıda ki bilgiler ışığında ve İşman ( 2011 )' da detaylı olarak ele alınan her bir modeldeki öğretmen rolleri aşağıdaki gibi tablo haline getirilerek özetlenmiştir.

Uzaktan Eğitimde Öğretmen Rollerini	Mektupla		Radyoyla		Televizyonla		Bilgisayarla		Karma	
	Tek		Tek	Çift	Tek	Çift	Tek	Çift	Tek	Çift
Psikolog	*		*	*	*	*	*	*	*	*
Öğretici	*		*	*	*	*	*	*	*	*
Öğretim Tasarımcısı	*		*	*	*	*	*	*	*	*
Teknoloji Uzmanı			*	*	*	*	*	*	*	*
Teknisyen			*	*	*	*	*	*	*	*
Yönetici	*		*	*	*	*	*	*	*	*
Site eğitmeni							*	*	*	*
Editör	*		*	*	*	*	*	*	*	*
Grafik tas.	*				*	*	*	*	*	*
Sos. Uzmanı	*		*	*	*	*	*	*	*	*
Danışman	*		*	*	*	*	*	*	*	*
Araştırmacı	*		*	*	*	*	*	*	*	*
Lider	*		*	*	*	*	*	*	*	*
Materyal üret.	*		*	*	*	*	*	*	*	*
Ölçme Değerlendirme Uzmanı	*		*	*	*	*	*	*	*	*
Sistem Uzmanı			*	*	*	*	*	*	*	*
Proje Yöneticisi	*		*	*	*	*	*	*	*	*
İletişim Uzmanı	*		*	*	*	*	*	*	*	*
Motivasyon Sgölayıcı	*		*	*	*	*	*	*	*	*
Uzaktan Eğitim Uzmanı	*		*	*	*	*	*	*	*	*
İçerik Tasarımcısı	*		*	*	*	*	*	*	*	*

### Uzaktan Eğitim Öğretmenleri ve Teknoloji

Uzaktan eğitim, bireylere kendi kendilerine öğrenme imkanı sağlayan, geleneksel eğitime göre daha esnek ve birey koşullarına uygulanabilir bir eğitimidir ( Oral, 2007 ) şeklinde tanımlanmıştır.. Uzaktan eğitim tanımında geçen esneklik ve birey koşullarına uygulanabilirlik kavramları, öğretmeni yakından ilgilendirmektedir. Teknolojik gelişmelere bağlı olarak uzaktan eğitimde yeni teknolojileri kullanma anlayışı da ortaya çıkmıştır ( Oral, 2007 ). Bu durumda öğretmen, özellikle teknolojinin uzaktan eğitime sunduğu olanakları kullanarak esnekliği yakalamalı ve bu sayede her türlü ortam ve koşulu bireyin koşullarına uydurmaya çalışmalıdır. Sonuç olarak, uzaktan eğitim öğretmeni teknolojiyle barışık olmak durumundadır. Öğretmen

teknolojinin varolan yönlerinden haberdar olmalı, gelişen ve yeni yönlerini ise araştırmacı kişiliğini kullanarak araştırmalı ve eğitim sistemine adapte edebilmelidir.

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# VECTOR CONTROL OF INDUCTION MACHINE WITH MODELS TAKING INTO ACCOUNT THE STATOR AND ROTOR FAULTS

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**Abstract-** With progress of the electric genius, the induction machines replace more and more the engines with requiring D.C current. However, the online diagnosis rotor and stator faults in the induction machines in order to reach a predictive maintenance have prompted the researchers to develop various techniques. In this work, we present the vector control of induction machine taking into account several faults such as short circuit between turns of stator and the broken bars of rotor. The modeling of induction machine is based on the theory of electromagnetic coupling of electrical circuits. In fact, these faults will be considered during the modeling in order to develop a tolerant control of induction machine, in others words, the control of induction machine holds in presence of stator faults.

**Key words:** Induction machine, Stator faults, Broken bars, Multi-turns Model, Vector control.

## 1. Introduction

The online diagnosis rotor and stator faults in the induction machines in order to reach a predictive maintenance have prompted the researchers to develop various techniques. The work in their majority is based on the signature (harmonic analysis) indicatory values such as current, torque using the theory of rotating fields and electrical circuits.

Moreover, the analysis methods of stator faults using the structural parameters of knowledge model to detect and locate failures. The key point to ensure the effectiveness of these methods is to choose a model of knowledge [V.SCA.1999, E.SCH.1999]. Indeed, the type of fault that has to be detected will be based on the model used [V.SCA.1999, E.SCH.1999]. Initial work relating parameter estimation began with relatively simple methods (model of Park for example) [G.DID.2004, F.FEL.1998]. The next step is therefore necessarily to pass to a more knowledge model of machine, while retaining the ability to identify the desired parameter. These models can be the three phases model [T.BOU.2003], which is not based on the assumption of a magnetically balanced machine, or models with 'n' phases (multi-turns model) [H.HEN.2003, D.KHO.2009, S.NAN.1999, V.SCA.1999, V.VIN.2003], that can reflect the operating of the machine over a large frequency range. On the other hand, it should be noted the need for a priori knowledge of the specific model of the induction machine. Moreover, the aging and depending on the environment, the representative model of the operating of the machine change. In addition, the diversity of defects (stator, rotor and supply defects) of the induction machine, they cannot be obtained by the same mathematical model. Indeed, every failure should be modelled separately by its own model [S.BEL 2007, X.CHA.2002, T.BOU.2001, F.FEL.1998, D.KHO.2009].

## 2. Induction machine modeling in presence of stator faults

To model the behavior of the short-circuits between coils, we will present another method for modelling of the induction machine, taking into account the changing parameters such as resistors and inductors, i.e. the matrix is stator resistance and the one of stator inductors are time-varying [X.CHA.2002, T.BOU.2001, D.KHO.2009, V.SCA.1999]. This model requires a precise and rigorous study of fault signatures of the induction machine.

In addition, the conventional modeling of a three-phase induction machine to the stator and the rotor wound (if the machine is cage made, we can consider the winding-phase equivalent), based on the classical assumptions. Under these assumptions, the machine can be modelled by the following equations:

$$[U_S] = [R_S][I_S] + [P\Phi_S] \quad (1)$$

$$[0] = [R_R][I_R] + [P\Phi_R] \quad (2)$$

$$[\Phi_S] = ([M_{SS}] + [L_{Sf}])[I_S] + [M_{SR}][I_R] \quad (3)$$

$$[\Phi_R] = [M_{RS}] + ([M_{RR}] + [L_{Rf}])[I_R] \quad (4)$$

One defines the coefficients of short-circuit as follows:

$$k_{sa} = \frac{N_{cc1}}{N_s} \quad k_{sb} = \frac{N_{cc2}}{N_s} \quad k_{sc} = \frac{N_{cc3}}{N_s}$$

The number of useful turns for the three stator phases is then given by:

$$N_1 = N_s - N_{cc1} = (1 - k_{sa})N_s = f_{sa}N_s$$

$$N_2 = N_s - N_{cc2} = (1 - k_{sb})N_s = f_{sb}N_s$$

$$N_3 = N_s - N_{cc3} = (1 - k_{sc})N_s = f_{sc}N_s$$

Matrices  $[R_S]$ ,  $[L_{Sf}]$ ,  $[M_{SS}]$ ,  $[M_{SR}]$  and  $[M_{RS}]$  depend on three coefficients  $f_{sa}, f_{sb}, f_{sc}$ . The inductors are given by the following terms:



With regard to the faults of short-circuit between turns, we have seen two cases of failures, where  $N_{cci} = 20$  and  $N_{cci} = 40$  the turns in short- circuit, therefore we will have respectively  $N_{cci} = 140$  and  $N_{cci} = 120$  turns that phase will be useful. Fig.2 presents the changing parameters (current, speed and torque) by considering these faults. Each fault has been applied whereas the machine was unloaded (at  $t = 0.8$  seconds). We notice that the current after the appearance of fault increases considerably compared to the current in steady state for the case of healthy machine. This increase is related to the number of turns in short-circuit. This is obviously the simultaneous decrease of resistance and the reactance phase of the stator. We also noted a slight disturbance at the speed and torque, and then they will be reinstated after a brief period.

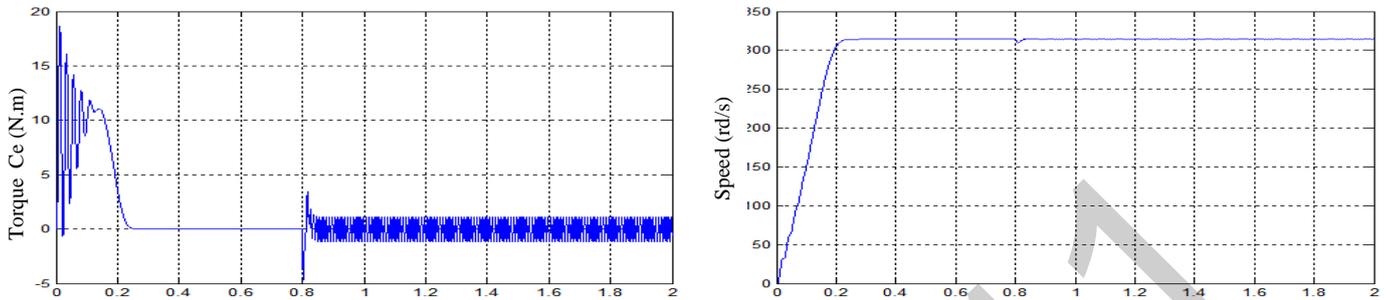


Fig.2. Results of 12.5% turns in short-circuit without control

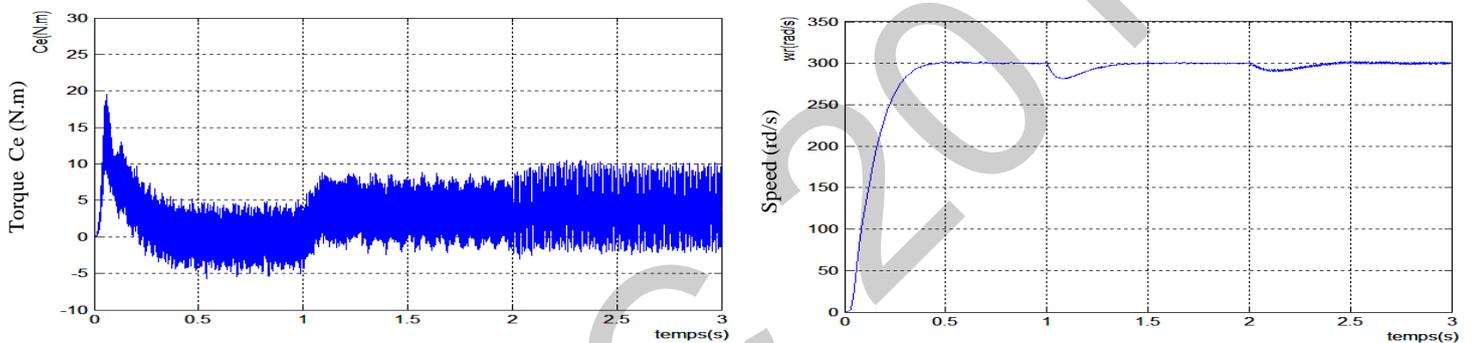


Fig.3 Results of 25% turns in short-circuit with vector control

In addition, we can see in the fig.3, that with tolerant control the speed of induction machine is established in 2 seconds after the appearance of stator fault (25% turns in short-circuit). The load it applied at 1 second.

### 6. Vector control with presence of rotor faults (Broken bars)

We present the influence of the rupture of bar on the walk of the asynchronous machine in vectorial order. After the machine has been fluxed, the reference speed is set to 100rad/s (fig.4 ). Then a load torque is applied at  $t=0.8s$ . When the machine is healthy and when torque is required, symmetrical rotor-bar currents appear with pulsation the slip frequency. At  $t=1.5s$ , we simulate a first bar is broken this is achieved by increasing its resistance. We only notice small oscillations on the speed. The second bar is broken a  $t=2.5s$ . We notice the appearance of fluctuations on the shapes of the torque. Speed remains always not very disturbed by this defect. For current I have one sees well a deformation during the rupture of the bar.

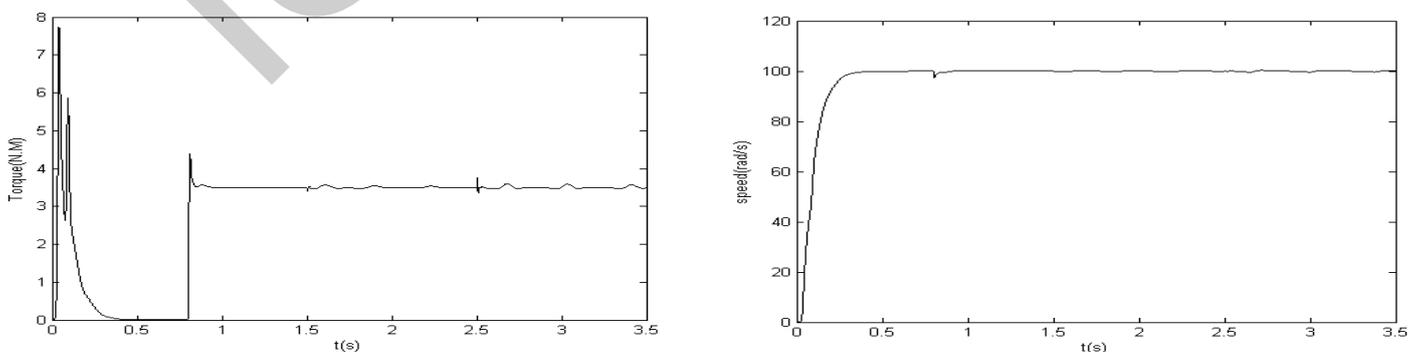


Fig.4 Results of two broken bars with vector control

## 7. Conclusion

This study allowed us to consider that the vector control can tolerate same less important faults such as: the shorts-circuit between turns or broken bars of rotor. This insures the operating of the induction machine even in failure mode (i.e. the induction machine with tolerant control can work like healthy machine in presence of faults).

Furthermore it is possible to use different methods of diagnosis for the detection and localization of the defects of the induction machine (based on the signatures of electrical and mechanical properties obtained from the model used for this study, namely: the sampled values of current stator and the rotational speed as well as the effective values of stator currents and voltages and the value of the rotational speed).

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## Appendix

$P_n$ : nominal power 1.1 kW

$V$ : stator voltage 220 V

$p$ : a number of poles 2

$f_s$ : stator frequency 50 Hz

$R_S$ : resistance of a stator phase 7.58  $\Omega$

$R_R$ : resistance of the rotor cage 6.3  $\Omega$

$L_R$ : rotor inductance 0.1612H

$L_S$ : stator cyclic inductance 0.5976H

$J_m$ : moment of inertia 0.0054 Nms<sup>2</sup>

$N_S$ : a number of turns per stator phase: 160

$M_{SR}$ : mutual inductance stator 26.5mH.

# VINEGAR MAKING BY TRADITIONAL METHOD IN THE SOUTH OF ALGERIA

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## ABSTRACT

The present study focused on the characterization of a final product called "vinegar" by people of the South of Algeria. It was produced for personal consumption via a traditional method.

The fermented beverage is made mainly by date raw material diluted in tap water (date:water ratio of 1:2) added with some ingredients as: 7 seed of (wheat, barley, coriander, harmel), a pinch of (salt, pepper). The process last 45 days at ambient temperature. Moreover, a modified experiment was carried out using only date to investigate the incidental influence of those ingredients supplemented.

Products of the two experiments were subject to physico-chemical and sensorial analysis. Samples of date vinegar collected have the same aspect (turbid), taste (sour) but different colour. The final product of the modified experiment emit ethylether odour comparatively to the strong date odour of the traditional's one.

Furthermore, vinegar resulted from the fermentation process of date alone had better quality with a higher acid acetic production and a lower residual ethanol content.

**Key-words:** vinegar-date-traditional process-sensorial quality.

## INTRODUCTION

The date palm tree (*Phoenix dactylifera*) is grown extensively in arid and semi-arid regions of the world, like the Arabian Peninsula, Egypt, Iran, Spain, Tunisia and South of Algeria (FAO, 2003).

Algeria is considered as one of the major date producing countries in the world with a yearly production of about  $400.10^3$  tonnes (DSAA, 2001).

Algeria is currently the 7<sup>th</sup> world producer and the first exporter of dates in value. Furthermore, the annual production has reached an average of 6 006 96 tonnes in 2009 with 2 812 65.7 tonnes for Deglet Nour variety, and about 2 094 14.3 tonnes for secondary or common dates with hard texture. These common dates are not consumed by humans, they are discarded or used in limited cases for animal feed (Ould El Hadj et al., 2001).

Dates are considered to be a favorable source for biological utilization because they contain much sugar and variant nutrients (Al Farsi and Lee, 2008; Biglari et al., 2008).

In the south of Algeria, a homemade product named "traditional vinegar" is largely used as a food flavouring and condiment or as a food preservative.

The objective of this study was to assess the physico-chemical characteristics and sensorial quality of two final product prepared respectively according a traditional method as applied in Sahara and a modified process.

## MATERIAL AND METHODS

### Origin of date fruit

This study was conducted on second-grade dates of the most abundant varieties in the South of Algeria (Biskra region): Mech-Degla. These fruits were collected at "Tamr stage" (full ripeness).

### Preparation of date vinegar

Two complete batch fermentation runs were carried out in plastic bottle of 1L capacity washed and rinsed with distilled water. Two fermenting medium was prepared with about 150 g of Mech-Degla dates without damages diluted in tap water (date:

water ratio of 1: 2). One of the fermentation medium was added with 7 seed of (wheat, barley, harmel, coriander), a pinch of (salt and pepper), and some nails according date quantities. A hole was made in the center of the bottles top for aeration and bottles were then incubated at room temperature (25 to 28°C) for 45 days. The end product of each bottle was filtered and analysed.

### Physico-chemical analysis of the final product

Reducing sugar content was determined using the dinitrosalicylic acid (DNS) method (Miller, 1959). Total soluble solid (TSS) was determined at 20°C using a hand refractometer with brix range model 50301130. The pH was measured using a digital pH meter (WTW inolab series Type) according to the AOAC, (1984). The total titratable acidity was determined by titration with 0,1 N NaOH and phenolphthalein as an indicator (Ough and Amerine, 1987). Alcohol concentration was determined by the potassium method (Bohringer and Jacob, 1964).

For the determination of mineral elements (Na,K,Zn,Fe,Cu,Mn,Ni,Cr,Cd,Pb), the ash was dissolved in 5 ml concentrated HCl and the volume made up to 200ml. All minerals were analysed by atomic absorption spectrophotometry (Rouessac, 2000).

### Sensorial evaluation

The end product of the fermentation process was evaluated for colour, taste, aspect and odour.

## RESULTS AND DISCUSSION

### Physico-chemical characteristics of the end product

Table 1 summarizes the results of total soluble solids (°Brix), pH, reducing sugars, % acetic acid and % ethanol for the two end product.

Table 1: Physico-chemical characteristics of the two end-product

Parameter / Process	pH	Acidity (g/ 100 ml)	°Brix	Residual reducing sugars (%)	Alcohol residual (g/100 ml)
1	3,41	0,99	17,7	0,5	4,58
2	3,40	1,14	15,2	0,21	3,69

**Process 1:** added with ingredients; **Process 2:** without ingredients.

The pH values found in our study after 45 days for the two continuous fermentation mediums are similar to the result reported by Ould El Hadj *et al.*, (2001) for the traditional vinegar produced with Harchaya date (dry variety). In contrast, they are lower than those of 100 samples of traditional balsamic vinegar (2,3-2,8) analyzed (Giudici *et al.*, 2009). This difference in the pH values could be considered as a distinctive characteristic of any traditional vinegar related to its production technology and organic acid profile (Giudici *et al.*, 2009).

Concerning acidity, the end product of the modified process (without ingredients) showed the higher content. Nevertheless, both values of the two fermenting process are lower than those obtained by Ould El Hadj *et al.*, (2001) for vinegar produced with three date varieties: Hchef of Deglet-Nour (2,5%), Harchaya (dry date) (3,03%) and Hamraya (2,5%). Also, Clavet (1912) noted higher acidity content for different vinegar made with wine (6 to 9%), cider (4%), white wine (5,6 to 7,9%). In the same way, Gonzalez and De Vuyst (2009) indicated higher values for vinegars from tropical Africa. The lack of acidity of the end product in our study may be probably due to the slow and incomplete acetous fermentation considering the high residual alcohol content observed with respectively 4,58% for the process 1 and 3,69% for the process 2. Likewise, Ould El Hadj *et al.*, (2001) noted that the residual alcohol content for three vinegar date variety's varies from 3,61 to 4,90.

As shown in the Table 1, the concentration of the residual reducing sugars of the final product of the process 1 is two fold higher than those of the second process. This could be related to the difference in the speed and the diffusion rate of the sugars through the date pulp. Furthermore, sugars are not completely metabolized depending upon the complex conditions of the biological fermentation.

As regards total soluble solids content, our values are higher than those indicated in the work of Ould El Hadj *et al.*, (2001) for vinegar produced respectively with Hchef Deglet Nour (8,3%), Harchaya (10%) and Hamraya (7%). This high content of solid soluble resulted from the higher residual content of alcohol and reducing sugars in the fermenting medium studied.

### Mineral composition of the end product

As indicated in the Table 2 and compared to the end product of the traditional method, Na, Ca and Mg contents were relatively high, while the K content was slightly low in the sample 2 produced without addition of ingredients. According to our results,

relatively higher contents of Ca and Mg were observed in onion vinegar with contrarily low sodium content (Horiucchi *et al.*, 2004). In addition, these authors suggest that this onion vinegar could be applied as nutraceutical food for prevention of hypertension disease.

Table 2: Contents of several main minerals and metals in the end product (mg/l)

Minerals Process	K	Na	Ca	Mg	Zn	Cu	Fe	Pb	Mn	Cr	Ni	Cd
1	4298	387,5	4,40	5,44	9,4	< 0,04	65.5	< 0,1	< 0,01	< <b>0,05</b>	< 0,05	< 0,01
2	3955	1037	62 ,81	24,50	3,95	< 0,04	< 0,06	< 0,1	< 0,04	< <b>0,05</b>	< 0,05	< 0,01

The analysis of mineral content gave an extremely high iron content of the product obtained with the traditional process as applied in Sahara. This product was not conform and may present a sanitary risk for consumers. In fact, the Algerian standard recommendation was (< 1mg/kg vinegar) (AOJ, 1997). However, the total Zn+Cu and lead were lower as required by the AOJ, (1997).

### Sensorial analysis

The results of the sensory evaluation of the two end product produced were presented in Table 3.

Table 3. Organoleptic characteristics of the end product.

Parameter Process	Colour	Aspect	Taste	Flavour
1	Brown	Turbid	Sweet and sour	Date odor ++
2	light brown	Turbid	Sweet and sour	Ethyl ether +

As can be seen, there is no difference in the aspect and taste of the two end product. Giudici *et al.*, (2009) suggest that in addition of acetic acid, other compounds play a key role in determining the sensorial properties of the vinegar, for example, citric acid possesses sweet and sour sensory notes; succinic acid has a salty-bitter taste; and sour, unripe and irritating/pungent flavours are ascribed to lactic acid, malic acid and acetic acid, respectively.

The colour of our product was brown and according several results reported for other foods, melanoidins are mainly responsible for determining the characteristic brown colour (Rivero-Pérez *et al.*, 2002; Piva *et al.*, 2008). Furthermore, our results shown a characteristic flavour for each sample produced. It was established that the flavour of vinegar depends on the raw materials, the constituents formed during fermentation and essentially about the contribution of some hundreds of volatile compounds (carbonyl compounds, ethers, acetals, esters, phenols, etc.) (Tesfaye *et al.*, 2009).

### CONCLUSION

Results of this study demonstrated that the two fermentation process conduct to a sweet and sour product but the acidity and residual alcohol content of those beverages are far from international values required for vinegars. The lack of acidity of the final product in this case may be due to the short time of the acetification step.

However, the use of date without adding the different ingredients considered in the traditional method as applied in the sahara give a product with better quality. Furthermore, the addition of nail could be toxic for the consumer health regarding the high content found in the end product of the process 1.

To conclude, we can say that there are several technological factors to take into account for vinegar production, such as room temperature, acetic acid bacteria used, composition of the fermentation medium, etc.

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# VIRTUALMATRiKS: A CONCEPTUAL MATHEMATIZATION PROCESS IN VIRTUAL LEARNING ENVIRONMENT

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## ABSTRACT

In the Virtual Learning Environment, students interact with the teacher and the other students. By interacting, students can enhance the understanding of mathematical concepts and its application in the real life. This study aims to develop a model of virtual learning environment based on Realistic Mathematics Education. The research questions are how to develop and implement this model and its effect on the learning outcomes. The results of development in this study are the model and device of VirtualMATRiKS. Students simulate the conceptual mathematization process by create the movie about problem solving. Then students share and discuss it through virtual-learning device. After validated by experts, the model and device were implemented in Semarang Senior High School. And the result is the model and devices qualify the effectiveness and practicality. This model gives a positive impact on student learning outcomes, and students can reach the Upper Limit of Zone of Proximal Development. This model can be applied and developed further in learning mathematics by considering into environment, conditions and students interest.

Keywords: *RME, Virtual-Learning Environment, Educational Movie, Conceptual Mathematization*

## INTRODUCTION

Teaching and learning mathematics are complex tasks. According to Freudenthal (1991), mathematics as human activity and mathematics must be connected to reality. Therefore, students should be able to understand the concepts of mathematics and and its application in the real world. But in fact, there are some problems in learning mathematics, such as some students are difficult to understand the concepts and problem solving, some students have low motivation in learning mathematics, and some students do not understand the application of mathematics in real life. By considering the expectations and problems, it is necessary to develop a model of learning environment that makes the learning activities become easier and more enjoyable so the students can reach the optimal learning outcomes. When referring to the Vygotskian perspective, learning outcomes and students' understanding can be increased as a result of interaction in learning. The interaction between teacher-student and student-student in learning, illustrates that social interaction in the form of discussion is able to provide students with opportunities to optimize the learning process. This interaction allows teachers and students to share and modify their ways of thinking. There is also a possibility for some students to showcase their own arguments as well as for other students the opportunity to try to capture the thought patterns of other students.

Activity is believed to be able to increase knowledge and understanding of the object was learned from the previous stage to a higher stage. Students can interact around the difficult task and share their effective problem-solving strategies, if there is an arrangement of classes and a form of learning environment. There are two forms of learning environment, namely physical learning environments and virtual learning environments. Virtual learning environment (VLE) developed by making the design of information spaces as learning environments. In the VLE, students interact with teacher and the other students, wherever and whenever. Teachers and students are familiar with the use of the system. Hardware and software that supports this system has been available. However, to achieve the purpose of learning mathematics, the development of the learning environment must be based on the characteristics and principles of mathematics and learning mathematics.

## THEORITICAL BACKGROUND

### Vygotskian Perspective

According to Vygotsky (1978), there are two important concepts in the sociocultural theory, the Zone of Proximal Development (ZPD) and scaffolding. ZPD is the distance between the actual developmental level as determined by independent problem-solving and the level of potential development as determined through problem solving under adult guidance or in collaboration with more capable peers (Vygotsky, 1978). It is a dynamic developmental state. At the lower limit of the zone are the tasks that children can accomplish independently, while at the upper limit is the space where more complex tasks can be realized by children through interactions with more knowledgeable others. Learning can evoke a variety of mental processes that can only be operated stored when a person interacts with an adult or collaborate with their peers. With these interactions, students can complete a complex task that can only be solved if students are given assistance by adults or collaborate with peers, the level is referred to as the upper limit of the ZPD. The process of giving assistance in this process is called scaffolding.

Scaffolding means providing large amounts of aid to students during the early stages of learning and then reducing the assistance and provide opportunities for children is to take over greater responsibility as soon as he can do it (Slavin, 1994).

Vygotsky (in John and Thornton, 1993) explains that learning occurs in two stages: first stage occurs when collaborating with others, and the next phase done on an individual basis in which occurs the internalization process. During the process of interaction occurs (teacher-student and student-student), the following capabilities should be developed: mutual respect, to test the truth of the statement of others, negotiate, and adopt the other opinion.

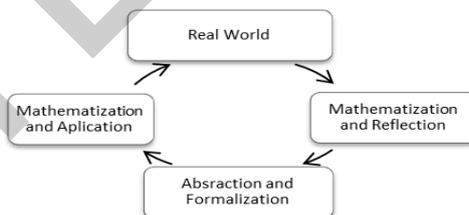
### Virtual Learning Environment

A Virtual Learning Environment is a collection of integrated tools enabling the management of online learning, providing a delivery mechanism, student tracking, assessment and access to resources (Dillenbour & al, 1999). In a virtual learning environment, students and teacher can interact anywhere, anytime and easy to find and share informations. Interaction can take many forms, including synchronous or asynchronous communication, one-to-one or one-to-many or many-to-many, text-based or audio and video, or even indirect communication such as sharing objects. Researchers have introduced the notion of “place” (Dourish & Chalmers in Dillenbour & al, 1999) to emphasize that space has a social impact. Places are settings in which people interact. (Munro, Höök & Benyon in Dillenbour & al, 1999). The representation of the learning environment ranges from text-based interfaces to the most complex 3D graphical output. 3D graphical representation is often used, because it can increase motivation, and triggering a positive attitude towards the environment. Dillenbour & al (1999) observed that virtual space imparts on users behaviour even when space is only described by text. In virtual environments, learning activities ranging from multiple-choice questionnaire for simulation and problem solving. The idea of learning activities in a virtual learning environment refers to something richer than the individual, closer to the idea of the project.

The difference between other constructivist environments and what virtual environments potentially offer can be described as making students not only active, but also actors, i.e. members and contributors of the social and information space. (Dillenbour & al, 1999). A virtual learning environment integrates a variety of tools supporting multiple functions: information, communication, collaboration, learning and management (Peraya & al. in Dillenbour & al, 1999). Virtual learning environments do not only integrate a variety of software tools but also integrate all the physical tools that can be found in a classroom. According Carabeanu (2006), a learning environment is considered adaptive if it is capable of: monitoring the activities of its users; interpreting these on the basis of domain-specific models; inferring user requirements and preferences out of the interpreted activities, appropriately representing these in associated models; and, finally, acting upon the available knowledge on its users and the subject matter at hand, to dynamically facilitate the learning process.

### Realistic Mathematics Education

Mathematics as human activity and mathematics must be connected to reality. These statements are the root of the Realistic Mathematics Education (RME). RME refers to the mathematics education approach which has been developed and applied in the Netherlands since 1971. Mathematics should be undertaken as an activity in the students experience mathematics as a meaningful subject and can better understand it (Freudenthal, 1991). Freudenthal emphasizes real activity in mathematical activities. Activities under consideration should consist largely of organizing or mathematization of subject matter and is taken from reality. Learners must learn mathematics with mathematization of subject matter from the real context and activity of mathematics, not learning from the traditional presentation of mathematics to the students as a ready-use system that is generalized. Real situations can include contextual problems or authentic Mathematically Contexts for students where they're having problems which are presented in relevant and real. The process of developing mathematical concepts and ideas that started from the real world called conceptual mathematization (de Lange, 1993). Schematic model of learning is described as follows.



Picture 1. Conceptual Mathematization (de Lange, 1993)

Through a process of progressive matematization, learners are given the opportunity to rediscover the insight, knowledge and mathematical procedures. Thus learners do the stages which in RME called horizontal and vertical mathematization. Gravemeijer (in Sembiring & al., 2008), suggests that there are three main principles of RME, namely: (a) Guided reinvention / progressive mathematizing, (b) the didactical phenomenology and (c) self-developed models. For the operationalization of the three main principles of RME, according Panhuizen (in Gravemeijer, 1994: 114-115), RME has five characteristics, namely: a) The use of contextual problems, b) The use of various models, c) Student contributions, d) interactivity, and e) intertwining (integrated). Strategy, which could be applied in the implementation of RME by Loucks-Horsley (1998): (1) a short learning process, (2) curriculum development, and (3) the use of technology. The results of research in the Netherlands showed that the RME has shown satisfactory results. RME has the potential to improve students' understanding of mathematics (Streefland, 1991).

### Activity Theory

All human actions are called activities. An activity involves an object. The object is to be transferred to the output of the activity. A subject performs an activity using a tool. The tool can be a physical or an abstract tool. The interactions between subject, object and community can all be mediated. Rules mediate the activity between the community and a subject. The activity may be collaborative, i.e. several subjects jointly do the activity using tools and dividing the work between each subject (Multisilta, 2008). In general, tools, rules and division of work mediate the relationship between the subject,

community and object. Tools, rules and division of work are artefacts that are used to achieve the outcome. Experiences and attitudes that influence one another (Uden, 2007). Activity can furthermore be divided into actions and an action on operations. In general, activities are based on high-level goals (for example, documenting a work process with images and video clips). The Shared Activities and Experiences framework originates from a need to describe sharing and experiences in social media in theoretical terms (Multisilta, 2008).

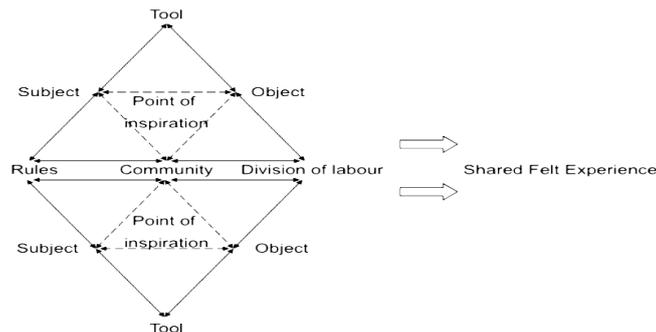


Figure 2. The Shared Experience and Activities Framework (Multisilta, J., 2008)

### Conceptual Framework and Research Question

Mathematics as human activity and mathematics must be connected to reality. Therefore, students should be able to understand mathematics concepts and its application in the real world. Students' understanding can be optimized through social interaction in the learning environment. There are two forms of learning environment, namely physical learning environments and virtual learning environments. In a Virtual Learning Environment (VLE), students can interact with the other wherever and whenever. In this learning environment, students do activities to learn and gain new knowledge and experience with solving problems, sharing information, and discuss. Thus, students are expected to reach the upper limit of the zone of proximal development (ZPD). Activities should be adapted to the characteristics of mathematics. Mathematical activity of solving contextual problem starts from the real world problem, mathematizing and reflecting the problem, abstraction and formalization, mathematizing in application and then bring back to the real world at the end process. In Realistic Mathematics Education (RME) approach, this process is called Conceptual Mathematization

This research questions are (1) how to develop and implement the model of VLE based on RME in Semarang Senior High Schools? and (2) Is the implementation of the model has a positive effect on student learning outcomes?

### RESEARCH METHOD AND PROCEDURES

This research is a development research that continued from previous research, MATRiKSMovie: building the nation character through movie-based RME (See also Cahyono, 2011). The purposes of this research is to develop the model of VLE based on RME in Semarang Senior High School. According to Cahyono (2006), model is defined as a conceptual framework used as guidance to do certain activity. Pouver (1974: 243) explain about model as assumption like metaphor formulized explicitly containing unresolves which depends each other. As a metaphor, model has never been seen as part of data represented. Model explains phenomena in a form which is not usual. Every model is needed to explain something more or different from data. This requirement is fulfilled by presenting data in forms of summary (type, diagram), configuration (structure), correlation (pattern), idealization and the combination of the four. Thus, model is metaphor which is solid and useful for the comparison of relation between the chosen data and the relation among the chosen unresolves of a logical construction.

In this study, validity, practicality and effectiveness criteria are defined as follows: validity refers to the extent that the design of the intervention should include "state of the art knowledge" (content validity) and the various components of the intervention are consistently linked to each other (construct validity), practicality refers to the extent that users (teachers and pupils) and other experts consider the intervention as appealing and usable in normal conditions, effectiveness refers to the extent that the experiences and outcomes from the intervention are consistent with the intended aims.

Following the work of Nieveen (1997) and Ottevanger (2001), the development and research activities in this research were conducted in three stages. The first stage is called the front-end analysis, the current situation of mathematics learning in Semarang Senior High School were analyzed. The second stage of the study is called the prototyping stage. This stage consisted to develop and validate the prototype, namely virtual-learning device, the lesson kit and formative evaluation. The third stage of the research is called the assessment stage. In this stage the final version of the model and device are implemented in Senior High School, and then the learning process and result are reflected and evaluated with the instrument.

### RESULT AND DISCUSSION

The first stage is called preliminary stage or front-end analysis, that the current situation of mathematics learning in Semarang senior high schools was analyzed. Result of the analysis in this stage are used as the basic for the development of model with valid, practical, and effective criteria. There are some problems in learning mathematics, such as some students are difficult to understand the concepts and problem solving, some students have low motivation in learning mathematics, and some students do not understand the application of mathematics in real life. Students and teachers need a medium to interact with easier, more enjoyable, and adjust to the development of information and communication technology. The results of the analysis indicate that some of the high school students still require visualization of abstract concepts and application of

concepts in the real world. One material that is considered difficult by students is a matter of trigonometry. Student difficulties understanding the concepts and solving problems related to trigonometry, including equations and trigonometric functions and applications of trigonometry in real life. Students at this age also tend to be less motivated in carrying out learning activities in mathematics and more interested in the entertainment and social networking because of the influence of age, social, environmental, facilities, and technology. Technological development encourages innovation in teaching and learning of mathematics by adjusting to conditions. By considering the expectations and problems, it is necessary to develop a model of learning environment that makes the learning activities become easier and more enjoyable so the students can reach the optimal learning outcomes. Learning outcomes and students' understanding can be increased as a result of interaction in learning.

In the second phase (prototyping stage), the result of analysis in first stage used to develop the prototype. Based on the preliminary analysis, the prototype being developed is a model and device of virtual learning mathematics based on RME, called VirtualMATRiKS. The prototype that need to develop, i.e virtual-learning device, lesson plan, teachers guide, students workbook, and the evaluation sheet. Preliminary description of the learning process is the students simulate of the conceptual mathematization process by creating the movie about problem solving. Then students experiencing by share and discuss the movie with other through virtual-learning device. It is based on the fact that mathematical activity of solving contextual problem starts from the real world problem, mathematizing and reflecting the problem, abstraction and formalization, mathematizing in application and then bring back to the real world at the end process. The activities of students in these activities is to demonstrate the process of solving problems related to the rediscovery of the mathematical concepts and applications of mathematical concepts in real life. Process in the production of educational films starting from a given theme as a problem (in the form of the rediscovery of the concept of mathematics, or mathematical applications), then the students discuss in a production team to develop problem-solving scenarios to be presented in the drama of human activity in problem solving, setting up properties which is needed in problem solving and presentation, to present the steps solving the problem by acting in front of the camera (as actrist or as a presenter), the product is presented in real video and/ or graphic animation according to student creativity and made simple with simple tools, so implementation of these activities in accordance with the allocation of time that has been planned in the lesson plan. The results of this learning process are portofolios and movie. Each team share the learning experience by uploading the movie in the Virtual Learning Environment device, then students discuss together about material with the guidance of teachers in the virtual learning environment. This activity can be done anywhere and anytime, with rules specified by the teacher.

Draft of prototype validated by experts (education, mathematics, media, evaluation) to obtain a valid prototype and ready to be implemented in learning process on the third stage. After validated, the prototype is corrected based on the suggestions given by experts, so getting a second prototype that is better than ever. Then the second prototype was simulated in the learning process. Simulation is used to obtain data on the implementation of models and tools in learning. The data come from teachers, students, and the observer. Simulation concludes with discussion and reflection to obtain feedback and know the lack of model and device as the basis for subsequent improvement. After repair and produce the final version of the prototype, and ready for use, then executed the third stage. The result of prototyping are the model of virtual learning environment and device of VLE. Learning environment that developed through this research is a hybrid learning environment (face-to-face learning and learning through elearning devices). Learning processes and devices were developed based on the philosophy, principles, and characteristics of RME and using IT-tools in the form of e-learning device that focus on providing support for teacher(s) and students in the learning process. E-learning device was developed with the software and computer networks. Syntax of the model are (1) Teachers provide instruction, convey learning goals, students in the class divides into groups, distribute the student activity sheet, (2) The teacher gives problems to be solved by the students, so students are able to construct the concept of matter being studied and/ or apply the concepts in real life, (3) Students discussing with his team to share tasks and create problem-solving scenarios in accordance with the creativity of each. (with teacher guidance). (4) Accordance with their respective duties, students creating a simple short film production process of solving the problem (the construction of concepts and/ or application of concepts). (5) Each team sharing the learning experience by uploading a movie in the VLE device (6) Students discuss their work together with the guidance of teachers in the virtual learning environment. This activity can be done anywhere and anytime, with rules specified by the teacher, (7) Each student gives a conclusion. (8) Teachers give clear, straighten the concept (if there is a less precise), and give final task of learning (projects, pop quizzes and/ or homework) using VLE device. Virtual learning device was developed and implemented by using software, hardware, and computer network, that supports text files, images, interactive media, mathematical formulas and video. The device also provides both synchronization and asynchronization communication communication feature.

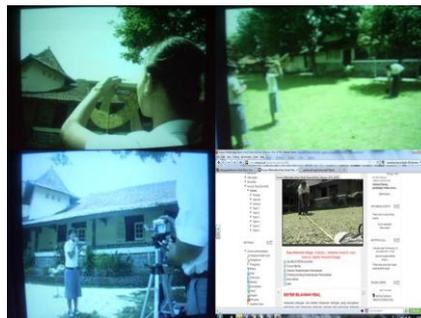


Figure 3. Practice problem solving in the real world, simple movie production, share and discuss in VLE device

The third stage of the research is called the assessment stage. In this stage the final version of the VirtualMATRiKS model and device are implemented in Senior High School, and then the learning process and result are reflected and evaluated

with the instrument. VirtualMATRiKS was implemented in a Semarang Senior High School class 10 in 2008 in the subject matter of Trigonometry.

The research result suggest that the average of reliability of learning equipment (virtual-learning device, lesson plan, teachers guide, students workbook, and the evaluation sheet) is 95,30%, that is a high reliability category, the capability of teacher in organizing the learning could be categorized as very good, with average score 3,52. The average of teacher's activities in the learning process is 3,54 or it reaches 88,48 % (category of very good). The average of students' activities in the learning process is 3,54 or it reaches 88,57 % (category of very good). Seeing the average of students' involvement of each meeting, it shows that there is an increase of students' involvement from 3.45 to 3.54 at the last meeting. The average of students' skill of process in the learning is 3.57 or it reaches 89.26% (category of very good).

According the calculation,  $\chi^2_{\text{calculation}} = 1,296$  which is significant at  $0,069 > 0,05$ , thus,  $H_0$  is accepted which means the data has normal distribution. Therefore, the statistic used is statistic of parametric. The result shows that the mathematics learning result data coming from upper, middle and lower groups in the experiment class and control class are normally distributed and are homogenous. By using *Univariate One Way Anova* to test the difference of averages between the upper, middle and lower groups. Based on the calculation, at the row group, the significant value is  $0,020 < 5\%$ , it means that the learning outcomes between experiment class and control class is different. At the column group, the significant value is  $0,000 < 5\%$ , it means that there is no difference of the learning outcomes among the three groups (upper, middle, lower). Then, there is no interaction because the value of significant is  $0,091 > 5\%$ .

By using *Regression Analysis*,  $F_{\text{calculation}} = 25,643$  with significant rate is 0,000. It shows that there is strong effect of skill of process toward the learning outcomes or  $H_0$  is rejected which means there is influence between skill of process and learning outcomes. From the calculation, the correlation between skill of process and learning outcomes is 63,5 % and the skill of process gives contribution toward learning outcomes 40,3%. Therefore, the skill of process strongly correlates with the

learning outcomes. The regression equation between skill of process and learning outcomes is  $\hat{Y} = 32,371 + 2,657 X$ , where  $Y$  = learning outcomes, and  $X$  = skill of process. From the calculation,  $F_{\text{calculation}} = 27,616$  with significant rate is. It shows

that there is strong effect of students' activity toward the learning outcomes or  $H_0$  is rejected which means there is influence between students' activity and learning outcomes. The correlation between students' activity and learning outcomes is 64,9 % and the students' activity gives contribution toward learning outcomes 42,1%. Therefore, the students' activity strongly correlates with the learning outcomes. The regression equation between students' activity and learning outcomes is  $\hat{Y} = 13,968 + 1,987 X$ , where  $Y$  = learning outcomes, dan  $X$  = students' activity.

From *Compare Mean One Sample t Test*, we find that  $t_{\text{calculation}} = 2,963$ . By using right side test, for  $\alpha = 5\%$  and  $df = n - 1 = 39 - 1 = 38$  we gain  $t_{(1-\alpha)(n-1)} = 2,021$ . Because  $t_{\text{calculation}} > t_{\text{table}}$ , then  $H_0$  is rejected. Therefore, it can be concluded that the average of learning outcomes  $\geq 65,0$ , thus, the students have mastered the material because they reach material comprehension. Therefore, learning process using this model can reach the purposes of learning (reach the material comprehension) with the average of learning result is 80,57.

The results of implementation show that the learning of mathematics through VirtualMATRIKS showed the good results. Activities and process skills of students in this learning is making a positive impact on student learning outcomes. The learning outcomes in this study referred to three aspects: cognitive, affective, and psychomotor. The cognitive aspect included pupils' achievement and reasoning, the affective aspect involved pupils' motivation, activity, and creativity, while the psychomotor included skills in problem-solving process. Scaffolding for students to reach the ZPD occurs when students interact with each other in processing of problem solving.

In the activities, students are trained to be creative and caring in problems solving, both social and environmental problems. Students work together in solving the problem. Students are able to communicate their ideas and dare to be responsible. This learning can build motivation, appreciation, contribution, interest, beliefs, creativity, confidence and perseverance and a sense of responsibility and communication skills. RME approach can build self-reliance, democracy, tolerance, humanism and honesty. Mathematical learning occurs during the film production process and during the discussion and interact with teacher or the others using VLE device. Activities and process skills of students in mathematics learning through VirtualMATRiKS in the high school has provided a positive effect on the results student learning (cognitive, affective, and psychomotor). Students learning outcomes in this learning environment are better than students learning outcomes in the conventional learning environment. There is a difference between understanding and student learning outcomes between before and after the learning process in that environment. After interacting via the VLE devices, understanding and student learning outcomes are higher than ever. Students can reach the upper limit of the ZPD.

## CONCLUSION AND SUGGESTION

Based on the results from the three stages of this study, it has been concluded that: The result of this research is a VLE model based on RME, namely VirtualMATRiKS. In this learning environment, the students simulate of the conceptual mathematization process by creating the movie about problem solving. Then students experiencing by share and discuss the movie with other through virtual-learning device. Model and device are effectively implemented in mathematics learning in

Senior High School, and this model gives a positive impact on student learning outcomes (cognitive, affective, and psychomotor). Students can reach the Upper Limit of Zone of Proximal Development.

Based on the conclusions of this study, it can be suggested that this model can be applied and developed further in learning mathematics by considering into environment, conditions and students interest.

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# WATER EFFECT ON DETERIORATIONS OF ASPHALT PAVEMENTS

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## ABSTRACT

Water has lots of adverse effects on pavement performance. In fact, moisture damage in asphalt pavements is global concern. Moisture damage can be defined as the loss of strength and durability in asphalt mixtures caused by the presence of water. Hence, it's the need to correctly identify the problem and isolate issues of contributing factors like material variability and construction practices for a better understanding of water effect on pavement deterioration. This study has discussed some of major failure mechanisms associated with the presence of water. In addition this study has also summarized some of the widely used methodology for the evaluation of water susceptibility. It was found that the empirical nature of test methods and the inherent variability of the results are the two primary challenges that impede the reliable characterization and assessment of water effect on pavement deterioration.

**Keywords :** Asphalt pavements, water effect, pavement deteriorations, stripping

## INTRODUCTION

Moisture damage can be defined as the loss of strength and durability in asphalt mixtures caused by the presence of water. Moisture damage is induced by the loss of bond between the asphalt cement or the mastic (asphalt cement, the mineral filler and small aggregates) and the fine and coarse aggregate. Moisture damage accelerates as moisture permeates and weakens the mastic, making it more susceptible to moisture during cyclic loading. Finally, moisture damage mechanisms results in the following distresses.

- Stripping: Debonding of aggregates and binder at the bottom of HMA layer.
- Bleeding: Formation of asphalt binder film on the pavement.
- Rutting: Surface depression along wheel path.
- Corrugation and Shoving: Plastic movement typified by ripples or an abrupt wave across the pavement surface.
- Cracking, Water Bleeding and Pumping.
- Raveling: Progressive disintegration of HMA layer.
- Localized failures: Progressive loss of adhesion between binder and aggregates or progressive loss of cohesion in aggregates and in binder.

Historically, six contributing mechanisms have been identified associated with moisture damage: detachment, displacement, spontaneous emulsification, pore pressure induced damage, hydraulic scour, and the effects of the environment on the aggregate–asphalt system. However, it is to be mentioned that moisture damage is not limited to a single mechanism but is the outcome of a combination of these mechanisms (Little and Jones, 2003). Santucci and Aschenbrener (2003) have identified the following factors that contribute to adverse effects of water in asphalt pavement.

**Table 1:** Factors Contributing Water Induced Distresses (after Santucci and Aschenbrener, 2003)

<b>Mix Design</b>	<ul style="list-style-type: none"> <li>• Binder and aggregate chemistry</li> <li>• Binder content</li> <li>• Air voids</li> <li>• Additives</li> </ul>
<b>Production</b>	<ul style="list-style-type: none"> <li>• Percent aggregate coating and quality of passing the No. 200 sieve</li> <li>• Temperature at plant</li> <li>• Excess aggregate moisture content</li> <li>• Presence of clay</li> </ul>
<b>Construction</b>	<ul style="list-style-type: none"> <li>• Compaction—high in-place air voids</li> </ul>

	<ul style="list-style-type: none"> <li>• Permeability—high values</li> <li>• Mix segregation</li> <li>• Changes from mix design to field production (field variability)</li> </ul>
<b>Climate</b>	<ul style="list-style-type: none"> <li>• High-rainfall areas</li> <li>• Freeze–thaw cycles</li> <li>• Desert issues (steam stripping)</li> </ul>
<b>Other Factors</b>	<ul style="list-style-type: none"> <li>• Surface drainage</li> <li>• Subsurface drainage</li> <li>• Rehab strategies—chip seals over marginal HMA materials</li> <li>• High truck ADTs.</li> </ul>

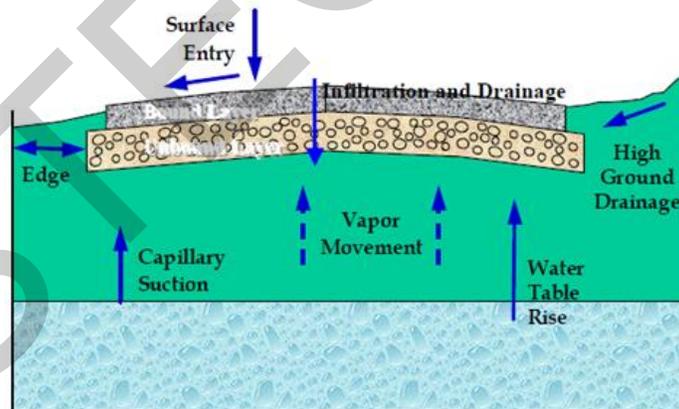
### Identification of the Problem

For a better understanding of water effect on pavement deterioration, it's the need to correctly identify the problem and isolate issues of contributing factors like material variability and construction practices. To this end, current study is intended to discuss the mechanisms associated with water induced damages in pavement. In order to fulfill this objective, this paper addresses following issues:

- Identification of the problem.
- Fundamental concepts- binder and aggregate interaction and representative failure mechanisms.
- Test methods to characterize moisture sensitivity.

### FUNDAMENTAL CONCEPTS

Before delving deeper in the mechanisms of water induced distresses, sources of water ingress and egress should be identified. Current engineering practice is predicated on the fact that water enters the pavement despite the efforts to prevent it. The presence of water in the pavement is mainly due to infiltration through the pavement surfaces and shoulders, melting of ice during freezing/thawing cycles, capillary action, and seasonal changes in the water table. The significance of the respective routes depends on the materials, climate, and topography. Elsayed and Lindly (1996) noted that prior to the study by Ridgeway (1982), high water table and capillary water were thought to be the primary causes of excess water in pavements. However, crack and shoulder infiltration, and to some extent subgrade capillary action, are also considered to be the major routes of water entry to the pavement (Dawson and Hill, 1998). A simplified schematic for routes of ingress and egress of water is provided in Figure 1.



**Figure 1:** Possible Sources of Water in Pavement (after Elsayed and Lindly, 1996)

The majority of studies on moisture or water damage in asphalt mixtures deals with an observed phenomenon called stripping. Stripping is the dis-placement of asphalt films from aggregate surfaces that occurs when the aggregate has greater affinity for water than the asphalt. It has been speculated that asphalt may be able to strip from an aggregate under dry conditions, especially after it has aged many years, but most losses of adhesion are attributed to the action of water.

The aggregates and asphalt for mixtures susceptible to stripping can be treated with a variety of anti-stripping additives; these additives commonly include the following:

- Liquid anti-stripping additives
- Portland cement
- Hydrated lime

Studies done by Terrel and Al-Swailmi (1994), Kiggundu and Roberts, (1988), Taylor and Khosla (1983) revealed at least five different mechanics of stripping: detachment, displacement, spontaneous emulsification, pore pressure, and hydraulic scour. Kiggundu and Roberts (1988) mentioned additional mechanisms that may play a significant role in moisture damage. These incorporate pH instability and the effects of the environment or climate on asphalt–aggregate material systems.

**Moisture Damage Theories**

No single theory properly explains moisture damage. Considering this, Kiggundu and Roberts (1988) attempted to combine some of the theories discussed earlier. They tabulated the primary and secondary contribution relationships shown in Table 2. This table attempts to relate theories that explain loss of adhesion to stripping mechanisms. For example, the mechanism of pH instability is, according to Kiggundu and Roberts, explained by both chemical reaction theory and physical and chemical components of interfacial energy theory. Detachment, as a second example, is assumed to be explained by physical and chemical aspects of interfacial energy theory as well as physical aspects of mechanical interlock theory. The physical aspects are manifested, according to Kiggundu and Roberts, by surface energy, while the chemical aspects are attributed to the effects of polarity of the molecules present at the common boundary. Even with this attempt to simplify the interaction of different theories and mechanisms, the interactive complexity of the processes becomes clearly evident. For example, surface bond is not solely a physical process because surface bond is dictated by the chemical nature of bonding at the asphalt and aggregate surface as well as by the presence of broken bonds or incomplete coordination of atoms due to broken bonds resulting in an increase in free energy.

**Table 2:** Proposed Relationships between Theories of Adhesive Bond Loss and Stripping Mechanisms (After Kiggundu and Roberts, 1988)

		THEORY								
		Mechanical Interlock			Chemical Reaction			Interfacial Energy		
Proposed Operating Mode		P	C	P-C	P	C	P-C	P	C	P-C
Stripping Mechanism	Detachment	S						S	W	
	Displacement					S		S		
	Spontaneous Emulsification				S	W				
	Film Rupture	S								
	Pore Pressure	S								
	Hydraulic Scouring	S								
	pH Instability					S				S

P= Physical C= Chemical P-C= Physical- Chemical S = Primary Contributor W= Secondary Contributor

**TEST METHODS TO CHARACTERIZE MOISTURE SENSITIVITY**

Numerous tests have been used to evaluate moisture susceptibility of HMA; however, no test to date has attained any wide acceptance (Roberts et al., 1996). In fact, just about any performance test that can be conducted on a wet or submerged sample can be used to evaluate the effect of moisture on HMA by comparing wet and dry sample test results

The tests that have been developed can be classified into two main categories based on the type of outcome: qualitative and quantitative. Qualitative tests provide a subjective evaluation of the stripping potential and include

- Boiling water test.
- Freeze–thaw pedestal test.
- Quick bottle test.
- Rolling bottle method.

The quantitative tests provide a value for a specific parameter such as strength before and after conditioning. These tests include

- Immersion–compression test.
- Indirect tensile test.
- Marshall immersion test.

- Double punch method.
- Resilient modulus tests.

On the other hand, the tests for identifying the moisture damage potential of an asphalt-aggregate mixture can be divided into two major categories based on mixture type: those on loose mixtures and those on compacted mixtures (Mansour et al., 2003). Tables 3 and 4 summarize the tests for moisture sensitivity on loose and compacted mixtures, respectively.

**Table 3: Moisture Sensitivity Tests on Loose Samples**

Test	ASTM	AASHTO	Other
Methylene blue			Technical Bulletin 145, International Slurry Seal Association
Film stripping			(California Test 302)
Static immersion	D 1664*	T182	
Dynamic immersion			
Chemical immersion			Standard Method TMH1 (Road Research Laboratory 1986, England)
Surface reaction			Ford et al. (1974)
Quick bottle			Virginia Highway and Transportation Research Council (Maupin 1980)
Boiling	D3625		Tex 530-C Kennedy et al. 1984
Rolling bottle			Isacsson and Jorgensen, Sweden, 1987
Net adsorption			SHRP A- 341 (Curtis et al. 1993)
Surface energy			Thelen 1958, HRB Bulletin 192 Cheng et al., AAPT 2002
Pneumatic pull-off			Youtcheff and Aurilio (1997)

**Table 4: Moisture Sensitivity Tests on Compacted Specimens**

Test	ASTM	AASHTO	Other
Moisture vapor susceptibility			California Test 307 Developed in late 1940s
Immersion-compression	D1075	T165	ASTM STP 252 (Goode 1959)
Marshal immersion			Stuart 1986
Freeze-thaw pedestal test			Kennedy et al. 1982
Original Lottman indirect tension			NCHRP Report 246 (Lottman 1982); Transportation Research Record 515 (1974)
Modified Lottman indirect tension		T283	NCHRP Report 274 (Tunnickliff and Root 1984), Tex 531-C
Tunnickliff-Root	D 4867		NCHRP Report 274 (Tunnickliff and Root 1984 )
ECS with resilient modulus			SHRP-A-403 (Al-Swailmi and Terrel 1994)
Hamburg wheel tracking			1993 Tex-242-F
Asphalt pavement analyzer			
ECS/SPT			NCHRP 9-34 2002-03
Multiple freeze-thaw			

### Tests on Loose Mixtures

These are the tests conducted on asphalt-coated aggregates in the presence of water. Examples incorporate boil, film strip, and static/dynamic immersion tests. Major advantage of these tests is that they are simple to conduct and less costly to run than tests conducted on compacted specimens. The major disadvantage is that the tests are not capable of taking the pore pressure, traffic

action, and mix mechanical properties into account. The results are mostly qualitative, and interpretation of the results becomes a subjective matter depending on the evaluator's experience and judgment. Loose mixture tests are best used for comparison between different aggregate- asphalt mixtures in terms of compatibility, strength of adhesion, and stripping. Mixtures failing in these tests, on the basis of some pre-established criteria, have the potential to strip and should be avoided. However, good results should not mean that a mix can be used, since the effects of the other contributing factors are overlooked in these tests.

In recent years, significant amount of research has been carried out to establish relationship between surface free energy and moisture damage potential. The principle behind using the concept of surface free energy is that the cohesive bonding within asphalt and the adhesive bonding between asphalt and aggregate are related to the surface free energy of the asphalt and aggregate. Researchers at Texas A&M University demonstrated the effectiveness of this concept by using three different aggregates (one granite and two limestone aggregates) and two of the SHRP asphalts (AAM and AAD). The permanent deformation on compacted specimens using compressive testing correlated well with measured values of surface free energy of the asphalts and aggregates used in the research when tested in dry and wet conditions.

### Tests on Compacted Mixtures

These tests are conducted on laboratory compacted specimens or field cores or slabs. Typical compacted mixture tests include indirect tensile freeze-thaw cyclic with modulus and strength measurement, immersion-compression, abrasion weight loss, and sonic vibration tests. The major advantage of these tests is that the mix physical and mechanical properties, water/traffic action, and pore pressure effects can be taken into account. Major disadvantages of these tests are the requirement of more elaborate testing equipment, longer testing times, and more laborious test procedures.

The AASHTO Standard Method of Test T283, "Resistance of Compacted Bituminous Mixture to Moisture Induced Damage," is one of the most commonly used procedures for determining HMA moisture susceptibility. This test is a modified version of Lottman Indirect Tension Test. The test involves curing of loose mixtures for 16 hours at 60° C, followed by an aging period of 2 hours at 135° C. At least six specimens are prepared and compacted. The compacted specimens are expected to have air void contents between 6.5% and 7.5%. Half of the compacted specimens are conditioned through a freeze (optional) cycle followed by a water bath. First, vacuum is applied to partially saturate specimens to a level between 55% and 80%. Vacuum-saturated samples are kept in a -18° C freezer for 16 hours and then placed in a 60° C water bath for 24 hours. After this period the specimens are considered conditioned. The other three samples remain unconditioned. All of the samples are brought to a constant temperature, and the indirect tensile strength is measured on both dry (unconditioned) and conditioned specimens. Test results are reported as a tensile strength ratio:

$$TSR = \frac{S_2}{S_1}$$

where,

TSR = Tensile strength ratio,

$S_1$  = average dry sample tensile strength and

$S_2$  = average conditioned sample tensile strength.

The Hamburg Wheel Tracking Device (HWT) is used to measure combined effects of rutting and moisture damage by rolling a steel wheel across the surface of an asphalt concrete specimen that is immersed in hot water. Originally, both beam and cylindrical samples were tested with device. However, with the increase in use of superpave gyratory compactor (SGC), researchers have adopted a testing protocol using cylindrical specimens compacted in the SGC as shown in Figure 2.

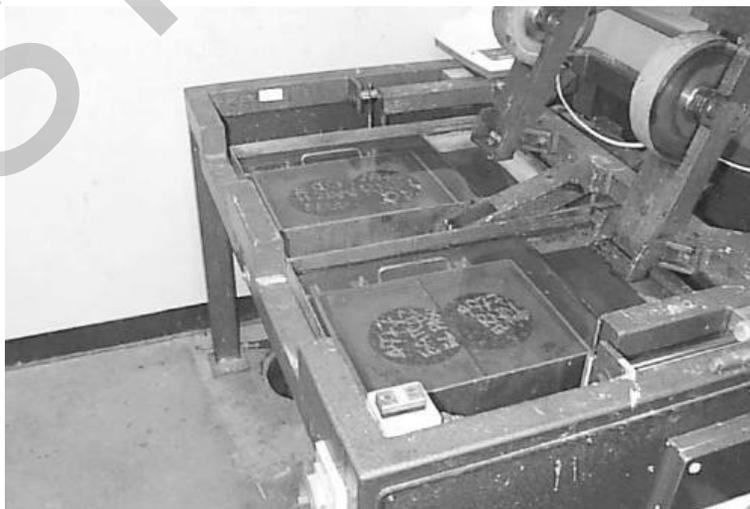


Figure 2: HWT) with Cylindrical Specimens

## CONCLUSIONS

Water effect on pavement deterioration is a complex phenomenon involving thermodynamic, chemical, physical, and mechanical processes that contribute to pavement deterioration. This study has discussed some of major failure mechanisms associated with the presence of water. In addition this study has also summarized some of the widely used methodology for the evaluation of water susceptibility. It was found that the empirical nature of test methods and the inherent variability of the results are the two primary challenges that impede the reliable characterization and assessment of water effect on pavement deterioration. This study successfully conveys the fact that water effect on pavement deterioration is an open ended problem which is to be solved by the broader understanding of representative failure mechanism and site-specific treatments applicable to the problem.

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## WOMEN OF MATHEMATICS

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### Abstract:

There were numerous women mathematicians in history and each made important contributions to the discipline. However the discipline of mathematics was a stifling environment for women. Contemporarily, the opinion of society and academics circles are still not very encouraging for women to be scientists or mathematicians. This presentation covers briefly the lives and legacy in mathematics of only six very well known women: Hypatia, Maria Gaetana Agnesi, Marie-Sophie Germain, Sonya Corvin-Krukovsky Kovalevsky, Emmy (Amalie) Noether and Florence Nightingale.

### Introduction:

For centuries women faced obstacles. Until the last century, women had no access to formal schooling, and even less access to mathematical ideas. Throughout history there has been a recurrent belief that at some fundamental level women were just not good at mathematics. It was argued that: Their brains were too small, dealing with mathematics would compromise their reproductive capacities and their hormones were not compatible with mathematical development.

There is no Nobel Prize in the field of Mathematics, instead there is the Fields Medal which is a prize awarded to two, three, or four mathematicians every four years. Since 1936 there has been no woman awarded this prize.

In 1966 IBM published a timeline poster titled: "**Men of Modern Mathematics**". The timeline covers the period from A.D.1000 to approximately A.D.1950, and the poster has biographical and historical items along with numerous pictures showing progress in various areas of science, including architecture. There was only one woman, Emmy Noether among the names. Her entry was: Emmy Noether, daughter of the mathematician Max, often called "Der Noether" as if she were a man. Yet her Göttingen professorship carried no salary, and [David] Hilbert (her mentor) had to fight to get her –a woman- in at all. She was fat, rough, and loud, but so kind, humorous and sociable that all who knew her loved her.

The engineers and architects who built the Eiffel tower were obliged to pay special attention to the elasticity of the metals. They inscribed the names of 72 scientists whose fundamental work in elasticity theory used that made the construction possible. Sophie Germain's name, the name of the most profound women of France whose work in elasticity theory was awarded by the French Academy, is excluded from this list because she is a woman.

The intellectual capacities of women were not only more formidable than men but they needed an extra dimension of stamina and determination to cope with the prejudice against women working in the areas of science and mathematics. Many women mathematicians use their mathematical talents and knowledge in other fields and many refrain from doing mathematical research in favor of social activities. In this sense it is unfair to restrict women's work in mathematics to their contributions as researchers and as teachers. The common denominator of women mathematicians is their extraordinary talent, superior genius and courage. S.Kovalevsky wrote three dissertations and S. Germain applied to Paris Academy of Sciences with three research papers. In most cases these women had to be not just twice but three times more scholarly accomplished than their male counter parts. Although their works are compatible in strength, purpose, resolution and dedication most of them were known by their dramatic aspects of their lives. Furthermore, some did not publish work under their own names and even if they did they were often forgotten. (Osen, 1984).

### Early Ages and Hypatia of Alexandria (370-415):

Mathematical history originated in Mesopotamia, Egypt and Greece. Around 4700 B.C. Babylonians who lived in Mesopotamia were quite competent in mathematics. We know that Egyptians were using a calendar in 4241 and the Ahmes papyrus dates from around 1650 B.C.. Mathematical games were a part of family enjoyment and Babylonian women had certain financial rights, could play a public role, become judges and secretaries. Most Egyptian women did not read and write and few women were able to become rulers. For this era we can only speculate that some women had access to knowledge in general and in particular to mathematical knowledge. There have been no prominent female names in mathematics from this era. This is also true for the great ancient civilizations of China and India. There have been a few women mathematicians or rather philosophers in the Hellenistic age. (Bell,1945). Thales is the first man in history known by his proofs instead of geometrical intuition. Pythagoras is the continuator of this approach and in his time, female mathematicians, philosophers and lecturers parallel to the evolution of social philosophy have surfaced. (Mozans 1913). Theona, Pythagoras's wife and their daughters, after the death of Pythagoras, carried out this system of thought. The Plato and Pythagoras School created a suitable environment for women to pursue a mathematical career and became academicians.

The first female mathematician known to us in history is Hypatia of Alexandria in Roman Egypt, from 4<sup>th</sup> century (AD 370 – AD 415). She became a professor at Alexandria University Museum Research Institution. Her father Theon, was a professor at Alexandria University, and tutored her in science, literature and philosophy. Hypatia was trained to be a perfect human being mentally and physically. Mathematics at that time was dealing with obscure problems as the locus of a given soul born under a certain planet. It was thought that mathematical calculations would determine the exact place of such a soul on a given future date. Hypatia wrote a number of commentaries on conic sections and treatises. She worked on Arithmetica of Diophantius. Hypatia belonged to a neo-Platonic school and her rationalism ran counter to the inflexible Christian beliefs. Hypatia was considered to be a

heretic and was murdered by a Christian mob who accused her of causing religious turmoil. She was tortured, humiliated and subjected to one of the cruelest assassinations of the history. (Dzielska, 1995; Audi, 1999).

For many centuries mathematics remained relatively quiescent in Europe. The period between the fall of Rome in A.D. 476 and A.D. 1453 saw a general decline in learning and civilization. During these long centuries, some small centers of culture developed first in one part of Europe, then in another. Italy was one such center; Gaul developed as another; Britain, Ireland, and Germany also emerged as intellectual centers.

### The “Witch” of Agnesi:

At the beginning of Renaissance, the opposition of women having any form of higher education continued. In most cases women did not learn to read and write. After the conquest of Constantinople, Istanbul, by the dissemination of knowledge to Europe and Italy, and invention of the printing press had a positive effect on the advancement of science and literature. Parallel to these in Italy women had the privilege of earning doctorates, had become lecturers, professors and chaired faculties in the universities of Bologna and Pavia. (Mozans, 1913). Maria Gaetana Agnesi (1718 – 1799), from Milan, is one of the most remarkable women in the history of mathematics. She knew several languages including Latin, Greek and Hebrew before she was nine years old. (Osen, 1984).

In 1748 she published her book *Analytical Institutions* on differential and integral calculus. The book integrates the works of Newton and Leibniz clearly. In this respect *Analytical Institutions*, constitutes a common ground/language for mathematicians, and should be considered to be the first modern Calculus book. The book has four volumes; briefly the first volume is on differential calculus. The second analyses infinitesimal quantities. The third is about integral calculus and the last one covers differential equations. In *Analytical Institutions*, she dealt with the equation  $yx^2 = a^2(a-y)$  or  $y = a^3/(x^2 + a^2)$  a versed sine curve. In her book she called this equation a ‘versiera’ a word derived from the Latin *vertere*, meaning ‘to turn’. In the English version of the book it was translated as witch, and the curve is known to be the “Witch of Agnesi”. (Stigler, 1974).

Maria had domestic responsibilities and was taking care of the household alone after her mother’s death. Interesting enough, she had 20 brothers and sisters, and it is said that, she wrote the first draft of this ground breaking book in order to tutor her youngest brother. This was the most important mathematical publication made by a woman up until this time. Though The French Academy examined her work in details and praised it, her admission to the Academy was denied on the bases that she was a woman. Her other collected works and lecture notes were also translated into English and French, published as books that were used for many years. The Bologna Academy of Sciences, which was more liberal than the French Academy, admitted her to be an honorary lecturer. It is not known for sure, if she has accepted this position or remained to stay in her home town Milan. She spent her last years in a charity, taking care of the sick and the persons in need. Some streets in Milan and other towns in Italy are named Maria Agnesi after her. (Beard, 1931).

### Monsieur LeBlanc:

The common factor of Archimedes, Monsieur LeBlanc, Lagrange, Legendre, Gauss, and Fermat is Marie-Sophie Germain (1776-1831) of Paris. Monsieur LeBlanc was Sophie’s pseudo name. She was a mathematician, physicist, and philosopher. In 1789 when Germain was 13, the Bastille fell, and the revolutionary atmosphere of the city forced her to stay inside. During this time, she read the works of Newton and Euler, *Traité d'Arithmétique* by Étienne Bézout and *Le Calcul Différentiel* by Jacques Antoine-Joseph Cousin. Germain, romanticized the death of Archimedes and his concentration over his work preventing him from noticing the soldier who has killed him. She became an admirer of mathematics and fancied its attraction which caused such a strong concentration. She learned Latin and Greek by herself so that she could read the works of Newton and Euler. Germain’s parents took severe measures to protect their daughter from harming her female body by studying and learning mathematics. Germain was insistent and her parents had to let her study the subject.

The École Polytechnique opened in 1794, but female students were not accepted. Germain obtained the lecture notes of the mathematics classes. She sent her work to, a faculty member, Joseph Louis Lagrange. She also wrote to Gauss about Fermat’s Last Theorem. In her letters she did not reveal that she was a woman and used the name of a student, Monsieur LeBlanc, a graduate from École Polytechnique. Monsieur LeBlanc was not a very good student. Reading her work, Lagrange was surprised with the progress made by his former student. (Lynn, 1984).

Around 1807, the French occupied the German town of Braunschweig, where Gauss was living. Germain, concerned that he might suffer the fate of Archimedes and wrote to General Pernety who was a family friend. General Pernety came to Gauss’ rescue, leaving him very pleased and surprised. He insisted to meet the person who made this happen. It was by this event; Germain had to reveal her real name to Gauss. (Lynn, 1984). If this was not happened, Germain’s work would have never been cited by her real name. She corresponded extensively with Lagrange, Legendre, and Gauss. Gauss appreciated her talent and supported her at all times.

Germain is one of the pioneers of elasticity theory. She worked on the curvature of elastic surfaces and her works led to the discovery of the laws of equilibrium and movement of elastic solids. Germain applied to Paris Academy of Science with three studies. The Academy was not willing to honor Germain the prize, she applied to the Academy again anonymously with two different articles, Lagrange offered his help with the first and Legendre helped her with the second. The second article was awarded an honorable mention. Later both Lagrange and Legendre worked on Germain’s results and published articles on the subject. Germain also proved or nearly proved several results that were attributed to Lagrange or were rediscovered years later. Two years later she applied again, but this time she published the work under her name before her submission to the Academy.

Germain won the grand prize from the Paris Academy of Sciences for her article "Memoir on the Vibrations of Elastic Plates" at her third attempt. (Todhunter and Pearson, 1960). The prize elevated Germain to be one of the most noted mathematicians of the world. Academy had a tradition of excluding women other than the wives of members. It was the main reason for the Academy's reluctance in giving the prize to her in the first place. Even after winning the contest, she was not allowed to attend the sessions, seven years later by the help of J. Fourier; she could be able to attend the meetings. (Lynn, 1984).

Her work on Fermat's Last Theorem provided a solid foundation for mathematicians in this field. She defined a certain prime number called Germain prime. Germain primes are those prime numbers  $p$  such that  $2p + 1$  are also primes. For example, 5 is a Germain prime because  $2 \times 5 + 1 = 11$ , is also a prime number, but the prime number 7 is not a Germain prime because  $2 \times 7 + 1 = 15$  is not prime. She conjectured that if there is an integer solution of the Fermat's equation  $x^p + y^p = z^p$  for Germain primes  $p$  then either  $x$ ,  $y$ , or  $z$  is a multiple of  $p$ . Germain proposed an extended version of her conjecture to the so called "Sophie Germain's Theorem". Her colleagues tested her conjecture for her list of primes one by one, unsuccessfully for years with the hope of proving Fermat's Last Theorem. This attempt would have shown there is no solution for Fermat's equation. (Del Centina, 2009).

Germain, made numerous and indispensable contributions to the field of mathematics and physics her examination of principles which led to the discovery of the laws of equilibrium and movement of elastic solids. In addition Germain studied chemistry, geography, history, philosophy and psychology. (Gray, 1978).

Because of her gender, she worked independently throughout her life. Germain's death certificate lists her as a "rentière – annuitant" (property holder), not a "mathématicienne." But her work was not unappreciated by everyone. Six years after her death, she had an honorary degree from University of Göttingen. Gauss noted: "[Germain] proved to the world that even a woman can accomplish something worthwhile in the most rigorous and abstract of the sciences and for that reason would well have deserved an honorary degree." (Mackinnon, 1990).

### **The Lady with the Lamp:**

Florence Nightingale (1820-1910) born in Florence, Italy. She is the founder of the modern nursing. She is known with her dedicated service to British soldiers at Selimiye Kaserne in Üsküdar, Turkey. She was called the lady with the lamp because she was making night shifts carrying a lamp. The nurse pledge named Nightingale pledge to honor her. It is because of her efforts that improved the care provided by hospitals nursing is accepted to be a vocation. In 1907 she founded the first secular nursing school in London. Florence, was raised in England during the Victorian Age, her father provided her a good education through tutors. It is not commonly known that she had a mathematical training. (Baly, 1986). She learned arithmetic, geometry, algebra, and before her involvement with nursing, spent her time tutoring children in these subjects at The British Museum. The British Museum has her lesson plans which are in her handwriting for teaching arithmetic and geometry. Her lesson plans show concern about the education of girls. "Girls' arithmetic has been neglected--their geography should be made arithmetical." Are among the quotes from her. She believed in teaching by questioning. How high is the reindeer? Are you as high? How high are you? 3 feet--how much is that? a yard-- are you a quadruped? How far is the topmost point of Europe from the Equator? How far do you come to school? Two miles-- now, if you were to walk two geographical miles a day, how long should you be walking to the equator? These are questions from her lecture notes. She was also humorous; after attending a political speech, she wrote: "I have invented a new system of Logarithms (finding the capacities of arithmetic not sufficiently extensive) to count the number of times 'Imperial Majesty' occurs in the speech...." (Cohen, 1984; Woodham-Smith, 1993).

Her mathematical approach saved the British army in 1855 at Scutari during the Crimean war and provided the data that led to hospital reforms. More significantly, she sought to improve sanitary conditions in the medical facilities. She proved her case through statistical analysis, using what she called "coxcombs," now known as "polar-area diagrams" or "Nightingale Roses". Her proof of the effectiveness of proper hygiene for the recovery from wounds and disease led to a reform of the entire military hospital system. (Goldie, 1987).

### **Sofia Vasilyevna Kovalevskaya**

Sonya Kovalevskaya (1850-1891) was born in Moscow. During politically unstable times, after the defeat of Russia in the Crimean war her family moved from Moscow to Palibiano. Sonya as a child enjoyed the countryside and living on a large estate. The estate was huge it had herds of cows and sheep, gardens, distilleries, a dairy farm and even a forest. The house was renovated and as result of a shortage in wall paper, one of the rooms' walls was bare. The walls of that room were covered with old manuscripts. The manuscripts were the old lecture notes in differential and integral calculus of Professor Ostrogradsky. This room was Sonya's favorite place to spend time. She used to spend hours looking at the formulas to figure out the order of the sheets and find a meaningful sequence among the formulas. Sonya was trained in foreign languages and mathematics. She was not allowed by her parents, to study mathematics seriously. But her interest in mathematics was keen so her father allowed her to study at the naval school in St. Petersburg, but her father opposed her to pursue her career in the subject. At that time in Russia a woman needed to have the permission of her father or husband to travel abroad. Moreover matriculation of women at any university was strictly forbidden. In order to get a better education in mathematics Sonya created a fictitious marriage, and together with her husband Vladimir Kovalevsky left her country and went to Heidelberg in 1868. With some trouble she enrolled as a provisional student at Heidelberg. Sonya later went to Berlin University in the hope of studying with Karl Weierstrass. Weierstrass was reluctant at first but was impressed by her studies accepted to tutor her privately at the University of Berlin. A Weierstrass's effort to enroll Sofya

in Berlin University proved to be useless. Opposition was too strong, the faculty and administration were totally against enrolling a woman. The private tutorials of Wierstrass continued for four years. Later she applied for a doctoral degree at University of Göttingen, she wrote three dissertations on partial differential equations, on the dynamics of Saturn's rings and on elliptic integrals. Her thesis on partial differential equations was awarded in absentia the degree of Ph.D. in mathematics. It is considered to be the first doctoral degree received by a woman in history. (Bell, 1937).

Sofya went to Russia in the hope finding a job. Severely disappointed of not finding a job with Viladimir she went to Palobino, to live with her family. Abandoning mathematics Sofya turned into a society lady for six years. But in 1880 in an attempt to find a job in mathematics, she presented a paper on Abelian integrals at a scientific conference. Her paper got the interest of Gosta Mittag-Leffler. He invited her to lecture at the University of Stockholm. In 1884 she was appointed to a five year position as "Professor Extraordinarius" (Professor without Chair) and became the editor of *Acta Mathematica*. In 1888 she won the *Prix Bordin* competition of the French Academy of Science. In 1889 she was appointed Professor Ordinarius (Professorial Chair holder) at Stockholm University, the first woman to hold such a position at a northern European university. Sofia became a liaison in the exchange of knowledge between Germany, France and Russia. After much lobbying on her behalf (and a change in the Academy's rules) she was granted a Chair in the Russian Academy of Sciences, but was never offered a professorship in Russia. (Bell, 1937; Belits, 2005).

She wrote ten papers in mathematics and mathematical physics and several literary works. The theorem in her dissertation, Cauchy-Kovalevski theorem, is considered to be the first significant result in partial differential equations. The "Kovalevsky top", which subsequently shown (by Liouville) to be the only other case of rigid body motion, beside the tops of Euler and Lagrange, that is "completely integrable". (Kochina, 1978). Many of her scientific papers were ground-breaking theories or the impetus for future discoveries.

### Der Noether:

Amalie Emma Noether (1882-1935) was born in Earlingen, Germany. She is often called "Der Noether" as if she were a man. Emmy's father was a professor at the University of Earlingen. She had training in household arts and the feminine graces. She is the first woman having a university degree in Europe. She had the permission of individual professors to audit classes and take the exams. Emmy had Poul Gordon as her tutor and wrote her Ph.D. thesis in 1907 under his supervision. In 1907 she started to teach at Earlingen University without any pay. In 1908 "Circolo Matematico di Palermo" and in 1909 the Germain Institution of Mathematics invited her. She accepted the invitations of Felix Klein and David Hilbert, and visited University of Göttingen, where she taught from 1913 to 1933. She gave courses offered by Hilbert without any pay. In 1919 she became a 'Privatdozent', in 1920 her works had the recognition and she was accepted to be a great mathematician. Two years later Emmy was nominated to a position of a 'nichtbeamteter ausserordentlich Professor'. She was invited and went to University of Moscow in 1928 and 1929 and in 1930 she went to the University of Frankfurt upon their invitation. 1932 she lectured at the International Congress of Mathematicians in Zürich. (Osen, 1974).

She had ground breaking results, introduced revolutionary theories of rings, fields and algebras, made significant contributions to the theories of algebraic invariants and number fields. She wrote the book, *Modern Algebra*, which is the foundation of the modern algebra. Her classic paper is *Idealtheorie in Ringbereichen (Theory of Ideals in Ring Domains, 1921)*, Noether developed the theory of ideals in commutative rings into a powerful tool with wide range of applications. She published major works on noncommutative algebras and hypercomplex numbers and united the representation theory of groups with the theory of modules and ideals. Her work on differential invariants in the calculus of variations, *Noether's theorem*, explains the fundamental connection between symmetry and conservation laws, which is break through in Theoretical Physics. She even had her name on publications in algebraic topology.

The adjective *Noetherian* is used to describe objects that satisfy an ascending or descending chain condition on certain kinds of subobjects. Noetherian group, Noetherian ring, Noetherian module, Noetherian topological space and Noetherian induction are among these.

She was a profound mathematician whose algebraic acumen was accepted by the world. University of Göttingen never paid her a real salary. Either she had been paid by her students or had very small payments for her lectures. She was an intellectual woman, a Jew, and a liberal. The Nazi government dismissed her along with Jews from university positions, and Noether moved to the United States in late 1933 to Bryn Mawr College in Pennsylvania. She also lectured at the Institute for Advanced Study in Princeton. These were the only times that Noether earned salary. But that did not last more than two years she died in April 1935 at an early age. (Kimberling, 1981; Auguste, 1981).

### A glimpse to the present situation

In January 2005 at the NBER (National Board of Economic Research) Conference "Diversifying the Science & Engineering Workforce: Women, Underrepresented Minorities, and their S&E Careers Lawrence Summers' remarks suggested that women might not have the same "innate ability" or "natural ability" as men.

1- Women with children are often unwilling or unable to work 80-hour weeks.

2- In math and science tests, more males earn the very top scores, as well as the very bottom scores. He said that while no one knew why, "research in behavioral genetics is showing that things people attributed to socialization" might actually have a biological basis -- and that the issue needed to be studied further.

3- It was not clear that discrimination played a significant role in the shortage of women teaching science and engineering at top universities. However, he concluded by emphasizing that Harvard was taking many steps to boost diversity. At that time L. Summers was the president of Harvard University. (Retrieved from WISELI-Women in Science and Engineering Leadership Institute University of Wisconsin-Madison <http://wiseli.engr.wisc.edu/archives/summers.php>).

Though Summers disseminated a letter of apology public statements, his remarks received strong reactions from women associations and academicians around the world. His remarks also became the starting point of several gender based research. Janet S. Hyde from Department of Psychology, University of Wisconsin and Janet E. Mertz from McArdle Laboratory for Cancer Research, University of Wisconsin School of Medicine and Public Health, in their article "Gender, culture, and mathematics performance" published in The Proceedings of the National Academy of Sciences of the United States of America (PNAS); asked the questions: Do gender differences in mathematics performance exist in the general population? Do gender differences exist among the mathematically talented? Do females exist who possess profound mathematical talent?

And answered them: "In regard to the first question, contemporary data indicate that girls in the U.S. have reached parity with boys in mathematics performance, a pattern that is found in some other nations as well. Focusing on the second question, studies find more males than females scoring above the 95th or 99th percentile, but this gender gap has significantly narrowed over time in the U.S. and is not found among some ethnic groups and in some nations. Furthermore, data from several studies indicate that greater male variability with respect to mathematics is not ubiquitous. Rather, its presence correlates with several measures of gender inequality. Thus, it is largely an artifact of changeable sociocultural factors, not immutable, innate biological differences between the sexes. Responding to the third question, we document the existence of females who possess profound mathematical talent. Finally, we review mounting evidence that both the magnitude of mean math gender differences and the frequency of identification of gifted and profoundly gifted females significantly correlate with sociocultural factors, including measures of gender equality across nations." (Hydea and Mertz, 2009).

Mathematics is still not free from gender bias. Women in mathematics need to cope with the prejudices of society at large, it is hard for them to find the jobs, receive the kind of community support and recognition which is important to mathematical development. Though their numbers are gradually increasing women are still under represented in high ranking positions.

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# YABANCI DİL ÖĞRETMENLERİ AKILLI TAHTA KULLANIMINA NE KADAR HAZIR? HOW READY ARE ENGLISH LANGUAGE TEACHERS FOR SMART BOARD USAGE?

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## Özet

Son yıllarda oldukça dikkat çeken ve ülkemizde de ilgi görmeye başlayan teknoloji destekli araçlardan birisi de “akıllı tahtadır”. Akıllı tahtanın temel özelliği bilgisayar ve projeksiyon bağlantısı ile çalışan etkileşimli bir yazı tahtası olmasıdır. Tahta ekranının interaktif özellikli dokunmaya duyarlı bir yapıya sahip olması önemlidir. Akıllı tahtanın eğitimde kullanılmasının yararları ile ilgili yapılan çalışmalar iki alana vurgu yapmaktadırlar. Bunlardan birincisi, akıllı tahtanın öğrenciyi daha fazla motive ederek ve çalışmaya katılmasını sağlayarak öğrenci etkililiğinin artırıyor olması ikincisi ise öğrenci etkileşimi, düşünme becerileri gibi çok yönlü özellikleri de içine alan öğrenme süreci ve kaynak sunumu üzerinde sağladığı etkidir (Hodge ve Anderson, 2007).

Milli Eğitim Bakanlığının “Temel İlköğretim” ve “Ortaöğretim” planlaması incelendiğinde öğretimde teknoloji kullanımı ve akıllı tahtaların yaygınlaştırılmasına büyük bir yatırım yaptığı görülmektedir (Somyürek vd, 2009). Akıllı tahtanın sağladığı olanaklar açısından kullanılması en uygun olabilecek alanlardan birisi yabancı dil öğretimidir. Bu nedenle, yabancı dil öğretmenlerinin akıllı tahtayı etkin bir şekilde kullanmaları için gerekli bilgi ve donanıma sahip olmaları gerekmektedir. Ayrıca, akıllı tahta kullanımı gibi bilgi teknolojileri kullanımındaki yenilik ve gelişmelerin hizmet öncesi öğretmen eğitiminde sunulması da birçok kaynakta tavsiye edilmektedir (örn. Alev, 2003).

Bu çalışmada, Yıldız Teknik Üniversitesi, Eğitim Fakültesi İngilizce Öğretmenliği bölümünde öğrenim gören öğretmen adaylarının akıllı tahta ve F@tih projesi hakkındaki bilgileri anket yolu ile veri toplanarak ortaya çıkarılmıştır. Toplam on yedi sorudan oluşan anket uzman görüşü alınarak araştırmacılar tarafından geliştirilmiştir. Çalışmaya “okul deneyimi” dersi kapsamında farklı ilköğretim ve liselere giden toplam 68 öğretmen adayı katılmıştır. Elde edilen bulgular sonucunda öğrencilerin düşünceleri saptanmış ve bu doğrultuda öğretmen eğitimi ve teknoloji kullanımı ile ilgili önerilerde bulunulmuştur.

**Anahtar Sözcükler:** Akıllı Tahta (AT), F@tih Projesi, Yabancı Dil Öğretimi

## Abstract

Smart Board is one of the technological devices which is broadly used in educational contexts including our country. Smart board is an interactive device combining whiteboard with the power of computer. With the simple touch of a finger it lets the teachers deliver dynamic lessons, write notes and save their works. Studies focusing on the advantages of smart board usage in education emphasize two fields. One of them is that smart boards increase students' participation by motivating the students and the second one is smart boards have an effect on learning process and resources including student interaction and thinking skills (Hodge and Anderson, 2007).

It is seen that the Minister of Education has made a big investment in order to expand use of technology and smart boards (Somyürek vd., 2009). When the opportunities provided by smart boards are taken into consideration, the most suitable field for smart board use may be foreign language teaching. Therefore, language teachers need necessary knowledge and skills to use this device in an effective way. Besides, it is suggested in the literature that developments in information technology and changes must be presented at pre-service training of teachers (eg. Alev, 2003).

This study aims to learn knowledge of candidate language teachers at Yıldız Technical University, the Faculty of Education, Foreign Languages Teaching Department on smart board and the project called F@tih. For this aim, a questionnaire developed by the researchers was used. The data collection tool consisted of 17 questions after taking views of experts. 68 candidate language teachers who visit different schools for school practicum participated in the study. Some suggestions are given related to teacher education and technology use with the help of gotten data.

**Key words:** Smart Board, F@tih Project, Foreign Language Teaching

## GİRİŞ

Bilişim teknolojilerinin son yıllardaki hızlı gelişimi eğitim sistemimizi de etkileyerek, sistemde bir takım yeniliklerin yapılması gereğini ortaya çıkarmıştır. Son yıllarda oldukça dikkat çeken ve ülkemizde de ilgi görmeye başlayan teknoloji destekli araçlardan birisi de “akıllı tahtadır”.

### Akıllı Tahta

Eğitim ve öğretim sürecinde kullanılan teknolojilerden biri olan akıllı tahta bilgisayar ve projeksiyon bağlantısı ile çalışan, büyük ve dokunmaya duyarlı bir ekrana sahip olan bir araçtır (Erduran ve Tataroğlu, 2009:14). Akıllı tahtanın ana bileşenlerini bir bilgisayar, bir projeksiyon aleti ve aynı zamanda sınıf tahtası işlevi de görebilen aktif bir yüzey oluşturmaktadır. Akıllı tahta ve projeksiyonda yüklü olan akıllı tahta programı çizimler, formüller, resimler, haritalar, şekiller vb. altyapının ders sırasında kolaylıkla sunulmasına imkan vermektedir. Akıllı tahta programı dışında bilgisayar ekranı olarak da kullanılabilir (Kaya ve Aydın, 2011: 181).

AT (akıllı tahta) ile öğretim düzenlenirken bazı yazılımların da beraberinde kullanılması gerekmektedir. AT satan firmalar bu yazılımları da satabilmekte ve öğretmenler bu programları kendi bilgisayarlarına yükleyerek kullanabilmektedirler. AT dijital ortamın çok amaçlı görev yapısı ile beyaz tahtanın boyut ve etkileşimini birleştirerek öğretmene çok yönlü ders işleme imkânı vermektedir. Tahta aynı zamanda kaleme ihtiyaç duyulmadan tahtanın ekranına yazı yazmasına ya da çizim yapmasına imkan sağlamaktadır. Öğretmen bu tahta yardımı ile ses, video, grafik gibi unsurları birarada kullanabilmekte ve bu sayede çoklu bir öğretim ortamı elde edilebilmektedir. AT ile internete bağlanılabilmekte ve sınıf içerisinde yapılan uygulamalar da kaydedilebilmektedir (Adıgüzel vd, 2011:459- 460). AT kullanıcısı bir bilgisayar görüntüsünü dokunarak ya da özel bir kalem kullanarak ekrana da yansıtabilir.

Eğitim açısından incelendiğinde akıllı tahtaların sunduğu etkileşim ortamının etkin öğrenmeyi desteklediği, boyutunun işbirlikçi ve grup içinde öğrenmeye yardımcı olduğu, görme ya da fiziksel yönden eksiklikleri olan öğrenciler için uygunluğu ve yapılanların kaydedilerek tekrar kullanıma ya da yapılandırılmaya imkan sağladığı bilinmektedir (Kennewell and Morgan, 2003:65).

### F@Tih Projesinin Kapsamı

Kısa adı ile F@Tih olarak bilinen “Fırsatları Artırma ve Teknolojiyi İyileştirme Hareketi” isimli proje Milli Eğitim bakanlığı tarafından yürütülmekte ve Ulaştırma bakanlığı tarafından desteklenmektedir. Üç yılda tamamlanması beklenen bu proje kapsamında 1. yıl ortaöğretim okulları, 2. yıl ilköğretim ikinci kademe, 3. yıl ise ilköğretim birinci kademe ve okul öncesi kurumlarının bilgisayar teknolojileri donanım ve yazılım altyapısının yanı sıra e-çerik ve bilgisayar teknolojileri ve internet kullanımı ihtiyaçlarının tamamlanması hedeflenmektedir. Ayrıca, öğretmen kılavuz kitaplarının güncellenmesi ve öğretmenler için hizmetiçi eğitimlerin hazırlanması da projenin hedefleri arasındadır (<http://fatihprojesi.meb.gov.tr/site>).

Bu projenin başarıya ulaşabilmesinde iki önemli etmen olduğu vurgulanmaktadır. Bunlardan birincisi bilgisayar okuryazarlığının özellikle gençler arasında yaygınlaştırılması ikincisi ise eğitimcilerin eğitimidir. Bu nedenle, öğretmenlerin sınıflardaki donanım ve e-çerikleri kullanma becerilerini geliştirmek amacıyla 608 bin öğretmene hizmet içi eğitim verilecektir (KobiEfor, 2010). Bu nedenle, Kayaduman vd. (2011)’m belirttiği gibi altyapıdaki mevcut durumun incelenmesinin yanı sıra öğretmenlerin yeterlilik durumlarının da incelenmesi gerekmektedir. Öğretmenlerin kendilerine bilgi teknolojileri kullanımı alanında özgüven düzeyleri, bilgisayar teknolojilerini kullanma durumları ve algıları araştırılması gereken öncelikli konular arasında gelmektedir. Buna ek olarak öğretmenlerin e-çeriği etkin bir biçimde kullanabilmeleri için öğretmen kılavuzlarının hazırlanması da tavsiye edilmektedir.

### Yabancı Dil Öğretiminde Akıllı Tahta Kullanımı

Yabancı dil öğretiminde bilgi teknolojileri kullanımı giderek yaygınlaşmakta ve öğretmenlerden yabancı dil derslerini bu teknolojilere uygun biçimde düzenlemeleri beklenmektedir. Akıllı tahta bu nedenle özellikle yabancı dil derslerinde son yıllarda birçok ülkede yaygın bir biçimde kullanılmaya başlanmıştır. Örneğin, Londra’daki ilköğretim okullarında AT kullanımı ve etkinliği üzerine yapılan kapsamlı ve uzun araştırma sonucunda AT’nin matematik, fen ve yabancı dil derslerinde kullanımının büyük oranda arttığı saptanmıştır (Moss vd, 2007:5).

Mathews-Aydinli ve Elaziz (2010), Türkiye’de İngilizce öğretiminde akıllı tahtanın kullanıldığı 13 okulda yaptıkları araştırmada öğretmen ve öğrenci görüşlerini toplamışlardır. Çalışmanın sonucunda hem öğretmenlerin hem de öğrencilerin akıllı tahta kullanımına ilişkin olumlu tutumlar geliştirdiği ve bu aracın yararlı olduğuna inandıkları bulunmuştur. Öğrenciler özellikle akıllı tahtanın dersleri daha ilginç hale getirdiğini düşünürken öğretmenler bu aracın kendilerine esneklik sağladığı görüşünde hemfikirdirler. Akıllı tahtanın

kullanım sırasında yapılanları kaydediyor olması en çok vurgulanan özelliği olmuştur. Akıllı tahtanın öğrencileri derse karşı motive ediyor olması hem öğrenci hem de öğretmen grubu tarafından vurgulanmıştır.

Almanya’da yabancı dil derslerinde akıllı tahta kullanımı ile ilgili yapılan araştırmada ders gözlemleri, video kaydı ve görüşmeler yolu ile öğretmenlerin akıllı tahta kullanımları ve tutumları öğrenilmeye çalışılmıştır (Schmid, 2010). Verilerin analizi a) akıllı tahta kullanımı için materyaller hazırlama, b) akıllı tahta aracılığı ile sunulan etkileşimi yönetme ve c) akıllı tahta teknoloji kullanımını dengeleme başlıkları yolu ile yapılmıştır. Araştırmanın sonucunda öğrencilere öğrenme ortamı ve akıllı tahta ile etkileşime geçebilecekleri fırsatların sunulduğu, öğrencilerin öğrenme sürecine akıllı tahta kullanımı ile etkin katılımlarının sağlandığı, farklı öğrenme biçimlerinin dikkate alındığı ve dil pratiği sağlandığı bulunmuştur.

Yabancı dil derslerinde akıllı tahta kullanan bir grup öğretmen ile yapılan bir başka araştırmada öğretmenler akıllı tahtanın yabancı dil derslerinde kullanımının olumlu bir etkiye sahip olduğunu belirtmişlerdir. Ayrıca, öğretmenler derslerdeki başarının ders öncesi hazırlık ile doğru orantılı olduğu ve öğretmenin sınıf içerisindeki rollerinin akıllı tahta kullanımı ile değiştiği görüşünde birleşmişlerdir (Gray vd., 2007). Araştırma sonucunda AT’nin iyi bir yabancı dil öğretimi için destekleyici olduğu sonucuna varılmıştır.

## YÖNTEM

Bu bölümde, öğretmen adaylarının akıllı tahta kullanımı ve F@t@h projesine yönelik bilgilerinin saptanması ve bazı değişkenlere göre değerlendirilmesi amacı ile yürütülen araştırmanın modeli, çalışma grubu, veri toplama aracı ve verilerin analizi hakkında açıklamalar verilmiştir.

Bu çalışmada, Yıldız Teknik Üniversitesi, Eğitim Fakültesi İngilizce Öğretmenliği bölümünde öğrenim gören öğretmen adaylarının demografik özellikleri ve akıllı tahta kullanımı, akıllı tahtanın öğretimdeki işlevlerinin öğretmen adaylarına göre önem sırası ve F@t@h projesine yönelik haberdarlıkları anket ile veri toplanarak ortaya çıkarılmıştır. Araştırmadan elde edilen verilerin istatistiksel analizinin yapılmasında SPSS paket programı kullanılmıştır.

### Araştırmanın Modeli

Araştırma, tarama modellerinden, tekil tarama modeline uygun olarak planlanmış ve gerçekleştirilmiştir. Tekil tarama modelinde; ilgilenilen olay, grup gibi birim ve duruma ait değişkenler, ayrı ayrı betimlenmeye çalışılır (Karasar, 2004).

Bu araştırmada da yansız seçilmiş grupların akıllı tahta kullanımı ve F@t@h projesine yönelik haberdarlıklarının ne olduğu ve çeşitli değişkenlere göre farklılık gösterip göstermediği ortaya konulmak istendiği için tekil tarama modeli seçilmiştir.

### Çalışma Grubu

Araştırmanın çalışma grubunu; 2011-2012 öğretim yılı güz yarıyılında Yıldız Teknik Üniversitesi Eğitim Fakültesi’nin Yabancı Diller Eğitimi Anabilim Dalı, İngilizce Öğretmenliği Bölümünde 4. sınıfta okuyan, toplam 68 öğrenci oluşturmuştur. Bu öğrencilerin seçiminde 4. sınıfa devam eden ve “Okul Deneyimi” dersi kapsamında farklı ilköğretim ve liselerde staj yapıyor olmalarına dikkat edilmiştir.

### Veri Toplama Aracı

Öğretmen adaylarının akıllı tahta ve F@t@h projesine dair görüşleri ile ilgili verilerin toplanması için bir anket uygulanmıştır. Bu araştırmada, kullanılan veri toplama aracı araştırmacılar tarafından geliştirilmiştir.

Toplam on yedi sorudan oluşan anket için uzman görüşüne başvurulmuştur. Uzman görüşü alınmasının ardından pilot çalışma ile anketin eksiklikleri giderilerek son şekli verilmiştir.

Veri toplama aracında öğrencilerin demografik bilgilerini belirleyecek sorular, Akıllı tahta kullanımı ve F@t@h projesinden haberdarlıkları ile ilgili soru maddeleri (16 tane) ve akıllı tahtanın öğretimde kullanım işlevlerinin öğrencilere göre önem sırasını belirleyecek soru (5 madde içeren bir soru) bulunmaktadır.

16 soruluk maddelerin yanıtlandırılmasında semantik tipte “Evet”, “Kısmen” ve “Hayır” seçeneklerinden oluşan bir derecelendirme ölçeği kullanılmıştır.

17. soruda ise öğrencilerden akıllı tahtanın öğretimdeki işlevlerinin kendilerine göre önemini “1” ile “5” arasında bir puan vererek derecelendirmeleri istenmiştir.

### Verilerin Toplanması ve Analizi

Araştırmanın verileri 2011–2012 öğretim yılı güz yarıyılında yapılan uygulamalar sonunda elde edilmiştir. Anketteki “Hayır” Seçeneği 1 puan üzerinden, “Kısmen” seçeneği 2 puan üzerinden ve “Evet” seçeneği 3 puan üzerinden hesaplanmıştır. Anketten elde edilecek en düşük puan 16, en yüksek puan ise 48’dir. Toplam puanın yüksek olması öğrencinin akıllı tahta kullanımı ve F@t@h projesinden haberdarlık düzeyinin yüksek olduğu anlamına gelmektedir.

Öğretmen adaylarının akıllı tahta kullanımı ve F@t@h projesine yönelik haberdarlıkları ile cinsiyet ve bilgisayar dersi alma durumları arasında anlamlı bir farklılık olup olmadığı bağımsız gruplarda t-testi ile tespit edilmiştir. Öğrencilerin yaşına göre farklılık gösterip göstermediğine ise varyans analizi ile bakılmıştır.

### BULGULAR ve YORUMLAR

Çalışma grubuna ait cinsiyet, yaş ve bilgisayar dersi alıp almamaları gibi demografik bilgiler aşağıdaki Tablo 1’de sayı ve yüzde olarak belirtilmiştir.

**Tablo 1: Demografik Bilgiler**

	Cinsiyet		Yaş			Bilgisayar Dersi Alma	
	Kız	Erkek	20-22 arası	23-24 arası	25-26 arası	Evet	Hayır
<b>Yüzde</b>	%65	%35	%82,4	%10,3	%7,3	%88	%12
<b>Sayı</b>	44	24	56	7	5	60	8
<b>Toplam</b>	68		68			68	

Çalışma grubunda 68 öğrenci yer almıştır. Tablo 1’e göre çalışma grubunun büyük çoğunluğunu kız öğrenciler oluşturmaktadır. Aynı şekilde öğrencilerin çoğunluğu 20-22 yaş aralığındadır. Öğrencilerin %88’lik gibi büyük bir kısmı öğrenim hayatı boyunca bilgisayar dersi aldığını belirtmiştir.

**Tablo 2: Cinsiyete Göre Akıllı Tahta Kullanımı Bilgisi Düzeyi**

Cinsiyet	N	Genel Ortalama	Standart Sapma	p
Kız	44	30,88	4,84272	,623
Erkek	24	33,91	5,27436	

Tablo 3’e göre kız öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması  $X=30,88$ , erkek öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması ise  $X=33,91$ ’dir. P değerine bakıldığında ( $p<,05$ ) istatistiksel olarak kız öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeylerinin erkek öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeylerinden anlamlı bir farkının olmadığı söylenebilir.

**Tablo 3: Bilgisayar Dersi Alma Durumuna Göre Akıllı Tahta Kullanımı Bilgisi Düzeyi**

Bilgisayar Dersi Alma Durumu	N	Genel Ortalama	Standart Sapma	p
Evet	60	32,00	5,12223	,650
Hayır	8	30,83	6,46271	

Tablo 4'e göre bilgisayar dersi alan öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması  $X=32$ , bilgisayar dersi almayan öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması ise  $X=30,83$ 'dür. P değerine bakıldığında ( $p<,05$ ) istatistiksel olarak bilgisayar dersi alan öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeylerinin bilgisayar dersi almayan öğrencilerin AT kullanımı hakkında sahip olduğu bilgi düzeylerinden anlamlı bir farkının olmadığı söylenebilir.

**Tablo 4: Yaşa Göre Akıllı Tahta Kullanımı Bilgisi Düzeyi**

Yaş	N	Ortalama	Standart Sapma	P
20-22 arası	56	31,98	5,24835	,915
23-24 arası	7	32,28	5,49892	
25-26 arası	5	31,20	4,76445	

Çalışma grubunda bulunan öğretmen adaylarının yaş ortalaması 21,64'tür. Tablo 5'e göre 20-22 yaş arası öğretmen adaylarının AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması  $X=31,98$ , 23-24 yaş arası öğretmen adaylarının AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması  $X=32,28$  ve 41-50 yaş arası öğretmen adaylarının AT kullanımı hakkında sahip olduğu bilgi düzeyi ile ilgili genel puan ortalaması ise  $X=31,20$ 'dir. P değerine bakıldığında ( $p<,05$ ) istatistiksel olarak öğretmen adaylarının AT kullanımı hakkında sahip olduğu bilgileri ile yaşları arasında anlamlı bir farkın olmadığı söylenebilir.

**Tablo 5: Akıllı Tahtanın Öğretimde Kullanım İşlevlerine Dair Önem Sırası ve Önem Puanı Ortalaması**

Akıllı Tahtanın öğretimde kullanılma işlevleri	Önem sırası					Ort.
	1	2	3	4	5	
1 Konu ile ilgili video göstererek dersi işleme	16 %23,5	11 %16,2	8 %11,8	10 %14,7	20 %29,4	3,1
2 Konu ile ilgili internetten araştırma yapma	7 %10,3	5 %7,4	12 %17,6	15 %22,1	26 %38,2	3,7
3 Konu ile ilgili görselleri (resim, harita vb) gösterme	9 %13,2	18 %26,5	14 %20,6	10 %14,7	14 %20,6	3,03
4 Konu ile ilgili PowerPoint sunuları ile dersi işleme	8 %11,8	14 %20,6	13 %19,1	13 %19,1	17 %25,0	3,2
5 Konu ile ilgili hazır alıştırma yapma	9 %13,2	7 %10,3	10 %14,7	15 %22,1	24 %35,3	3,5

Öğretmen adaylarının "Derslerinizde Akıllı Tahta kullanıyor olsaydınız Akıllı Tahtanın belirtilen özelliklerinden en çok hangisini kullanmaya ihtiyaç duyardınız? Lütfen önem sırasına göre 1 ile 5 arasında puanlayınız." sorusuna verdikleri cevabın analizi Tablo 6'da yer almaktadır.

Buna göre, öğretmen adayları için akıllı tahta aracılığı ile video göstererek ders işlemenin önem derecesi ortalaması 3,1'dir. Video göstererek ders işleme %23,5'lik bir oranla 1. derecede ve %29,4'lük bir oranla 5. derecede bir önem taşımaktadır.

Akıllı tahta aracılığı ile internetten araştırma yapma önem derecesi ortalaması 3,7'dir. İnternetten araştırma yapma %10,3'lük bir oranla 1. derecede ve %38,2'lik bir oranla 5. derecede önemli bulunmuştur.

Akıllı tahta aracılığı ile görseller göstermenin önem derecesi ortalaması 3,03'tür. Görseller gösterme %13,2'lik bir oranla 1. derecede ve %20,6'lık bir oranla 5. derecede önemli bulunmuştur.

Akıllı tahta aracılığı ile Powerpoint sunuları üzerinden ders işlemenin önem derecesi ortalaması 3,2'dir. Powerpoint sunuları üzerinden ders işleme %11,8'lik bir oranla 1. derecede ve %25'lik bir oranla 5. derecede önemli bulunmuştur.

Akıllı tahta aracılığı ile hazır alıştırma yapma öğrencilere yaptırmanın önem derecesi ortalaması 3,5'tir. Hazır alıştırma yapma %13,2'lik bir oranla 1. derecede ve %35,3'lük bir oranla 5. derecede önemli bulunmuştur.

Ayrıca, öğretmen adaylarının F@tih projesinden haberdarlık düzeyi incelendiğinde çalışma grubunun %70,6 'sının F@tih projesi hakkında bilgiye sahip olmadıkları, % 13,2'sinin proje hakkında kısmen bilgiye sahip oldukları ve % 16,2'sinin ise F@tih projesi hakkında bilgi sahibi oldukları ortaya çıkmıştır.

## SONUÇ VE ÖNERİLER

Yıldız Teknik Üniversitesi, Yabancı Diller Eğitimi, İngilizce öğretmenliği bölümünde öğrenim gören toplam 68 öğrenci ile yapılan bu çalışmada, öğretmen adaylarının “Akıllı Tahta” kullanımı ve F@tih projesi ile ilgili bilgi düzeylerinin ve kendileri bu aracı kullandıklarında ihtiyaç duyacakları özelliklerin tespit edilmesi amacı ile likert bir anket geliştirilerek veri toplanmıştır.

Elde edilen verinin değerlendirilmesi sonucunda AT kullanımı bilgi düzeyi ile cinsiyet ve yaş değişkenleri arasında anlamlı bir ilişki olmadığı görülmüştür. Aynı biçimde bilgisayar dersi alan öğrenciler ile almayan öğrenciler arasında AT kullanımı bilgi düzeyi arasında anlamlı bir ilişki bulunmamaktadır.

Araştırma kapsamında öğretmen adaylarının AT işlevlerinden bazılarını önem sırasına göre sıralamaları istenmiştir. Verilen beş işlevden “konu ile ilgili görselleri gösterme” önem sırasında birinci gelmekte bu işlevleri sırası ile “konu ile ilgili video göstererek dersi işleme”, “konu ile ilgili PowerPoint sunuları ile dersi işleme”, “konu ile ilgili hazır alıştırmaları öğrencilere yaptırma” ve “konu ile ilgili internetten araştırma yapma” işlevleri takip etmektedir.

Bu çalışma, Yıldız Teknik Üniversitesi, İngilizce öğretmenliği son sınıf öğrencileri ile sınırlıdır. Sonraki çalışmalarda Türkiye’de bulunan diğer üniversitelerin öğrencileri de çalışmaya dahil edilebilir. Öğretmen adaylarının bilgi düzeyleri ve görüşleri öğrenildiği gibi farklı illerde ve farklı kademelerde yabancı dil öğreten öğretmenlerin de bilgi, görüş ve uygulamalarını öğrenmek amacı ile araştırmalar yürütülebilir.

Bu çalışmada sınırlı sayıda öğretmen adayından veri toplanmasına karşın elde edilen veri yardımı ile şu önerilerde bulunulabilir;

- 1) Öğretmen yetiştiren yükseköğretim kurumlarında bilgisayar ya da bilgi teknolojileri ile ilgili derslerde AT ve kullanımı ders içeriğine alınmalıdır. Öğretmen adaylarının etkili bir biçimde AT kullanımlarına yardımcı olacak ödev ve projeler hazırlanmalıdır.
- 2) Öğretmen yetiştiren kurumlarda alan ve eğitim derslerinde öğretim görevlilerinin AT kullanması hem öğretmen adaylarına örnek olacak hem de öğretmen adaylarının bu konu ile ilgili bilgi ve tutumlarının gelişmesi sağlanacaktır.
- 3) Yabancı dil öğreten öğretmenler için AT'nin yabancı dil öğretiminde kullanımı ile ilgili hizmetiçi eğitim ve seminerler hazırlanmalıdır.
- 4) Öğretmenlerin ve öğretmen adaylarının okullarda AT kullanımı teşvik edilmelidir.
- 5) Düzenlenecek eğitim programlarında bu araştırma kapsamında öğretmen adaylarının belirttiği gibi en fazla ihtiyaç duydukları veya önemli olduklarını düşündükleri konulara göre içerik hazırlanmalıdır.
- 6) Öğretmen adayları için F@tih projesinin kapsamı ve hedeflerini içeren tanıtım broşürleri ve seminerler hazırlanmalıdır.

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# YAPI İÇ MEKÂNLARINDA GÜRÜLTÜ VE İNSAN SAĞLIĞI İLİŞKİSİNE YÖNELİK TASARIM

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## Özet

İnsan, yaşamını sürdürürken çevresi ile sürekli iletişim halindedir. İnsan yaşamında önemli bir etkisi olan ve insanların günlük yaşam aktivitelerini gerçekleştirdikleri mekânlar olan yapılar, insan sağlığına olumlu ya da olumsuz etki etmektedir. Yapıları oluşturan mekânlardaki iç çevresel faktörlerdeki değişken olumsuz etkiler insanda homeostazisi bozarak hastalık yapıcı etkiye neden olabilmektedir. Bu olumsuz etkilerden; insan çevresinde oluşan gürültü, insanın homeostatik dengesini bozarak strese neden olur ve hastalanmasını sağlar. Bu çalışmada, insanların işitme sağlığını ve algılamasını olumsuz etkileyen, fizyolojik ve psikolojik dengesini bozabilen, iş verimini azaltan, çevrenin hoşluğunu ve sakinliğini yok ederek niteliğini değiştiren gürültünün istenmeyen etkilerini azaltmaya yönelik önlemlerin göz önünde bulundurulmasının önemi vurgulanmıştır.

**Anahtar kelimeler** : Yapılar, Homeostatik denge, Gürültü

## THE DESIGN FOR NOISE AND HUMAN HEALTH RELATIONSHIP IN STRUCTURE'S INTERIORS

### Abstract

Human are in constant communication with its surroundings while maintaining their lives. Buildings, the places people continue activities of daily living and have a significant impact on human life, effect positive or negative effect in human health. Variable adversely affects, environmental factors in the rooms consisted of structures, can lead to disease-causing effect corrupting homeostasi. This is one of the negative effects of noise which occur in the environment, causes stress and ill people provides disturbing the. In this study, it is emphasized that the noise which business efficiency, reducing the quality of by destroying the calm consideration of measures to mitigate the adverse effects of changing of environment, impairing the physiological and psychological balance and adversely affect the ear health and sensing of a person.

**Keywords** : Structures, homeostatic balance, Noise.

### 1. GİRİŞ

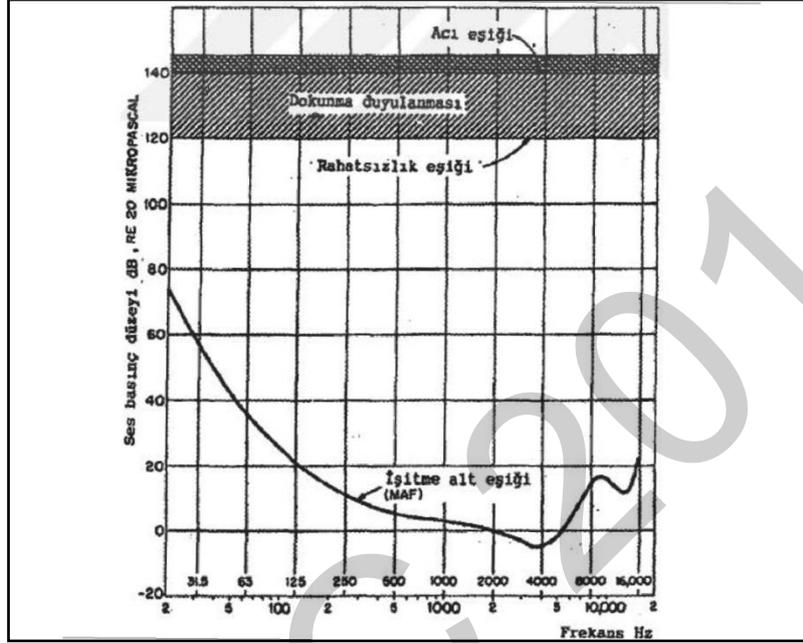
İnsanlık tarihi boyunca bireyin, yaşamını devam ettirdiği yapılarda, geçirdiği zaman, yaşamının önemli bir bölümünü oluşturmakta ve mekânların iç koşulları fiziksel ve ruhsal olarak insan sağlığını etkilemektedir. Yapılan çalışmalar fiziksel çevresiyle uyum içinde bulunan insanların verimlerinin yüksek düzeyde olduğunu, fizik ve ruh sağlıklarının da yıpranmadığını kanıtlamaktadır. İnsanlar yaşam deneyimlerinin büyük bir kısmını, oluşturdukları yapay fiziksel çevreler olan yapılarda gerçekleştirmektedirler. Söz konusu mekânların fiziksel koşulları; yaşayanların sağlığına etki ederek, olumlu ya da olumsuz etkide bulunur. Fiziki çevrede oluşan ses ölçülebilen fiziki çevre ögesidir. Ses, belirli sınırlar içinde kaldığı sürece insan bünyesi ona uyum sağlar. İnsan sağlığına olumsuz etki edecek seviyede oluşan ses, gürültü olarak tanımlanır. Gürültü, kişinin denge mekanizması olan "homeostazisi" bozarak strese yol açar ve bunun sonucunda hastalanmasına neden olur. Bu nedenle tasarımcı, insanların işitme sağlığını ve algılamasını olumsuz etkileyen, fizyolojik ve psikolojik dengesini bozabilen, iş verimini azaltan, çevrenin hoşluğunu ve sakinliğini yok ederek niteliğini değiştiren yapı içi ve dışı kaynaklı gürültünün istenmeyen etkilerini azaltmaya yönelik önlemleri göz önünde bulundurulmalıdır [1,2].

Bu çalışmada amaç; fiziksel çevresi ile sürekli etkileşim içinde bulunan bireyin, fiziksel çevre faktörlerinden gürültünün, insan sağlığı üzerindeki etkilerini ortaya koymak ve gürültünün iç mekânlarda denetimine yönelik öneriler sunmaktır.

## 2. TANIM

Kısaca ‐istenmeyen ses‐ olarak tanımlanabilen gürültü, düzensiz yapılı ve farklı frekans bileşenlerine sahip olan ve genellikle zamana göre değişen, birbiriyle belli bir uyum göstermeyen gelişigüzel titreşimlerdir. Sesin gürültü olarak kabul edilip edilmemesi, ses basınç düzeyine, frekansına, süresine, zamanlamasına, ses kaynağının nitelik ve niceliğine, kişinin ruh haline ve yaratılışına bağlıdır. Ses ne kadar nitelikli ve hoş gider olursa olsun, yeğinliği fazla ise gürültü olarak kabul edilir.

Gürültü şiddeti sonomete ile ölçülür ve desibel (dB) ile ifade edilir. Normal bir kulak 0-10 dB arasını rahatça duyar, 120-140 dB ise en şiddetli seslerdir (Şekil 1). Frekansa gelince normal insan kulağı 16-20.000 Hz arasını duyar. Bunun alt ve üstüne infrason ve ultrason olarak tanımlanır ve insan kulağı bu sesleri duymaz.[1]



Şekil 1. İnsan Kulağının Sesi Algılama Alanı [3]

## 3. GÜRÜLTÜ VE İNSAN SAĞLIĞI İLİŞKİSİ

Gürültü, özgün bir akustik biçim kavramıdır. Belli bir kaynaktan köken alıp, değişik özellikler göstererek ortaya çıkar. Yine belli şartlardan etkilenerek geçtiği bir iletim yolunu takip eder ve bir alıcıya ulaşır. Gürültü, kişinin denge mekanizması olan ‐homeostazisi‐ bozarak strese yol açar ve bunun sonucunda hastalanmasına neden olur. Homeostazis; insanın biyolojik yapısının, yaşam koşullarına uyum sağlarken, dengelerin korunmalarını sağlayan kendi kendini düzenleme süreci olarak tanımlanır (Şekil 2). İnsan vücudu etkileşime hazır, açık bir sistemdir ve sürekli dinamik bir enerji ile insanın iç ve dış çevresinin etkileşimi sonucu, iç çevreyi dengede tutmaktadır. Homeostazi sonucunda kurulan dinamik denge, çevrenin sürekli denetim altında olmasını gerekli kılar [2].

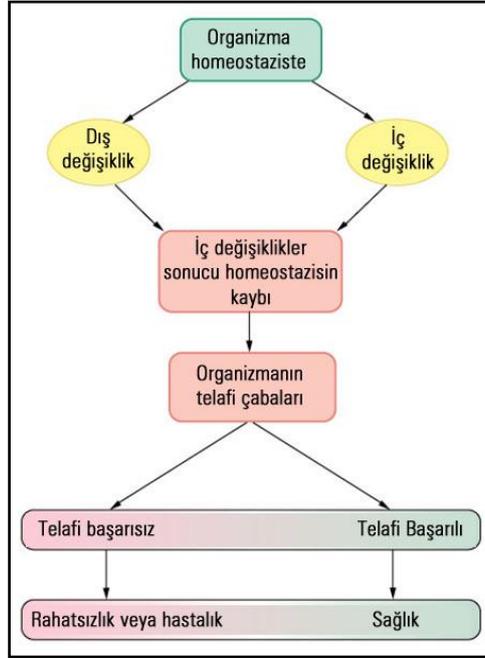
1971'de Dünya Sağlık Örgütü (WHO) tarafından gürültünün, insan sağlığına karşı ana bir tehdit olarak görülmesi gerektiği bildirilmiştir. Gürültünün iş verimine olan etkisi, yapılan işe ve akustik öğelere göre farklılık gösterir. Gürültülü ortamlarda bulunan kişiler arasında, 84 dB den sonra hoşgörüsüzlük, düşmanca davranma ve yardım etme düşüncesinin azaldığı ortaya çıkmaktadır. Gürültü etkisi kesilse bile kişilerde genel bir depresyon hali devam ettiği görülmektedir [1].

Yüksek düzeydeki gürültü, iş üzerindeki başarıyı etkilemese bile rahatsızlık, iletişimde kopukluk ve uzun süreli sağlık etkilerine yol açabilir. Yapılan araştırmalar 95 dB ve üzerinde gürültü düzeyine maruz kalan insanlarda somatik hastalıkların arttığını göstermektedir.

Gürültü, insan ilişkisi iki ayrı biçim gösterir:

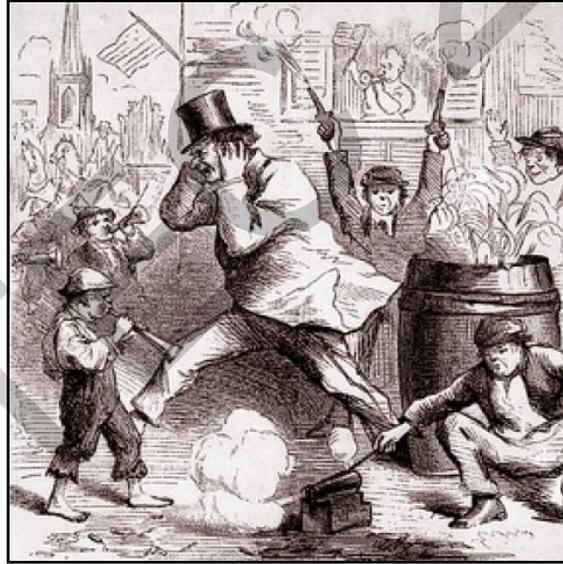
1-İnsanın gürültüyü değerlendirme özelliklerine bağlı cevaplar: İnsanın işitsel değerlendirme özelliklerine, psikolojik durumuna bağlı olarak ortaya çıkan cevaplardır.

2-İnsanın gürültüden etkilenimi sonucu ortaya çıkan, zarar etkisi cevaplar: İşitsel duyumda ortaya çıkan bozulmalar, işitsel duyum dışında fizyolojik bozulmalar ve psikolojik, zihinsel bozulmalar biçiminde verilen cevaplardır.



Şekil 2. Homeostazis ve Kontrolü [2]

Bireylerde oluşan rahatsızlık durumu, gürültünün fiziksel özellikleri ve dinleyicinin sosyolojik ve demografik özelliklerine göre farklılık gösterir (Şekil 3). Gürültünün insan üzerindeki olumsuz etkisinin büyüklüğü sesin fiziksel özellikleriyle doğrudan ilişkilidir. Yüksek frekanslı gürültü rahatsız edicidir. Devamlı veya kısa sürelerle periyodik olarak tekrarlanan gürültü, kısa süreli ve geçici olanlardan daha fazla rahatsız edicidir (Tablo 1).



Şekil 3. Gürültünün Etkisi

Tablo 1. Gürültü Hasarları [1]

Gürültü Derecesi	Gürültü hasarları				
	Konforsuzluk	Rahatsızlık	Sıkılma Duygusu	Kızgınlık	Konsantrasyon ve Uyku Bozukluğu
<b>1.derece gürültüler</b> (5 dBA)					
<b>2.derece gürültüler</b> (fizyolojik) (65-90 dBA)	Kalp Atışının Değişimi	Solunum Hızlanması	Beyindeki Basıncın Azalması		
<b>3.derece gürültüler</b> (90-120 dBA)	Fizyolojik Gürültü	Baş ağrısı			
<b>4.derece gürültüler</b> (120-140 dBA)	Fizyolojik Gürültü	Baş ağrısı			
<b>5.derece gürültüler</b> (140> dBA)	Kulak Zarının Patlaması				

## Gürültünün İşıtmeye etkisi

- 1) Akustik Travma
- 2) Geçici Duyma Kaybı
- 3) Kalıcı Duyma Kaybı biçiminde görülebilir. Gürültünün etkisi ile oluşan, geçici duyma kaybında eski duyarlılığa dönüş söz konusu olabilir, buna karşın kalıcı duyma kaybında dönüşüm söz konusu değildir [5].

## Gürültünün Fizyolojik Etkileri

Fizyolojik olarak gürültü insan vücudunda kısa ve uzun süreli etkiler biçiminde görülmektedir.

- 1.Kısa Süreli Etkiler; gürültü kesildikten hemen sonra ortadan kalkan, kalp hızının artması göz bebeğinin büyümesi, istemli kasları kapsayan refleksler, nefes alma hızında değişiklikler gibi etkilerdir.
- 2.Uzun Süreli Etkiler; gürültü kesildikten uzun süre sonra bile, gözlemlenebilen fizyolojik açıdan pek çok rahatsızlığa yol açan etkilerdir. Gürültünün uzun süreli etkisi kişide stres yaratır ve bunun sonucunda hastalık gelişir.

## Gürültünün Psikolojik Etkileri

Yorgunluk, sıkıntı, sinirlilik, gerginlik, uykuya dalma güçlüğü, ani uyanmalar, uykusuzluk, öğrenmede azalma, saldırgan davranış, depresyon, hafızada değişiklikler, sosyal davranışlarda değişiklikler biçiminde kişi üzerinde psikolojik etkileri görülmektedir.

## Gürültünün Performans Etkileri

Çalışma ortamında yüksek düzeyli, ani ve kesikli gürültülerin kişilerde dikkatin dağılması sonucu, yapılan işin zamanında ve doğru yapılamamasına bununla birlikte iş kazalarının yaşamasına neden olabilir.

Fiziksel Etkenler	<ul style="list-style-type: none"> <li>• İşıtme Hasarı</li> </ul>
Fizyolojik Etkenler	<ul style="list-style-type: none"> <li>• Vücuttaki Bozukluklar</li> <li>• Kalp Atışının Bozulması</li> <li>• Metabolizmada Bozukluk</li> <li>• Uyku Bozukluğu</li> <li>• Sinir Sistemi Dejenerasyonu</li> </ul>
Psikolojik Etkiler	<ul style="list-style-type: none"> <li>• Aşırı Tepkiler</li> <li>• Hoşnutsuzluk</li> </ul>
Performans Etkileri	<ul style="list-style-type: none"> <li>• Eylem Üzerindeki Etkisi</li> <li>• Konuşma ile Girişim Olayının Olması</li> <li>• Dinlenme ve anlaşma güçlüğü</li> <li>• Konsantrasyonun kesilmesi</li> <li>• Dinlenmenin Etkilenmesi</li> </ul>

## 4. YAPI İÇ MEKÂNLARINDA GÜRÜLTÜ DENETİMİ

Yaşamı birçok yönde olumsuz etkileyen gürültü ile mücadeleye çok eski zamanlarda M.Ö 600'lerde Sybaris kentinde başlanmıştır. 1158-1603 yılları arasında İngiltere Kraliçesi I. Elizabeth'in döneminde aile kavgalarının gece saat 22:00'den sonra yapılmasının resmen yasaklanmış olması, 1403'de Bern şehrinde gürültü ile ilgili kısıtlamaların getirilmesi; 1515'de Zürih şehrinde geceleri sokakta gürültü yapılmaması koşulu getirilmesi, 1730'larda, arabacıların kışın saat 21:00 den sonra dansların yasaklanması gürültünün kişileri rahatsız eden etkilerine karşı alınan ilk önlemler olarak göze çarpmaktadır.

Yapılarda gürültü yapılarında gürültü kaynakları yapı dışı ve yapı içi kaynaklı olmak üzere iki başlıkta toplanır. Yapı dışındaki tüm gürültüler dış çevre gürültüsünü oluşturur. Eğer dış gürültü bina cephesinden içeri girerken fon gürültüsünün üzerinde bir düzey oluşturuyorsa bunun denetlenmesi gerekir. Bu denetimde en etkili yol bina cephesinin ses geçiş kaybını arttırmaktır [4].

Yapı içi gürültüler ise yapının işlevine ve kullanıcılara bağlı olarak ayırım gösterirler. Yapı içi mekanlarında oluşan gürültü:

1. Havada Doğan Gürültüler
  - (a) Kullanıcıların konuşmaları, bağırmaları ve ağlamaları ile oluşan gürültüler
  - (b) Elektrikli aletlerin çıkardığı gürültüler
2. Katılarda Doğan Gürültüler
  - (a) Döşemede doğan darbe gürültüleri;
    - i.Sert zeminlere düşen sert nesnelerin oluşturduğu gürültüler
    - ii.Kullanım eşyalarının itilip çekilmesi ile oluşan gürültüler
    - iii.Kullanıcıların hareketleri sonucunda oluşan topuk sesi

- iv. Bina girişi ve merdivenlerde oluşan gürültüler
- v. Mutfak çalışmasında oluşan gürültüler

(b) Yapı ile katı bağlantısı olan nesnelere çıkardığı gürültüler

- i. Hidrofor, pis su motoru gibi gürültüler
- ii. Tesisat ve teknik donatıların gürültüleri
- iii. Kapı ve pencerelerin kullanımında oluşan gürültüler
- iv. Havalandırma kanallarında oluşan gürültüler yapı içinde katılarda oluşur [1].

İnsan sağlığını gürültünün olumsuz etkilerinden koruyabilmek için;

1. Yapılarda, katlarda ayırıcı duvarlar, döşemeler için ses yalıtımı kriterleri belirlenip sonrasında bu değer kontrol edilmelidir.
2. Yapılarda, yüksek gürültü düzeyli mekânlarda ya da özellikle ses yalıtımı yapılması istenilen mekânlarda, yapı elemanlarının (kapı, pencere, duvar v.b.) birim ağırlıkları artırılarak ses geçişi engellenebilir. Bu yeterli gelmezse ek önlemler alınmalıdır.
3. Yapılarda, katlarda ayırıcı duvarlar, döşemeler için ses yalıtımı kriterleri belirlenip sonrasında bu değer kontrol edilmelidir.

## 5. SONUÇLAR

İnsan sağlığını sürdürülebilmesi için dış çevresi ile uyum halinde bulunmalıdır. Olumsuz dış çevre koşulları insan sağlığını bozucu bir etkiye sahiptir. Yapının iç çevresinde oluşan ya da dış çevreden yapı içini etkileyen denetimsiz kaldığı sürece insan sağlığına olumsuz etki eden gürültüler, insanların işitme sağlığını ve algılamasını olumsuz etkileyerek, fizyolojik ve psikolojik dengelerini bozan, iş verimini, çevrenin hoşluğunu ve sakinliğini yok eden bir etki yaratmaktadır. Bu nedenle, yapı iç mekânlarında insanların, kendilerini fiziksel ve ruhsal yönden rahat hissedebilmeleri için gürültünün insan üzerindeki etkisi göz önünde bulundurulmalı ve tasarımcı ses denetiminin sağlandığı akustik konfor koşullarının sağlandığı mekânlar oluşturmalıdır.

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# INFLUENCE OF HARDENING OF STERILIZED STAINLESS STEEL ON CORROSION RESISTANCE

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## Abstract

The purpose of the tests was to determine whether and how sterilisation process of samples made of AISI 316L stainless steel with different strain impacts their corrosion resistance. Tests were made on steel samples that had been electrochemically polished in order to assure proper surface roughness. In order to evaluate the influence of sterilisation on physical and chemical properties of steel surface, tests of corrosion resistance were made by means of potentiodynamic method. The tests were made in alternative solution simulating human blood – artificial plasma. Recorded anodic polarisation curves created the ground for determination of typical parameters describing pitting corrosion resistance, that enabled to evaluate steel wire corrosion behaviour under sterilisation conditions.

## INTRODUCTION

Final quality of implants made of AISI 316L steel depends among other things on their chemical composition, metallurgical quality, work hardening, functional characteristics and the set of physical and chemical properties of the surface. The issue of creation of proper physical and chemical characteristics is mainly focused on the methods that substantially reduce unfavourable phenomena which take place on the phase boundary: implant – tissue. Surface layer is formed thanks to application of various technologies of surface engineering. Implant surface treatment is conditioned by technological capabilities of the manufacturer and his knowledge of biomechanical determinations as well as knowledge of implant reactivity during insertion and product utilisation. Other important criteria of product forming or application include: economical, industrial and clinical.

One of the most frequently used final process of surface modification of implants made of AISI 316L steel is chemical passivation and steam sterilisation. This treatment aims at implant surface modification through minimisation of the amount of corrosion products that penetrate to the tissue [1-3]. Corrosion resistance is the basic property of the material, vital for its applicability for medical purposes. Types of corrosion, revealed on the ground of macro- and microscopic observations after different periods of implant immersion in blood environment, have not been systematised yet. Stochastics of changes of conditions determining initialization and development of implant corrosion in blood environment is specific, and the image of damage is often different to the one obtained under simulated laboratory conditions. Metallic materials corrosion resistance is determined through comparative tests that are carried out by means of accepted testing methods under laboratory conditions, simulating real biological environment. It is determined on the ground of potentiodynamic tests, potentiostatic tests and by means of impedance spectroscopy. On the ground of the analysis of the results, it is possible to determine such features as corrosion potential, corrosion current density, potential values as well as density of corrosion currents that correspond to the respective passive ranges, perforation potential of passive layer, repassivation potential polarisation resistance. Analysis of the obtained results enables full corrosion characteristics of the implant in the specific environment [4-7].

Therefore, this study presents carried out tests the purpose of which was to determine the influence of surface modification method under sterilisation conditions of AISI 316L steel with various hardening on its corrosion resistance in blood environment. These tests were carried out by means of potentiodynamic method that enables determination of features typical of corrosion resistance.

## METHODS AND PROCEDURES

Steel AISI 316L delivered in the form of supersaturated steel rod with diameter  $d_0 = 5,6$  mm, which was drawn to the diameter  $d_1 = 1,5$  mm was used in the tests. Both, chemical composition and alloy structure, were in accordance with the recommendations of ISO 5832-1:2007. Strain in drawing process, expressed as a logarithm, was  $\square_d = 2,64$ .

Next, the way of surface preparation was differentiated through application of mechanical treatment – grinding ( $R_a = 0,40 \square m$ ), electrochemical polishing ( $R_a = 0,12 \square m$ ) and chemical passivation ( $R_a = 0,12 \square m$ ). Surface roughness tests were made by means of linear mechanical contact measurement method with application of profile measurement gauge SURTRONIC 3+ by Taylor/Hobson. Measurement was made on sections  $l = 0,8$  mm long with accuracy  $\pm 0,02 \square m$ .

Samples of wire rod and wire, prepared in such a way, were then subject to steam sterilisation in autoclave Basic Plus by Mocom at the temperature of  $T = 134^\circ C$ , pressure  $p = 2,1$  bar for  $t = 12$  min. Next, the samples representing successive stages of surface preparation were subject to pitting corrosion tests. The tests were carried out in accordance with recommendations of PN-ISO 17475. Pitting corrosion resistance was evaluated on the ground of registered anodic polarisation curves by means of potentiodynamic method and with the employment of electrochemical testing system VoltaLab® PGP 201 by Radiometer that was a part of measuring set. Prior to the commencement of tests, all samples were cleaned in 96% ethanol in ultrasound washer. The tests began with determination of opening potential  $E_{OCP}$ . Next, anodic polarisation curves were registered, beginning with the potential of  $E_{start} = E_{OCP} - 100$  mV. Potential changed in anodic direction at the rate of 1 mV/s. When anodic

current density of  $i = 1 \text{ mA/cm}^2$  was obtained, polarisation direction was changed. This way return curve was registered. The tests were carried out in alternative solution of artificial blood plasma simulating human blood with chemical composition presented in Table 2. Solution temperature during the test was  $37 \pm 1^\circ\text{C}$ , a  $\text{pH} = 7,0 \pm 0,2$ .

Table 1. Chemical composition of the artificial plasma according to PN – EN ISO 10993-15 standard

Components	NaCl	CaCl <sub>2</sub>	KCl	MgSO <sub>4</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> HPO <sub>4</sub>	NaH <sub>2</sub> PO <sub>4</sub>
Components concentration, g/l distilled water	6,8	0,2	0,4	0,1	2,2	0,126	0,026

RESULTS

The first stage of tests comprised pitting corrosion tests for wire rod samples with diameter  $d_0 = 5,6 \text{ mm}$ , made of AISI 316L steel with ground surface. Opening potential established at the level of  $E_{\text{OCP}} = -420 \text{ mV}$ . Electrochemical polishing caused the increase of potential to  $E_{\text{OCP}} = 0 \text{ mV}$ , and chemical passivation process further increase to  $E_{\text{OCP}} = +26 \text{ mV}$ . The course of anodic polarisation curves for ground, electrochemically polished as well as electrochemically polished and chemically passivated surface is presented in Fig. 1, and values of parameters describing resistance to corrosion – in Tab. 2.

Value of corrosion potential for samples that were only subject to mechanical working was  $E_{\text{corr}} = -90 \text{ mV}$ . The process of electrochemical polishing caused increase of corrosion potential to  $E_{\text{corr}} = -39 \text{ mV}$ . Whereas for samples that were in addition subject to chemical passivation, the value of corrosion potential was  $E_{\text{corr}} = -24 \text{ mV}$ . Determined values of polarisation resistance  $R_p$  and corrosion current density  $i_{\text{corr}}$  were, respectively – Tab. 2:

- for ground samples:  $R_p = 51 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,051 \text{ }\mu\text{A/cm}^2$ ,
- for polished samples:  $R_p = 360 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,007 \text{ }\mu\text{A/cm}^2$ ,
- for polished and passivated samples:  $R_p = 636 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,004 \text{ }\mu\text{A/cm}^2$ .

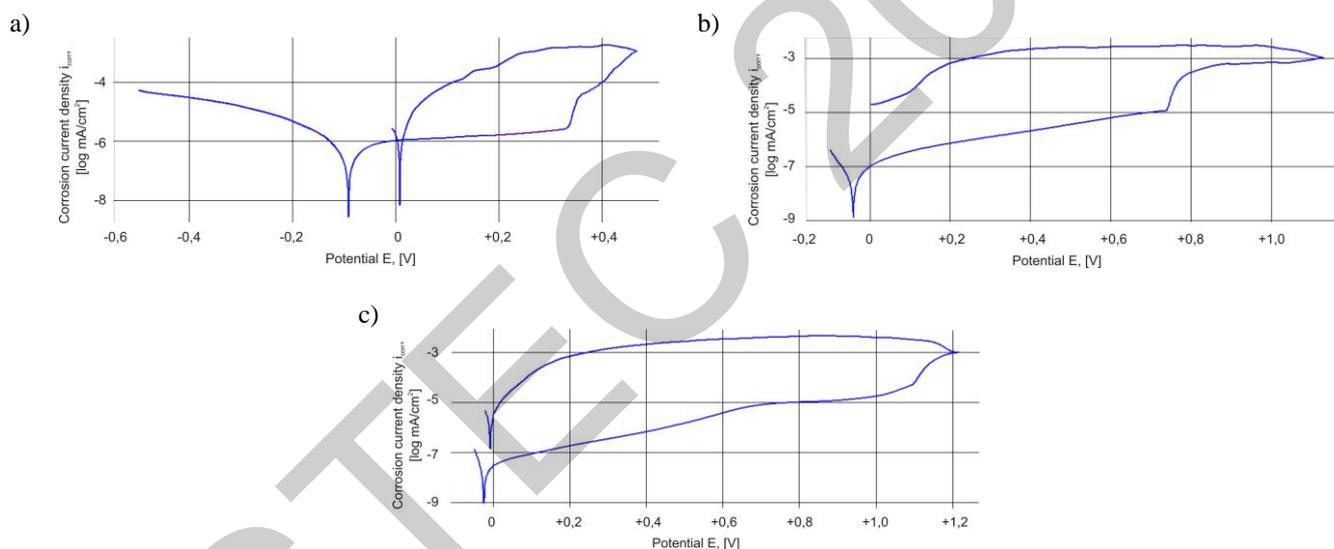


Fig. 1. Anodic polarization curves for AISI 316L samples ( $d_0 = 5,6 \text{ mm}$ ) of surface: a) ground, b) ground and electrochemically polished, c) electrochemical polished and passivated

Chemical passivation of samples surface most of all increased the value of breakdown potential from  $E_b = +338 \text{ mV}$  for ground surface to  $E_b = +1100 \text{ mV}$  for passivated surface – Tab. 2, Fig. 1 and 3.

Next stage comprised the tests of corrosion resistance of wire with diameter  $d_0 = 1,5 \text{ mm}$  with ground, electrochemically polished and electrochemically polished and passivated surface. Anodic polarisation curves registered for this group of samples are presented in Fig. 2.

Corrosion potential value for samples subject only to mechanical working was  $E_{\text{corr}} = -277 \text{ mV}$ , and after additional application of electrochemical polishing it increases to  $E_{\text{corr}} = -113 \text{ mV}$ . Chemical passivation caused further increase of corrosion potential to the value of  $E_{\text{corr}} = -85 \text{ mV}$ . Other typical features describing pitting corrosion resistance were, respectively – Tab. 2, Fig. 2 and 3:

- for ground samples:  $R_p = 84 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,30 \text{ }\mu\text{A/cm}^2$ ,
- for polished samples:  $R_p = 218 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,012 \text{ }\mu\text{A/cm}^2$ ,
- for polished and passivated samples:  $R_p = 908 \text{ k}\Omega\text{cm}^2$ ,  $i_{\text{corr}} = 0,003 \text{ }\mu\text{A/cm}^2$ .

Chemical passivation of samples surface also had some impact on the increase of breakdown potential from  $E_b = +377 \text{ mV}$  for ground surface to  $E_b = +664 \text{ mV}$  for passivated surface – Tab. 2, Fig. 2 and 3.

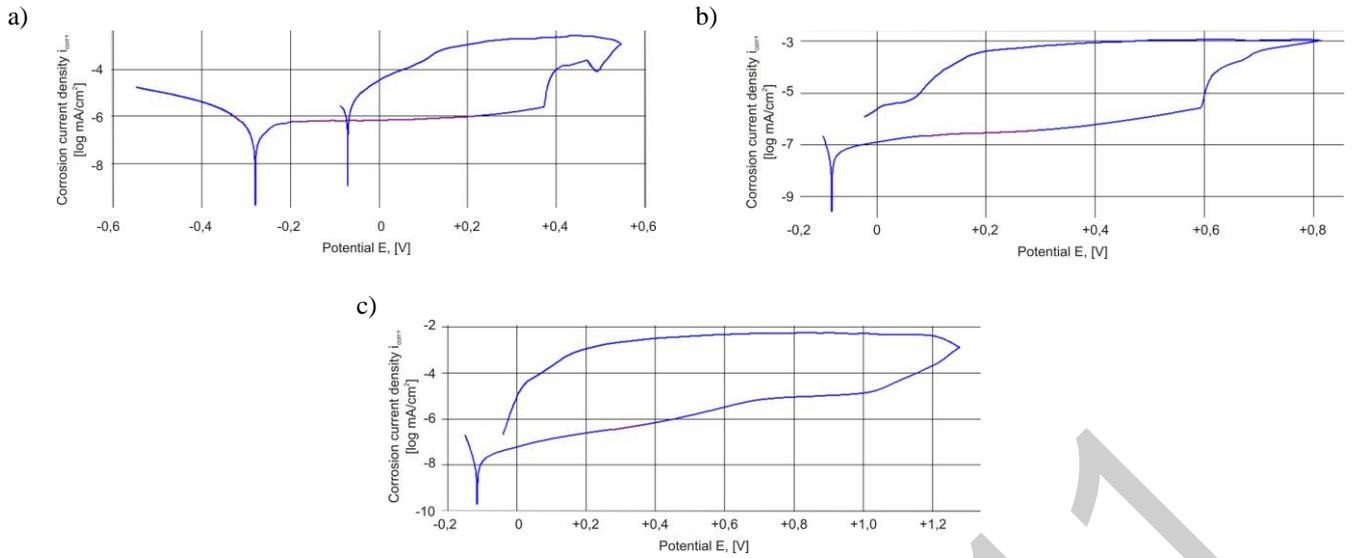


Fig. 2. Anodic polarization curves for AISI 316L samples ( $d_0 = 1,5$  mm) of surface: a) ground, b) ground and electrochemically polished, c) electrochemical polished and passivated

Table 2. Results of corrosion resistance

Diameter d, mm	Method of surface preparing	Open potential $E_{ocp}$ , mV	Corrosion potential $E_{corr}$ , mV	Polarisation resistance $R_p$ , $k\Omega \cdot cm^2$	Corrosion current density $i_{corr}$ , $\mu A/cm^2$	Breakdown potential $E_b$ , mV
5,6	Ground	-420	-90	51	0,51	338
5,6	Electrochemical polished	0	-39	360	0,07	743
5,6	Chemical passivated	26	-24	636	0,04	1100
1,5	Ground	-490	-277	84	0,30	377
1,5	Electrochemically polished	-42	-113	218	0,12	600
1,5	Chemical passivated	-33	-85	908	0,03	664

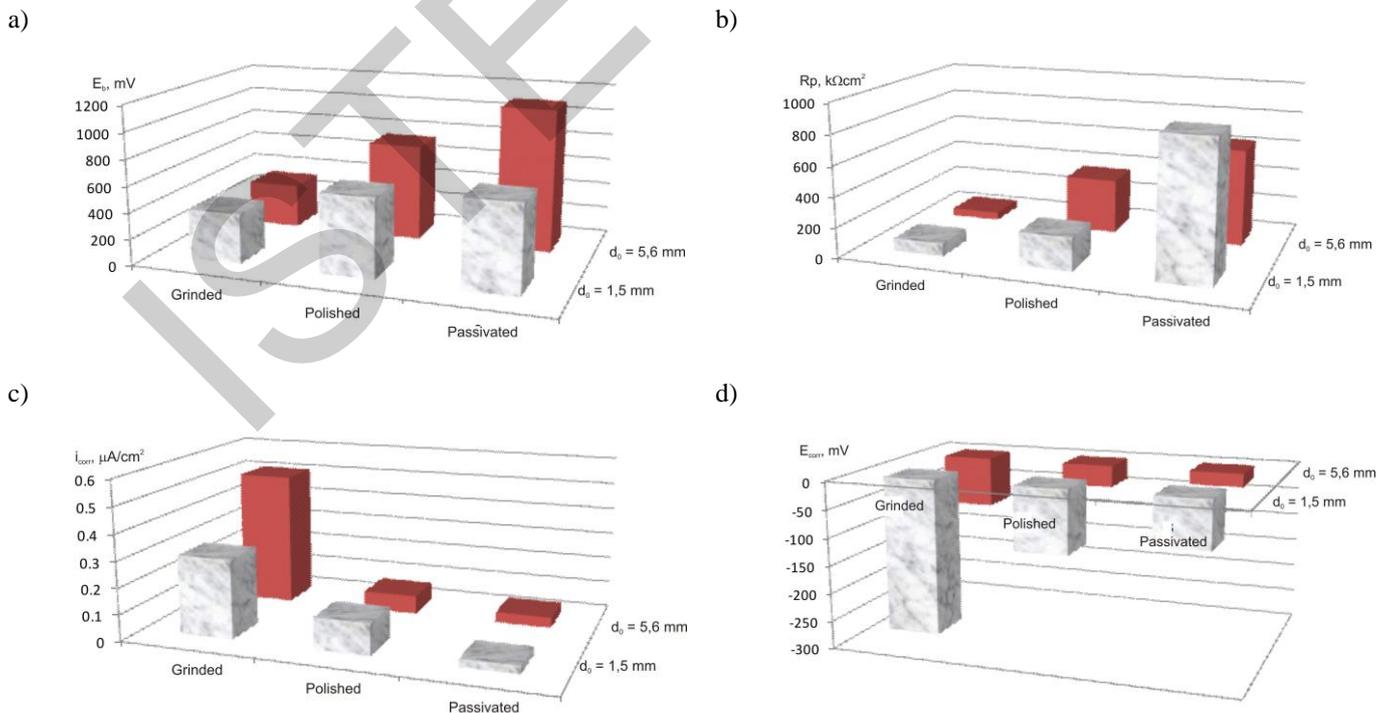


Fig. 3. The course of changes of typical features describing pitting corrosion resistance: a) breakdown potential  $E_b$ , b) polarisation resistance  $R_p$ , c) corrosion current density  $i_{corr}$ , d) corrosion potential  $E_{corr}$

## CONCLUSIONS

An important issue in the process of forming functional characteristics of instruments and implants used in vascular surgery is the selection of mechanical properties of metallic biomaterial and its physical and chemical characteristics of its surface. Physical and chemical characteristics of implant surface should be adapted to the features of human tissues. Evaluation of corrosion resistance of metallic biomaterials is one of the basic criteria for instruments and implants biotolerance evaluation. Therefore, corrosion resistance tests of AISI 316L steel that is currently used for implants in vascular surgery were presented in this study. Corrosion tests carried out in artificial blood plasma solution enabled to obtain information how electrochemical corrosion resistance of AISI 316L steel with modified surface changes as the result of strain in the drawing process.

Comparative analysis of anodic polarisation curves showed that work hardening has a substantial influence on corrosion characteristics. Supersaturated steel rod ( $d_0 = 5,6$  mm) features higher corrosion resistance. With the increase of strain in drawing process to  $\epsilon_c = 2,64$  (for wire with diameter of  $d_1 = 1,5$  mm), decrease of perforation potential and polarisation resistance were observed, as well as increase of corrosion current density, which is an unfavourable phenomenon. These results explicitly prove deterioration of corrosion resistance with the applied work hardening.

Corrosion resistance also depends on the way of product surface preparation. Obtained results show that the process of polishing and chemical passivation increased electrochemical corrosion resistance to a great extent for supersaturated steel rod as well as for the wire with diameter of 1,5 mm. Both, supersaturated steel rod and the wire with surface that was chemically passivated, featured the best corrosion characteristics.

To sum up, it must be highlighted that irrespective of work hardening applied and differences in the way of surface preparation, pitting corrosion was present on the samples. Test results prove that there is the need for protective layers application on implants made of the tested steel and used in invasive cardiology.

## ACKNOWLEDGMENTS

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# CORROSION RESISTANCE OF PREMODELED GUIDEWIRES MADE OF STAINLESS STEEL

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## Abstract

The purpose of the study is to evaluate resistance to electrochemical corrosion of wire made of stainless steel, designed for use in cardiology treatment. The influence of strain formed in the premodeling process and methods of wire surface preparation to corrosive resistance in artificial plasma solution were analysed. Wire corrosion tests were carried out in the solution of artificial plasma with the use of the system for electrochemical tests VoltaLab®PGP201. Resistance to electrochemical corrosion was evaluated on the ground of recorded curves of anodic polarization by means of potentiodynamic method. Potentiodynamic tests carried out enabled to determine how the resistance to pitting corrosion of wire changes, depending on strain formed in the premodeling process as well as on the method of wire surface preparation. Deterioration of corrosive properties of wire along with the increase in the formed strain hardening was observed.

## INTRODUCTION

Tests within the range of biomedical engineering carried out currently focus mainly on adequate selection of physical and chemical properties of materials that shall meet extremely restrictive criteria of their biological evaluation. It also refers to materials that will be used for production of surgical instruments which are used among other things for the correct location of implants in the human body or electrodes during heart electrotherapy. One of such instruments are guide wires used for implantation of heart pacemakers. The first external heart pacemaker was implanted in 1958 by a Swedish heart surgeon Ake Senning in cooperation with its manufacturer Rune Elmeqvist. Electrodes of the device were then placed on the epicard wall, not inside the heart. It was a ground-breaking moment in the development of electrotherapy whose treatment efficiency was proved both by scientific research as well as clinical practice [1-3]. The level of the development in the area of microelectronics is nowadays so high that it enables to make use of devices that are substantially smaller, with substantially greater programming options, and electrodes of pacemakers have become much thinner and more durable. In order to provide proper electrical stability and correction of conduction disturbances in a way that enables to obtain electrical operation of the heart as similar to the regular condition as possible, the tests are still being carried out to improve and modify the existing equipment and instruments.

Guide wires, the purpose of which is to insert endocavitary electrodes, are of crucial importance [3]. Wires made of stainless steel with diverse diameters and mechanical properties are mostly used for this purpose. Currently on the market there are many such guide wires that differ not only as far as material used is concerned, but most of all because they feature different forms and geometrical features. Such a huge variety of geometries is caused more by patent and market issues than by real clinical considerations. They haven't been normalised so far. Each company manufactures guide wires using their own catalogue series of types, determining their typical features and properties. However, clinical practice shows such limitations connected with currently used materials for guide wires. They are first and foremost connected with biocompatibility. Material inserted into blood-vascular system cannot cause changes to electrolyte composition, irreversible damage to protein structure, release of morphotic blood elements and it also should not initiate the process of coagulation, toxic and immunological reactions. Thus, the interest of manufactures in adequate surface treatment is increasing, in order to limit the occurrence of those unfavourable phenomena. [4].

Guide wires used commercially in electrotherapy are usually in the form of wires and are made of stainless steel of 18-8 type [5]. The analysis of the course of atrial lead implantation shows that guide wire prior to its implantation is deformed permanently. Therefore, in this study the tests were carried out that aimed at determination of influence of plastic strain of the wire on its corrosion resistance in blood environment. In order to simulate working conditions guide wires were deformed in the angle bend test by the angles:  $\alpha$ : 30°, 60°, 90°, 120° and 150°, respectively, on the radius of  $r = 3$  mm. The tests were carried out by means of potentiodynamic method which enabled to determine typical parameters describing resistance corrosion of the guide wire. Parameters obtained in the measurements were compared with non-deformed guide wire, which made the ground for the assessment of applicability of stainless steel X10CrNi18-8 for such type of medical product.

## METHODS AND PROCEDURES

Guide wires, commercially used in hospitals, made of stainless steel of X10CrNi18-8 type, in the form of wire with diameter of  $d = 0,4$  mm and length  $l = 680$  mm – Fig. 1, were used for the tests. Prior to the test, guide wires were sterilised with pressurised water steam in autoclave at the temp.  $T = 134^{\circ}\text{C}$  for  $t = 12$  min.

Potentiodynamic tests began with determination of opening potential  $E_{OCP}$  when there was no current. Then, anodic polarisation curves were registered, and the measurement commenced with the potential equal  $E_{start} = E_{OCP} - 100$  mV. Potential changed in anodic direction at the rate of 1 mV/s. When the density of anodic current reached  $i = 1$  mA/cm<sup>2</sup>, polarisation direction was changed. This way return curve was registered. Registered curves made the ground for determination of typical parameters describing resistance to pitting corrosion, i.e.: corrosion potential  $E_{corr}$  (mV), breakdown potential  $E_b$  (mV), repassivation potential  $E_{cp}$  (mV), polarisation resistance  $R_p$  (kΩ·cm<sup>2</sup>), corrosion current density  $i_{corr}$  (μA/cm<sup>2</sup>). Measurements were carried out with the use of measurement system VoltaLab®PGP201. Saturated calomel electrode NEK served as the reference electrode, whereas platinum electrode served as the auxiliary electrode. The tests were carried out in the solution of artificial blood plasma at the temperature of  $T = 37 \pm 1^\circ\text{C}$  – tab. 1.

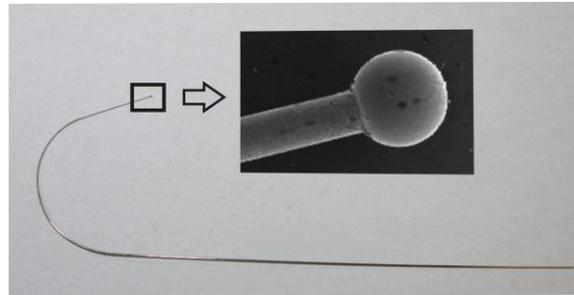


Fig. 1. Guide wire with the tip profiled at the angle  $\alpha = 150^\circ$

Table 1. Chemical composition of the artificial plasma according to PN – EN ISO 10993-15 standard

Components	NaCl	CaCl <sub>2</sub>	KCl	MgSO <sub>4</sub>	NaHCO <sub>3</sub>	Na <sub>2</sub> HPO <sub>4</sub>	NaH <sub>2</sub> PO <sub>4</sub>
Components concentration, g/l distilled water	6,8	0,2	0,4	0,1	2,2	0,126	0,026

### RESULTS

On the ground of the carried out potentiodynamic tests it was determined that corrosion potential for non-deformed guide wires established at  $E_{corr} = -73$  mV – Fig. 2a. Polarisation brought about rapid increase of anodic current intensity at the potential  $E_b = +760$  mV – Fig. 2a and 3. When the value of anodic current reached 1 mA/cm<sup>2</sup>, the direction of samples polarisation was changed, which enabled to register the return curve. Anodic polarisation curve, registered in such a way, featured the presence of hysteresis loop which proved the presence of pitting corrosion. Moreover, on the ground of Stern method, polarisation resistance and corrosion current density were determined, and they were  $R_p = 69,5$  kΩcm<sup>2</sup> and  $i_{corr} = 0,374$  μA/cm<sup>2</sup> respectively – tab. 2.

Table 2. Results of corrosion resistance

Bend angle $\alpha$ , °	$E_{OCP}$ , mV	$E_{corr}$ , mV	$R_p$ , kΩcm <sup>2</sup>	$i_{corr}$ , μA/cm <sup>2</sup>	$E_b$ , mV
0	-95	-73	69,5	0,374	+760
30	-102	-108	84,2	0,309	+725
60	-117	-24	95,5	0,272	+562
90	-129	-81	67,9	0,383	+517
120	-144	-68	76,2	0,341	+403
150	-148	-65	77,2	0,337	+380

Next, samples were analysed after application of strain at the angle of  $\alpha$ : 30°, 60°, 90°, 120° and 150°, respectively. Corrosion potential fell in the range of  $E_{corr} = -108 \div -24$  mV – Fig. 2b-2f, whereas values of breakdown potential were smaller than the values obtained for non-deformed guide wires and fell within the range of  $E_b = +380 \div +725$  mV – Fig. 2b-2f and 3. Next, values of polarisation resistance and corrosion current density were differentiated depending on bend angle. These values are, respectively, in the range for  $R_p = 67,9 \div 95,5$  kΩcm<sup>2</sup>,  $i_{corr} = 0,272 \div 0,383$  μA/cm<sup>2</sup> – tab. 2.

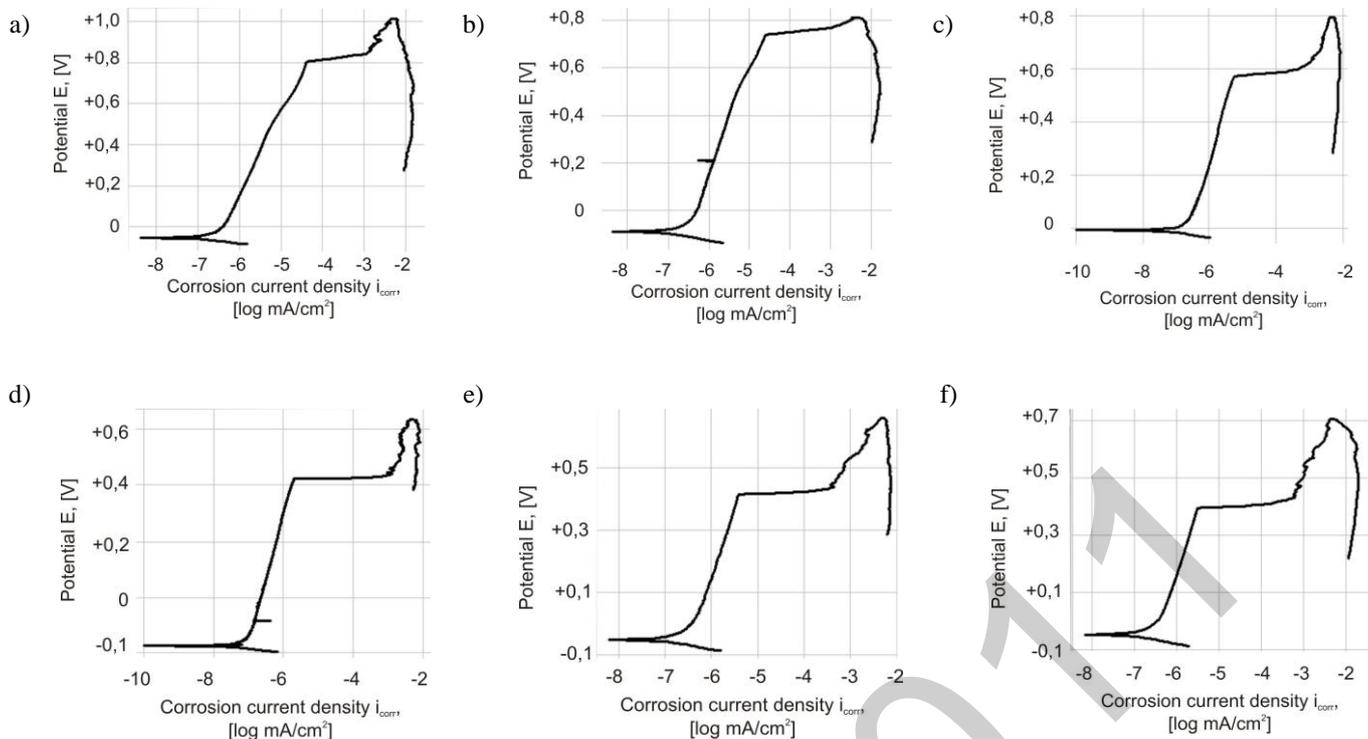


Fig. 2. Anodic polarisation curves determined for guide wire with bend angle:  
 a)  $\alpha = 0^\circ$ , b)  $\alpha = 30^\circ$ , c)  $\alpha = 60^\circ$ , d)  $\alpha = 90^\circ$ , e)  $\alpha = 120^\circ$ , f)  $\alpha = 150^\circ$

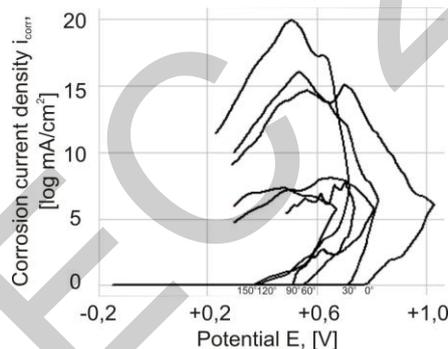


Fig. 3. Value of perforation potential for the angle of guide wire bending angle:  
 a)  $\alpha = 0^\circ$ , b)  $\alpha = 30^\circ$ , c)  $\alpha = 60^\circ$ , d)  $\alpha = 90^\circ$ , e)  $\alpha = 120^\circ$ , f)  $\alpha = 150^\circ$

## CONCLUSIONS

Modern society experiences increasing blood and vascular system diseases morbidity rate, including bradyarrhythmia. Therefore implantation of cardiological pacemakers cardioverters – defibrillator is becoming more and more popular every year. Pacemaker is a device used for electrical stimulation of heart rate. It is used when sinuatrial node, as the result of various diseased, ceases to serve its purpose, which leads to bradycardia and in turn it may lead to the symptoms of brain ischaemia or heart failure. Other reason for implantations are also atrioventricular blocks (lat. dissociatio atrioventricularis) (so called heart blocks).

Popularity of heart electrotherapy leads directly to the increase of patients who undergo such treatment. Success of electrotherapy depends on a range of factors, and one of them is proper selection of instruments and auxiliary materials. Of crucial importance for proper realisation of cardiological pacemaker implantation are guide wires whose purpose is to insert endocavitary electrodes. Tests regarding guide wires manufacturing technology are carried out in order to obtain products with proper performance characteristics, including also their improved biocompatibility.

Potentiodynamic tests carried out in artificial blood plasma were the source of information about corrosion resistance of guide wires with diversified bend angle. It was estimated that increase of strain decreases the value of perforation potential  $E_b$  by ca. 400 mV, that is an unfavourable phenomenon – Fig. 3. Registered values of corrosion potential, current density or polarisation resistance were not much different for deformed and non-deformed guide wires.

Presence of pits, which were probably created as the result of passive layer perforation in the area of the biggest stress located on the external side of the bend, was found on the surface of the wire after corrosion tests. Therefore, it is believed that production engineers should focus their work on modification of guide wires surface in order to increase their resistance to

electrochemical corrosion. Creation of suitable protective layers would enable to eliminate unfavourable phenomena in the blood and vascular system and substantial improvement of biocompatibility of used steel wires.

#### ACKNOWLEDGMENTS

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## CELECOXIB DERIVATIVES AS POSSIBLE ANTIINFLAMMATORY, ANTICANCER AND ANTI-HCV AGENTS

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**Keywords:** Hepatitis C virus NS5B, Celecoxib, Sulfonylthiourea, Sulfonyliminothiazolidinone, Anticancer activity, Antiinflammatory activity

### ABSTRACT

A series of novel *N*-(3-substituted aryl/alkyl-4-oxo-1,3-thiazolidin-2-ylidene)-4-[5-(4-methylphenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl]benzenesulfonamides [**2a-e**] have been synthesized by the addition of ethyl  $\alpha$ -bromoacetate and anhydrous sodium acetate in dry ethanol to *N*-(substituted aryl/alkyl carbamothioyl)-4-[5-(4-methylphenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl]benzenesulfonamides [**1a-e**], which was synthesized by the reaction alkyl/aryl isothiocyanates with celecoxib. The structures of the isolated products were determined by the spectral methods and evaluated for anti-Hepatitis C virus (HCV) NS5B RNA dependent RNA polymerase (RdRp) activity, analgesic and anti-inflammatory activities. In addition, the selected compound [**1a**] was screened by the National Institutes of Health (NIH) for anticancer activity against 60 human tumor cell lines.

### INTRODUCTION

COX-2 is the key inducible enzyme in the conversion of arachidonic acid into prostaglandins (Dubois et al., 1998) and is elevated in a number of human cancers (Aoki et al., 2002, Fujiwaki et al., 2002, Gupta et al., 2001, Kulkarni et al., 2001, Kirkpatrick et al., 2002). Celecoxib, a selective COX-2 inhibitor, is currently Food and Drug Administration-approved for chemoprevention in familial adenomatous polyposis based on demonstrable inhibition of colon polyp formation, further solidifying the use of this agent in cancer therapy (Steinbach et al., 2000). Celecoxib is a COX-2 class anti-inflammatory agent with little or no gastric side effects. Pyrazole compounds such as celecoxib are known to possess anti-HCV and anti-inflammatory properties (Rostom et al., 2003, Riyadh et al., 2010, Bekhit et al., 2005). Previous studies have reported that sulfonylthioureas and 4-thiazolidinones possess antibacterial, anticonvulsant, anti-inflammatory, anticancer and antidiabetic activities (Masereel et al., 1997, Englert et al., 2001, Rostom, 2006). Sulfonylthioureas and 4-thiazolidinones synthesized in our laboratory have also exhibited the aforementioned. This observation

motivated us design and synthesize potent new compounds. In the current study, new sulfonylthiourea derivatives [**1a-e**] were prepared starting from celecoxib. In the second part, sulfonyliminothiazolidinone [**2a-e**] derivatives were synthesized by the reaction of ethyl  $\alpha$ -bromoacetate and anhydrous sodium acetate in dry ethanol with the sulfonylthioureas [**1a-e**]. Some of the compounds were obtained by the microwave assisted synthesis method, also known as Green Chemistry. After purities of the synthesized compounds were evaluated by Thin layer chromatography (TLC), the structures of the compounds were confirmed by elemental analysis and spectral (UV, IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , HR-MS) data.

The effect of the compounds on the enzymatic activity of the HCV NS5B polymerase were investigated in the Department of Biochemistry and Molecular Biology of New Jersey Medical School-UMDNJ. Analgesic and anti-inflammatory activities, gastric ulcerogenic studies and lipid peroxidation tests of the compounds were evaluated in the Department of Pharmacology at Inonu University. The anticancer activity of the selected compound [**1a**] was elucidated at the NIH.

## EXPERIMENTAL

### CHEMISTRY



#### *Synthesis of N-(substituted aryl/alkyl carbamothioyl)-4-[5-(4-methylphenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl]benzenesulfonamides [1a-e]*

A solution of the appropriate isothiocyanate (0.00275 mol) in dry acetone (5 mL) was added to a stirred mixture of the Celecoxib (0.0025 mol) and anhydrous potassium carbonate (0.005 mol) in dry acetone (20 mL), and the reaction mixture was heated under reflux for 20-25 h. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the reaction mixture was dissolved in water and acidified with hydrochloric acid (2 N). The resulting precipitates were filtered, dried and recrystallized.

#### *Synthesis of N-(3-substituted aryl/alkyl-4-oxo-1,3-thiazolidin-2-ylidene)-4-[5-(4-methylphenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl]benzenesulfonamides [2a-e]*

##### **Method I (thermal)**

Ethyl  $\alpha$ -bromoacetate (0.0011 mol) and anhydrous sodium acetate (0.002 mol) were added to a solution of the appropriate sulfonylthiourea derivative **1a-e** (0.001 mol) in absolute ethanol (20 mL) and the reaction mixture was heated under reflux for 2-4 h. The precipitated solid was collected and recrystallized.

**Method II (microwave for 2d and 2e)**

A mixture of the appropriate sulfonylthiourea derivative **1a-e** (0.001 mol) in absolute ethanol (20 mL), ethyl  $\alpha$ -bromoacetate (0.0011 mol) and anhydrous sodium acetate (0.002 mol) was placed in the microwave oven and irradiated at 270 W for 10-15 min. The reaction mixture was left to cool to room temperature. The precipitated solid was collected and recrystallized.

**PHARMACOLOGY****Effect on HCV NS5B polymerase enzyme inhibition**

The ability of the compounds to inhibit HCV NS5B RdRp activity was investigated *in vitro* by poly(A)-U12 extension assays described in experimental section (Kaushik-Basu et al., 2008). The compounds **1a-e** and **2a-e** were reconstituted in DMSO as 50 mM stocks, and serially diluted in DMSO to obtain working stocks.

Wedelolactone, a known inhibitor of HCV NS5B activity (Kaushik-Basu et al., 2008), was used as a positive control *in vitro*. Preliminary screening was carried out at 100  $\mu$ M to identify a wider range of compounds. Celecoxib, the parent molecule, included in this investigation for comparison with its derivatives, exhibited the lowest activity against NS5B of ~10%. All other compounds except **2a** and **2e** exhibited varying degrees of inhibition ranging from ~19% to 83% at 100  $\mu$ M concentration (Table 1). Of these, compounds **1c** and **1d** were the most active, with  $IC_{50}$  values of 36  $\mu$ M and 45  $\mu$ M.

**Table 1:** Effect of the compounds on HCV NS5B RdRp activity *in vitro*.

Compound	Ar/R	Anti-NS5B Activity (% Inhibition, 100 $\mu$ M)	$IC_{50}$ ( $\mu$ M)
<b>1a</b>	Ethyl	49.4	36.2 $\pm$ 1.2 45.5 $\pm$ 1.2
<b>1b</b>	Phenyl	53.5	
<b>1c</b>	Benzyl	82.3	
<b>1d</b>	4-nitrophenyl	68	
<b>1e</b>	4-trifluoromethylphenyl	14.6	
<b>2a</b>	Ethyl	8.2	
<b>2c</b>	Benzyl	19.4	
<b>2d</b>	4-nitrophenyl	31.3	
<b>2e</b>	4-trifluoromethylphenyl	9.4	
<b>Celecoxib</b>		9.5	

**Anti-inflammatory activity**

Pharmacological investigations conducted in the present study included assessment of anti-inflammatory and analgesic activities as well as the ulcerogenic risk and antioxidant activity upon acute administration. To determine the anti-inflammatory profile of the synthesized compounds, the carrageenan-induced hind paw edema model in mice was used (Koster et al., 1959).

The analgesic activity of the compounds was studied employing the acetic acid-induced writhing test in mice (Kasahara et al., 1985). In both screening tests, 100 mg/kg (body weight) doses of the test drugs were orally administered to the animals, as a first step. All compounds exhibiting  $\geq 15\%$  effectiveness in relieving symptoms, were considered for further evaluation, and the experiments were repeated at two different dose levels (50 and 200 mg/kg) (Tables 2 and 3).

Procedures involving animals and their care were conducted in conformity with international laws and policies and animal studies accepted by Inonu University Ethical Council (2011/A17). All compounds screened for ulcerogenic activity were also analyzed for lipid peroxidation (LPO) by the method of Ohkawa et al. (1979) as modified by Jamall and Smith (1985).

**Table 2.** Analgesic effects of the test compounds at a 100 mg/kg dose, against acetic acid-induced abdominal constriction test, ulcer score and the lipid peroxidation levels in stomach of mice.

Compounds	Writhing test Mean $\pm$ SEM (% inh.)	Ulcer score (200mg/kg)	Lipid peroxidation (nmol TBARS /g wet weight)
Control	17.4 $\pm$ 3.7	0/5	387.7 $\pm$ 27.9
Celecoxib (25 mg/kg)	8.0 $\pm$ 1.3 (54) *	0/5	417.8 $\pm$ 23.3
ASA (200 mg/kg)	4.4 $\pm$ 0.9 (74.7) **	3/5	436.1 $\pm$ 17.1
1a	5.6 $\pm$ 0.9 (67.8) **	0/5	387.7 $\pm$ 12.8
1d	14.0 $\pm$ 3.0 (19.5)	0/5	429.2 $\pm$ 23.2
1e	24.0 $\pm$ 3.0 (-37.9)	0/5	406.9 $\pm$ 27.0
2c	11.8 $\pm$ 1.4 (32.2)	0/5	330.4 $\pm$ 9.7
2d	12.0 $\pm$ 2.6 (31)	0/5	350.2 $\pm$ 9.9

### Evaluation of anticancer activity in vitro

Primary anticancer assays were performed according to the US NCI protocol as described elsewhere (Holbeck, 2004). Briefly, effect of the compounds on the growth parameters of the different cancer cell lines was evaluated relative to equivalent amounts of DMSO treated controls and expressed as percent growth. Cellular cytotoxicity was evaluated under identical conditions to rule out inhibition of cell growth as a consequence of compound toxicity. The cells were treated with the compounds at concentration of  $10^{-5}$  M for 48 h. Compound **1a** inhibited the growth of HOP-92 cells by  $\sim 20.78\%$ . Lung cancer cells NCI-H322M and melanoma Malm-3M cells exhibited significant cytotoxicity.

**Table 3.** Dose-dependent anti-inflammatory effects of the compounds against carrageenan-induced hind paw edema model in mice at different doses

Compounds	Dose mg/kg (per os)	Swelling in thickness ( $\times 10^{-2}$ mm) $\pm$ SEM (percent inhibitory activity)			
		90 min	180 min	270 min	360 min
Control		72.0 $\pm$ 6.6	92.0 $\pm$ 8.1	121.0 $\pm$ 9.8	129.0 $\pm$ 7.8
Celecoxib 25 mg/kg		57.0 $\pm$ 6.9 (20.8)	42.0 $\pm$ 3.3** (54.3)	94.0 $\pm$ 10.4 (22,3)	103.0 $\pm$ 7.5 * (20,1)
1a	100mg/kg (n=3)	58.1 $\pm$ 6.6 (19,4) 70.0 $\pm$ 6.5	72.9 $\pm$ 11.9 (19,7) 72.0 $\pm$ 5.1	72.7 $\pm$ 16.7 (39,5) 90.0 $\pm$ 9.3 *	77.9 $\pm$ 11.7 ** (39,7) 100.0 $\pm$ 6.5 *
	50 mg/kg (n=5)	54.6 $\pm$ 7.9 (25.0)	74.2 $\pm$ 8.2 (19,3)	117.5 $\pm$ 9.8	97.4 $\pm$ 5.6 ** (24,5)
1d	200mg/kg (n=5)	95.9 $\pm$ 10.2 70.0 $\pm$ 4.7 45.9 $\pm$ 10.9 (36.2)	100.6 $\pm$ 5.8 (18,3) 77.0 $\pm$ 2.0 (16,3) 65.3 $\pm$ 6.4 (29.0)	110.7 $\pm$ 11.0 112.0 $\pm$ 7.3 98.2 $\pm$ 9.8 (19.0)	88.7 $\pm$ 9.3 * (31,2) 125.0 $\pm$ 5.9 91.0 $\pm$ 3.3 ** (29,5)
		88.4 $\pm$ 2.6 47.0 $\pm$ 3.3 * (34,7) 76.9 $\pm$ 5.7	83.9 $\pm$ 3.4 57.0 $\pm$ 6.2 ** (38,0) 83.0 $\pm$ 6.8	88.7 $\pm$ 11.4 (26,7) 92.0 $\pm$ 1.2 * (23,9) 110.5 $\pm$ 7.5	83.4 $\pm$ 9.6 ** (35,4) 106.0 $\pm$ 6.7 (17,8) 103.7 $\pm$ 5.2 * (19,6)
2c		83.4 $\pm$ 8.7 65.0 $\pm$ 6.1 69.5 $\pm$ 8.3	90.6 $\pm$ 11.7 74.0 $\pm$ 8.8 (19,5) 75.6 $\pm$ 8.3 (17,8)	91.7 $\pm$ 16.7 (24,2) 95.0 $\pm$ 10.0 (21,4) 133.2 $\pm$ 14.3	118.2 $\pm$ 7.1 10.0 $\pm$ 7.1 120.1 $\pm$ 5.3
		73.2 $\pm$ 11.1 47.0 $\pm$ 3.3 * (34,7) 80.6 $\pm$ 9.4	100.6 $\pm$ 5.8 47.0 $\pm$ 3.7 ** (48,9) 86.0 $\pm$ 9.4	98.2 $\pm$ 16.7 (21,6) 89.0 $\pm$ 6.5 * (26,4) 121.0 $\pm$ 12.8	120.9 $\pm$ 9.3 110.0 $\pm$ 6.7 108.6 $\pm$ 5.6
2d					

### CONCLUSION

In this study, we have identified compound **1c** as a promising anti-HCV NS5B inhibitor. Sulfonylthiourea derivatives were found to be more potent than sulfonyliminothiazolidinones, while celecoxib, the parent compound was the least active of all compounds examined in this investigation. All the four selected compounds (**1a**, **1d**, **1e**, **2d**) produced a higher inhibition of oedema formation in the carrageenan-induced rat paw oedema. The anti-inflammatory activity of celecoxib derivatives is in the range of 19.4 to 36.2 % for 90

min. It was observed that **1a** exhibited potent analgesic activity in comparison to standart drug ASA (acetylsalicylic acid). All tested compounds showed significant reduction in ulserogenic activity (0/5), whereas the standart drug ASA showed high severity index (3/5). In conclusion **1a** showed negligible cell growth inhibition at  $10^{-5}$  M concentration against variety of cell lines.

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## ENHANCED VINDOLINE PRODUCTION IN *CATHARANTHUS ROSEUS* YOUNG SHOOTS CULTURES BY SALT STRESS

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### Abstract

The Madagascar periwinkle (*Catharanthus roseus*) produces pharmaceutically valuable monoterpenoid indole alkaloids. This plant is the only commercial source of the antitumor dimeric alkaloids, vinblastine and vincristine, which are formed by the condensation of catharanthine and vindoline subunits. The high economic value of this alkaloids, along with the low amounts recovered from *Catharanthus* plants, has prompted significant efforts to produce them through cell culture technology. However, undifferentiated cultures has shown the inability to produce vindoline, in vitro shoot cultures have been proposed to overcome this hurdle. The aim of the present work is to enhance vindoline synthesis by application of salt stress (NaCl) as elicitor.

The sodium chloride (NaCl) is used to treat young shoot cultures with various concentration and contact times. Shoot exposure to salt stress shortened the time required for the maximal vindoline accumulation to 16 d. The production of vindoline was increased by 2g/l of NaCl to 1.2 and 0.973 mg/g DW respectively with contact times of 10 hours and 24 hours by 2g/l of NaCl. This production was about 2 fold higher than control with contact times of 10 hours.

**Key words:** *Catharanthus roseus*, elicitation, indole alkaloids, shoot cultures, Sodium chloride, vindoline

# GROWTH PERFORMANCE OF JAPANESE QUAIL USING TREATED ENTEROMORPHA MEAL IN DIETS

By

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## Abstract:

We have about 10 years experience in using seaweeds for poultry diets in different ways and by different methods. This study could be a contribution to our program.

Enteromorpha is one of the most common seaweed growing on the Egyptian Mediterranean coasts. About 5 species of this genus grow abundantly on hard substrates.

They contain high fiber contents as well as suitable wide range of nutritional compounds and essential elements.

The Japanese quail comes as one of the promising poultry industry in Egypt.

This study aimed to evaluate the different methods of treatments on the nutritional value of Enteromorpha meal given to the Japanese quail.

The duration of growing period lasted 5 weeks of age (7-42 day) by using one day old Japanese quail chicks hatched in poultry research station.

A total number of 600 unsexed 7day old Japanese quail were separated into 5 groups, each group, 120 birds had been classified in 3 replicate of 40 birds. Four groups were fed on 10% of Enteromorpha in the meal. One was untreated while 3 treated with freezing, boiling and acetic acid methods. The last group was fed by 100% normal growing diets as control group.

Results have demonstrated the effects of Enteromorpha treatment in diets on growth performance of the Japanese quail.

Japanese quail which fed by treated Enteromorpha with acetic acid during all experimental periods were recorded significantly as the highest live body weight (LBW) and the best feed conversion ratio compared to either other treatments or control.

In conclusion we can recommend the addition of the treated wide spread seaweed, Enteromorpha to the diet of poultry in Egypt.

**Key words:** Seaweeds ,Enteromorpha, Japanese quail, growth performance, feed intake

## INTRODUCTION

The use of Seaweeds have been expanded since ancient times as food, fodder and fertilizer and as sources of medicinal drugs, they continue to be widely consumed as food in Asian countries (Mishra *et al.*, 1993). In particular, certain edible seaweeds contain significant quantities of lipids, protein, vitamins and minerals (Norziah & Ching, 2000; Sanchez- Machado *et al.*, 2002)

There is, therefore, interest in the use of edible seaweeds in the development of low-cost, highly nutritive diets for human and animal nutrition, especially animal nutrition since sea vegetables are able to accelerate the growth of some species such as big oysters, tilapia, salmon, trout, etc., all of great commercial interest (Fleming *et al.*, 1996; Hahn, 1989).

In some green seaweeds such as the species belonging to the genus *Ulva* and *Enteromorpha* the protein content can represent between 10 and 26% of dry weight of the plant. According to Lahaye and Jegou (1993), *Ulva lactuca* contained 15.8 and 8.0% soluble fibers, respectively, and 24.2 and 32.6% insoluble. For *Enteromorpha compressa* these values were 14.9 and 15.9%, and 21.6 and 28.7%, respectively. For both algae, soluble fibers appeared to be xylorhamnoglycuronan sulfates and insoluble fibers were essentially composed of glucans. Fibers in both algae were hydrophilic but the water-holding capacities were higher after extraction of soluble fibers. Water-soluble fibers, particularly those from *E. compressa*, demonstrated low intrinsic viscosities at 37°C in buffers and were affected by pH The higher protein contents are recorded in green and red seaweeds (on average 10-30 % of the dry weight).

Haroon A. M. *et al.* (2000) found that the lipid content in *Enteromorpha spp.*, was low and varied slightly from 3.47±1.76% of DW to 4.36± 2.17% of DW at. The protein content varied from 9.42±4.62% of DW at to 20.60±5.00% of DW.. The level of carbohydrate was very high compared to that of lipid and protein and varied from 29.09± 6.44% of DW to 39.81± 11.15% of DW. The presence of cell wall polysaccharides limits the efficiency of classical procedures of protein extraction (Jordan & Vilter, 1991). The degradation of cell wall polysaccharides by enzymes is a procedure frequently used for protoplast production (Cachot *et al.*, 1994). On the other hand, El-Khimsawy *et al.* (2006) improved the protein extraction from *Ulva sp.* and *Geledeum sp.* by acetic acid, sodium hydroxide and enzymes treatments.

The aim of this research was investigating the effect of treated *Enteromorpha* meal on the Japanese quail diets and also, the effect of these treatments on growth performance.

## MATERIALS AND METHODS

### Collection samples of *Enteromorpha* spp and Analytical methods.

Samples of *Enteromorpha* spp. were collected freshly from the coast of Mediterranean Sea of Alexandria. Seaweeds were washed using tap water several times in order to get rid of associated salts and sand. The test material was dried at 60°C for 72 h in across flow drier, then grinded and kept in bags until being analyses and used in the preparation of the experimental diets.

The moisture level, crude protein, crude fiber, ether extract and ash contents were determined for each sample according procedures outlined by Association of Official Analytical Chemists (A.O.A.C, 1995).

### Physical and chemical treatments procedures.

Each treatment was performed on 3 replicates of 100 g, of algal powder.

**Untreated *Enteromorpha* (T1):** *Enteromorpha* powder was added to Japanese quail diets without treatment.

**Treating *Enteromorpha* by Freezing (T2):** Dried algal powder was immersed in 1000 ml distilled water in an Erlenmeyer flask and freezed at -20°C for 24h and then dried again at 60°C for 24 h.

**Treating *Enteromorpha* by Boiling (T3):** Dried algal powder was immersed in 1000 ml distilled water in an Erlenmeyer flask and heated at 100°C for 2h then dried again at 60°C for 24 h.

**Treating *Enteromorpha* by acetic acid(T4):** Dried algal powder was immersed to 1000ml of 1% acetic acid solution (v/v) in an Erlenmeyer flask and heated at 120°C for 2 h in an autoclave then it was dried at 60°C for 24 h.

### Growth trial:

Experimental work was conducted at a poultry experimental station, Faculty of Agriculture, Al-Azhar University, Nasr City, Cairo, Egypt during 2011.

The duration of growing period was 5 weeks (7-42 day) by using initially one day old Japanese quail chicks hatched in poultry research station.

A total number of 600 unsexed 7day old Japanese quail were distribution into 5 groups, each 120 birds (3 replicate each 40 birds). Four groups were fed on 10% of *Enteromorpha* in the meal. One was untreated while 3 treated with freezing, boiling and acetic acid methods. The last group was fed by 100% normal growing diet as control group. All diets were isocaloric isonitrogenous containing 23% CP and 2900 kcal. ME/Kg diet according to NRC, 1994. Food and water provided for birds freely.

### Experimental diets

Chemical composition of treated *Enteromorpha* spp. is showed in Table (1).

Table (1): Chemical composition and digested nutrients in *Enteromorpha* spp. with or without tested treatments.

Treatment	CP %			EE %			NFE %			CF %	ASH %	ME k.cal/kg
	%	D.C.* %	D.CP%	%	D.C.* %	D.EE%	%	D.C.* %	D.NFE%			
Untreated (T <sub>1</sub> )	21.76	8.97	1.95	4.66	25.76	1.20	22.86	25.47	5.82	30.43	18.58	419
Freezing (T <sub>2</sub> )	21.82	48.22	10.52	4.62	58.38	2.70	24.49	80.59	19.74	30.51	18.56	1453
Boiling (T <sub>3</sub> )	21.72	52.09	11.31	4.59	64.55	2.96	26.03	82.82	21.56	29.07	18.59	1582
Acetic acid (T <sub>4</sub> )	21.09	57.88	12.21	4.48	60.68	2.72	36.89	83.29	30.73	15.71	21.83	1962

CP= Crud Protein, EE= Ether Extraction, NFE= Nitrogen Free Extraction, CF= Crud Fiber. D.C = Digestion coefficient.

ME= metabolically energy was calculated according to Harper *et al*, (1977) as following equation:

$$ME \text{ (kcal/kg diets)} = [(D.NFE*4)+(D.CF*4)+(D.CP*4)+(D.EE*9)]*10$$

- El-Khimsew *et al*, (2006)

### Collecting data and measurements of growth performance

**Body Weight (BW) and Body Weight Gain (BWG):** Chicks of Japanese quail were individually weighted at the start of experiment (at 7 day old) to nearest gram in each of group, and the weight repeated every week in early morning before receiving any feed or water till the end of experimental growing period (6<sup>th</sup> weeks of age). Live body weights (LBW) for each group were totaled and divide on the number of chick to obtain the average live body weight. Also, gain in weight was calculated by subtracting the average final live body at the beginning and the end of each week of age.

**Feed intake (FI):** Feed were provided for each group alone by satisfied amount, and the residual feed was weekly collected, weighted and subtracted from offered one to obtain feed intake.

Table(2): Composition of experimental diets of Japanese quail.

Ingredients	(T <sub>1</sub> ) 10%	(T <sub>2</sub> ) 10%	(T <sub>3</sub> ) 10%	(T <sub>4</sub> ) 10%	Control
Yellow corn, ground	54	54.5	54.5	55	59
Corn Gluten, 60%	10	8	8	8	3
Soybean meal, 44%	13	16	16	16	27
Broiler concentrates,52%*	10	10	10	10	10
Vitamins**	0.20	0.20	0.20	0.20	0.20
Minerals***	0.20	0.20	0.20	0.20	0.20
NaCl	0.10	0.10	0.10	0.10	0.10
Vegetable oil	2	0.5	0.5	0	0
Limestone	0.5	0.5	0.5	0.5	0.50
Untreated (T <sub>1</sub> )	10	0	0	0	0
Freezing (T <sub>2</sub> )	0	10	0	0	0
Boiling (T <sub>3</sub> )	0	0	10	0	0
Acetic acid (T <sub>4</sub> )	0	0	0	10	0
Total (Kg)	100	100	100	100	100
Crud Protein %	24.07	24.07	24.06	24.04	24.02
M.E Kcal/ Kg	2904	2897	2908	2920	2925
Calcium	0.84	0.85	0.85	0.85	0.8
Nonphytat phosphorus	0.47	0.47	0.47	0.47	0.49
Lysine	1.32	1.38	1.38	1.38	1.26
Methionine + cystine	1.19	1.18	1.18	1.17	0.76

\*Concentrate analysis: 52% CP, 2400 ME kcal/kg, 2.0% EE, 3.0% CF, 7.1% Ca and 3.7% P, 1.6% Methionine + Cystine, 3.0% Lysine.

\*\*Each kg contained: VA 6000000 IU, VD<sub>3</sub> 1250000 IU, VE 15000 mg, VB<sub>1</sub> 1000 mg, VB<sub>6</sub> 1000 mg, VB<sub>12</sub> 6 mg, Nicotinic acid 15000 mg, Pantothenic acid 5000 mg, Biotin 50 mg, Folic acid 500 mg and choline chloride 50% 400 mg.

\*\*\*Each kg contained: Mn 35 mg, Fe 40 mg, Cu 3.5 mg, Zn 25 mg, Iodine 0.25 mg, Selenium 0.075 mg, Cobalt 0.10 mg, CaCO<sub>3</sub> 1000 mg.

**Feed conversion ratio (FCR):** FCR was measured as the amount of feed consumed per unit of weight gain. Feed conversion ratio was calculated by using the following formula.

$$\text{Feed conversion ratio} = \text{Total feed intake (g)} / \text{Weight gain (g)}.$$

## RESULTS

**Body weight:** Results indicated Enteromorpha addition in diets, averages of body weight of Japanese quail as shown in Table (3) affected by treatment methods of Enteromorpha. Japanese quail which fed treated Enteromorpha with acetic acid (T<sub>4</sub>) during all experimental periods were recorded significantly the highest LBW compared to either other treatment or control with except, at 2<sup>nd</sup> week the difference between (T<sub>4</sub>) and (T<sub>3</sub>) was insignificant. Birds fed untreated Enteromorpha recorded significantly the lowest LBW compared to either other treated or control.

As shown in Table (3) birds fed freezing (T<sub>2</sub>) recorded significantly lower (LBW) compared to control during all experimental periods.

Table (3): Effect of treated Enteromorpha addition in diets on body weight (BW)

Treatments	Age of Japanese quail birds/ weeks					
	W <sub>1</sub>	W <sub>2</sub>	W <sub>3</sub>	W <sub>4</sub>	W <sub>5</sub>	W <sub>6</sub>
T <sub>1</sub> (Untreated)	20.33 <sup>A</sup>	36.49 <sup>D</sup>	70.03 <sup>E</sup>	97.13 <sup>D</sup>	127.33 <sup>E</sup>	148.09 <sup>E</sup>
T <sub>2</sub> (Freezing)	20.41 <sup>A</sup>	39.09 <sup>C</sup>	77.71 <sup>D</sup>	106.03 <sup>C</sup>	138.02 <sup>D</sup>	163.71 <sup>D</sup>
T <sub>3</sub> (Boiling)	20.39 <sup>A</sup>	45.05 <sup>A</sup>	88.54 <sup>B</sup>	122.27 <sup>B</sup>	165.66 <sup>B</sup>	195.06 <sup>B</sup>
T <sub>4</sub> (Acetic acid)	20.44 <sup>A</sup>	45.78 <sup>A</sup>	92.28 <sup>A</sup>	130.11 <sup>A</sup>	175.54 <sup>A</sup>	207.08 <sup>A</sup>
Control	20.47 <sup>A</sup>	43.02 <sup>B</sup>	85.45 <sup>C</sup>	120.77 <sup>B</sup>	161.89 <sup>BC</sup>	190.34 <sup>C</sup>

**Feed intake:** Results indicated the averages of feed intake of Japanese quail as shown in Table (4) as affected by treatment methods on Enteromorpha. The results indicated that there were significant differences among treatment methods of Enteromorpha of feed intake at all weeks during experiment.

At the 2<sup>nd</sup> and 3<sup>rd</sup> week of age, data in Table (4) show that tested treatment is not significantly affected feed intake, but untreated Enteromorpha and treatments by Acetic acid (T<sub>4</sub>) significantly decreased feed intake at 2<sup>nd</sup> and 3<sup>rd</sup> week. At the 4<sup>th</sup> week, untreated Enteromorpha (T<sub>1</sub>) detected significantly the highest feed intake than either control or other treatments with significant difference between them. While treatments by Acetic acid (T<sub>4</sub>) and control detected significantly the lowest feed intake compared to other treatments, with insignificant difference between them.

At 5<sup>th</sup> week, untreated Enteromorpha detected significantly highest feed intake compared to control. Boiling (T<sub>3</sub>) treatment recorded significantly less feed intake than control. Freezing (T<sub>2</sub>) and acetic acid (T<sub>4</sub>) treatments were not affected feed intake compared to control.

At 6<sup>th</sup> week, there were insignificant effect of Enteromorpha treatments by acetic acid (T<sub>4</sub>) and boiling (T<sub>3</sub>) on feed intake compared to control, while treatments of freezing (T<sub>2</sub>) Enteromorpha detected significantly less feed intake than control. On the other hand untreated Enteromorpha detected significantly highest feed intake compared to control.

Table (4): Effect of treated Enteromorpha addition in diets on feed intake (FI)

Treatments	Age of Japanese quail birds/ weeks				
	W <sub>2</sub>	W <sub>3</sub>	W <sub>4</sub>	W <sub>5</sub>	W <sub>6</sub>
T <sub>1</sub> (Untreated)	35.1 <sup>B</sup>	93.27 <sup>AB</sup>	144.08 <sup>A</sup>	129.91 <sup>A</sup>	160.91 <sup>A</sup>
T <sub>2</sub> (Freezing)	43.43 <sup>A</sup>	95.97 <sup>A</sup>	115.72 <sup>B</sup>	115.14 <sup>B</sup>	144.33 <sup>C</sup>
T <sub>3</sub> (Boiling)	45.22 <sup>A</sup>	88.55 <sup>B</sup>	101.17 <sup>C</sup>	110.95 <sup>C</sup>	153.71 <sup>B</sup>
T <sub>4</sub> (Acetic acid)	43.71 <sup>A</sup>	87.11 <sup>AB</sup>	85.8 <sup>D</sup>	115.33 <sup>B</sup>	151.86 <sup>B</sup>
Control	44.95 <sup>A</sup>	91.19 <sup>AB</sup>	86.29 <sup>D</sup>	117.49 <sup>B</sup>	154.77 <sup>B</sup>

**Feed conversion ratio:** Results indicated in Table (5) revealed that averages of feed conversion ratio of Japanese quail from the second week up to 6<sup>th</sup> week of age, and the results the results indicated that at the all weeks of age birds fed treated Enteromorpha by acetic acid (T<sub>4</sub>) was detected significantly best feed conversion ratio compared to control, with except, at 2<sup>nd</sup> and 6<sup>th</sup> week the effect of treatment was insignificant. During the first tow weeks of experimental feed conversion ratio was not significantly affected by boiling treated Enteromorpha (T<sub>3</sub>), while during the last three weeks it were significant worse affected. On the other hand, untreated Enteromorpha and that treated by freezing recorded significant worsen feed conversion ratio compared control.

Table (5): Effect of treated Enteromorpha addition in diets on feed conversion ratio (FCR)

Treatments	Age of Japanese quail birds/ weeks				
	W <sub>2</sub>	W <sub>3</sub>	W <sub>4</sub>	W <sub>5</sub>	W <sub>6</sub>
T <sub>1</sub> (Untreated)	2.17 <sup>B</sup>	2.78 <sup>A</sup>	3.51 <sup>A</sup>	4.30 <sup>A</sup>	7.75 <sup>A</sup>
T <sub>2</sub> (Freezing)	2.32 <sup>A</sup>	2.48 <sup>B</sup>	3.21 <sup>B</sup>	3.59 <sup>B</sup>	5.62 <sup>B</sup>
T <sub>3</sub> (Boiling)	1.83 <sup>D</sup>	2.04 <sup>CD</sup>	2.57 <sup>C</sup>	2.56 <sup>D</sup>	5.23 <sup>D</sup>
T <sub>4</sub> (Acetic acid)	1.72 <sup>DE</sup>	1.87 <sup>E</sup>	2.19 <sup>E</sup>	2.53 <sup>D</sup>	4.81 <sup>E</sup>
Control	1.99 <sup>C</sup>	2.15 <sup>C</sup>	2.47 <sup>CD</sup>	2.84 <sup>C</sup>	5.47 <sup>C</sup>

**General conclusion of effect of treatments and levels of Enteromorpha on growth performance of Japanese quail:** Results detected in Table (6) showed the effect of treatment method of Enteromorpha on performance parameters of growing Japanese quail indicated that averages of total final body weight ranged between (148.09 g) for group T<sub>1</sub> and (207.08 g) for group T<sub>4</sub> with significant differences among the other treatment groups. Birds fed algae treated by acetic acid (T<sub>4</sub>) detected final live body weight (LBW) significantly higher than control; while other tested treatments detected final live body weight (LBW) significantly lower than control.

Also results indicated that the group of quail which fed on diet containing treated Enteromorpha by acetic acid (T<sub>4</sub>) showed that the highest value (186.64 g) of body weight gain significant with other groups, and the lowest value (127.76 g) were recorded by group which fed on diet containing Enteromorpha untreated.

Concerning total feed intake data of Table (6) revealed that group T<sub>1</sub> was recorded the highest total feed intake (565.27 g), while the group of T<sub>4</sub> was recorded the lowest value (479.81 g).

As aspect of feed conversion ratio as an average during whole experimental period results shown in table (6) indicated that birds fed treated Enteromorpha by acetic acid (T<sub>4</sub>) recorded feed conversion ratio better than that fed on all other treatments.

Data presented in Table revealed that mortality percentage during the whole experimental period ranged between 3.30 to 7.45%, and almost all mortalities was recorded in the present study could attributed to accidental factors during handling of birds and not treatment performance.

Table(6): Effect of treated Enteromorpha addition in diets on growth performance of Japanese quail as an average during whole experimental period.

Treatments	Nutrient utilization parameter				
	LBW	BWG	FI	FCR	MR
T <sub>1</sub> (Untreated)	148.09 <sup>E</sup>	127.76 <sup>E</sup>	565.27 <sup>A</sup>	4.10 <sup>A</sup>	6.65 <sup>B</sup>
T <sub>2</sub> (Freezing)	163.71 <sup>D</sup>	143.30 <sup>D</sup>	509.59 <sup>B</sup>	3.44 <sup>B</sup>	5.80 <sup>C</sup>

T <sub>1</sub> (Boiling)	195.06 <sup>B</sup>	174.67 <sup>B</sup>	497.60 <sup>C</sup>	2.85 <sup>D</sup>	5.80 <sup>C</sup>
T <sub>2</sub> (Acetic acid)	207.08 <sup>A</sup>	186.64 <sup>A</sup>	479.81 <sup>D</sup>	2.62 <sup>E</sup>	3.30 <sup>D</sup>
Control	190.34 <sup>C</sup>	169.87 <sup>C</sup>	490.69 <sup>C</sup>	2.98 <sup>C</sup>	5.00 <sup>B</sup>

LBW=live body weight, BWG=body weight gain, FI= feed intake, FCR= feed conversion ratio, MR= mortality ratio.

## DISCUSSION

Results obtained in present study indicated that addition of untreated *Enteromorpha* in Japanese quail diets significantly decreased LBW. These results are in agreement with those obtained by El-Khimsawy (1983), Carrilo (1990) and Rose and Doming (1990) who found that the body gain of chicks significantly gradually decreased by increasing in seaweeds level in the diet. Ventura *et al.* (1994) found that *Ulva rigida* is not a suitable ingredient for poultry diets when it used as level of 10 % or higher. They added that as dietary seaweeds increased growth rate was decreased. The growth depression which results from low organic matter digestibility of seaweeds. El-Khimsawy (1983) reported that digestibility of untreated algae was low.

Findings of present study showed that physical treatments (freezing or boiling) improved Japanese quail growth compared untreated seaweeds. These results may be due to the effect of treatment on seaweed cell walls, hence improved seaweeds digestibility and its protein quality. Mitsuda (1963) found that algal protein quality as long as chemical composition was affected by processes. He added that nitrogen retention in algal protein when algae treated by cooking at 100° C were increased than untreated algae. Also, Becker 1978 found that availability of lysine in algae treated with freezing was better than untreated algae. El-Khimsawy, 1978 found that freezing processing was efficient for breaking down cell wall of algae which resulted in more protein release from the cell.

Results obtained in present study indicated that chemical treatment by acetic acid had best effect on LBW than physical treatments or untreated algae (*Enteromorpha*) in Japanese quail. These results may be due to the efficient effect of chemical processing on cell wall of algae Taylor *et al.*, 1953. Cohn and Edsall (1943) found that addition of acids to organic materials extract containing soluble protein to reach the pH of the iso-electric point of protein lead to precipitating the protein. El-Khimsawy, (1978) used each sodium hydroxide or hydrochloric acid to release more protein extraction from seaweeds. Fleurence, (1999) reported that protein extraction from most seaweeds in difficult due to the presence of large amounts of anionic cell wall polysaccharides.

Concerning feed intake results obtained in present study indicated that untreated *Enteromorpha* in Japanese quail diet increased feed intake compared to control. These results may be due to low available nutrients in untreated *Enteromorpha* becomes low its digestibility, hence the birds tend to increase feed intake to covering its nutrients requirements, (El-Khimsawy, 2001). These results are in agreement with those reported by Schaible (1970) who stated that birds eat more of a less palatable mixture than one that seems more palatable.

In general, results obtained in present study are in agreement to those found by El-Deek *et al.* (1987) and Carrillo *et al.* (1990) who reported that seaweeds in chicks and Japanese quail increased feed intake. Hintz *et al.* (1966) found that alfalfa of green seaweeds is not a high energy feed becomes of its low digestibility. These results are in agreement with those obtained by El-Khimsawy (1978) who found that chicks fed on diet containing crude seaweeds mixture tend to increase feed intake than that contain seaweeds extraction or control. The increasing of feed intake as affected by freezing treatment, obtained in present study may be due to freezing treatment may be brocked cell wall of seaweeds, but did not facilitated the nutrients solubility, hence the diet was poor in quality accordingly the birds increased feed intake in order to covering its requirements. The decreasing feed intake as affected by *Enteromorpha* treated by acetic acid (T<sub>4</sub>) and boiling, as a results obtained in present study, may be due to each acetic acid and boiling lead to increasing fat solubility. Increasing of fat in poultry diet decreased feed intake (El-Khimsawy, 2001).

As aspect of feed conversion, it is knowable that feed conversion value depends on each live body gain and feed intake. Results obtained in present study indicated that all tested diets detected worse feed conversion ratio, except one that treated by acetic acid. These results may be due to increase feed intake but improvement of feed conversion by *Enteromorpha* treated by acetic acid may be due to decreasing feed intake besides that increasing live body weight.

Feed conversion value of *Enteromorpha*, or generally of seaweeds, were variable in literature according to treatment and procedure used for seaweeds processing.

Inal *et al.* (1995) found that maxi crop, an extract from the seaweed increased feed intake and decreased feed conversion efficiency. Raju and sreemannarayana (1995) found that *Ulva* in rabbit diet did not affected feed conversion. Padhi *et al.* (2003) reported that seaweeds in laying hen diet did not influence feed conversion. El-Deek and Brikaa (2009) reported that addition of seaweeds up to 12% in ducks diet did not affected feed conversion. El-Zabalawy (2010) found that *Ulva* treated by acetic acid in Japanese quail diet increased feed intake and decreased feed conversion efficiency.

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# STUDY OF THE KINETICS OF BIOMASS GROWTH AND HYOSCYAMINE ACCUMULATION IN HAIRY ROOTS OF THREE SPECIES OF *DATURA SP.*

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## ABSTRACT

*Solanaceae*, particularly species of the *Datura* genus, are rich in tropane alkaloids including hyoscyamine. This study examines the relationship between biomass and hyoscyamine accumulation in hairy roots of three species of *Datura sp.* The experiment was conducted *in vitro* on hairy roots induced by *Agrobacterium rhizogenes* "strain A4".

The results show that the biomass growth in the hairy root and the hyoscyamine accumulation are inversely proportional. Thus, for the three studied species, the maximum of accumulation of hyoscyamine is reached between the 20<sup>th</sup> and 22<sup>nd</sup> days. It occurs when the biomass of hairy root reached its stationary growth phase.

**Keywords:** biomass growth, *Datura sp.*, hyoscyamine accumulation, kinetic.

## THE PRODUCTION OF CELLULASE FROM NOVEL IDENTIFIED CELLULOMONAS SP.

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### ABSTRACT

The objective of this study is to improve the production of cellulase by screening novel cellulose-hydrolytic bacteria. Five novel cellulase-producing bacteria were isolated and identified through 16S rRNA sequence as *Cellulomonas* sp. The activity of enzymes (mainly xylanase and endoglucanase) was almost present extracellularly and the production of enzyme was dependent on substrate (xylan, rice straw and wastepaper) utilized for growth. *Cellulomonas* sp. strain TSU-03 produced the highest activity of xylanase and endoglucanase at 885.5 and 620 U/mg protein when rice straw and xylan was used as sole substrate, respectively.

**Keywords:** Cellobiase, Cellulase, Endoglucanase, Exoglucanase, Xylanase

### INTRODUCTION

Currently, production of bioethanol from agricultural residues is a suitable alternative, in view of fast depletion of fossil fuels (Lo et al. 2009). However, bioethanol is not extensively utilized with the common reason that the cost of fermentation process. Therefore, the chance to obtain cheap ethanol will depend on the successful screening and improvement of cellulase-producing strain. The goal of this study aim to isolation of novel cellulase producing microorganism as well as the production of cellulase was also investigated.

### MATERIALS AND METHODS

#### Bacterial isolation

Soil samples were collected from different locations of Phatthalung, Thailand for the isolation of cellulase-producing bacteria. Hydrolytic bacteria was identified under CMC- and xylan-BHM medium as described previously by Lo et al. (2009) and Sangkharak et al. (2011).

#### 16S rRNA gene analysis and phylogenetic analysis

Pure bacterial cultures were obtained and the nucleotide sequence of the 16S rRNA gene of isolated bacteria was amplified by PCR employing DNA polymerase. The universal primers 27F (5'-GAGTTTGATCCTGGCTCA-3') and 1,525R (5'-AGAAAGGAGGTGATCCAG-3') numbered according to the *E. coli* 16S rRNA gene sequence were used. Amplification and sequence analysis of the 16s rRNA was performed as previous described (Porwal et al. 2008).

The DNA sequences of isolated bacteria were deposited in the EMBL database under accession numbers HQ670717–HQ670721.

### The production of cellulase enzyme on different cellulosic materials

Lignocellulosic materials obtained from Southern of Thailand (Phatthalung, Thailand) such as 1% of rice straw, wastepaper and xylan were selected as the carbon source. Rice straw and wastepaper were pretreated before used following of the method describe by Sangkharak (2011).

### Enzyme assay

Endoglucanase and xylanase activity was determined following to the method described by Nitisinprasert and Temmes (1991). Exoglucanase (avicelase) activity was determined according to the method described by Miller (1959) and Lo et al. (2009). Cellobiase activity was determined colorimetrically by the glucostat enzyme assay method (Raabo and Terkildsen 1960).

## RESULTS AND DISCUSSION

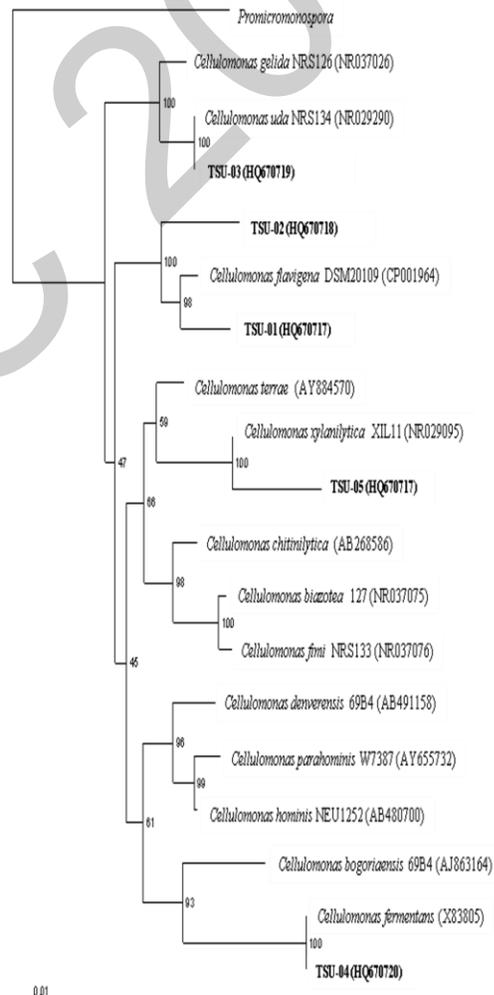
### Isolation and identification of the isolated bacterial strains

Five strains hydrolyzing cellulolytic materials were isolated from agricultural soil and designated as strain TSU 01-05. All strains were a gram positive and rod-shaped bacterium. The 1.5-kb fragment comprising of 16s rRNA gene were also determined for five isolates. All sequences showed >95% identity with 16S rRNA gene of a previously analyzed *Cellulomonas* sp. A comparison of 16S rRNA gene from isolated strains to 16S rRNA of other bacteria belonging to the family “*Cellulomonadaceae*” is shown in Figure 1.

### Production of cellulase from isolated strains with cellulosic mater

The effect of different carbon source (rice straw, wastepaper and xylan) on the production of cellulolytic enzyme by *Cellulomonas* sp. TSU 01-05 was summarized in Table 1.

*Cellulomonas* sp. strain TSU-03 showed the ability to produce high level of enzyme activity compared to other *Cellulomonas* sp. as previous reported.



**Figure 1** Phylogenetic analysis of isolated bacteria TSU 01 - 05 and selected bacteria in alpha subdivision of the division *Cellulomonadaceae* generated from an alignment of 1.5 kb of 16S rRNA obtained from GenBank database (accession number in parentheses).

**Table 1** Production of cellulolytic enzyme including xylanase, endoglucanase, exoglucanase and cellobias by *Cellulomonas* sp. TSU 01 – 05 with rice straw (a), wastepaper (b) and xylan (c) as sole carbon source at different location (extracellular, intracellular and cell bound).

<i>Cellulomonas</i> sp.	Enzyme activity (U/mg protein)											
	Xylanase			Endoglucanase			Exoglucanase			Cellobiase		
	Extra-cellular	Intra-cellular	Cell bound	Extra-cellular	Intra-cellular	Cell bound	Extra-cellular	Intra-cellular	Cell bound	Extra-cellular	Intra-cellular	Cell bound
<b>(a) Rice straw</b>												
TSU 01	12.4	20.7	25.9	32.5	16.6	10.0	12.0	25.8	10.5	10.0	10.2	10.2
TSU 02	10.1	15.4	32.2	33.3	14.5	10.6	14.7	20.3	10.0	11.1	10.0	10.0
TSU 03	885.5	11.2	132.2	280.9	12.2	12.4	17.6	19.6	14.3	10.1	11.3	10.0
TSU 04	198.3	12.8	10.0	125.4	11.0	14.0	12.2	22.3	10.5	16.4	10.5	11.5
TSU 05	550.2	18.5	111.6	131.6	11.5	12.2	10.2	20.6	11.2	14.0	10.0	10.4
<b>(b) Wastepaper</b>												
TSU 01	22.1	10.4	12.5	50.1	10.2	11.1	20.1	12.3	11.5	14.2	10.5	15.6
TSU 02	19.1	12.1	10.3	45.2	10.2	10.3	21.2	11.4	10.6	12.6	19.6	11.5
TSU 03	856.2	11.5	12.0	258.5	12.1	10.2	10.5	14.5	12.1	11.4	11.5	10.6
TSU 04	214.7	11.6	10.2	139.2	10.5	12.1	15.4	19.6	13.5	13.8	12.4	11.5
TSU 05	375.4	10.2	10.4	140.5	10.3	12.4	10.2	10.8	10.5	10.2	13.0	10.5
<b>(c) Xylan</b>												
TSU 01	45.1	200.6	10.2	74.4	33.5	22.5	10.9	12.2	10.0	10.0	10.5	8.8
TSU 02	32.9	202.4	10.0	42.2	29.9	39.3	11.0	10.3	10.2	10.5	11.4	9.1
TSU 03	820.0	26.3	19.2	620.0	10.4	18.7	10.5	15.1	10.2	8.8	10.5	10.2
TSU 04	40.2	30.0	20.5	55.4	33.4	19.6	12.1	10.0	11.1	8.8	8.9	10.0
TSU 05	250.0	21.1	12.4	155.1	22.6	21.0	22.4	12.1	10.2	11.2	12.2	9.5

## CONCLUSION

*Cellulomonas* sp. isolated in his study offer a good prospect for cellulolytic enzyme production and this process can be applied as a part of industrial application using lignocellulosic materials (rice straw, wastepaper, xylan). *Cellulomonas* sp. strain TSU-03 produced the highest activity of xylanase and endoglucanase at 885.5 and 620 U/mg protein when rice straw and xylan was used as sole substrate, respectively.

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# LOCAL WISDOM OF BEES CAPTURE AND ECONOMICS VALUE OF HONEY AT PRA BUDDHA CAVE COMMUNITY A BOUNDARY BETWEEN

Trang and Nakhon Si Thammarat Province.

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## Abstract

Local wisdom of people in this community is a giant honeybee hunting and taking honey for sale. This occupation has a long legacy with the establishment Pra-Buddha Cave community. The giant honeybee hunting in community is still going on which consists of the people who had knowledge and experience that need to be teamwork. The first of step is observation of reason, tracking, equipment preparation, method of the giant honeybee hunting, belonging to the giant honeybee, honeybee hunters team and hunter's beliefs. The intellectual of the giant honeybee hunting has been a contemporary historical legacy since the ancient time. It is reflected in the nature of the observation, test, application, recollection and instruction in the living. In addition, the local knowledge is guideline for conservation and natural resource management in a systematic way at the community to be with the Pra-Buddha Cave community. Furthermore, the economic value of honey in Pra-Buddha Cave community was calculated by market price approach is that showed the result of 71,917 bath per year

**Keywords:** Local wisdom, The giant honeybees, *Apis dorsata* F. (Hymenoptera: Apidae) hunting, Pra-Buddha Cave Community, Economic Valuation

## INTRODUCTION

Thailand is the abundance of natural resources and biodiversity including wood, various vegetation types and large number of animals. Biological diversity makes Thailand is the source of the intellectual maturation of the nature. Pra-Buddha Cave community (total area 14 km<sup>2</sup>) was located in Koa-Pu Koa-Ya National Park boundary between Moo. 6, Tambon Nong Bua, Rasada District, Trang Province and Moo. 6, Tambon Nam Tok, Tung Song District, Nakhon Sri Thammarat Province. This community is more than one hundred years old. People in this community were usually useful natural resources from the past until now (Chaiwichit, (interview), 2009). The main occupation of people in this community is Para rubber and fruits

plantation. Other occupation and also important is giant bees hunting for bring honeybee for sale. An outstanding professional of people in this community is a giant honeybee hunting and taking honey for sale. This occupation has a long legacy with the establishment Pra-Buddha Cave community (Sawi, (interview), 2009). At present, the giant honeybee hunting in the community is still going on but the local people who had knowledge and experience are decrease because the giant honeybee hunting is difficult. The giant honeybee hunting needed to be teamwork for many steps. From the recent research, we studied and collected the giant honeybee hunting wisdom of Pra-Buddha Cave community Moo. 6, Tambon Nong Bua, Ratsada District, Trang Province and Moo. 6, Tambon Nam Tok, Tung Song District, Nakhon Sri Thammarat Province. We also approach the study and conservation of the giant bee of Pra-Buddha Cave community follow by local wisdom. The provident knowledge on the giant honeybee hunting would be with the community. This will lead to understand about the wisdom of giant honeybee hunting and also make local people to posses a hundred-year-old knowledge (Sompong, (interview), 2009) Moreover, this research will be produced value added in community. This knowledge should be with community to bring about local wisdom of the giant honeybee hunting understanding and feel to be jealous of local wisdom source. In the future if has no promote and disseminate local wisdom of honeybee hunting for youth and villagers, the ancient smart honeybee hunting knowledge may be lost from the community.

#### **OBJECTIVE**

1. To study the local wisdom of people is a giant honeybee hunting and the guideline of conservation in Pra-Buddha Cave community
2. To study the economic value of honey in Pra-Buddha Cave community

#### **METEDOLOGY**

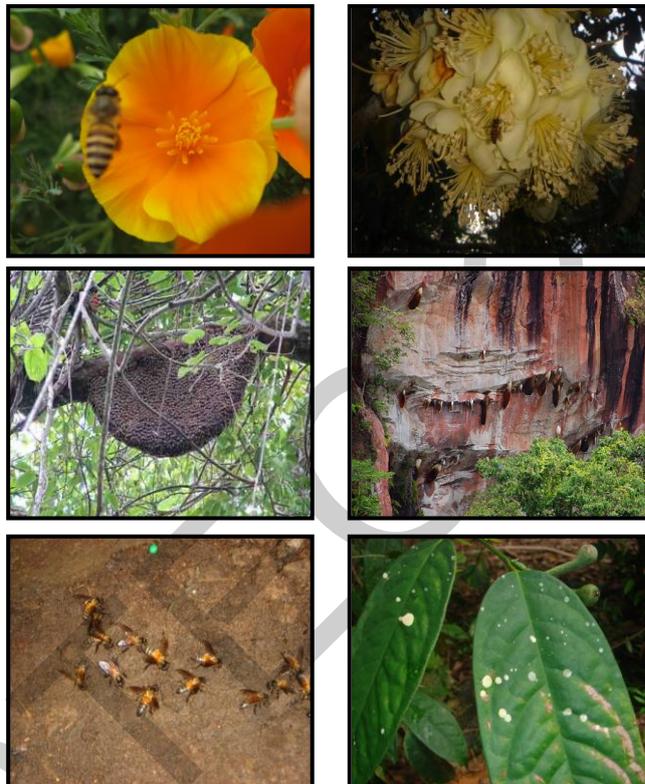
The research was done using a survey research, by collecting data on knowledge and local wisdom from the people who the key information interviews consisted three groups as the main group information, the support group information and the general group in the community, by using questionnaire, informal semi-structure, interview, participating observation.

Furthermore, the economic value of honey in Pra-Buddha Cave community was calculated using market prices approach which consider the cost of equipment, the time and labor capture bee, and the cost of fuel used to seek and monitor honeycomb. Therefore, the calculation of net benefit was counted from the total amount of honey subtract with the cost of bee capture.

#### **RESULTS**

The purpose of research were: 1) To study the local wisdom of people is a giant honeybee hunting and the guideline of conservation in Pra-Buddha Cave community 2) to study the economic value of honey in Pra-Buddha Cave community. According to the survey and collect the data on knowledge and local wisdom from the people that an outstanding professional of people in this community is a giant honeybee hunting and taking honey for sale. This occupation has a long legacy with the establishment Pra-Buddha Cave community. At present, the giant honeybee hunting in the community is still going on but the local people who had knowledge and experience are decrease because the giant honeybee hunting is difficult. The giant honeybee hunting need to be teamwork which there are various knowledge.

The first step is observation of reason, the giant bees start immigrants to live in the community area around in March to June of every year which the variety of wild flowers will be bloom in this season. It is suitable for build the honeycomb for reproduction. Next, monitoring the honeycomb has four ways 1) Observe the trees that the giant bees have been build honeycomb last year because the giant bees would often come back to build honeycomb at the same in next year. 2) The giant bees will be are and seek the water. 3) Observe behavior of the giant bees that finding the honey bees of wild flowers. 4) Observe behavior of the giant bees while bring the small bee go out to evacuate. After this, the bee hunters prepare equipment such as "mong" (local name), container, knife for cutting honeycombs and PP rope. All of equipment must be non-toxic for the giant bees. Then, they make Puk-Kum that is a symbolic for show the belongings. Finally, the bee hunters carefully climb the tree.



**Fig. 1. The method of the bee hunter monitor the giant honeycomb**

Besides, the total amount of honey was found to be 200 bottom in village which the price of honeybee approximately 500 bath per bottom. There was the cost around 28,083 baht per year. Thus, the economic value of the honey in Pra-Buddha Cave community was calculated using local market price that showed the net benefit of 71,917 baht per year.

## CONCLUSIONS

From the results showed the long and continue local wisdom of the giant honeybee hunting and to be sustainable conservation of biodiversity. Moreover, this research was produced value added in community. The local wisdom of giant bees hunting of Pra-Buddha Cave community was accumulated the experience and knowledge developing continuously and take it to solve the problem.

For guidance on the giant bees conservation follow by folk wisdom was belief that the same traditional and remain with the community since the past. Some belief was a trick of the giant bees hunter in the past for the giant bee conservation remain with Pra-Buddha Cave community. Moreover, this trick made the giant bees come back to build honeycomb at the same area from past to present

In addition, its also created a unity the villagers. Including used the materials which do not destroy the giant bees. At this time, some belief about the giant honeybees hunting will be disappeared because of villager's lifestyle in this community has been changed such as using the material is available and easy, so the giant honeybees hunters should be the rules agree within the community for conservation is the natural resources that continue remain in the community.

### **ACKNOWLEDGEMENTS**

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Sawi Promkang. 2009. (interview), 13 January 2009.

# INFLUNCE OF SYNTHESIS TIME ON MICROSTRUCTURE OF SiC NANOFIBERS FROM RICE HUSK

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## ABSTRACT

SiC nanofibers have been anticipated to have high specific strengths for applications as reinforcements in composite materials. The interfacial strength between the fibers and the metal matrix plays the key role in producing the composites having higher interlaminar shearing strength. The purpose of this work is to synthesis of SiC nanofibers from mixture of graphite and charcoal of rice husk using iron and aluminum as the catalysts by current heating technique in argon atmosphere in holding time for 10 to 60 minutes. Microstructural characterization by scanning electron microscopy showed that the diameters of fibers were typical 50 to 500 nm. The results of energy dispersive x-ray found that the fiber contained mainly Si, C, Fe, Al and O.

**Keywords:** Silicon carbide, nanofibers, microstructure

## 1. INTRODUCTION

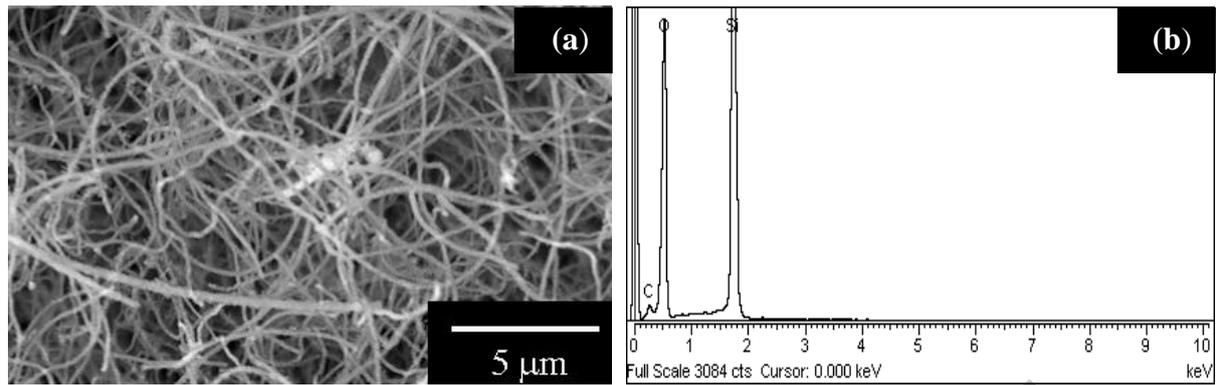
SiC nanofibers have been widely recognized as nanomaterials with high strength, corrosion resistance and exceptional high temperature stability (Ward *et al.*, 2001). Furthermore, SiC nanofibers have been excellent mechanical and field emission properties, which fine potential application in various nanocomposite materials and in field emission nanoscale device (Deng *et al.*, 2006). Recently, SiC nanofibers have been successfully synthesized from rice husk by chemical vapor deposition (CVD) and vapor liquid solid (VLS) techniques in electrical furnaces (Liu *et al.*, 2004). In general, Fe, Co, Ni and Al metals have been widely used as the catalyst to support on the growth of the nanostructure in these techniques (Lai *et al.*, 2000, Ferro *et al.*, 2004 and Chen *et al.*, 2008). The objective of this study was to investigate the holding time condition in the preparation of SiC nanofibers from mixture of rice husk charcoal and graphite by current heating technique with Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> as catalysts in Ar-atmosphere (Singjai *et al.*, 2002).

## 2. METHODS AND PROCEDURES

The rice husk was dried in an oven at 120 °C for 24 hours (Qiao *et al.*, 2002). A furnace was used for conversion of rice husk into rice husk charcoal in Ar-atmosphere (Krishnarao *et al.*, 2007). A slow heating rate of 10 °C min<sup>-1</sup> was applied up to 800 °C for 30 minutes. The raw material containing rice husk charcoal (50 wt%), graphite (46 wt%) and Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> (2 wt%) as a catalyst was complicated using a stainless-steel die at a hydraulic pressure of 0.5 ton into a rod-shape. The compacted sample was approximately 6.6 mm. in diameter and 20 mm. in length. The rods were subjected to a current heating apparatus, the synthesis was done at 35 V, 15 A in holding time at 10-60 minutes. The products were characterized using scanning electron microscopy (SEM, JEOL, JSM-6335F) and energy dispersive x-ray (EDX, Oxford Instruments) techniques.

## 3. RESULTS

SEM micrograph of a raw materials rod from mixture of 50 wt% charcoal and graphite was synthesized by current heating technique in argon atmosphere at holding time for 30 minutes in Figure 1a. It was found that fibers are long chain and regular. The diameter of fibers is ranging from 120 to 400 nm by using the energy dispersive x-ray attached to SEM. The chemical composition of fibers was analyzed by EDX as shown in Figure 1b. The fibers contained mainly Si, C and O.

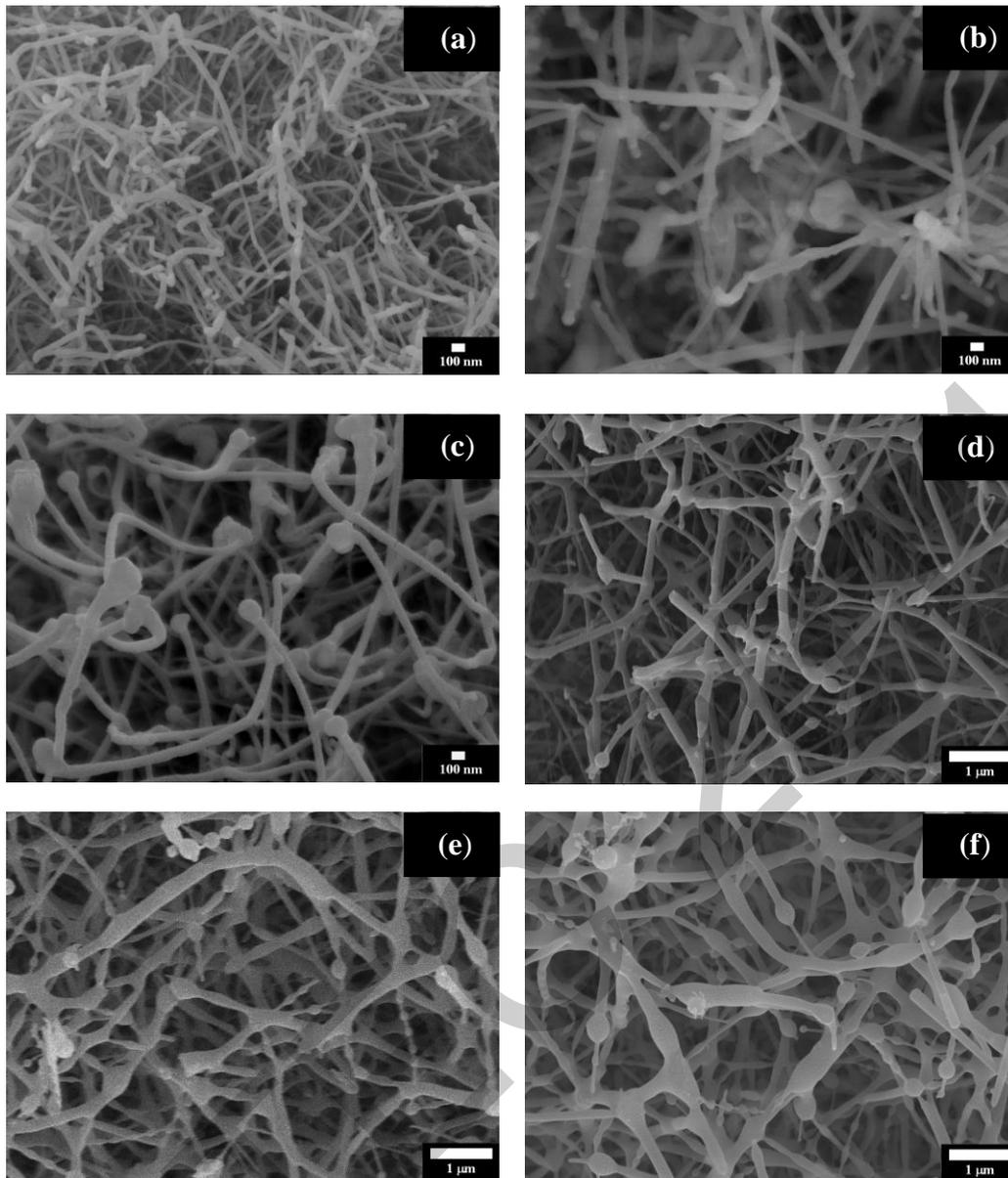


**Figure 1.** The raw materials rod from mixture of 50 wt% charcoal and graphite was synthesized by current heating technique. (a) SEM micrograph and (b) EDX spectrum.

The raw materials rod from mixture of 50 wt% charcoal, 46 wt% graphite, 2 wt % Fe and 2 wt% Al was synthesized by current heating technique in argon atmosphere by holding time at 10, 20, 30, 40, 50 and 60 minutes. SEM micrographs are presented in Fig. 2. The average fibers could be observed in Table 1. The results show that with increasing the holding time from 10 to 60 minutes, the fibers size tended to increase. As shown in Fig. 2a, the holding time for 10 minutes can be observed that the fibers do not complete growth. The fibers diameter is about 78 nm. The holding time for 20 minutes is presented in Fig 2b. The fibers are cylindrical in shape with diameters around 102 nm. Furthermore, it can be observed that the beaded tip was form. SEM micrograph shows in Fig. 2c and 3. The beaded tip of fibers could be clearly seen in holding time for 30 minutes with the diameter of fibers is about 55 nm. The growth of fibers can be explained by VLS mechanism. The VLS start with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single-crystalline fibers (Liang *et al.*, 2000).

**Table 1.** Diameter average of fibers at different holding time

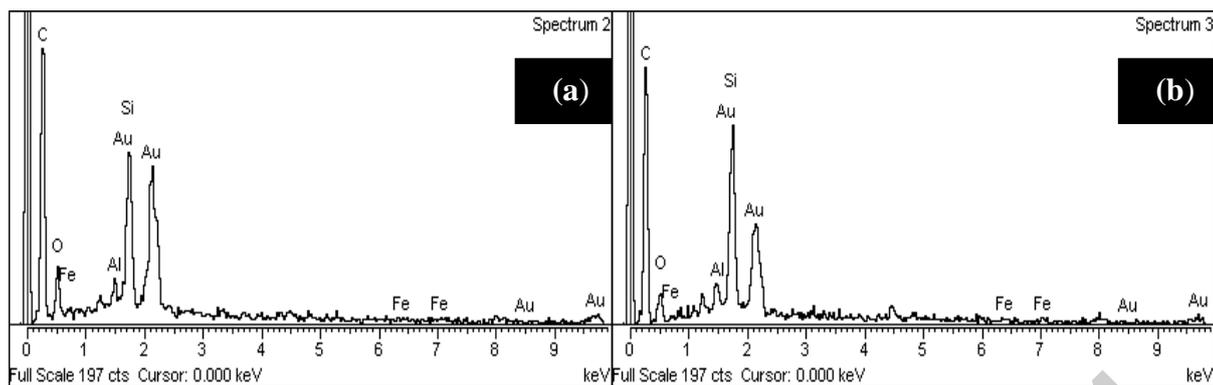
Holding time (minutes)	10	20	30	40	50	60
Diameter average (nm)	78	102	109	234	379	469



**Figure 2.** The SEM image of the raw materials rod from mixture of 50 wt% charcoal, 46 wt% graphite, 2 wt % Fe and 2 wt% Al by current heating method at different holding time. (a) 10 minutes, (b) 20 minutes, (c) 30 minutes, (d) 40 minutes, (e) 50 minutes and (b) 60 minutes.



**Figure 3.** The SEM image of the raw materials rod from mixture of 50 wt% charcoal, 46 wt% graphite, 2 wt % Fe and 2 wt% Al by current heating method for 30 minutes.



**Figure 4.** EDX analysis of the raw materials rod from mixture of 50 wt% charcoal, 46 wt% graphite, 2 wt % Fe and 2 wt% Al by current heating method for 30 minutes. (a) tip bed of nanofiber and (b) nonfiber.

Fig. 4a and 4b show EDX analysis of fibers by holding time for 30 minutes. It was found that the beaded-tip and fiber contained Al, Fe, Si, C and O.

#### 4. CONCLUSIONS

The silicon carbide nanofibers have been successfully prepared through current heating technique in argon atmosphere from the rice husk charcoal, graphite,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  mixture by holding time at 10 to 60 minutes. It can be clearly seen that beaded SiC nanofibers is formed completely at holding time up 30 minutes with diameter of  $\sim 109$  nm.

#### 5. ACKNOWLEDGEMENT

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# UTILIZATION OF MC-CDMA IN WIRELESS RAYLEIGH CHANNEL

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## ABSTRACT

Recent advances in wireless communications have made use of Multi-Carrier Code Division Multiple Access (MC-CDMA) technique to allow for high data rate transmission. Many papers have studied the performance of IEEE 802.11 Wireless Local Area Networks by using simulation under different modulation. The multi-path Rayleigh channel represents a hostile environment for WLANs communication. So, we have proposed the MC-CDMA system to overcome the impact of this kind of wireless channel. The focus of this study is to simulate a modified physical layer based on the Wi-Fi parameters combined with a stage of spread spectrum. We investigated the modified physical layer performance on the basis of Bit Error Rate. This parameter is discussed and compared with CDMA system based on the IEEE 802.11b standards. The numerical results show that the MC-CDMA is a powerful multi-carrier multiple access technology since it's provide better performance in noisy conditions.

**Key words:** WLAN, WI-FI, MC-CDMA, Rayleigh fading channel.

## 1. INTRODUCTION

With the rapid development of wireless communications, two trends are gaining in popularity. One is the use of Code Division Multiple Access (CDMA) and the other is the use of Orthogonal Frequency Division Multiplexing (OFDM). CDMA achieves soft capacity limit by using the same bandwidth all time by assigning different spreading codes to each user. The only limitation is the self interference and multi-user interference. One of the reasons for this impairment is contributed by the channel. OFDM is another technology adopted by the digital broadcasting society to counter the Inter Symbol Interference (ISI) problem. OFDM has received considerable attention for its advantages in high bit-rate transmission over frequency-selective channels. It has also several desirable attributes, such as high spectral efficiency, robustness with respect to multi-path delay spread all of which are making OFDM to be incorporated in various wireless standards. The presence of a Cyclic Prefix (CP) completely eliminates ISI (Schulze & Lüders, 2005; Bahai & Saltzberg, 2002; Hanzo et al., 2003; Nassar et al., 2002; Li & Stuber, 2006). For future wireless applications, researchers have also started a new trend of combining these two techniques with the intention of obtaining advantages of both, and the proposed new technique is generally termed Multi-Carrier Code Division Multiple Access (MC-CDMA) (Hara & Prasad, 1997). The MC-CDMA is seen as an attractive and practical solution to enhance the throughput and/or robustness for future high-speed indoor Wireless Local Area Networks (WLAN).

In this article, we evaluate performances in terms of Bit Error Rate (BER) of WLAN system based on IEEE 802.11 which is also often referred to as "Wireless Fidelity". Knowing that, today's Wi-Fi is gaining a lot of popularity because is deployed in home, office, restaurants, airports, university campus, streets and is recognized as one of the main access technologies to the Internet. For this reason we chose it like an example for our study. So, the focus of this study is to simulate a modified Physical Layer (PHY) based on the IEEE 802.11a combined with a stage of spread spectrum. This modified layer particularly concentrates on IEEE 802.11a standard because its physical layer design is considered to be more robust against harsh propagation conditions. According to the IEEE specification the WLAN should transmit the data in frames, but the preamble and the header are not implemented in our simulations. Only the part which contains the data to be transmitted is implemented with Matlab software. Basically, the proposed scheme is based on Pseudo Noise code.

The rest of the article is organized as follows: Section 2 gives a short Wi-Fi overview. Section 3 describes the MC-CDMA technique. Section 4 gives a detailed presentation of the simulated scheme. Section 5 gives the simulation results and section 6 draws the conclusion.

## 2. WI-FI OVERVIEW

WLANs provide wideband wireless connectivity and allow high-speed data transfer without the need for wires or cables installation (Smith et al., 2011). WLANs can be used in different environments such as home users, public and enterprise applications. The first and most fundamental challenge for WLANs comes from the transmission medium itself. Wireless communication channels constitute a hostile propagation medium, which suffers from fading.

In June 1997 the Institute of Electrical and Electronics Engineers (IEEE) defined an international interoperability standard, called IEEE 802.11 wireless LAN, also known as Wi-Fi. This standard specifies a number of Physical Layers (PHYs). Two of these PHY are based on radio communication and use the 2.4GHz band, license free ISM (Industrial, Scientific and Medical bands) and the others PHY uses infrared light. All three PHYs support a data rate of 1Mbps and optionally 2 Mbps. In 1998, Lucent Technologies and Harris Semiconductor proposed a standard called Complementary Code Keying (CCK) to achieve 5.5Mbps and 11Mbps transmit rates. The IEEE adopted the CCK and released a new standard, named IEEE 802.b, in 1999

Motivated by the demand for higher data rates and by the opening of new unlicensed spectrum in the 5GHz band for the use of a new category of equipment called Unlicensed National Information Infrastructure (UNII) devices, a new IEEE 802.11 working group started working on third generation of WLANs. In July 1998, this group selected OFDM as a transmission technique. In 2000, the standard was ratified and called IEEE 802.11a. It defines data rates between 6 and 54Mbps. To make sure that these data rates are also available in 2.4GHz band, mid 2003 IEEE standardization group finalized a similar standard for this band named IEEE 802.11g. The growing success of IEEE 802.11b and IEEE 802.11a products together with the demand for even higher bit rates confirms the need for research to high data-rate extensions for WLANs (IEEE part1, 1999; IEEE part1, 2007).

## 3. MC-CDMA

Recently MC-CDMA has become a hot topic in mobile communications research since it has the benefits of both OFDM and CDMA. In MC-CDMA symbols are modulated on many subcarriers to introduce frequency diversity instead of using only one carrier like CDMA. Thus MC-CDMA is robust against deep frequency selective fading compared to DS-SS (Hanzo et al., 2003). Each user data is first spread using a given high rate spreading code in the frequency domain. A fraction of a symbol, corresponding to a chip of the spreading code, is transmitted through a different subcarrier. Hence each OFDM subcarrier has a data rate identical to the original input data rate. The transmitted signal of the  $i^{\text{th}}$  data symbol of the  $j^{\text{th}}$  user  $s_i^j(t)$  is:

$$s_i^j(t) = \sum_{k=0}^{N-1} b_i^j c_k^j e^{2\pi(f_0 + kf_d)t} p(t - iT) \quad (1)$$

where:  $N$  is the number of subcarriers,  $b_i^j$  is the  $i^{\text{th}}$  message symbol of the  $j^{\text{th}}$  user,  $c_k^j$  represents the  $k^{\text{th}}$  chip,  $k = 0, 1, \dots, N-1$ , of the spreading sequence of the  $j^{\text{th}}$  user,  $f_0$  is the lowest subcarrier frequency,  $f_d$  is the subcarrier separation and  $p(t)$  is a rectangular signaling pulse shifted in time given by:

$$p(t) = \begin{cases} 1 & \text{pour } 0 \leq t \leq T \\ 0 & \text{ailleurs} \end{cases} \quad (2)$$

If  $1/T$  is used for  $f_d$ , the transmitted signal can be generated using the IFFT, as in the case of an OFDM system. There for, if the original symbol rate is high enough to become subject to frequency selective fading, the input data have to be serial-to-parallel converted into  $P$  parallel data sequences and each serial-to-parallel output is multiplied with the spreading code of length  $N$ . Then each sequence is modulated using  $N_s$  subcarriers. Thus, all  $N_s = P \cdot N$  subcarriers are also modulated in baseband by the IFFT.

## 4. Proposed MC-CDMA schemes description

In our simulations, the channel coding is not used. The proposed system uses MC-CDMA in the physical layer. The 20 MHz channel is split into 52 subcarriers (48 subcarriers for data and 4 pilot subcarriers), like in the IEEE 802.11a OFDM physical layer. Figure 1 illustrates the MC-CDMA simulation model. The input data stream is first mapped into BPSK and then is multiplied by the spreading code of length  $N$  (the same symbol is transmitted in parallel through several subcarriers). Each chip of PN code modulates one subcarrier. The number of subcarriers in this scheme equals the length of spreading code. All data corresponding to the total number of subcarriers are modulated in baseband by IFFT and converted back into serial data. Then a cyclic prefix is inserted between the symbols to combat the ISI and the inter-carrier interference (ICI) caused by multi-path fading. Finally, the signal is transmitted trough the channel. The channel consists of a multi-path fading with AWGN (10-Tap Rayleigh fading model is used as the channel).

At the receiver the inverse operation is employed.

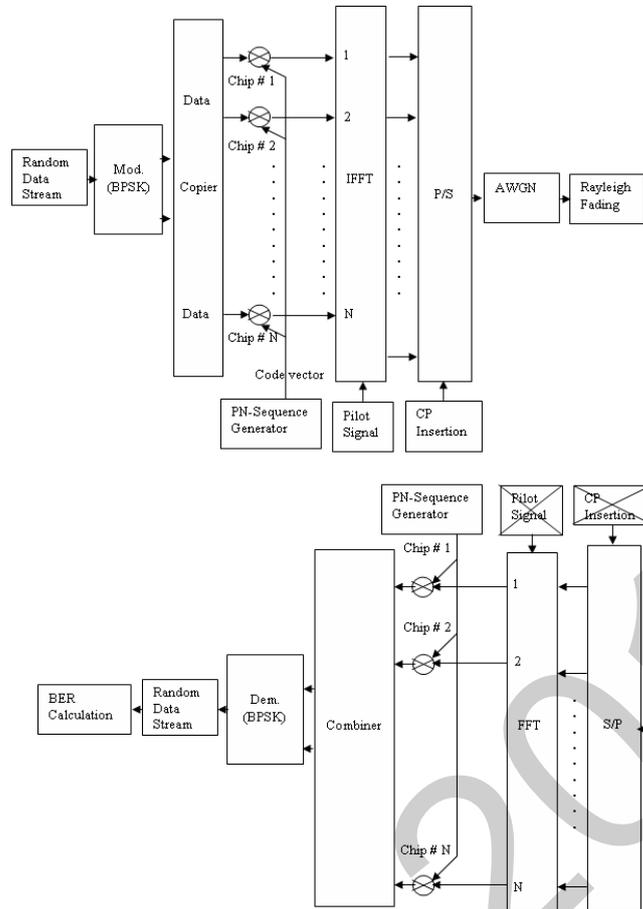


Fig.1. The simulation block diagram of MC-CDMA

Simulation parameters of the PHY layer are presented in table 1.

Table 1. Simulation parameters

Parameter	Value
Channel Bandwidth	20 MHz
Subcarriers Spacing	0.3125 MHz
Symbol Interval	4μs = 3.2μs + 0.8μs
Guard Interval	0.8μs
FFT size	64
Number of subcarriers	52
Spreading factor	52
Spreading code	PN

## 5. SIMULATIONS, RESULTS AND ANALYSIS

### 5.1 Simulations environment

The simulations are designed and implemented using Matlab. Performance is evaluated by transmitting randomly generated data stream over a channel. The stream is then received, demodulated and BER is calculated each time for every simulation. Multi-path appears in conditions where the transmitted signal experiences reflections, diffractions, and scattering. This is due to obstacles between transmitter and receiver. A channel in mobile communications can be simulated in many different ways. In our simulations, we have considered the two most commonly used channels: the Additive White Gaussian Noise (AWGN) model and a Rayleigh fading channel model. The channel model is based on the worst case scenario, assuming that no line-of-sight path is available between the transmitter and the receiver. On the other hand, a wideband fading channel can be modeled as a sum of several differently delayed, independent Rayleigh fading process. The corresponding channel impulse response is described as:

$$h(t, \tau) = \sum_{p=1}^P a_p R_p(t) \delta(\tau - \tau_p) \quad (3)$$

where:  $a_p$  is the normalized amplitude,  $R_p(t)$  is the Rayleigh fading process,  $\tau_p$  is the delay of the p-th path.

5.2 MC-CDMA simulation results

The graph of BER versus Es/No is shown in figure 2. The model is based on MC-CDMA with PN code. The graph indicates that the transmission quality don't depend on Es/No.

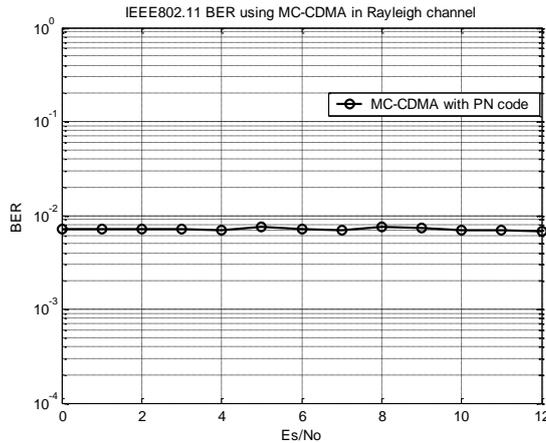


Fig.2. The BER vs. Es/No of MC-CDMA model in Rayleigh channel

The objective of this work is to investigate the performance of the MC-CDMA in the Wi-Fi environment. So to evaluate this study we will compare it with a second scheme based on CDMA. Figure 3 illustrates the general block diagram of the transceiver for the CDMA in IEEE 802.11b we used. The input data stream is first mapped into DBPSK and then the output is spread by Barker code. The spread signal is then passed through a matched filter adapted to the rectangular shape of the data; IEEE 802.11b systems utilize raise cosine filter. Finally, the data are sent to the receiver over the channel. The data are sent to the receiver over the same channels used before. At the receiver the inverse operation is employed

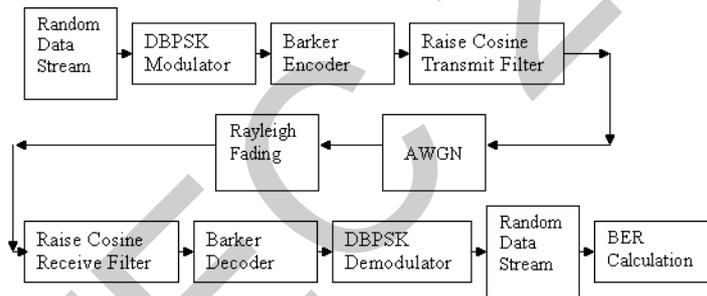


Fig. 3. Simulation Block diagram of the transmitter and receiver for the CDMA in IEEE 802.11b

The graphs in figure 4 indicate that the transmission quality is degraded for CDMA model when compared with the MC-CDMA in the Rayleigh channel.

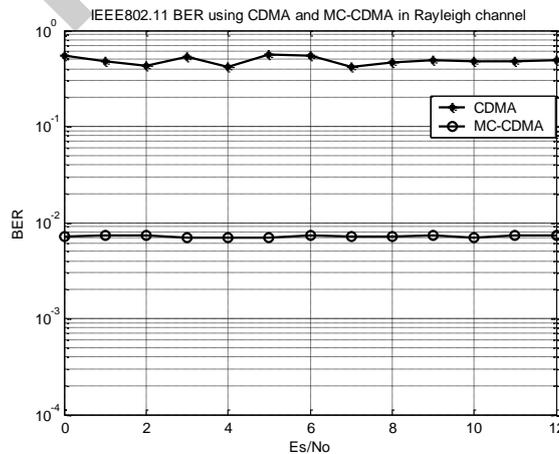


Fig.4. The BER vs. Es/No of CDMA and MC-CDMA models in Rayleigh channel

The MC-CDMA performs best in that it shows the least BER while CDMA is the worst for the same modulation.

## 6. CONCLUSION

In this article, we are proposing a modified version of the IEEE 802.11 system, based on MC-CDMA as PHY layer. This modified layer particularly concentrates on IEEE 802.11a standard because its physical layer design is considered to be more robust against harsh propagation conditions. A Rayleigh fading channel model is used to resemble the real world scenario. In this case the transmission quality is degraded because of the multi path effects.

The simulation results were plotted in terms of BER versus  $E_s/N_0$  for the performance of the MC-CDMA. From the performed simulations, the numerical results show that the MC-CDMA is a powerful multi-carrier multiple access technology, capable of significantly outperforming its CDMA counterpart with an adequate spreading sequence code.

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# INFLUENCE OF CARBON BLACK ON THE CHARACTERISTICS OF HDPE

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## Abstract

The materials studied are based thermoplastic polyethylene. Their use is involved particularly in pressure pipes for water supply (potable or waste water) and gases, protective tubes for cables and pipes without pressure for the removal from wastewater. These materials are therefore forced to undergo multiaxial stress loadings at different speeds. Our contribution is to highlight the effect of carbon black, for that we have methods to characterize the mechanical behavior of materials and neutral after addition of carbon black for two types of loads in quasi-static.

## Keywords:

Polymer, carbon black, mechanical characteristics

## 1 INTRODUCTION

Generally, polymers are damaged by UV rays from the sun. To this end, adds an inhibitor: carbon black or dye with stabilizer is necessary. In this work, we investigate the influence of black carbon on mechanical properties. The mechanical behavior of virgin materials and reloaded was characterized for two types of stress: traction and resilience. Evolutions characteristics of elasticity, plasticity and fracture were identified. Comparisons between the different loading modes helped highlight the complex effect of black carbon on the characteristics of the materials studied.

## 2 PREPARATION OF MATERIAL

The HDPE of the study was made initially in the form of granules (Figure1). It was then extruded to make plates (Figure 2, 3,) and to extract éprouvettes (Figure 4). The extrusion conditions are determined to ensure cooling as homogeneous as possible in the plates. The extrusion conditions limit the maximum thickness of plates about 6 mm.



Figure 1: Granule of HDPE.



Figure 2: Press



Figure 3: Addition of black of carbon.

## GEOMETRY OF TEST SPECIMENS

The smooth specimens were collected initially from the plates the thickness  $B$  is 2 mm, the width  $W$  is 6mm. Effective area is so  $12\text{mm}^2$ .



Figure 4: Tensile specimens according to ASTM

3 PHYSICAL-CHEMICAL ANALYSIS

3.1 Determination of softening point

This test indicates the actual temperature at which the product begins to soften, that is to say, beyond which penetration is increasing rapidly. This temperature is called the Vicat softening point is that when a needle with a flat section of 1mm<sup>2</sup> penetrates 1mm into a sample plate with a thickness of 3mm with a load of 1kg and a uniform rate of temperature rise (Figure 5; 6)

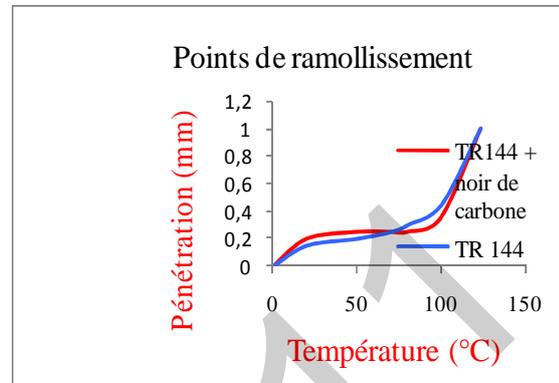


Figure 5: A view of the mechanism of softening

Figure 6: Diagram of penetration as a function of temperature.

3.2 Determination of density

The determination of the density of HDPE is made with a precision of one ten-thousandth. To determine this, cut a small piece of a plate specially made for and soak in isopropanol, then dip it in the column density and height read after 15 min of stabilization. Density is determined by referring to two different colors and floats of known densities. The distances between the different elements are determined using a ruler and a marker the calculation is done using the formula 1.

$D = Y/Z(B-A) + A$       Z : distance between the two floats A and B ; B : 2nd density float ; A: density of 1 float ; Y : distance between the specimen and float to low density.

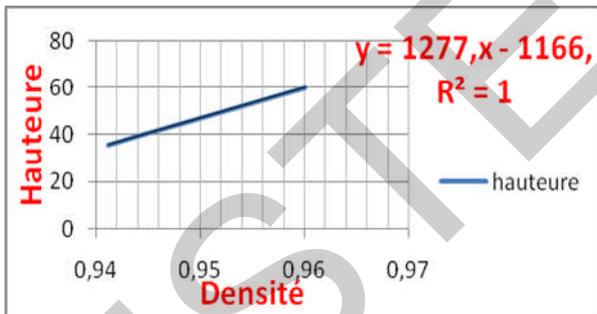


Figure 8: Diagram of the variation in the density function of the height of the columns

3.3 Determination of the melt index

The method describes the technique adopted to determine the rate of extrusion of polyethylene through a hole of denial specified in the prescribed conditions of pressure and temperature.



Figure 9: Appareil Melt flow index.

Désignation	Melt index g10	Density g/cm <sup>3</sup>	Hardness
TR144	0.15	0.9453	58.33
TR 144+ 2.5 NC	0.16	0.9563	66
S502	0.35	0.9559	67.66
S502+ 2.5 NC	0.40	0.9655	66
6030	1.2	0.9634	61.33
6030+ 2.5 NC	2	0.9683	66

TABLE 1: Result physicochemical tests of materials expressly studied

4 RESULTS TEST

Tensile tests at room temperature and impact tests were conducted at the Laboratory of unit « ENIP POLYMED SKIKDA ALGERIE » in collaboration with the « University Badji Mokhtar Annaba Algeria »

4.1 Tensile test

The figure 11 show the damaged specimen after the tensile test



Figure 10: Testing Machines Sun500.



Materials	A <sub>e</sub> %	A <sub>r</sub> %	σ <sub>e</sub>
TR144	5.9.	478.39	19.74
TR 144+ NC	6.12	348.8	20.34
5502	5.34	322.87	22.62
5502 + NC	4.45	12.87	24.19
6030	4.4	126.86	26.65
6030 + NC	4.14	6.38	26.41

Table 2: Summarizes the results of the tensile test

Figure 11: Damages specimen after the tensile test.

Digraphs of Figures 12-17 represent the different characteristics.

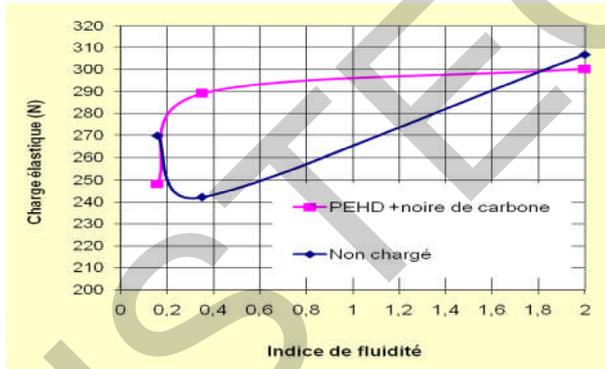


Figure 12: Diagram of elastic load.

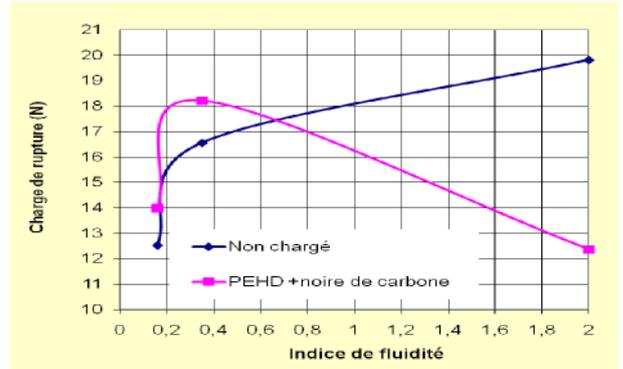


Figure 13: Diagram of breaking load.

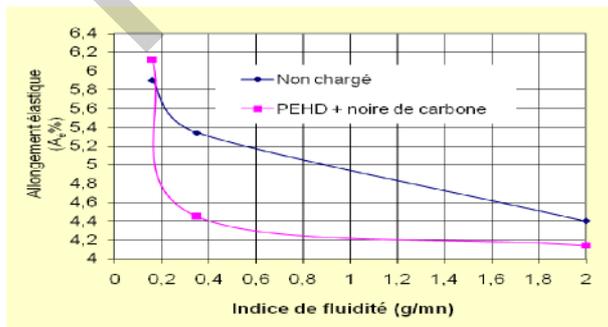


Figure 14: Diagram of elastic elongation.

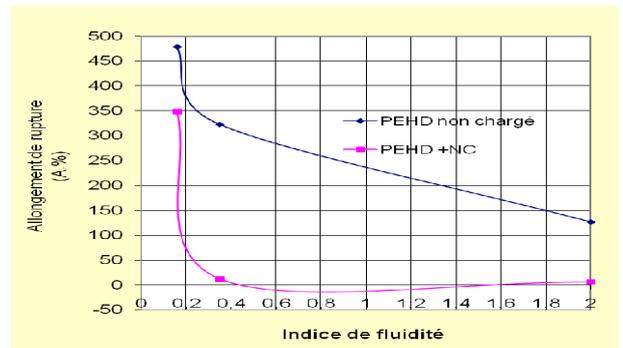


Figure 15: Diagram of breaking elongation.

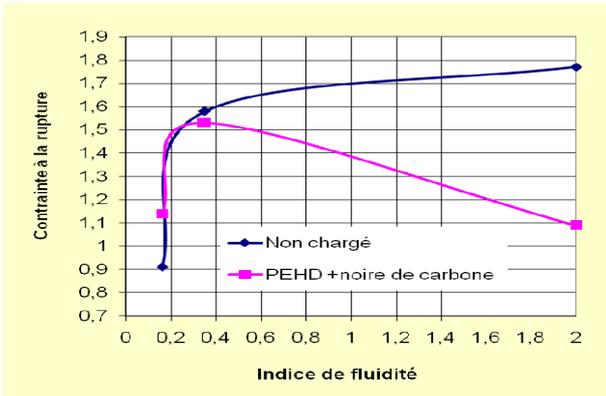


Figure 16: Diagram of Elastic stress.

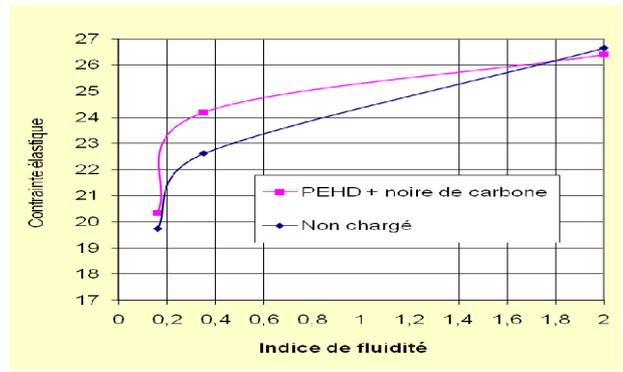


Figure 17: Diagram of breaking stress.

4.2 Test of resilience

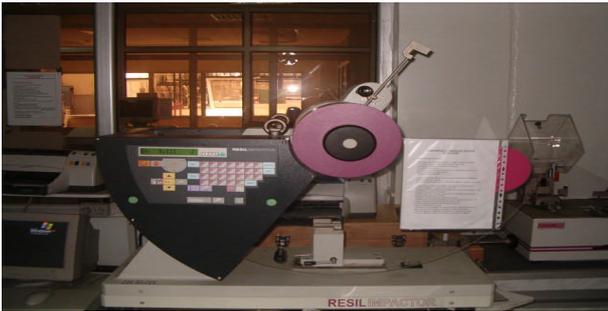
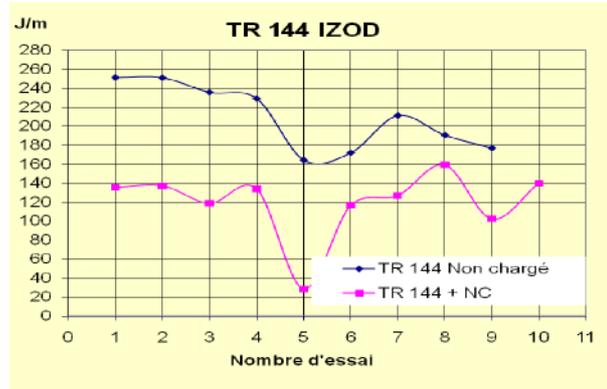
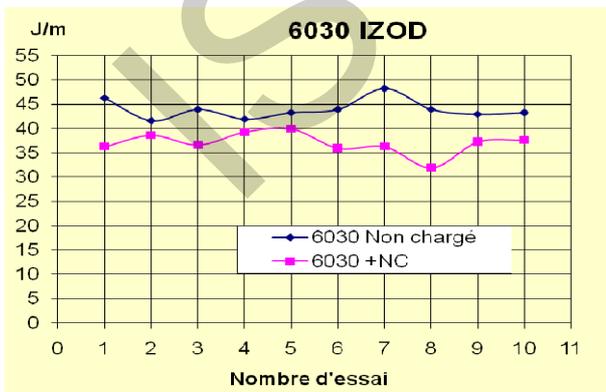
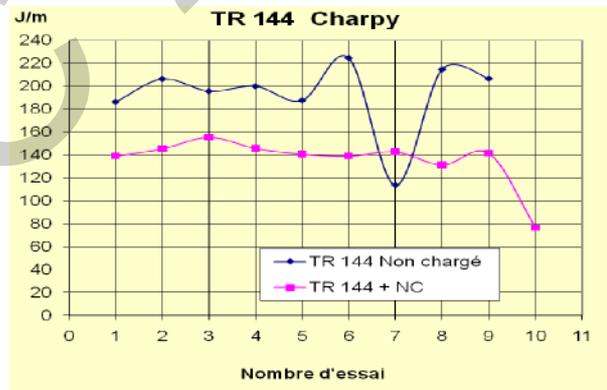
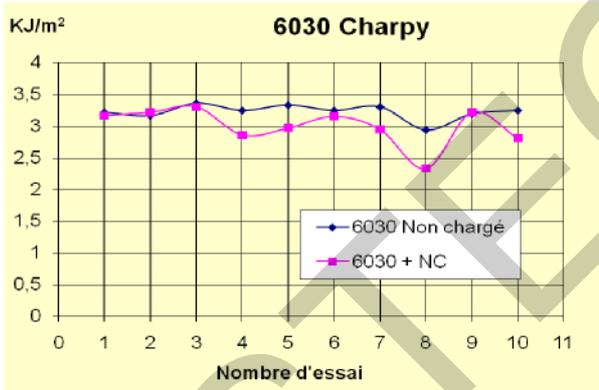


Figure 18: Charpy sheep.



Figure 19: Photograph of the damaged specimens.

Digraphs of Figures 20-24 represent the different characteristics of the impact test.



5 CONCLUSIONS AND FUTURE DEVELOPMENTS

The changes of mechanical properties have been identified based on reloading. Comparisons between the different loading modes helped highlight the complex effect of carbon black on properties of materials tested. All these observations at both micro and macro enabled us to propose the first models of the macroscopic behavior observed in these trials. These models, once incorporated into codes of industrial computing wil allow us to study the effects of charging.

## 6 ACKNOWLEDGEMENTS

The authors thank the Laboratory Unit ENIP POLYMED SKIKDA ALGERIA for their assistance.

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# LAMİNE KOMPOZİT MALZEMELERİN BALİSTİK DAVRANIŞLARININ DENEYSEL METOTLA İNCELENMESİ

## EXPERIMENTAL INVESTIGATION OF BALLISTIC BEHAVIOR OF LAMINATED COMPOSITE MATERIALS

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### ÖZET

Günümüzde savunma sanayi büyük önem taşımaktadır. Sanayiye yatırım yapan ülkeler gerek askeri gerekse ekonomik açıdan önemli seviyelerde bulunmaktadır. Savunma sistemlerinde kullanılan koruyucu zırhların geliştirilmesi adına birçok çalışma yapılmaktadır. Kompozit malzemeler, zırh sistemlerinin geliştirilmesinde önemli rol oynamaktadır. Bu çalışmada kompozit malzemelerden elde edilen zırhların balistik davranışları incelenmiştir. 3 farklı katman, tüm kombinasyonlarda sıralanarak 6 tane deney numunesi hazırlanmıştır. Bu katmanlar; kevlar, karbon fiber ile lamine edilmiş alüminyum bal peteği ve iki arka arkaya konulmuş kontrplaktır. Safir T14 uzun namlulu tüfek ve Yavaşalar 36 kalibre tek kurşun fişek kullanılarak numunelerin balistik davranışları incelenmiştir. Çalışmanın sonucunda aynı malzemelerin farklı şekilde dizilişleri ile birbirinden çok farklı davranışlar gösterdiği saptanmış ve iki numunenin, hedefi mermiden korumada yeterli düzeyde olduğu tespit edilmiştir.

### ABSTRACT

Nowadays, defense industry is of great importance. Countries that made investments in this industry are in the significant levels both military and economic fields. Many investigations are being made to develop protective armors that used in defense systems. Composite materials play an important role in the development of armor systems. In this study, ballistic behavior of armors investigated that produced from composite materials. Six specimens prepared by different combination of three different layers that are Kevlar, carbon fiber laminated honeycomb and two plywood. Safir T14 long-barreled rifle and Yavasalar 36 caliber one cored projectile were used to define ballistic behaviors of the specimens. As a result of this study it is obtained from those different combinations of the same materials show different ballistic behaviors and two armors were enough strength for protecting target from the projectile.

*Keywords: Armour, composite materials, carbon fiber, ballistic*

### 1. GİRİŞ

Günümüz teknolojisinin temelinde, malzeme alanındaki iyileştirilmeler ve yeni buluşlar için yapılan çalışmalar yatmaktadır. Malzeme bilimi, gelişen teknolojik koşullar içerisinde tek bir mühendislik dalı olmaktan çıkıp, metaller, ametaller, kimyasallar, organikler, inorganikler, polimerler vb. dallara ayrılmıştır. Bu gruplaşmanın içerisinde kompozit malzemeler, en önemli ve geniş uygulama alanına sahip çalışma sahasını oluşturmaktadır. Uzay mühendisliği, havacılık, otomotiv, tekstil ve savunma sanayi gibi önemli endüstri kolları, kompozit malzemelerin önemini benimsetmiş ve gelişimden üst seviyede faydalanmıştır. Kompozit malzeme, genel tanımı itibariyle, biri matris diğeri de takviye olmak üzere iki veya daha fazla malzemenin bir araya gelmesiyle oluşturduğu, daha üstün özelliklere sahip olan malzemedir. Oluşturulan bu karışım, içerdiği matrisin mekanik veya fiziksel özelliklerinden farklı bir özelliğe sahiptir. Kompozit malzemeler, kendisini oluşturan bileşenlerin niteliklerinden daha üstün bir yapıya sahip olduğu için, mühendislik alanında büyük bir öneme sahiptir [1]. Savunma ve silah sanayi, tüm dünyada önemli bir yere sahiptir. Bu endüstriye yatırım yaparak teknolojisini geliştiren ülkeler hem askeri açıdan hem de ekonomik açıdan dünyada çok önemli konumlarda bulunmaktadır. Askeri deneylerin ve buluşların büyük çoğunluğu gizlilik içinde yapılmaktadır. Bu nedenle her ülkenin milli savunma ve silah sanayiine önem vermesi gerekmektedir [2].

Askeri sistemler, özellikle kara kuvvetlerini destekleyenler, daha hızlı, daha çevik ve daha mobil olmaya yönelik gelişmektedir. Bunun bir sonucu olarak, gelişmiş hafif vücut zırhı ve hafif araç zırhı talebi, yeni zırh malzemelerin gelişmesine neden olmuştur. Yüksek performans fiber malzemelerinden, her iki uygulama için de faydalanılmaktadır. Örneğin yumuşak, esnek fiber kumaşları olarak vücut zırhlanması veya rijit polimer matrisli kompozitlerinde takviye malzemesi olarak hafif araç zırhlanmasında kullanılabilir. Tüm tarihsel gelişme boyunca hafif ve esnek malzemeler araştırılarak, daha hafif vücut zırh sistemleri ile mobiliteyi artırmak ve aynı zamanda belirli tehditlere karşı koruma sağlanması hedeflenmiştir. Bu amaçla ilk malzemeler arasında deri ve hatta ipek metal plakalar ile birlikte kullanılarak, ihtiyaç duyulan korumaya ulaşılmaya çalışılmıştır. Metallerin tamamen vücut zırh sistemlerinden kalkması, Kore savaşına kadar gerçekleşmemiştir. Bu noktada, ikinci dünya savaşı süresince geliştirilmiş olan, bir naylon kumaş yelek ve bir E-cam fiber/etil selüloz kompozit yelek, kullanıma alınmıştır. Bu yelekler bomba ve parçaların neden olduğu yaralanma ve ölümlerin büyük bir kısmına karşı koruma

sağlamıştır. Naylon ve E-cam fiberler, düşük maliyetlerinden ötürü, günümüzde hala bazı uygulamaları bulmasına rağmen, yüksek performans fiberleri, birçok fiber takviyeli zırh uygulamaları için standart haline gelmiştir. Yüksek performans fiberleri tipik olarak örülmüş kumaş halinde yelekler, örülmüş veya örülmemiş olarak polimer matris kompozitlerinde takviye malzemesi halinde başlık amaçlı kullanılabilir [3].

Savunma amaçlı olarak üretilen ürünlerden beklenen temel özellikler vardır. Bunlardan en önemlileri beklenen tehditlere karşı koruma sağlama, hafif olması ve ekonomik olmasıdır. Bazı uygulamalarda da; zırhın sürekliliği istenir. Yani peş peşe gelen tehditlere karşı, her seferinde benzer bir koruma sağlanmalıdır [2]. Bir kumaş zırhın balistik performansı, kumaşın ve çarpan merminin fiziksel özelliklerine bağlıdır. Kumaşın fiziksel özellikleri, iplik elastisite modülü, iplik çekme gerilimi, iplik kırılma gerinimi, iplik doğrusal yoğunluğu ve dokuma yapısı gibi başlıkları içerir. Mermi karakteristikleri, kütle ve şekilden oluşmaktadır. Balistik kumaş malzemelerinin katmanları, bölgesel yoğunluğu artırmak ve kullanışlı zırhlar üretmek üzere kaplanmaktadır. Bu kumaş tabakaların balistik davranışları, modele göre optimize edilebilirse daha da kullanışlı olabilir [4]. Ağırlık kavramı, balistik zırh tasarımında önemli bir parametredir. Hafif zırhlar, enerji korunumunun ve hareket kabiliyetinin artırılması için önemlidir. Metalik malzeme olarak, yüksek dayanımlı çelikler, alüminyum alaşımlar, titanyum alaşımlar zırh yapımında yaygın olarak kullanılmıştır. Çünkü bu malzemeler, yüksek mukavemet, iyi şekillendirilme ve buna bağlı yüksek tokluk, kaynak edilebilirlik ve yüksek balistik performans parametrelerinin kombinasyonlarına sahiptir. Bunun yanında, monolitik metalik malzemeler genel olarak ağırdır [5]. Tasarımcılar ve zırh kullanıcılarının her ikisinin de karşılaştığı iki ilginç seçim; ağırlıktan kaynaklanan rekabet koşullarının nasıl en iyi şekilde dengeleneceği, belirli bir tehdit seviyesinde zırh paketi için kalınlık ve maliyet parametreleri. Tekil tabaka olarak üretilen bir zırh sistemi ufak çaplı kalibredeki mermiler için iyi bir dayanım gösterebilir. Bunun yanında, zırh delici mermileri alt etmek için çoklu katmalı örneğin kompozit destekli sert seramik ön yüzeyli zırh sistemleri gereklidir ve yaygın olarak kullanılmaktadır. Bu tip mermiler, sertleştirilmiş çelik veya tungsten karpit gibi sert çekirdek malzemesi içerirler ve seramik yüzey çarpma sırasında merminin etkisini azaltır ve aşındırır. Kompozit destek ise yavaşlamış olan merminin kinetik enerjisini absorbe eder ve ayrıca seramik ve mermi parçalarını tutarak daha fazla hasara neden olmasını engeller [6].

Yüksek mukavemetli kumaşlar, daha öncede bahsedildiği gibi, esneklik ve hafifliğin önemli olduğu balistik koruma sistemlerinde yaygın olarak kullanılmaktadır. Çalışmalar neticesinde, içyüzeysel sürtünme, bu tür kumaşların çarpma enerjisini absorbe kabiliyetini etkilemektedir. Tan [7] ve arkadaşları, tek katmanlı Twaron kumaşının balistik performansı üzerine deneysel çalışmalar yapmıştır. Bu çalışmalarında, farklı kalibredeki mermilerle, karşılıklı iki kenarlarından sıkıştırılmış dikkörtgen kumaş numuneleri üzerinde çarpma testleri yapmışlardır. Bu çalışmaları göstermiştir ki, gelişen mermi tipleri-kumaş sürtünmesi, çarpma sırasındaki enerjinin sönmülmesinde önemli bir mekanizmadır. Briscoe ve Motamedi [8], üç farklı Kevlar kumaş tipinin balistik performansları bakımından sürtünme karakteristiklerini incelemiştir. Kullanılan kumaş tipleri için anlaşılmıştır ki, sürtünme derecelerinin artırılmasıyla bağlantılı olarak, hedefi delmek için gerekli hız da artmalıdır. Yüksek sürtünme derecesine sahip olan kumaş, daha fazla enerjiyi absorbe eder [9]. Genellikle seramik tabakalı sert ön yüzey ve fiber destekli arka plakanın kombinasyonu olarak tasarlanan modern zırhlar, balistik ve yapısal gereksinimleri sağlamak üzere geliştirilirken aynı zamanda yaklaşık %30-40 oranında ağırlık tasarrufu sağlamaktadır [10]. Yüksek modüllü polietilen fiberlerinin gelişimi, kumaş zırhların etkisini artırmış ve bu fiberlerden yapılan kompozit zırhların balistik performansına olan ilgiyi meydana getirmiştir. Çoğunluklu olarak araştırmalar, yüksek dayanımlı fiber-seramik tabakaları üzerine yapılmıştır. Fakat pek az çalışma, metal ve yüksek mukavemetli fiberlerin kombinasyonunu keşfetmek üzere yapılmıştır [5]. Kompozit malzemeler belirli bir düşük ağırlıkta gösterdikleri mekanik özellikleri ile bilinmektedir. Bu özellikleri mühendislere, performans kaybı olmadan, ince ve sert yapılar tasarlamada yardımcı olur. Kompozit malzemelerin birçok faydası olmasına rağmen, çok karmaşık bir çarpma davranışı gösterirler ve artan yük çekme kapasitelerini güçlü bir şekilde etkileyen görünmez darbelere karşı oldukça hassastırlar [11].

Örülmüş kompozit materyaller birçok uygulamada birincil yapı bileşeni olarak kullanılmaktadır. Bu tip yapıların hasar analizleri, yapı tasarımlarının önemli bir bölümünü oluşturmaktadır. Avantajlarının yanında, örgülü kumaş kompozitlerinin karmaşık yapısı analizleri ve simülasyonları oldukça zorlaştırmaktadır. Örgülü kompozitlerin modellenmesi üzerine yapılan çalışmaların büyük kısmı, malzemelerin elastik özelliklerini öngörmek amacıyla yapılmıştır. Fakat pek az çalışma hasar davranışları üzerinde durmuştur. Bu nedenden ki, örgülü kumaş kompozitlerin ilerleyen hasar davranışları karmaşık bir olgu olmaktadır. Bu olgu, matris malzemesinin kumaş ile geometrik açıdan doğrusal olmayan uyulanması ve etkileşimdeki bileşenlerin gerilme yığılmasıyla hasar birikimlerinden oluşmaktadır [12]. Ticari ve sanayi uygulamalarında yaygın olarak kullanılan yüksek performans organik kumaş malzemesi aramid, polimerik reçine sistemleri ile mekanik ve kimyasal etkileşimi sınırlayan pürüzsüz ve düzgün bir yüzey sağlar. Kumaş ve reçineyi birbirinden karakteristik olarak ayıran bu özellik ara yüzeyde bir form oluşmasını imkânsızlaştırır. Aramid ile diğer organik kumaş ve farklı reçine sistemleri arasındaki ara yüzey etkileşimlerini artırmak için çok sayıda çalışma yapılmıştır [13]. Çarpmayı absorbe eden malzemelerin önemli bir sınıfı olarak kumaşlar ve esnek lifli kompozitler, kurşungeçirmez yelekler ve diğer vücut zırh sistemlerinde yaygın olarak kullanılmıştır. Bu malzemelerin kişisel koruma uygulamalarında kullanılmış olması, bu malzemelerin ve bu malzemelerden yapılan bileşenlerin mekanik tepkilerini anlamak üzere deneysel çalışmaların geliştirilmesini acilen gerektirmektedir. Kevlar\_KM2 kumaşı, yüksek sertlik, hafiflik ve yüksek dayanımları sayesinde kişisel koruma uygulamalarında geniş olarak kullanılmıştır. Bir kumaş zırh sisteminin deformasyon sürecini anlamak için malzeme özelliği, kumaş yapısı, mermi geometrisi, çarpma hızı, çoklu tabaka etkileşimi, uzak alan sınır koşulları ve sürtünme gibi birçok konu araştırılmalıdır (Chesseman ve Bogetti, 2003). Bu faktörlerin içinde, malzeme özellikleri zırhın etkenliğini belirlemede kritik önemdedir [14].

Tabakalı balistik kompozit malzemeleri, koruyucu başlıklarda veya seramik ve diğer malzemelerin katkısıyla koruyucu gövde zırhlarında kullanılabilir. Standart sert plaka korumalı vücut zırhları genellikle mermiyi kırmak ve yavaşlatmak için seramik

plaka ve mermiyi durdurmak ve seramik parçalarını tutmak için çok katlı kompozit panelden oluşan çoklu tabakalardan yapılır. Zırh, dinamik deformasyondan kaynaklanan potansiyel yaralanmayı azaltmak için kullanılan sarsıntı karşıtı tabaka içerebilir. Çarpma sırasında zırhta oluşan maksimum deplasman, arka yüz işareti (BFS) olarak tanımlanır ki bu balistik performans için önemli bir parametredir. Aramid içeren iki tip yaygın kompozit kumaş, vücut koruyucu zırhlarda kullanılabilir. Bunlar Kevlar ve polietilen asıllı Spectra veya Dyneema'dır. Dokuma yada tek yönlü liflerin katmanları termoplastik veya ısı ile sertleşen polimer matrislerle bağlanmaktadır [15].

Balistik deneyler sırasında, genellikle hedef malzemesinin radyal olarak hareketinin gerçekleştiği sünek delik genişlemesi görülmektedir. Bu sebepten dolayı, hedef malzemenin akma mukavemetinin yüksek olması, nüfuziyet direncinin de yüksek olmasına sebep olmaktadır. Yüksek tokluk ve sünekliliklerinden dolayı, metallerin çoklu çarpmaya karşı koyma kabiliyetleri oldukça yüksektir. Bununla birlikte metaller yumuşak malzemelerdir ve çarpışma esnasında hemen hemen merminin bütün kinetik enerjisi, hedefin deformasyonu ile sönmülenir. Seramikler ise metallere göre çok daha gevrek ve çoklu çarpmalara karşı mukavemetlerinin zayıf olmasına rağmen; düşük yoğunluk, yüksek rijitlik, yüksek sertlik ve yüksek basma mukavemetlerinden dolayı zırh sistemlerinde yaygın olarak kullanılırlar. Balistik çarpmada, çarpma yüzeyindeki yükler, basma niteliğinde olduğu için, burada yüksek sertlik ve rijitlik önem kazanmaktadır. Düşük yoğunluk, yüksek sertlik ve rijitliklerinden dolayı seramikler, genellikle zırh kombinasyonlarının ön yüzeyinde kullanılmaktadırlar. Çok yüksek sertlik ve elastisite modüllerinden dolayı seramikler, yüksek hızlı ve zırh delici mermileri hasara uğratabilmektedirler. Ancak bu işlevi yerine getirirken, parçalanırlar ve kullanımları tekil çarpma durumu ile sınırlı kalır. Buna karşılık tanecik takviyeli metal matrisli kompozitler, seramikler ve metallerin sunduğu özelliklerin karışımına sahip oldukları için, bu malzemelerin balistik performanslarının incelenmesi, önemli bir araştırma konusu olarak karşımıza çıkmaktadır [1].

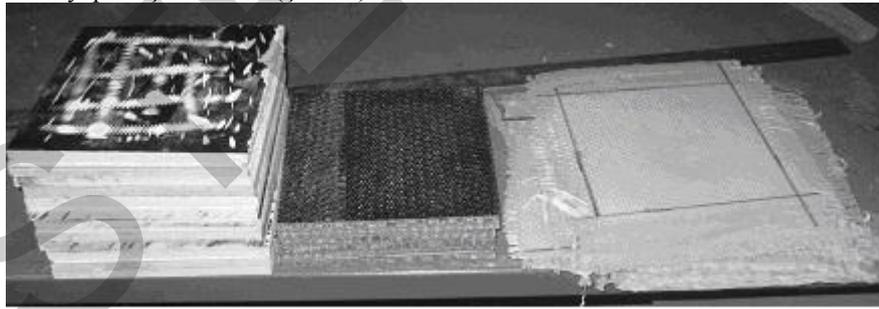
Günümüzde zırh yapımında en yaygın olarak çelik kullanılmaktadır. Çelik hakkındaki teknolojik bilgi birikiminin genişliği ve üretiminin diğer malzemelere nazaran daha ucuz olması, tercih edilmesindeki en büyük etkenlerdir. Fakat hafif zırh tasarımında, yüksek yoğunluğu sebebiyle çelik uygun değildir. Bu durum araştırmacıları, daha iyi malzeme geliştirmeye ve farklı malzeme kombinasyonları üretmeye teşvik etmiştir [4]. Bu çalışmada, farklı kombinasyonlarda dizilen kompozit zırh numunelerinin, balistik çarpmaya karşı olan davranışları deneysel olarak incelenmiştir. Deneyler sonucunda kullanılan iki kombinasyonun, merminin hedefe ulaşmasını engellediği ve sabit koşul için yeterli zırh görevini üstlendiği tespit edilmiştir.

## 2. MATERYAL ve METOT

### 2.1. Malzemeler ve Özellikleri

Literatür araştırması sonucu, üç farklı malzeme seçilmiş ve bu malzemelerin farklı kombinasyonlarda sıralanması ile altı adet deney numunesi hazırlanmıştır. Seçilen malzemeler şunlardır:

- Katmanlardan oluşan ve piyasada plywood olarak isimlendirilen kontrplak,
- Karbon fiber ile lamine edilmiş alüminyum bal petek yapısı (honeycomb),
- Epoksi reçine uygulaması yapılmış keklar 49 (Şekil 1)



Şekil 1. Kullanılan malzemeler; (a) Kontrplak, (b) Bal petek yapısı, (c) Kevlar

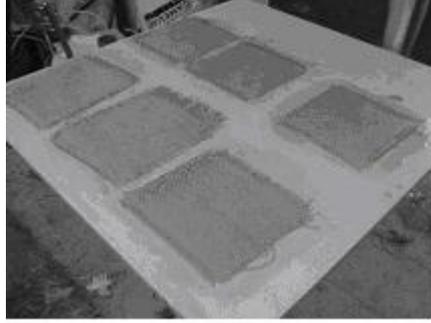
Numunelerin hazırlanma aşamasında iki adet 10 mm kalınlığında kontrplak yapılandırılarak kullanılmıştır. 10 mm kalınlığındaki kontrplak 9 katmandan oluşmaktadır. Katmanlar huş ve kayın ağacından yapılmıştır ve 0°-90° açılarla dizilmiştir. 10 mm kalınlığında alüminyum bal petek yapısı kullanılmıştır. Yapının iki yüzeyi de karbon fiber ile lamine edilmiştir. Bal petek yapısında Al5052 kullanılmıştır. Al5052'nin yoğunluğu 2680kg/m<sup>3</sup>, çekme dayanımı 290MPa, elastisite modülü 70000MPa'dır. 3 kat 49 serisi keklar kullanılmıştır. Kevların yoğunluğu 1440kg/m<sup>3</sup>, çekme dayanımı 3000MPa, elastisite modülü 112,4GPa'dır. Kevlar'a epoksi reçine uygulaması yapılmıştır. Kullanılan epoksinin markası ve modeli "Huntsman Ly 3505" dir. Çekme dayanımı: 85-90MPa, elastisite modülü: 3500-3900MPa'dır. Reçinenin içerisine katılan sertleştirici katkı maddesinin markası ve modeli Huntsman XB3405'dir. Hacim olarak 60 birim keklar için 40 birim epoksi uygulanmıştır. Katmanları yapıştırmak için Araldite 2021 epoksi yapıştırmacı kullanılmıştır.

### 2.2. Test Numunelerinin Üretim Aşamaları

Deney numunelerinin boyutu 200mm X 200mm'dir. Bal peteği yapısı ve tahtalar bu boyutta kesilmiştir. Kevlar ise epoksi uygulaması yapılmadan önce 250mm X 250mm boyutunda kesilmiştir. Epoksi uygulandıktan sonra kenarlarından spiralle kesilerek 200mm X 200mm boyutuna getirilmiştir. Bal peteği yapısının yüzeyine laminasyon işlemi için öncelikle adheziv film

yapıştırıcı uygulanmıştır. Film yapıştırıcının üzerine prepreg karbon fiber yapıştırılmıştır. Ardından 180°C sıcaklıkta ve 4bar basınçta fırına verilerek 30 dakika boyunca prepreg ürünün kürleşmesi sağlanmıştır.

Kevlara, epoksi uygulaması yapmak için pürüzsüz yüzeye sahip, yüzeyi kaplamalı bir tahta kullanılmıştır. Tahtanın üzerine bir sünger yardımıyla polivaks kalıp ayırıcı sürülerek 15 dakika beklenmiştir. Ardından kuru bir bezle yüzeyi iyice silinerek parlatılmıştır. Kevlara uygulanacak olan epoksi, ağırlık olarak %60 kevlar, %40 matris malzemesi olarak hazırlanmıştır. Matris malzemesi ise 100 birim epoksi, 42 birim sertleştirici olacak şekilde karıştırılarak hazırlanmıştır. Ardından hazırlanan epoksi, tahtanın üzerine bir rulo fırça yardımıyla sürülmüştür. Epoksinin üzerine kevların ilk katı konulmuştur. Kevların üzerine rulo fırça yardımıyla epoksi sürülmüştür. Bu işlem 2. ve 3. kat kevlar için tekrarlanmıştır. Diğer 5 numune için de epoksi uygulaması aynı şekilde yapılarak yaklaşık 10°C sıcaklıkta 12 saat kürleşmeye bırakılmıştır(Şekil 2).



Şekil 2. Epoksi uygulanmasından sonra kevlar malzemesinin görünüşü

Hazırlanan bu katmanlar farklı kombinasyonlarda dizilerek yapıştırılmıştır. Yapıştırıcının balistik teste bir etkisinin olmaması için sadece malzemelerin kenarlarına uygulanmıştır. Pürüzsüz yüzeylerde yapıştırıcının başarılı olabilmesi için zımparalama yapılmıştır. Yapıştırıcının daha iyi ara yüzey oluşturması için numuneler sıkıştırılmıştır(Şekil 3). Hazırlanan numune sıralaması ise Tablo 1 de verilmiştir.



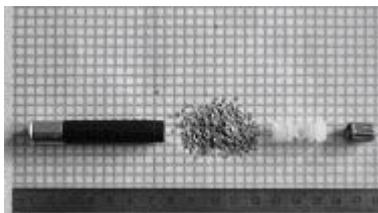
Şekil 3. Hazırlanan numunelerin sıkıştırılması

Tablo 1. Numunelerin Katman Sıralaması

Numune	Katman Sıralaması
1	Kontrplak, kevlar, bal peteği
2	Bal peteği, kevlar, kontrplak
3	Kevlar, bal peteği, kontrplak
4	Kevlar, kontrplak, bal peteği
5	Kontrplak, bal peteği, kevlar
6	Bal peteği, kontrplak, kevlar

### 2.3. Deneysel Çalışma

Deneysel çalışmada, Safir T14 Classic uzun namlulu av tüfeği kullanılmıştır. Tüfeğin kütlesi 2850gr olup; namlu uzunluğu 51cm, toplam uzunluğu ise 96cm'dir. 36 kalibrelik namlu çapına sahip tüfekte namlu çıkış hızı 700m/s olarak verilmiştir [17]. Test sırasında mermi tipi olarak Yavaşalar markalı YAF 36 CAL. SLUG model fişek kullanılmıştır (Şekil 4). Fişekün kurşun ağırlığı 7.5gr, piriñç yüksekliđi 16mm ve kovan yüksekliđi 65mm'dir[18].



Şekil 4. Yavaşalar YAF 36 CAL. SLUG fişek[i17]

Zırh, daha önce hazırlanan çelik bir çerçevenin içerisine civata yardımıyla sıkıştırılmıştır (Şekil 5). Deney düzeneği atış esnasında rijit bir davranış sergilemektedir. Standartlara göre uzun namlulu silahlarda 15 metre mesafeden atış yapılması gerekmektedir; ancak güvenlik gerekçesiyle 10m mesafeden atış yapılmıştır. Atış, gerçek koşulları canlandırmak amacıyla bir kişi tarafından yapılmış, tüfek her hangi bir düzenek kullanılarak sabitlenmemiştir.



Şekil 5. Deney Düzeneği

### 3. SONUÇLAR

Bu çalışmada malzemelerin dizilişlerinin balistik dayanıma olan etkisi araştırılarak zırh numunelerinin sönümlene kabiliyetleri incelenmiştir. Her bir numune için atışlar yapıldıktan sonra elde edilen sonuçlar ışığında malzeme davranışları gözlemlenmiştir. Birinci numunede mermi, zırhı delmiştir. Kontrplak malzemede ve bal peteği yapısında ciddi hasar meydana gelmiştir. Merminin zırhın arkasından çıkarken bal petek yapısının üzerinde bulunan karbon fiber malzemeyi parçalamıştır. Bu dizilişin uygun olmadığı alınan hasardan ve Şekil 6'den anlaşılmaktadır.



Ön Görünüş

Arka Görünüş

Kesit Görünüş

Şekil 6. Birinci Numunenin Görüntüleri

İkinci numunede de mermi, zırhı delmiştir. Şekil 7'de görüldüğü gibi bal peteği yapısının üzerinde yaklaşık olarak mermi çekirdeğinin çapı kadar bir delik açmıştır. Kontrplak malzemede merminin çıktığı yerin etrafı parçalanmıştır. Birinci numunede olduğu gibi bu numunede de delaminasyon oluşumu gözlenmektedir.



Ön Görünüş

Arka Görünüş

Kesit Görünüş

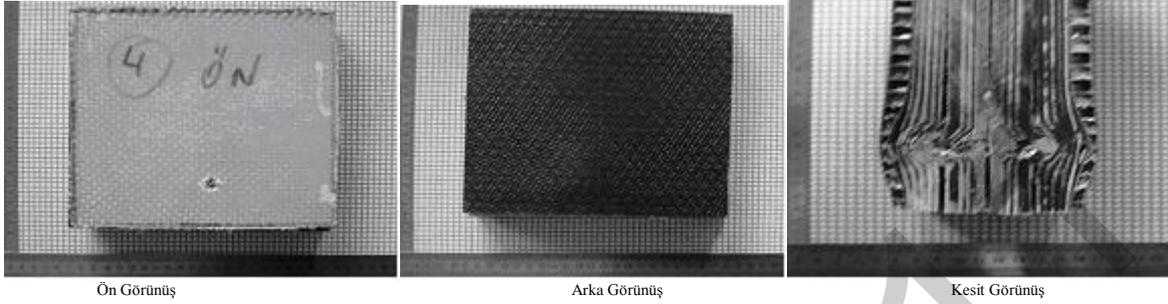
Şekil 7. İkinci Numunenin Görüntüleri

Üçüncü kombinasyonda, diğer bir sert malzeme olan epoksi uygulanmış kevlar 49 kullanılmış ve arkasına ikinci numunedeki gibi, diğer sert malzeme tercih edilmiştir (Şekil 8). İkinci deneydeki duruma benzer şekilde, sertleşmiş kevlar işlev görmemiş ve merminin ilerleyişini engellememiştir. Diğer katmanlar ise sönümlene işlemini gerçekleştirememiştir.



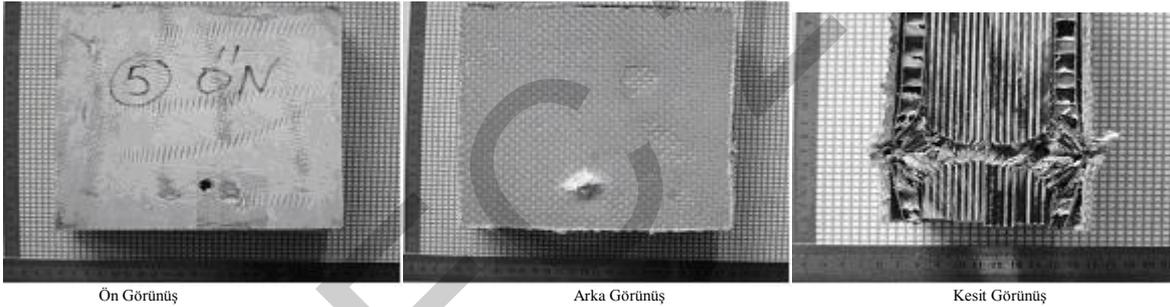
Şekil 8. Üçüncü Numunenin Görüntüleri

Dördüncü numunede, atış sonucunda merminin çekirdeği zırhın içinde kalmıştır (Şekil 9). Mermi çekirdeği, arka taraftan çıkamamıştır. Merminin çekirdeğinde yüksek miktarda plastik şekil değişimi gözlemlenmektedir. Zırhın arka kısmında bulunan bal peteği yapısında basma gerilmelerinin etkisiyle hücrelerde plastik deformasyon gözlemlenmiştir. Bal peteği yapısı arkaya doğru plastik olarak şekil değiştirerek sehim oluşturmuş ve bir derinlik izi meydana gelmiştir. Mermide plastik deformasyon gözlemlendiğinden tam ortadan kesilerek incelenen numunelerdeki mermi nüfuziyet miktarları farklıdır. Mermi çekirdeği Şekil 11'in kesit resminde mermi isabet ekseninin merkezinden kesilen numunenin sağ tarafı için 26mm ilerleme, sol tarafı için ise 28mm ilerleme tespit edilmiştir.



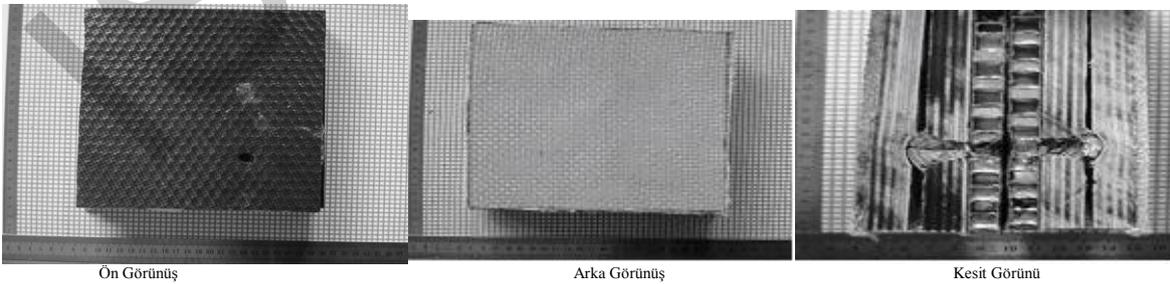
Şekil 9. Dördüncü Numunenin Görüntüleri

Beşinci numunede ilk numuneye benzer biçimde ilk olarak yumuşak olan kontrplak katmanı kullanılmış ve sonda bulunan sert katmanların yeri değiştirilmiş ve ilk deneydeki gibi mermi kompozit zırhı delerek dışarı çıkmıştır (Şekil 10). Tüm katmanlarda yüksek miktarda hasar oluşmuştur. Mermi zırhın arkasından çıkmıştır. Özellikle tahta ve bal peteği yapısındaki önemli miktarda parçalanma ve plastik şekil değişimi gerçekleşmiştir.



Şekil 10. Beşinci Numunenin Görüntüleri

Altıncı numunede mermi çekirdeği zırhın arkasından çıkmamıştır. Dördüncü numunenin atışa göre ters konumlandırılmış hali olan bu zırhta, bal peteği yapısı, aralıklı hava ile dolu petek dokusu ve karbon fiber ilk katmanı yardımıyla ilk darbeyi bertaraf etmiş ve biraz daha esnek olan epoksi uygulanmış kevlar 49'un arka taraftan yaptığı destek ile mermiyi hedeften koruyabilmiştir. Mermi çekirdeği Şekil 11'in kesit resminde mermi isabet ekseninin merkezinden kesilen numunenin sağ tarafı için 21mm ilerleme, sol tarafı için ise 22mm ilerleme tespit edilmiştir.



Şekil 11. Altıncı Numunenin Görüntüleri

#### 4. TARTIŞMA ve ÖNERİLER

Birinci, ikinci, üçüncü ve beşinci numuneler mermiyi engellemede başarısız olmuş; dördüncü ve altıncı numune merminin zırha nüfuz ederek sönmülmesini sağlamıştır. Birinci numunede kontrplak önde, kevlar ortada, bal peteği ise en arkadadır. Hasar oluşumuna baktığımızda, mermi ahşap malzemeye çarptığı anda yüksek hızından dolayı malzemede kayma gerilmeleri oluşturmuş ve yaklaşık mermi çapı kadar bir delik açmıştır. Ahşap malzemenin ortalarına kadar bu şekilde malzemeyi delen mermi, daha sonra hızını bir miktar kaybetmiş ve bu noktadan sonra basma gerilmeleri oluşturarak malzemede eğilme hasarı oluşturmuştur. Kevların rijitliğinin izafi olarak ahşap malzemeden fazla olmasından dolayı, mermi çekirdeği kevlara çarptığı

anda plastik deformasyonun etkisiyle ezilip, çapı iyice artmıştır. Daha sonra, mermi çekirdeği, karbon fiber katmanını ve bal peteği yapısını da parçalayarak dışarı çıkmıştır. İlk katmanda diğerlerine nazaran daha yumuşak bir malzeme olan kontrplak kullanımı merminin hızını kesememiş, arkada bulunan sert katmanlar bu durumda işlevini yitirmiştir.

İkinci numunede bal peteği önde, kevlar ortada, kontrplak en arkadadır. Yüksek hızla gelen mermi, bal peteği yapısı ve kevlarla çarpıp, bu malzemelerde kayma gerilmeleri oluşturmaktadır. Oluşan bu gerilmeler, 2 malzemede de mermi çapına yakın bir delik oluşturmaktadır. Bu sırada, mermi plastik olarak şekil değiştirmekte ve mermi çekirdeği ezilerek çapı büyümektedir. Daha sonra mermi, ahşap malzemeye çarpmakta ve azalan hızından dolayı burada basma gerilmeleri oluşturmaktadır. Mermi, ahşap malzemede ilerlerken, ahşap malzemenin arkasında oluşan çekme gerilmelerine karşı destekleyici bir malzeme olmadığı için ahşap malzeme katmanlarından ayrılmakta ve mermi arka yüzeyi parçalayarak çıkmaktadır. İlk kademede sert bir malzeme olarak bal peteği kullanılmış, fakat ikinci kademede devreye giren epoksi uygulanmış sert kevlar sönmüleme yapmak yerine merminin etkini azaltmadan durumu amplife etmiştir.

Üçüncü numunede kevlar önde, bal peteği ortada, kontrplak ise en arkadadır. İlk olarak kevlar ve bal peteği yapısına yüksek hızla çarpan mermi, bu malzemelerde kayma gerilmelerinin etkisiyle yaklaşık mermi çapı kadar delik meydana getirmektedir. Burada enerjisinin bir kısmını kaybeden mermi çekirdeği, kontrplağa çarptığında malzemede ağırlıklı olarak basma gerilmeleri oluşturmaktadır. Kontrplağın arkasında destekleyici bir katman olmadığı için kontrplağı parçalayarak zırhın arka tarafından çıkmıştır.

Dördüncü numunede kevlar önde, kontrplak ortada, bal peteği en arkada bulunmaktadır. Mermi çekirdeğinin kevlarla temas etmesiyle birlikte, kevların yüksek enerji absorbe etme özelliği sayesinde merminin hızı azalmaktadır. Aynı zamanda mermi çekirdeği plastik olarak şekil değiştirerek yayvanlaşmaktadır. Temas alanı artan mermi çekirdeği, ahşap malzemede ağırlıklı olarak basma gerilmelerine sebep olmaktadır. Aynı zamanda ahşap malzeme üzerinde daha geniş bir şok dalgası oluşturmaktadır. Bunun sonucunda enerjisinin büyük bir kısmı ahşap malzeme tarafından absorbe edilmektedir. Yüksek basma gerilmelerine karşı ahşap malzemenin iyi bir davranış gösterdiği söylenemez. Fakat burada oluşan basma gerilmelerine karşı koymasının ve parçalanmamasının temel nedeni arka tarafta destekleyici katman olarak bal peteği yapısının bulunmasıdır. Bu dizilimin uygun olduğu görülmüştür. İkinci ve üçüncü numunelerde, ilk iki katman sert malzemelerden oluştuğu halde mermi geçişi engellenememiştir. Bu durum için, ilk sert katman olan epoksili kevlar 49, darbeyi hafifletirken sönmüleyici kısım olan kontrplak bölgesinin gücünü arkadan destek olarak kullanılan bal peteği yapısı sağlamaktadır.

Beşinci numunede kontrplak önde, bal peteği ortada, kevlar en arkadadır. Mermi ahşap malzemeye çarptığı anda yüksek hızından dolayı malzemede kayma gerilmeleri oluşturmuş ve yaklaşık mermi çapı kadar bir delik açmıştır. Ahşap malzemenin ortalarına kadar bu şekilde malzemeyi delen mermi, daha sonra bir miktar hız kaybetmiş ve bu noktadan sonra malzeme üzerinde basma gerilmeleri oluşturarak eğilme hasarı meydana gelmiştir. Bal peteği yapısına temas ettiği anda plastik deformasyonun etkisiyle yayvanlaşan merminin oluşturduğu basma gerilmeleri, bal peteği yapısında büyük miktarda plastik deformasyon meydana getirmiştir. Daha sonra kevlarları parçalayarak zırhın arkasından çıkmıştır.

Altıncı numunede bal peteği önde, kontrplak ortada ve kevlar en arkada bulunmaktadır. Yüksek hızla gelen mermi, bal peteği yapısına çarpıp, bu malzemede kayma gerilmeleri oluşturmaktadır. Oluşan bu gerilme, malzemede mermi çapına yakın bir delik oluşturmaktadır. Bu sırada, mermi plastik olarak şekil değiştirmekte ve mermi çekirdeği ezilerek çapı büyümektedir. Temas alanı artan mermi çekirdeği, kontrplakta ağırlıklı olarak basma gerilmelerine sebep olmaktadır. Arkadaki kevların desteği ve önde bulunan bal peteğinin daha sert olması nedeniyle dördüncü numuneye göre daha az nüfuziyet ve daha fazla koruma sağlanmıştır. İkinci 10 mm kalınlığında kontrplağın yüzeyinde basma gerilmelerinin etkisiyle ezilme meydana gelmiş; yalnız mermi bu katmana nüfuz edememiştir. En arka katmanda bulunan kevlarlarda her hangi bir hasar meydana gelmemiştir. Bunun sonucunda mermi enerjisinin tamamı kontrplak tarafından absorbe edilmekte ve mermi zırh içerisinde kalmaktadır.

Numunelerin balistik davranışlarına baktığımızda, ahşap malzemenin zırh içerisindeki konumu, zırhın başarılı olmasındaki temel etkidir. Ahşap malzemenin önde olduğu numuneler başarısız olmuştur. Çünkü yüksek hızla gelen mermi çekirdeği, malzeme üzerinde kayma gerilmeleri oluşturmaktadır. Ahşap malzemenin kayma gerilmelerine karşı dayanımı düşük olduğundan büyük miktarda deformasyon oluşmakta ve ahşap malzemenin enerji absorbe etme özelliği büyük oranda azalmaktadır. Bu nedenle ahşap malzemenin önde kullanılması uygun değildir. Ahşap malzemenin ortada olduğu numuneler başarılı olmuştur. Çünkü mermi çekirdeği zırhın ilk katmanına çarptığı anda plastik şekil değiştirmekte ve çapı büyüyerek daha geniş bir alana etki etmektedir. Numunelerdeki hasar mekanizmalarına baktığımızda bunu net bir şekilde görebilmekteyiz. Ahşap malzemeyi arka kısımdan basma gerilmelerine karşı destekleyen bir malzeme olduğunda, ahşap malzeme çok yüksek miktarda enerji absorbe etme özelliği kazanmaktadır. Yapılan testler de bu durumu destekler niteliktedir. Ahşap malzemenin arkada olduğu numuneler başarısız olmuştur. Bal peteği yapısı ve kevlarları delerek ahşap malzemeye ulaşan mermi, enerjisinin büyük bir kısmını kaybetmiş olmasına rağmen, ahşap malzeme arkasında destekleyici herhangi bir katman olmadığı için ahşap malzemeyi parçalayarak dışarı çıkmıştır. Burada yapılan yorumlar, sadece tek numune üzerinde oluşan hasarlara bağlı olarak yapılmıştır. Kesin bir hasar değerlendirilmesi ancak bu deneylerin tekrarlanması ile yapılabilir. Çünkü silahtan atılan mermilerin aynı hızda çıkmaması ve üretilen zırhların aynı özellikte olmaması gibi parametrelere bağlı olarak zırhların balistik davranışları değişecektir.

Sonuç olarak, farklı kombinasyonlara sahip lamine kompozit malzemeler ile yapılan balistik deneylerinde önde rijit, ortada absorbe kabiliyeti olan ve sonda, ara malzemeyi destekleyen bir yapıya ihtiyaç duyulduğu anlaşılmaktadır. Buna göre yapılan

altıncı numunenin (bal peteği, kontrplak ve kevlar sıralaması) ise çalışmadaki en uygun ve mermiyi bertaraf edecek kompozit laminasyon olduğu tespit edilmiştir.

## 5. EKLER

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# INVESTIGATION OF CO<sub>2</sub> ADSORPTION ON ACTIVATED CARBON PREPARED FROM OLIVE STONE

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## ABSTRACT

In this study, the utilization of activated carbon to remove carbon dioxide from flue gas originated from coal burning power plants was investigated. Being different from other similar studies, olive stone was used as raw material, which is derived from olive and olive oil wastes in large amounts due to its high surface area, high amount produced in Turkey, sustainability and low economic value. Before the activation process, olive stones were impregnated with H<sub>3</sub>PO<sub>4</sub> solution that has a concentration of %35 and %50. Impregnated olive stones were activated in different conditions which vary for activation temperature from 400°C to 500°C and activation time 1 or 2 hours. Activated carbon samples were then subjected to different modes of modifications which involved thermal treatment at 650°C and 850°C, reflux with nitric acid that has the concentration of %50 to increase the surface chemical groups which have more basic character that is thought to be more efficient for CO<sub>2</sub> adsorption since CO<sub>2</sub> is an acidic gas. Modifications were also performed by metal doping with iron, copper and vanadium. After whole modification processes samples went through CO<sub>2</sub> adsorption process with different temperatures and pressures to investigate their affects on adsorption and determine the proper conditions. The results showed that the adsorption temperature and pressure had significantly effect on the amounts of CO<sub>2</sub> adsorbed. Textural characteristics of activated carbons and doped metals also played an important role on adsorption of CO<sub>2</sub>.

**Keywords:** Activated carbon, olive stone, metal doping, CO<sub>2</sub> adsorption

## INTRODUCTION

Forecasts of global energy use in the 21<sup>st</sup> century suggest an increasing dependence on fossil fuels, such as coal, oil and natural gas, which will result in increasing CO<sub>2</sub> emissions, and therefore, rising CO<sub>2</sub> concentrations in the atmosphere. Currently, carbon capture (direct and indirect capture) and carbon sequestration technologies (storage in terrestrial ecosystems, geological formations, and oceans) are being developed to achieve zero emissions when using carbon based fuels. CO<sub>2</sub> capture and separation from flue gas or fuel gas is the first step towards carbon sequestration. Porous materials, like molecular sieve and zeolites, as well as activated carbons, are suitable candidates for CO<sub>2</sub> capture by physical adsorption, due to their highly developed porous structure (Maroto-Valer et al., 2005).

Although structural properties including surface area and pore size distribution are effective on the adsorptive capacity of activated carbon (AC) but when specific interactions of adsorbate/ adsorbent play role in the adsorption process, other features such as surface chemistry should also be taken into consideration (Gauden & Wisniewski, 2007; Pastor-Villegas & Duran-Valle, 2002; Swider & Rolison, 1999). The surface chemistry of the activated carbons can be efficiently modified by chemical impregnation which together with the intrinsic nature of the activated carbon can highly increase the adsorption capacity (Manocha, 2003).

According to the nature of the adsorbate, the surface chemistry of activated carbon can be modified by creating acidic or basic groups (Sun et al., 2007). As CO<sub>2</sub> is an acidic gas, the presence of basic species can cause a priori basic character of the carbon surface which promotes the CO<sub>2</sub> capture capacity (Alvim-Ferraz & Todo-Bom, 2003; Lach, 2007). It has been shown that the capacity of activated carbons to adsorb CO<sub>2</sub> – which is based on physical adsorption – can be increased by introducing nitrogen functional groups into their structure. The incorporation of these functionalities may be achieved by two techniques: impregnating the surface with appropriate chemicals or introducing nitrogen into the carbon structure. Impregnation is frequently used although this could lead to the blockage of the porous structure, which would reduce the adsorption capacity of the activated carbon. Nitrogen can be incorporated into the carbon structure by preparing activated carbons from N-containing polymers or by heat treatment of the carbons with gaseous ammonia (Pevida et al., 2008).

Impregnation of activated carbons by metal oxides as metallic species can be an efficient way to improve the surface adsorption characteristics of activated carbons. However, further works are needed in order to clarify activated carbon impregnating effect on CO<sub>2</sub> adsorption. However, the introduction of metallic species as surface additives can modify the adsorptive properties of activated carbons, the used method might results negative effects on adsorption capacity (Somy et al., 2009).

Although activated carbon is widely used as an adsorbent in many applications, to reach the full potential of activated carbons, many problems still need to be solved considering the required adsorption process. In this study activated carbon samples were subjected to different modes of modifications which involved thermal treatment at different temperatures, reflux with nitric acid and metal doping with iron (Fe), copper (Cu) and vanadium (V) to increase the surface chemical groups. The aim was to assess the effect of such modifications on the capacity of the activated carbon to capture CO<sub>2</sub>.

## EXPERIMENTAL

### Carbon Sample and Activation

Olive stones are used as raw materials for activated carbon production. Since chemical activation method was chosen to activate the raw material,  $H_3PO_4$  was utilized as chemical agent. Merck-85%  $H_3PO_4$  solution was diluted with distilled water to 35% and %50 and then olive stones were impregnated with  $H_3PO_4$  solution that has the concentration of %35 and %50, at 80 °C for 4 hours after reaching the desirable temperature with continued stirring (Yavuz et al., 2010). After impregnation, samples were dried in an oven at 110 °C during the night and were named as AC35 and AC50 (activated carbons impregnated with %35 and %50  $H_3PO_4$ ). The reason of impregnation with  $H_3PO_4$  was the availability to make the process in low temperatures by one step, possibility of recovering whole amount of  $H_3PO_4$  and  $H_3PO_4$ 's ability to decrease the amount of mass loss.

Olive stones that were impregnated with  $H_3PO_4$  and known as AC35 and AC50 were activated in different conditions which vary for activation temperature and activation time to see the surface area of different types of activated carbons (Çetinkaya, 2008). The samples which was impregnated with  $H_3PO_4$  that has a concentration of %35 and %50 were placed in a ceramic sample case in a horizontal quartz reactor and went under a thermal process at 400 °C with 5 °C/ min. heating rate, under  $N_2$  flow (300ml/min. flow rate) for 2 hours after reaching the desirable temperature. The samples were named as AC35-400-2 and AC50-400-2. The sample which was impregnated with  $H_3PO_4$  that has a concentration of %50 went under a thermal process at 500 °C with 5 °C/ min. heating rate, under  $N_2$  flow (300ml/min. flow rate) for 1 hour after reaching the desirable temperature and named as AC50-500-1. After heat treatment with ammonia, samples were washed with boiling distilled water until no further change in pH could be detected and dried over one night at 110 °C. Dried samples were then subjected to different modes of modifications which involved thermal treatment, reflux with nitric acid and metal doping with different metals.

### Surface Treatments

After BET surface area analysis of activated carbons, it was found that AC50-400-2 sample had the large surface area (1734, 77  $m^2$ /gr while others had 1615, 15 and 1646, 48  $m^2$ /gr ). Considering the amount of adsorption of  $CO_2$  mostly depends on the surface area and especially micro porosity (micro pore volumes) of the activated carbon, in scope of the characterization's results, AC50-400-2 sample was chosen for implementing further modifications.

- AC50-400-2 sample was placed in a ceramic case and in a horizontal quartz tube and held under  $N_2$  flow (300 ml/min.) for 1 hour after reaching the desirable temperature at 650 °C and 850 °C with a heating rate of 10°C/min. After thermal process samples were named as AC50-400-2-650-1 and AC50-400-2-850-1 (Muniz et al., 1998).
- AC50-400-2 sample was treated at reflux in %50 wt  $HNO_3$  for 4 hours at 90 °C. Then the oxidized sample was washed with distilled water until no further changes in pH could be detected and dried in an oven at 110 °C. Finally, sample was heat treated up to 850 °C with a heating rate of 10°C/min. in  $N_2$  flow with a flow rate of 300ml/min. for 1 hour. Modified sample was named as AC50-400-2-ref%50wt-850-1 (Muniz et al., 1998).
- In regard to former literature studies, AC samples were impregnated with vanadium, copper and iron in order to increase the carbon dioxide adsorption capacity of AC samples.  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Cu(NO_3)_2 \cdot 3H_2O$  and  $V_2O_5$  catalysts (Merck) were doped to AC samples by pore volume impregnation method (Tseng & Wey, 2006). Ferric nitrate and copper nitrate powders were diluted with distilled water to obtain certain metal concentrations (weight ratios of 0.5%, 1% and 2% for copper nitrate; 2%, 4%, and 5% for iron nitrate over AC). These solutions were prepared with distilled water; however vanadium pentaoxide solution was obtained by oxalic acid solution (Shimoda et al., 1985). AC samples were added to ferric nitrate and copper nitrate solutions (with the ratio of solution to AC being 8 ml:1 g) and put into water bath which was equilibrated at 343 K. On the other hand, vanadium pentaoxide mixed with oxalic acid ( weight ratios of 1%, 2% and 4% vanadium pentaoxide mixed over AC) was put into water bath until the color of the solution turns into blue from yellow, and then AC was added to the solution. According to pore volume impregnation method, stirring was maintained until the complete evaporation of the liquid phase insured. After the impregnation process, firstly the samples were dried at 383 K during all night; secondly calcination step was carried out to transform the metal nitrates into metal oxides. Calcination procedure was performed at 673 K for 4 hours by placing a ceramic pan containing the impregnated AC samples. After the calcination procedure, the samples were cooled down to room temperature in inert gas atmosphere (Çetinkaya, 2008).

### Sample Characterization

BET surface area analysis of the samples was measured by  $N_2$  adsorption-desorption isotherms at 77 K using a Quantachrome adsorption apparatus, Autosorb-1. Prior to the BET measurements, the samples were outgassed at 573 K under high vacuum during all night.

### $CO_2$ Adsorption

The adsorption capacity of the produced activated carbons was determined using a gas adsorption analyzer with volumetric method by using HPVA-100 (TA Instrument). In a typical adsorption study, about 125 mg of sample was placed in a small cell and every sample held under a pressure rate between 1 to 10 bars at room temperatures.

## RESULTS AND DISCUSSIONS

### Effect of Adsorption Temperature on CO<sub>2</sub> Adsorption

Fig. 1 shows the CO<sub>2</sub> adsorption capacities of the activated carbon (AC-50-400-2) measured at different adsorption temperatures (25, 50 and 100 °C). It can be seen that the adsorption capacity decreases rapidly with increasing adsorption temperature. This behavior is typical of a physical adsorption process, where both the surface adsorption energy and the molecule diffusion rate increase with increasing temperature. As a consequence, the adsorbed gas on the surface of the activated carbon becomes unstable, resulting in the desorption of adsorbed CO<sub>2</sub> molecules (Maroto-Valer, 2005). In the present study, the CO<sub>2</sub> capture capacity of the activated carbon at 25 °C is about 2 times higher than that at 100 °C (34,1 mg-CO<sub>2</sub>/g-adsorbent vs. 17,8 mg-CO<sub>2</sub>/g-adsorbent). However, typical flue gas temperatures are typically up to 150 °C and therefore, it is necessary to develop sorbents that can operate at higher temperatures (Maroto-Valer, 2005).

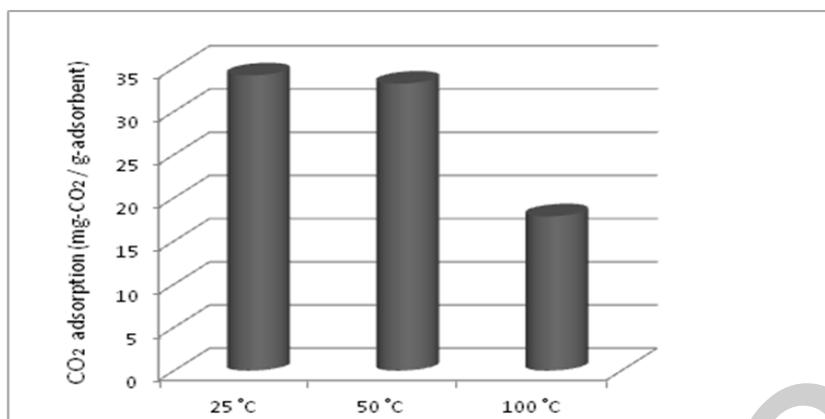


Figure 1. Effect of temperature on the CO<sub>2</sub> adsorption for activated carbon (AC-50-400-2)

### Effect of Adsorption Pressure on CO<sub>2</sub> Adsorption

Fig. 2 shows the CO<sub>2</sub> adsorption capacities of the activated carbon (AC-50-400-2) measured at different adsorption pressures between 1-20 bars. It can be seen that the adsorption capacity increases rapidly with increasing adsorption pressure. This behavior was observed for all the activated carbons produced in this work. According to the other articles on CO<sub>2</sub> adsorption with activated carbon, the same behavior can be seen that with increasing pressures, amount of adsorption of CO<sub>2</sub> increases too (Somy et al., 2009; Pellerano et al., 2009; Zhang et al., 2010; Guo et al., 2006).

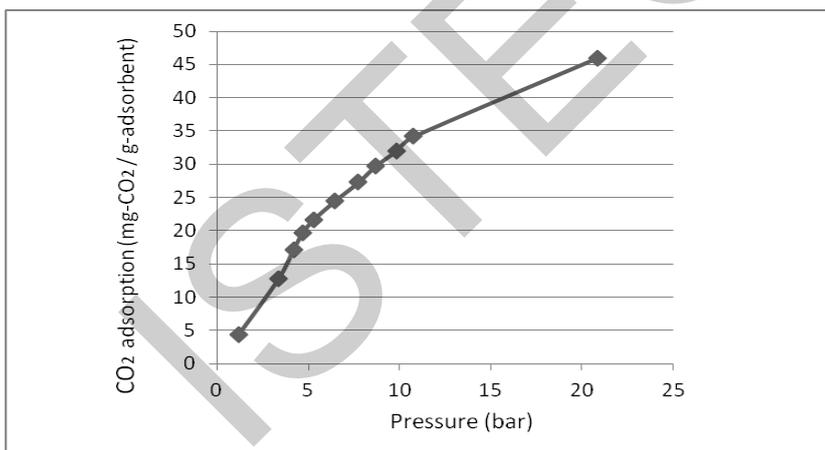


Figure 1. Effect of pressure on the CO<sub>2</sub> adsorption for activated carbon (AC-50-400-2)

### Effect of Surface Treatments on CO<sub>2</sub> Adsorption

#### Thermal Treatment

As seen from Table 1, the thermal modification makes an increasing impact on the adsorption amount of activated carbons. The CO<sub>2</sub> adsorption capacity decreased with increasing modification temperature. The sample that was modified at 650 °C has a larger surface area (BET), micropore volume and micropore surface area in comparison to the raw activated sample and modified sample at 850 °C and it can be explained that the higher amount of CO<sub>2</sub> adsorption for this sample is due to the fine pore structure, better surface area, micropore volume and micropore surface area. But for the sample that was modified at 850 °C, despite of having lower surface area, micropore volume and micropore surface area; it has higher amount of adsorption than the raw activated carbon has. It can be due to having some surface functional groups on the surface of activated carbon that can contribute to the chemical adsorption of CO<sub>2</sub> (Maroto-Valer, 2005).

Table 1. Porous structure properties of the activated carbon (AC-50-400-2) and its thermal treated counterparts

Sample	Adsorption amount at 25 °C and 10 bars (mg CO <sub>2</sub> / g adsorbent)	BET surface area (m <sup>2</sup> /g)	Micropore volume (cc/g)	Micropore surface area (m <sup>2</sup> /g)
AC-50-400-2 (raw activated carbon)	34,17	1734,77	0,806	2267,43
AC-50-400-2-650-1	45,63	1846,45	0,901	2534,94
AC-50-400-2-850-1	43,31	1201,40	0,578	1625,35

#### Nitric Acid Reflux

BET surface area of the sample treated with nitric acid is significantly less than the rest of the samples, suggesting that the oxidation with nitric acid is a very aggressive treatment that destroys the microporous carbon structure by blocking pores. The aim of this surface treatment is to create functional base groups on the surface of activated carbon. Some authors observed that the presence of sites of basic character increased the capacity of active carbons to adsorb CO<sub>2</sub> (Muniz et al., 1998). However some articles could manage to show this effect (Muniz et al., 1998), in our work according to our adsorption results this treatment failed to increase the adsorption of CO<sub>2</sub>. As reported elsewhere, dipping of activated carbon in a solution of additives may cause pore blocking in the structure of activated carbon which can cause decrease in adsorption capacity (Somy et al., 2009).

Table 2. Porous structure properties of the activated carbon AC-50-400-2 and its nitric acid treated counterpart

Sample	Adsorption amount at 25 °C and 10 bars (mg CO <sub>2</sub> / g adsorbent)	BET Surface area (m <sup>2</sup> /g)	Micropore volume (cc/g)	Micropore surface area (m <sup>2</sup> /g)
AC-50-400-2 (raw activated carbon)	34,17	1734,77	0,806	2267,43
AC50-400-2-ref%50wt-850-1	27,89	319,41	0,144	404,97

#### Metal impregnation

Table 3 shows the textural characteristics of the carbon parent sample and the samples impregnated with catalysts. It can be seen that both the micropore surfaces, as well as the micropore volume, decrease when the carbon is doped. The decrease in surface area and micropore volume shows that apparently the catalyst is distributed in the pores and also impregnation process causes pore blockage (Carabineiro et al., 2003). Therefore, CO<sub>2</sub> adsorption capacity of the carbon samples is expected to decrease. But considering the aim of modification is to create basic surface functional groups and providing that surface characteristic causes the increasing of CO<sub>2</sub> adsorption, all doped samples can refer to that aim except Fe of 5 %wt and V of 1%wt.

#### Vanadium

Activated carbon samples were impregnated with vanadium over activated carbon ratios of 1 % wt, 2 %wt and 4 %wt. The adsorption results were shown in Table 3. It is seen from table that vanadium loading (2 %wt and 4 %wt) improved the adsorption capacity of activated carbon samples. It can be concluded that the doping slightly increases the surface basic groups, probably as a consequence of the preparation process. Also it can be clearly seen from the results that textural properties have no impact on adsorption.

#### Copper

Copper was impregnated to activated carbon samples, the weight ratio of copper to activated carbon being 0.5 %, 1 % and 2 %. Obtained samples were exposed to adsorption processes, the results were given in Table 3. As shown in table, the best adsorption capacity for copper was obtained with the 2 % ratio. It can be explained with its higher surface area and especially micropore volume and micropore surface area in comparison to other Cu doped carbons. Although the textural properties of raw activated carbon is better than Cu doped carbons, doped carbons have higher adsorption capacities. It's due to the basic character surface functional groups were created on the surface.

#### Iron

Activated carbon samples were impregnated with iron over activated carbon ratios of 2 % wt, 4 %wt and 5 %wt. Samples impregnated with iron showed reduction on the adsorption with increasing ratio. But considering the raw activated carbon, adsorption amount of CO<sub>2</sub> is slightly higher. According to previous articles, the presence of Fe causes a marked increase on SO<sub>2</sub> adsorption capacity of activated carbon, and the highest efficiency was obtained with vanadium addition. This property of these metals may due to their typically high catalytic effect (Davini, 2001). Contrary of this study, Tseng et al. obtained that iron gave the second best result after vanadium (Tseng et al., 2003) and copper showed a lower activity increase. In this

experiment, metal activity orders are different from previous researches. In other research based on CO<sub>2</sub> adsorption with doped activated carbon, iron showed the highest adsorption results, vanadium was second and copper was third (Carabineiro et al., 2001). In our study, Cu is the strongest and V is the weakest metal to increase adsorption of CO<sub>2</sub>. Based on the opinion of SO<sub>2</sub> surface treatments and doping methods can refer to CO<sub>2</sub> adsorption experiments since they have similar acidic characters, the same results could be expected.

Table 3. Porous structure properties of the activated carbon AC-50-400-2 and its metal doped counterpart

Sample	Adsorption amount at 25 °C and 10 bars (mg CO <sub>2</sub> / g adsorbent)	BET surface area (m <sup>2</sup> /g)	Micropore volume (cc/g)	Micropore surface area (m <sup>2</sup> /g)
AC-50-400-2 (raw activated carbon)	34,17	1734,77	0,806	2267,43
Cu 0,5 % wt	44,13	1702,05	0,805	2265,12
Cu 1% wt	41,50	1248,23	0,626	1761,00
Cu 2% wt	47,41	1723,75	0,822	2313,01
V 1% wt	32,54	1120,58	0,524	1473,98
V 2% wt	34,65	926,30	0,446	1253,75
V 4% wt	39,76	924,99	0,433	1218,08
Fe 2% wt	43,22	1130,15	0,521	1465,54
Fe 4% wt	37,33	885,03	0,403	1134,97
Fe 5% wt	32,38	972,71	0,434	1221,52

## CONCLUSION

The adsorption of CO<sub>2</sub> on the activated carbon is mainly a physical adsorption process and the adsorbed amount decreased with increasing adsorption temperature. Also increasing pressure values cause higher adsorption of CO<sub>2</sub> between 1-10 bars.

Three surface treatment methods, including thermal treatment, metal impregnation and reflux with nitric acid (HNO<sub>3</sub>) were used to modify the surface properties of the activated carbons to increase their CO<sub>2</sub> capture capacity.

The thermal treatment increases the surface area of the activated samples, at lower temperature (650 °C).

Reflux with nitric acid results in a dramatic decrease of the surface area of the activated carbon, probably due to pore blockage and surface coverage. Both the thermal treatment and metal impregnation can increase the CO<sub>2</sub> capture capacity of the activated carbons, due to the possibility of introduction of basic surface functional groups on the surface.

Doped metal content of activated carbon is one of the most important parameters affecting to its CO<sub>2</sub> adsorption efficiency. Vanadium, copper and iron doping to activated carbon caused an improvement effect for its CO<sub>2</sub> adsorption capacity. The optimum percentage of doped metal over activated carbon changes per metal: 4 % wt for vanadium, 2 %wt for copper and 2 %wt for iron. The best results are obtained with copper and iron. Finally, metal impregnation improves the adsorption capacity of activated carbon due to their catalytic activity level.

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## METAPHORIC INTERPRETATIONS OF ADULT LEARNERS ON LIFE LONG LEARNING

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### ABSTRACT

Learning is a process of accumulated knowledge from experiences of individuals. It is a long process from harmonic picture of experiences. The concept of lifelong learning for adult learners becomes crucial to reveal their experiences in constructing knowledge. The story telling approach as research tool was used in this research. To capture interpretations of adult learners on lifelong learning in higher education, personal experience and voice of adult learners are gathered through stories and dialogue. This research relies on qualitative research design that twelve adult learners participated to this research. They are master degree students who are currently studying Educational Planning, Management, Administration and Economics Programme at Education Faculty. In this research, adult learners reflected that life long learning becomes as sky, computer, airplane, jumping to mountain, newborn baby, technology, flower, ship. Further to this, adult learners perceived themselves as life long learners that they are searching for new opportunities of learning through experiences especially in work context.

Learning is continual process which is the part of the lifelong process. Learning is transformation of information and experience into skills as Bramioh (2010) pointed out that learners can be succeed if they have a firm belief of their potentiality and capability to perform tasks within experiential learning environment.

Learning captures intellectual process and the socially embedded knowledge construction to cope with life and deal with problems in order to internalize transferable skills. Significantly, the role of the work and job context that we have are the significant indicators to generate skills, behaviors and attitudes and extend our potential as adult learners.

Within a life long learning process as it is associated with work context, learning and practice within the work shape our development and capability development (Devins, Smith & Holden, 2011; Knapper and Cropley, 2000). Harris (1999, p.165) claim that lifelong learning initiatives include development programmes, networks, counseling services, adult learning programmes which adults can develop their potential through socially, learning based programmes. Furthermore, life long learning process is currently a part of instructional strategies in higher education that significantly adult learners gain capability and skills through events, programmes from life long learning programmes (Day, Lovato, Tull & Ross-Gordon, 2011; Merrill, 2004).

As literature pointed out that life long learning programmes and activities are very significant to personal and professional for learners, sharing knowledge and exchanging ideas are the relevant process within life-long learning process. It is necessary to consider negotiation, sharing with others in order to co-construct knowledge and transform information for skills development.

In this respect, storytelling approach is the popular learning method within the classes in order to share knowledge, reflect own interpretations and gain better understanding from others' experience and point of views during learning process (Day, Lovato, Tull & Ross-Gordon, 2011; Merrill, 2004).

Story telling approach is the tool for revealing potential and understanding in a detailed explanation through imagination. It is a kind of metaphorical attempt for negotiating, sharing and gaining better understanding, constructing knowledge within classes, significantly in higher education. Also, it is appropriate for the adult learners who are capable to discuss, negotiate and have life experience with concrete examples.

The meaning of experiences and constructed knowledge can be revealed and exchanged with others by the language which consists of metaphorical interpretations. In exchanging knowledge, sharing ideas and experiences, people can use culturally embedded symbols, myths, and metaphors. In this respect, metaphors are the symbolic tools to reveal experience with a meaning. Within a learning process, metaphors can foster constructing knowledge, exchanging ideas based on a critical understanding. Metaphors are important as the way we reflect what we think, interpret about our views, and meanings to the specific experience.

Further to this, story telling approach is metaphoric tool to reveal what adult learners think, understand, construct within their learning process. As the role of storytelling approach, metaphors in to life long learning process shed a light to have theoretical framework for this research, this research opens academic discussion on how storytelling approach and metaphoric reflection help construction of knowledge in learning process for adult learners within higher education classes.

In this respect, this research paper aims to reveal metaphoric interpretations of adult learners on life long learning in higher education practices. The following research questions are answered in this research paper;

- Q1. How do adult learners define life long learning?
- Q2. How do adult learners perceive life long learning as metaphor?
- Q3. How do adult learners perceive life long learning to foster their professional development?

## **METHODOLOGY**

Constructing knowledge requires a process that relies on experiences, interpretations of learners. Adult learners' experiences have a great role to accomplish merits of co-construction of knowledge in today's context (Braumoh, 2010). As life long learning refers developing educational practice in order to foster learning throughout life, the understandings of adult learners were examined through story telling approach in this research study (Braumoh, 2010; Nielsen, 2006). Reflections on stories and dialogue telling approach as the story telling approach facilitates epistemological and methodological stance for the research that adult learners reflected their interpretations on life long learning through metaphors (Burchell, Dyson, 2000; Labonte, 2011). They reported their metaphoric interpretations on life long learning and they reflected their experiences in relation to co-construction of knowledge about the life long learning philosophy (Greer, Cavallaro, 2001).

The mode of research as a story telling that focuses on experiences and imaginations, thoughts of the adult learners about life long learning. In this respect, story telling approach emphasizes on personal experience and voice of adult learners to enhance education practices within research process (Labonte, 2011). As stories facilitates show and tell on sharing their experiences and interpretations, metaphors are used in this research for reflecting definitions about life long learning (Burchell, Dyson, 2000; Paechter, 2004).

Gathering ongoing reflections through stories, giving reflections on life long learning through explaining metaphors by adult learners justified the chosen research approach as a qualitative research journey in this research (Bochaver, Fenko, 2010; Marshall, 1999, Paechter, 2004). In this research, case study which is used as seeking for the answers of "how" or why questions in order to make exploratory interpretations through metaphors (Yin, 1994).

Twelve adult learners participated to this research that they selected purposively within this research journey. They are master degree students who are currently studying Educational Planning, Management, Administration and Economics Programme at Education Faculty. Twelve adult learners reported their experiences on life long learning by reflecting metaphors after getting in-depth understanding about life-long learning philosophy based on seminar that was presented by course instructor (Shaw, Mahlios, 2011; Diehl, Reese, 2010). Data was collected through self-reports that adult learners provide insights on the interpretations and reflection on life long learning (Silverman, 2005). Back translation was done to the collected qualitative data and data analyzed through content analysis (Silverman, 2005).

The research relied on the mode of the course which was entitled as “Management Effectiveness and Life Long Learning”. In this course, adult learners who were from master degree course on educational planning, management and administration, adult learners as research participants reported their imaginative thoughts and co-constructed knowledge within their professional development.

## **RESEARCH FINDINGS**

The research findings covered interpretations of adult learners about life- long learning, being life-long learners.

### **Metaphoric Interpretations on Life Long Learning**

One of the adult learners reported that new born baby is a metaphor for life long learning. This signifies starting learning from childhood by gaining knowledge step by step. New born baby have started to learn walking, talking through development. Adult learner 1 emphasized that life long learning represents to proceed development. Further to this, adult learner 2 stated that life long learning is as a technology. In here, technology represents a sign of development, reaching out knowledge, communication, learning.

Further to this, adult learner 3 reflected that life long learning is as a computer. It is considered as an updating knowledge in contemporary trends. Furthermore, adult learner 4 reported life long learning as a metaphoric way which is jumping to mountains. It is defined as learning through developing within safety environment in order to reach out right manner. Adult learner 5 stated that life long learning is information technology that diffuses learning, development.

In summary, adult learners reported various interpretations through metaphoric perspective which sky, flower, ship in the sea, airplane, raining. In this respect, they interpreted life long learning as accumulated knowledge from experiences, ongoing development and changes, adaptation to feed their personal and professional development within global standards and competitive world.

### **How Adult Learners Interpret Themselves as Life Long Learner**

Adult learners defined themselves as life long learner according to their life context. They reflected their understanding to themselves based on their experiences, thoughts. Adult learner 1 as life long learner pointed out that s/he is the learner who updates learning and knowledge according to global changes. Life longer is defined as adopting changes. Adult learner 2 defined the role of life long learner as discovering self day by day. Developing capabilities from experiences, realizing changes to empower abilities are part of life-long learning process. Adult learner 3 defined himself as an innovation of learning. Participant stated that being life long learning refers as learning by discovering. Adult learner 4 defined life long learner as gathering knowledge from collaborative environment through knowledge sharing. Further to this, adult learner 5 defined life long learner as learning through learning activities in work environment.

According to interpretations on being life-long learning, although adult learners reported different way of experiences for their roles, it can be clearly stated that they have a consciousness of being life long learner for their personal and professional development.

## **CONCLUSION AND DISCUSSION**

As constructing meaning is learning, focusing on learners’ thinking and learning through metaphors is essential in current learning-teaching process. In this respect, creating an environment of providing learning from attributed experience plays a great role. Story telling approach is important that learning is facilitated as a social activity and contextual. Especially, adult learners have potential to make dialectic method while constructing meaning as learning through their experiences (Johnson, 2001). Story telling as research tool was used to reveal interpretations of adult learners about life-long learning philosophy. They reported their metaphoric interpretations on life long learning and they shaped knowledge, attitudes through story telling approach (Labonté, 2011). Being a part of this activity as involving in story telling approach and the being part of the qualitative research naturally contributed to the personal and professional development of the adult learners.

The study of Shaw, Mahlios (2011) provides an insight on metaphors as a cognitive tool to know and understand how reality is and how we interpret reality. Metaphors supports adult learners better understand their change

process as well that adult learners understand and internalized their change and development process on their learning through metaphors in this research.

In this research, adult learners reflected that they saw life long learning as sky, computer, airplane, jumping to mountain, newborn baby, technology, flower, ship. They interpreted life long learning as ongoing development and adaptation to changes. Adult learners defined themselves as life long learners as being searching for new opportunities and learning through experiences especially in work context.

In further studies, the number of the participants as adult learners can be increased and action research approach can be conducted to realize changes and the progress of the adult learners in both social and professional roles.

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# AN ANTHROPOMETRIC STUDY OF THE SCHOOLCHILDREN IN TRNC PRIMARY SCHOOLS

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## ABSTRACT

The present study aimed at comparing the anthropometric characteristics of the schoolchildren with the characteristics of the school furniture used in the classrooms. A sample of 1095 students aged between 7 and 11 from 12 schools in the Turkish Republic of Northern Cyprus (TRNC) was participated in the study. The participants were initially given an information form and a comfort rating scale. After the completion of these, they were invited for anthropometric measurements. For the anthropometric measurements the researchers have used a Harpenden Anthropometer. The body-parts measured included knee height, popliteal height, buttock-popliteal length, hip breadth, elbow-seat height and shoulder height. The characteristics of the furniture used in the classrooms were identified by taking measures of different dimensions of the furniture. The outcomes of the present research would suggest implications for furniture designers and school managements. Moreover the findings could be used as a reference for following up the development of the schoolchildren's anthropometry.

**Keywords:** Anthropometrics, furniture design, schoolchildren, mismatch

## INTRODUCTION

Ergonomics can be defined as a scientific area that takes into account the match between human physical, cognitive and physiological capacity and the tools, equipment and physical environment that he interacts with (International Ergonomics Association, 2000). The ergonomics perspective is about considering the factors in a system that may form a risk for human health and well-being and eliminating or reducing them for improving work performance.

Preceding the Second World War many countries, especially the Unites States and some of the European countries have started applying ergonomics in different areas, (E.g. industry, education, hospitals etc.) in order to improve safety, health and productivity (Wilson, 2000). With the development of technology the importance of ergonomics practice has increased. Ignoring ergonomics issues may lead to musculoskeletal disorders (MSDs); psychological problems originated by stress, human error and reduced productivity. For example, Oztug et al. (2007) found that a group of office workers experiencing musculoskeletal symptoms reported reduced work productivity up to 40%.

Educational environments are of the areas where the risk factors behind the aetiology of the MSDs can be seen. Since initiating the action of "Ergonomics for Schools (<http://www.ergonomics4schools>)" there has been a significant increase in the number of studies performed in the field. A number of studies have been performed investigating the suitability of the desks and chairs to the student's anthropometry. Moreover, some of the researchers have studied the effects of carrying schoolbags on musculoskeletal symptoms (Watson et al., 2003; Whittfield, Legg, & Hedderley, 2005). With respect to the Legg (2007) the number of studies performed in the area of school ergonomics were not at satisfactory level.

In schools, as places where children spent most of their time, there is a need for designing the environment and educational equipment in a way that would keep the children safe (Cowie & Oztug, 2008) and provide opportunity for high quality education. Studies performed within the last decade have demonstrated the importance of providing the students with suitable furniture that would match their anthropometric characteristics. An Australian study (Milanes & Grimmer, 2004) found that back pain was prevalent among the students who were exposed to unsuitable desks and chairs in the classroom. Furthermore; spinal problems can be prevented by training the students on achieving right sitting and standing postures.

In Turkish Republic of Northern Cyprus (TRNC) the level of ergonomics awareness has not reached at desirable level yet. The number of studies performed is very limited. In addition to this, to the authors' awareness, no studies have been published in the indexed journals related to ergonomics issues in schools. The aims of the present research were as follows:

- Determining the anthropometric characteristics of the primary school students
- Determining the characteristics of the desks and chairs used in the classrooms
- Identifying the level of mismatch between student anthropometric characteristics and furniture used
- Obtaining how schoolchildren rate the level of desk-chair comfort when seated during the lessons

## METHODS

### Sample

1095 schoolchildren aged between 7 and 11 years old from 12 primary schools based in different districts of TRNC had volunteered to take part in the study. The schools were identified based on their location and consent was sought from the principals prior to the study. The ethics committee of the Ministry of Education of TRNC has approved the study. Primary schools in TRNC have five class levels; therefore one class from each level was identified randomly wherever there were multiple classes. The students were informed about the procedures and the measurements were taken on the voluntariness basis. The measurements were performed by two research students who were trained prior to data collection. The training sessions were continued until the researchers had reached to the desired level of consistency in repeated measurements.

### Instruments

The instruments used in the study consisted of a student information form, discomfort rating scale, a Harpenden Anthropometer (Holtain Limited, Wales, UK), a steel measurement tape, a wooden adjustable stool and data sheets.



Figure 1. Harpenden Anthropometer

### Data collection

#### Information form

Initially all the students were given an information form that was combined with a comfort rating scale. The information form inquired about gender, age, school name and the class level of the students. Finally a faces rating scale (IASP, 2001) was provided for comfort ratings. At this section the students from levels 3, 4 and 5 were asked “how comfortable do you feel while seated during the lessons” and asked marking the scale wherever it was appropriate. The test-re-test reliability of the comfort rating scale was performed with students from classes 3,4 and 5 during two consecutive weeks and the results demonstrated a highly reliable scale ( $n=53$ ,  $r=0,75$ ).

#### Measurements

All the measurements were taken while the students were seated on the adjustable stool provided and their shoes were off. The stool was adjusted to the level where the knees and right elbows of the subjects were bent at  $90^\circ$ . The body dimensions measured were as follows:

Knee height (1): The vertical distance from the floor to the upper surface of the knee with knee flexed at  $90^\circ$ .

Popliteal height (2): The vertical distance from the floor to the floor to the popliteal angle at the underside of the knee.

Buttock-popliteal length (3): Horizontal distance from the back of the uncompressed buttocks to the popliteal angle, at the back of the knee, where the back of the lower legs meet the underside of the thigh.

Hip breadth (4): Maximum horizontal distance across the hips in the sitting position.

Elbow-seat height (5): Vertical distance from the seat surface to the underside of the elbow.

Shoulder height (6): Vertical distance from the seat surface to the acromion (i.e. the bony point of the shoulder).

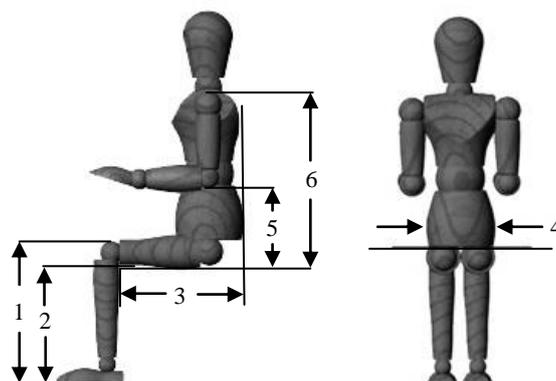


Figure 2. Anthropometric data obtained: knee height (1), popliteal height (2), buttock-popliteal length (3), hip breadth (4), elbow-seat height (5), shoulder height (6).

The classroom furniture used in schools that were in different sizes was also measured. The dimensions measured are as follows:

Seat height (Sh): The distance from the floor to the highest side of the seat.

Seat depth (Sd): The horizontal distance from the back of the sitting surface of the seat to its front edge.

Seat width (Sw): The horizontal distance from one side of the sitting surface to the other.

Backrest height (Bh): The vertical distance from the back edge of the sitting surface to the top edge of the backrest.

Desk height (Dh): The vertical distance from the floor to the top front edge of the desk.

Desk under-surface height (DUh): The vertical distance from the floor to the bottom of the front edge of the shelf under the writing surface.

Desk under-surface distance (DUd): The horizontal distance from the front edge of the shelf under the writing surface to the front edge of the writing surface.

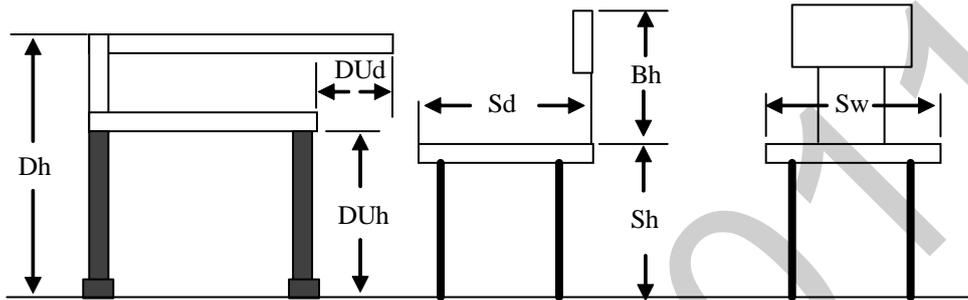


Figure 3. Illustration of furniture dimensions measured. Sh= seat height; Sd= seat depth; Sw= seat width; Bh= Backrest height; Dh= Desk height; DUh= Desk under-surface height; Dud= Desk under-surface distance

### DATA ANALYSIS AND RESULTS

All the data collected by means of measurements were recorded on the data sheets. The data on the data sheets has been entered in to the SPSS v17.0 and made ready for further statistical analysis. The project is still in progress; therefore the further stages will consist of using descriptive statistics such as maximum, minimum, mean and standard deviation values for the 1095 students from class1 to class 5. Furthermore, the degree of mismatch between the student's body measures and furniture characteristics will be calculated in terms of percentages.

### DISCUSSION

The results of the present study would provide an opportunity for understanding how appropriate the present furniture used in the schools in TRNC. It may also lead to understand how the interaction between the students and the school furniture effect perceived levels of comfort during the lessons. As it is demonstrated by Milanese and Grimmer (2004) the cause of musculoskeletal symptoms experienced by adolescent students may be attributed to school furniture design. Murphy and Buckle (2002) found that both back and neck pain were prevalent in English schools that could be attributed to high levels of trunk and neck flexion. The authors also reported that children were usually working in flexed postures. High levels of flexion found to increase the possibility of reporting short-term low-back pain. Saarni et al. (2007) demonstrated this issue by performing an experimental study. The working postures of the schoolchildren were video recorded at baseline, before new furniture introduced and followed thereafter. The results demonstrated that there had been an improvement in the back and neck postures of the intervention group compared to control group.

### CONCLUSIONS

Up to date only a few studies have been found to consider ergonomic issues in schools in TRNC. The present research has been conducted at primary school level and included schoolchildren aged between 7 and 11. Further research is necessary to study children from other age groups.

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