JOURNAL OF SCIENTIFIC PERSPECTIVES

JSP

International Peer-Reviewed and Open Access Electronic Journal

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Volume : 3 Year : 2019 Issue : 3

E-ISSN : 2587-3008

DOI : 10.26900

JOURNAL OF SCIENTIFIC PERSPECTIVES JSP

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JOURNAL OF SCIENTIFIC PERSPECTIVES JSP

International Peer-Reviewed Journal

Volume: 3
Issue: 3
July 2019

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **165-176**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.017
Research Article

THE SYNTHESIS OF SPHERICAL SHAPE AMINO FUNCTIONALIZED PEI-TGIC COVALENT ORGANIC FRAMEWORKS: SYNTHESIS, CHARACTERIZATION, AND METHYL ORANGE ABSORPTION

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Received: 27 June 2019; Accepted: 17 July 2019

ABSTRACT

In here, the synthesis of covalent organic framework (COF) from the reaction of polyethyleneimine (PEI) and triglycidyl isocyanurate (TGIC) in dimethylformamide at 90 ^{o}C were carried out. The surface are, pore volume and pore size values of PEI-TGIC COFs observed as 23.4 m^2/g, 0.143 cm^3/g, and 22.5 nm, respectively. Moreover, the surface charge of PEI-TGIC COFs increased to +46.1±2.6 mV from +18.3±1.7 mV, after protonation of amine groups of PEI-TGIC COFs. Moreover, the potential usage of PEI-TGIC based COFs in absorption methyl orange (MO) dye from aqueous media was testing. It was observed that, the PEI-TGIC COF absorbed 156.6±4.9 mg/g MO, and the protonated PEI-TGIC (p-PEI-TGIC) COFs absorbed 202.4±5.3 mg/g MO from aqueous media in 30 min. The MO absorption by PEI-TGIC COF fitted with pseudo-first-order kinetic model, whereas MO absorption by p-PEI-TGIC COF fitted with pseudo-second-order kinetic model.

Keywords: *Covalent organic framework, COF, PEI-TGIC, methyl orange absorption*

1. INTRODUCTION

In recent years, scientists have set out from nature's ability to create complex systems; have made great progress in the production of many materials with advanced functions by combining units in different shapes and structures [1-3]. By way of example, many materials have been synthesized from zero dimension materials [4] to three-dimensional materials [5], inorganic materials [6] to organic materials [7], irregular amorphous materials [8] to regular crystalline materials [9], non-porous materials [10] and porous materials [11] by using weak bonds such as p-p bonds [12] and stronger bonds such as covalent bonds [13]. For porous structure synthesis, exciting progress has been made in coordination chemistry and material science, and metal organic frameworks (MOFs), which are coordinated polymers have been synthesized using metal ions and organic ligands [5]. In addition, with recent significant developments, new generation amorphous materials of various pore sizes have been synthesized such as hyper crosslinked polymers (HCPs) [14], internal microporous polymers (PIMs) [15], conjugated microporous polymers (CMPs) [16], cryogels [17] and son on [18]. With these developments in the synthesis of porous structures; the synthesis of covalently bonded crystalline porous structures has been a new field of research for researchers. Studies have shown that the most important strategy for this purpose is the use of rigid units with multiple connections by covalent bonds [19]. Finally, in 2005, the first covalent organic frameworks (COFs) were synthesized by Yaghi and co-workers, with crystallin, and porous structure and high surface area [7].In brief, COFs are two- or three-dimensional porous crystal structures synthesized by regulation of organic subunits [7, 20, 21]. Although they were used for gas absorption [22] and separation [23] when first synthesized, advances in this area have enabled COFs to be used in a wide range of applications, from solar collectors [24] to optoelectronic devices [25], sensors [21] to catalysts [20], and environmental applications [26] to medical applications [27].

Dyestuffs are organic pollutants which are widely used in textile, paper, printing industry and home paints, produced about 7×10^5 metric tons annually and sold in the market with more than 100.000 types [28, 29]. Wastewater containing dyes is one of the most problematic organic pollutants due to their high toxicity, suspended structures, and color. Reduction of light penetration as a result of coloring of dyes adversely affects activity for photosynthetic organisms in aquatic life [30-33]. However, it can be toxic to some living things in aquatic life, in the presence of aromatics, metals, chlorides, and so on [30-33]. Because of their synthetic origin and complex structure, dyes are stable and difficult to biologically degrade. Dyes can be classified as, anionic - direct, acid and reactive dyes; cationic - basic dyes; and nonionic - disperse dyes [30]. Among these, water-soluble reactive and acid dyes are the most problematic dyes [34, 35]. In addition, despite the low concentration of basic dyes, giving too much color with negatively affects water and water organisms [36, 37].

In this study, the prepared of isocyanurate based amine functionalized (PEI-TGIC) COFs were successfully synthesized in dimethyl formamide at 90 ^{o}C. The prepared COFs were treated with HCl to protonation of amine groups on PEI-TGIC COFs. The PEI-TGIC COFs were characterized by using Fourier Transform Infrared (FT-IR) spectrometer, surface area and porosity measurements, zeta potential, and thermogravimetric analyzer (TGA) measurements. Moreover, the prepared PEI-TGIC based COFs were used as an absorbent for methyl orange removal from aqueous media.

2. EXPERIMENTAL

2.1 Materials

The branched polyethyleneimine (PEI, 50% in water, Mn:1800, Aldrich) and triglycidyl isocyanurate (TGIC, Aldrich) were used for synthesis of covalent organic frameworks.

Dimethyl formamide (DMF, 99%, Merck) was used as solvent for COF synthesis. Hydrochloric acid (HCl, 36.5%, Sigma Aldrich) was used to protoation of PEI-TGIC COFs. Potassium chloride (KCl, 99%, Merck) was used for zeta potential measurements. Methyl orange (MO, ACS reagent, 85% dye content, Fluka) was used for absorption studies.

2.2 Synthesis of PEI-TGIC covalent organic framework

The synthesis of PEI-TGIC COF was carried out in DMF at 90 ºC by using epoxy – amine ring opening reaction [17]. In brief, 3.93 mmol of TGIC was dissolved into 100 mL of DMF and 23.8 mmol of PEI (2 mL of PEI solution %50 in water), and stirred at 90 ºC, at 800 rpm mixing rate for 2 h. The prepared PEI-TGIC COFs were precipitated in excess amount of acetone, and washed with acetone, acetone-water, water, and acetone again, to remove unreacted reactants. The prepared and washed PEI-TGIC COFs were dried by using heatgun and stored at closed tubes for further usage.

Moreover, the prepared PEI-TGIC COFs were treated with 1 M HCl acid to protonation of amine groups of to obtain higher positively charged PEI-TGIC COFs. Then, protonated PEI-TGIC (p-PEI-TGIC) COFs were washed with water once, acetone twice, and dried by using heat gun.

2.3 Characterization of PEI-TGIC covalent organic framework

Functional group determination of TGIC and PEI-TGIC COFswere carried out by Fourier Transform Infrared (FT-IR, Nicolet iS10, Thermo) spectroscopy with using attenuated total reflectance (ATR) module. The range of wavelength is in between 4000 and 650 cm^{-1}.

The thermal behavior of PEI-TGIC and p-PEI-TGIC COFswere determined and comparedeach other with thermogravimetric analysis through using Thermogravimetric Analyzer (TGA, /DTA 6300, Exstar).Initially, moisture is removed from the sample through heating from 25 ºC to 100ºC. Then the temperature alteration is set to raise 10ºC per minute from 90ºC to 1000ºC.

Zeta Potential Analyzer (BIC, Brookhaven Inst. Corp.) is used for the determination of the particle charges. The aqueous solutions of PEI-TGIC and the p-PEI-TGIC COFwere diluted with 10^{-3}M KCl solution to prepare for analysis of zeta potential.

Particle size and shape are observed through using Scanning Electron Microscope (SEM, JEOL JSM-5600). The synthesized, washed and freeze-dried PEI-TGIC COFs were placed into carbon tape attachedaluminum stub and coated with gold to a few nanometer thicknesses under vacuum. The images were taken with an operating voltage of 20 kV.

Specific surface area, pore volume, and pore size determination of PEI-TGIC COF were carried out with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods by using Micrometritics, Tristrar II, Surface area and porosity device. Before analysis, the PEI-TGIC COF was dried in freeze-dryer (Christ Alpha 1–2 LD plus), and prior to measurementspassed through N_2 gas for 8 h to remove moisture and other contaminants at 80 °C using a Flow Prep 060 Degasser.

2.4 Absorption studies

The absorption study of MO from aqueous solution was done by following literature with some modification [17]. For this purpose, 0.05 g of each PEI-TGIC and p-PEI-TGIC COFs were used as absorbents. Besides, the 100 mL of 250 ppm MO aqueous solution were prepared and 0.05 g of each PEI-TGIC and p-PEI-TGIC COFs were added into solutions after taking zero time samples from solutions. Then, the samples from solution were taken in certain time intervals and were read by using UV–vis spectrophotometer (UV–Vis, T80+, PG Instruments)

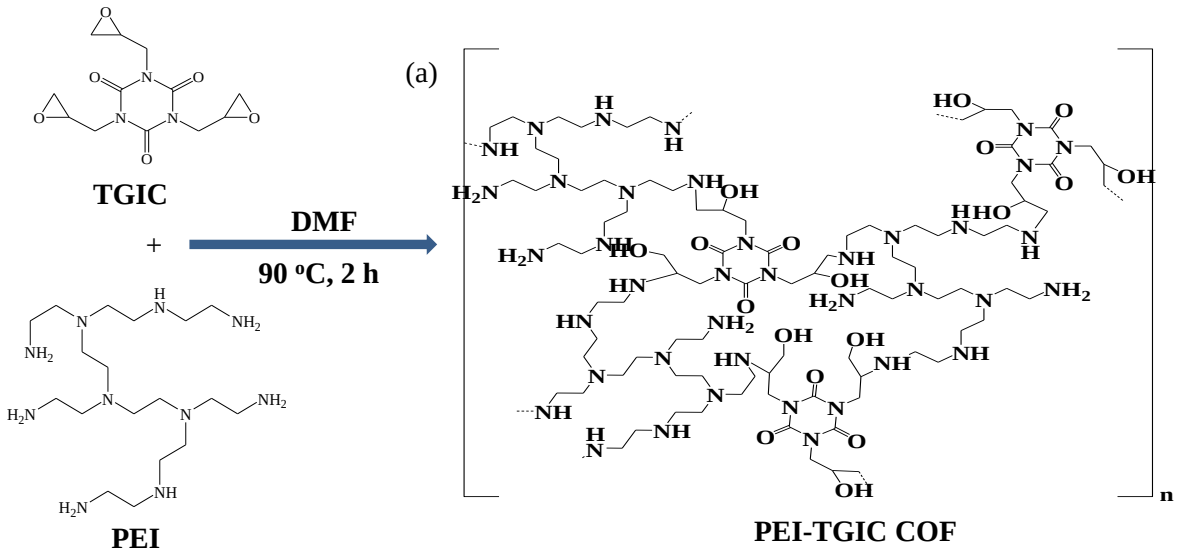
after 25 times dilution at 464 nm wavelength. The absorbed amount of MO dyes from prepared PEI-TGIC, and p-PEI-TGIC COFs were determined from the decreasing on absorbance values of diluted samples at 464 nm wavelength for MO.

3. RESULTS AND DISCUSSION

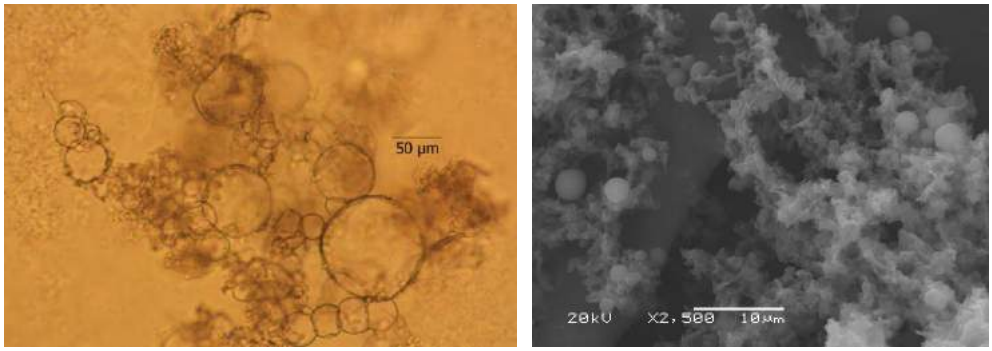
3.1 Synthesis and characterization of PEI-TGIC COFs

In recent years, the reactions of epoxy and amine groups are widely used for modification and synthesis of new polymeric structures [38]. In brief, the reaction involves the nucleophilic addition reaction of amine to epoxy groups [39]. The hydrogen atoms of primary and secondary amine groups provide to opening of oxirane ring of the epoxy components with nucleophilic addition reaction [40-42]. In here, the branched PEI molecules was used with the 1:2:1 ratio of primary, secondary, and tertiary amine groups content to reacted with tri epoxy groups contain TGIC molecule to synthesis of PEI-TGIC COFs. The molecular structure of PEI and TGIC, and schematic presentation of reaction between PEI and TGIC are given in **Figure-1 (a)**. It was seen from **Figure-1 (a)**, the amine primary and secondary amine groups on branched PEI molecule bonded with epoxy groups of TGIC with the nucleophilic addition reaction. On the other hand, the obtained optic microscope and SEM images are given in **Figure- 1 (b)**.

Figure-1. (a) the schematic presentation of synthesis of PEI-TGIC COF, and (b) the optic microscope and SEM images of PEI-TGIC COFs.



(b)

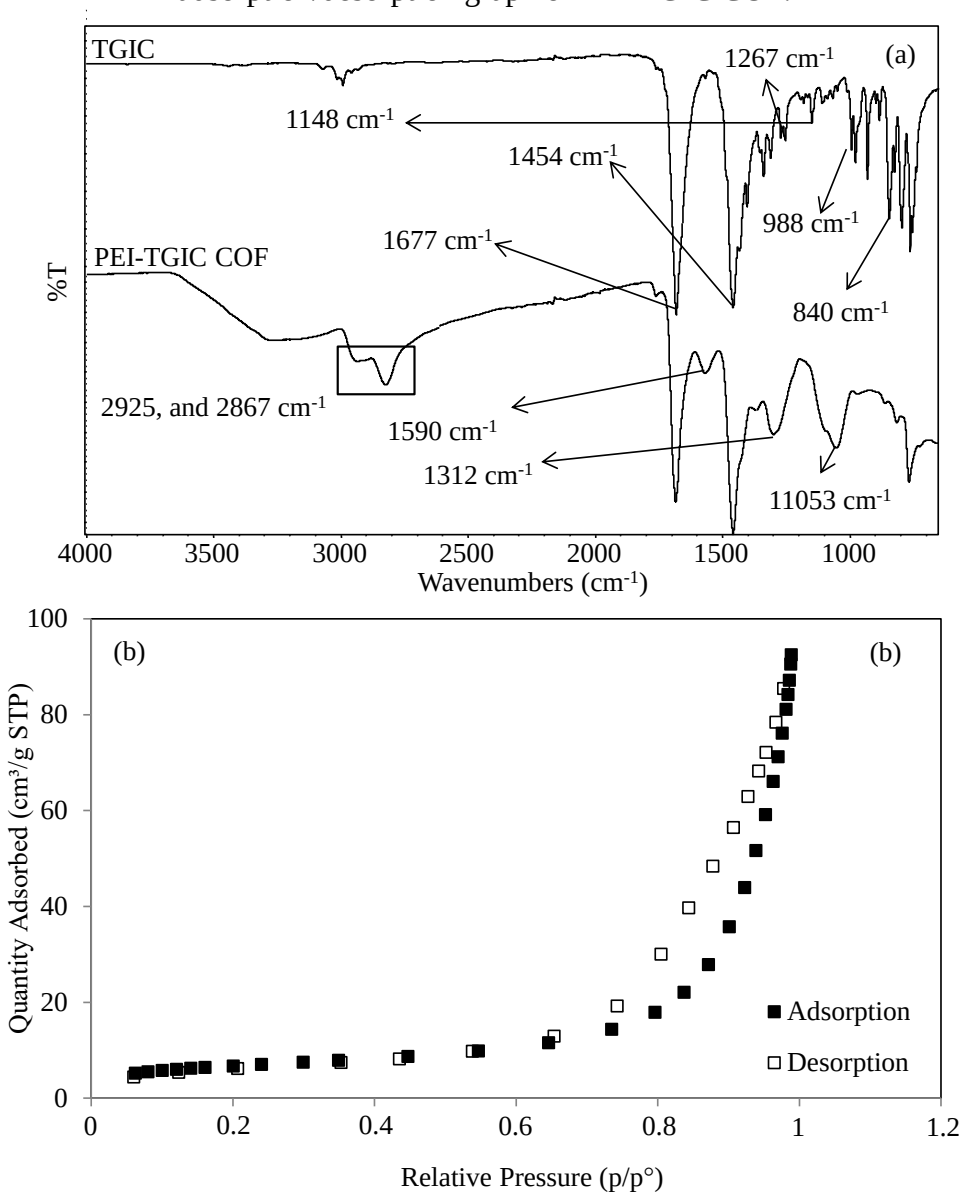


It was clearly seen from optic microscope and SEM images of PEI-TGIC COFs, the COFs are spherical shape with poly dispersed size ranges. The optic microscope images of PEI-TGIC COFs were taken from the aqueous solution of COFs, and it was seen that, the sizes of

COFs between 20-100 μm in aqueous media, whereas the SEM images which are taken from dried from of PEI-TGIC COFs shown that the sizes of PEI-TGIC COFs are between 0.5-5 μm. It can be said that, from optic microscope and SEM images the prepared PEI-TGIC COFs can be swollen easily in aqueous media with almost 20 fold increasing on size of dried from. On the other hand, the yield % of reaction was gravimetrically calculated as 78±4.1 % from the mass of reactant and product.

To confirm of synthesis of PEI-TGIC COF, the FT-IR spectrum of TGIC and PEI-TGIC were recorded and compared for the observing disappeared and appeared peaks after PEI-TGIC COF synthesis. It was clearly seen from **Figure-2 (a)**, the FT-IR spectrum of TGIC shown some characteristic peaks such as C=O stretching at 1677 cm^{-1}, CH_2 stretching at 1454 cm^{-1}, 1267 cm^{-1} asymmetric epoxy ring stretching, 1148 cm^{-1} C-N-C peak from aromatic ring, 988, and 840 cm^{-1} asymmetric epoxy ring bending, respectively. On the other hand, it was clearly seen that, the peaks from epoxy ring is disappeared and turned to –OH peaks at 1310, and 1053 cm^{-1}, and the peaks from amine groups at 1590 cm^{-1} was also observed after synthesis PEI-TGIC COFs.

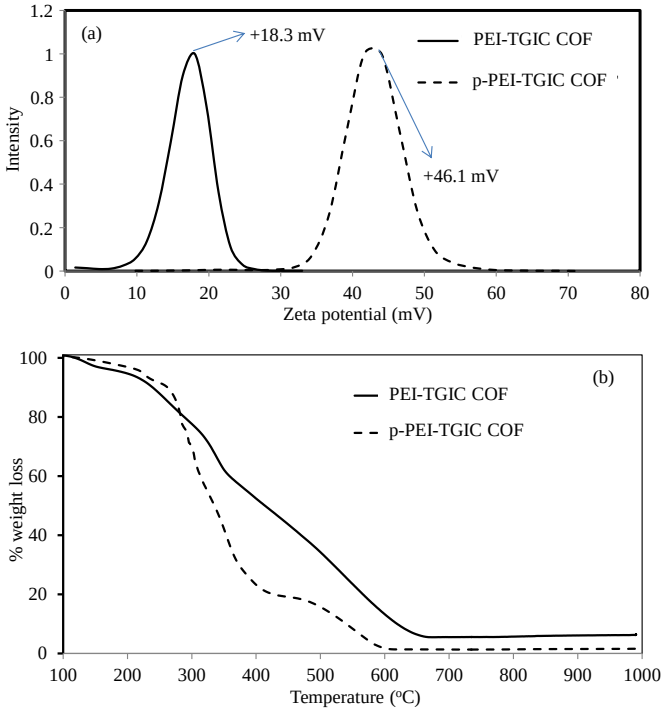
Figure- 2. (a) The FT-IR spectrum of TGIC and PEI-TGIC COF, and (b), N_2 adsorption/desorption graph of PEI-TGIC COF.



Besides, the surface area, pore size and pore volume values of PEI-TGIC COFs were determined by using N_2 absorption/desorption measurements and corresponding graph is given in **Figure 2 (b)**. The shape of obtained hysteresis loop were H3, and it H3 type hysteresis loopindicated that the narrow slit-shaped pores were obtained in prepared PEI-TGIC COFs [43, 44]. Moreover, the surface area was determined as 23.4 m^2/g from N_2 absorption/desorption measurements of PEI-TGIC COFs with using BET method. Also, the pore volume and pore size values of PEI-TGIC COFs were determined as 0.142 cm3/g, and 22.5 nm, respectively, from N_2 absorption/desorption measurements of PEI-TGIC COFs with using BJH method. The porous structure of prepared provides a considerable number of reactive sites on PEI-TGIC COFs.

Besides, the prepared PEI-TGIC COFs were treated with 100 mL of 1M HCl at room temperature about 2 h to protonate amine groups. The change on surface charges were determined by using zeta potential measurements and corresponding graph is given in Figure 3 (a). It was observed that, the surface charge of PEI-TGIC COF is determined as +18.3±1.7 mV, whereas increased to +46.1±2.6 mV after HCl treated to prepare p-PEI-TGIC COF. The increasing on surface charges approximately 2.5 fold confirm that the amine groups of PEI-TGIC COF was successfully protonated.

Figure- 3. The changing on (a) surface charges, and (b) thermal stability of PEI-TGIC after protonation.

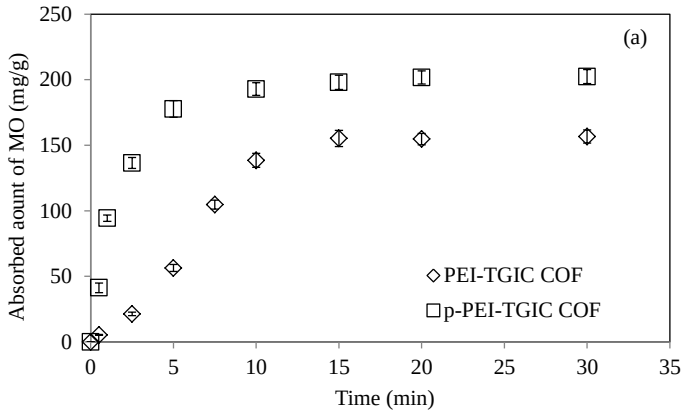


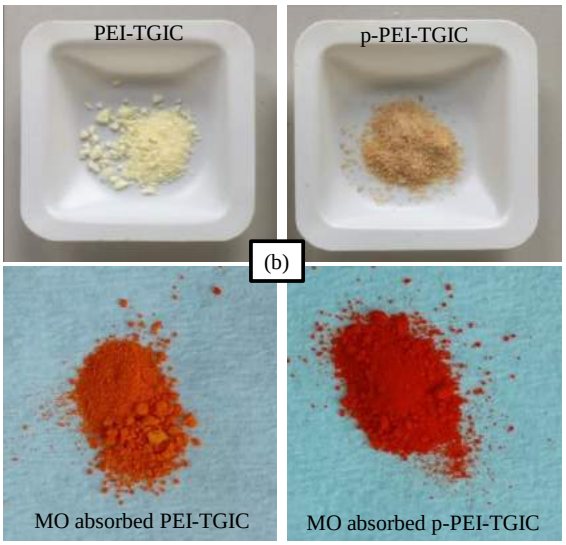
Furthermore, the thermal stability of PEI-TGIC, and p-PEI-TGIC COFs were compared each other from their corresponding TGA thermograms in **Figure 3 (b)**. The bare PEI-TGIC COFs shown three degradation steps as started for first degradation step is between 100-154 ºC with 3.2% weight loss, the second degradation step is between 213-326 ºC with 30.7% weight loss, and the last degradation step between 350-611 ºC with 93.6% weight loss, and finally the 93.7% weight loss was observed at 1000 ºC. Differently from bare form of PEI-TGIC, the p-PEI-TGIC COFs shown lower thermal stability in three degradation steps as observing of the first degradation step is between 100-228 ºC with 2% weight loss, the second degradation step I between 258-405 ºC with 80.6% weight loss, and the third degradation step is between 473-602 ºC with 98.4% weight loss, whereas it was observed 98.6% weight loss at 1000 ºC, respectively.

3.2 The potential usage of PEI-TGIC COFs as an absorbent

In literature, there is so many publication has been reported about removing of toxic organic dyes such as oxidation, reduction, and absorption/desorption or organic dyes [45-47]. The oxidation or reduction of organic dyes has some disadvantages such as using some catalysts as metal nanoparticles, or extinguishment of reusability potentiality of dyes. On the other hand, the absorption or desorption of organic dyes from waste waters provide reusability potentiality of organic dyes with desorption processes. Therefore, the potential usage of prepared PEI-TGIC and p-PEI-TGIC COFs were investigated for MO dyes from aqueous media. The absorption of MO studies was carried out from 100 mL 250 ppm MO solution with the addition of 0.05 g of PEI-TGIC and p-PEI-TGIC COFs. The absorbed amount of MO was calculated by reading of the taken samples from MO solution in certain time intervals with UV-Vis spectrometer at 464 nm wavelength for MO dyes. The samples were 25 times diluted before reading on UV-Vis spectrometer. The corresponding graph is given in Figure 4 (a). It was observed from **Figure-4 (a)** that, the PEI-TGIC COFs were absorbed 56.4±26 mg/g MO in 5 min, and 156.6±4.9 mg/g MO dyes from aqueous media in 30 min (in equilibrium). On the other hand, the absorbed amount of MO by p-PEI-TGIC was determined as 177.6±6.3 mg/g in 5 min, and 202.4±4.3 mg/g in 30 min. It was observed that, the rate of absorption and amount of absorbed MO higher for p-PEI-TGIC COFs than bare PEI-TGIC COFs, due to higher positive surface charges of p-PEI-TGIC interactions with negatively charged MO dyes.

Figure- 4. (a) The adsorption graph of PEI-TGIC, and p-PEI-TGIC COFs MO dyes [0.05 g COF, 100 ml, 250 ppm MO], and (b) digital camera images of PEI-TGIC, and p-PEI-TGIC COFs and theri MO absorbed forms.





The digital camera images of PEI-TGIC, p-PEI-TGIC and their corresponding MO absorbed forms are also given in **Figure- 4 (b)**. It was clearly seen that, the white color of PEI-TGIC COFs turned to brownish color after HCl treatment, and also the orange color of MO absorbed form of p-PEI-TGIC COFs darker then PEI-TGIC COFs that confirm that higher amount absorption of MO dyes by p-PEI-TGIC COFs.

The absorption kinetic of MO by PEI-TGIC and p-PEI-TGIC COFs were determined by using well-knownpseudo-first-order (Eq. 1), and pseudo-second-order (Eq. 2) models, respectively following corresponding equations [48];

$$\log (q_e-q_t) = \log Q_t - (k_1/2.303)t \quad (1)$$

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (2)$$

where; "qe" is absorbed amount of molecule at equilibrium (mg/g), "qt" isabsorbed amount of molecule at at t time (mg/g), k_1 is rate constant for pseudo-first-order model (min_{-1}), and k_2 is constant for pseudo-second-order model ($g.mg^{-1}.min$). The calculated values of qe, k_1 and k_2 values from the plots of log (q_e-q_t) vs t for pseudo-first-order model, and t/q_tvs t fro pseudo-second-order model, are summarized in **Table 1** for MO absorption by PEI-TGIC, and p-PEI-TGIC COFs, respectively. It was observed for MO absorption by PEI-TGIC COFs that, 210.6 mg/g and 333.3 mg/g q_e values for pseudo-first-order, and pseudo-second-order kinetic models, whereas experimental q_e value is 156.6±4.9 mg/g. Moreover, the k_1, and k_2 values were also determined as 0.227 min^{-1}, and $1x10^{-4}$ g.min-1.min, with 0.971, and 0.584 corelation coefficient (R^2) values for pseudo-first-order, and pseudo-second-order kinetic models, respectively.

Table- 1. Pseudo-first-order and pseudo-second-order constants and correlation coefficients for adsorption of MO by PEI-TGIC, and p-PEI-TGIC COFs.

Material	Exp.	Pseudo-first-order-model			Pseudo-second-order-model		
	q_e (mg/g)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g mg^{-1} min)	q_e (mg/g)	R^2
PEI-TGIC COF	156.6±4.9	0.227	210.6	0.971	$1x10^{-4}$	333.3	0.584
p-PEI-TGIC COF	202.4±5.3	0.264	149.7	0.978	$3x10^{-3}$	217.4	0.998

It can be said that from results, the MO absorption by PEI-TGIC COFs fitting with pseudo-first-order kinetic model. On the other hand, the absorption of MO by p-PEI-TGIC COFs q_e values were calculated as 149.7, and 2017.4 mg/g forpseudo-first-order, and pseudo-second-order kinetic models, whereas experimental q_e value is 202.4±5.3 mg/g. The R^2 values with 0.978, and 0.998, k_1 and k_2 values with 0.264 min^{-1}, and $3x10^{-3}$ g.min-1.min were calculated forpseudo-first-order, and pseudo-second-order kinetic models, respectively. It was observed that, the MO absorption by p-PEI-TGIC COFs fitting with pseudo-second-order kinetic model.

The validity of kinetic model can be done from R2 values, and also the Sum of Square Error (SSE %) were also used in literature from the corresponding equation (Eq. 3) [48];

$$SSE\ \% = (\Sigma(q_{e,exp} - q_{e,cal})^2/N)^{1/2} \quad (3)$$

Where,"N" is the number of data points. "$q_{e,exp}$" and "$q_{e,cal}$" (mg/g) are the experimental and calculated adsorption capacities, respectively. The numerical fitting is good if R^2 is ~1.0 and SSE is ~ 0.0. The SSE values were calculated as 18 and 58.9 for pseudo-first-order, and

pseudo-second-order kinetic models for MO absorption by p-PEI-TGIC, and 17.6, and 5 for pseudo-first-order, and pseudo-second-order kinetic models for MO absorption by p-PEI-TGIC COFs. The validity of fitted kinetic models of MO absortion by PEI-TGIC, and p-PEI-TGIC COFs were proven with SSE calculation.

4. CONCLUSION

In this study, it was reported that, the synthesis of novel spherical shape, porous PEI-TGIC COFs with23.4 m^2/g surface area, 0.143 cm^3/g pore volume, and 22.5 nm pore size, and its protonated form p-PEI-TGIC COFs were successfully carried out. The surface charge increased to 46.1±2.6 mV from 18.1±1.7 with the protonation of PEI-TGIC COFs. The prepared PEI-TGIC and p-PEI-TGIC COFs absorbed 156.6±4.9 mg/g, and 202.4±5.3 mg/g MO from its aqueous solution. On the other hand, the absorption kinetic of MO by PEI-TGIC COFs fitted with pseudo-first-order model with 0.971 R^2 values, whereas absorption kinetic of MO by p-PEI-TGIC COFs fitted with pseudo-second-order model with 0.998 R^2 values. Therefore, the cationic-based COFs of PEI-TGIC and p-PEI-TGIC have great potential for the removal of negatively charged dyes, pesticides, herbicides, and heavy toxic metal ions different oxidation states from aquatic environments.

Conflict of Interest Statement

The authors declare no conflict of financial, academic, commercial, political, or personal interests

Acknowledgements

The authors are grateful for the financial support by Canakkale Onsekiz Mart University Scientific Research Commission (FBA-2016-727).

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **177-188**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.018
Research Article

EXPERIMENTAL SETUP FOR AC MOTOR SPEED CONTROL BY USING PLC

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Received: 10 July 2019; Accepted: 25 July 2019

ABSTRACT

PLC is widely used in industrial control application. For this reason, PLC education has an important place in the content of universities and it is explained in different engineering department.

In this paper, AC motor speed control by using PLC experimental setup is designed and implemented. Through this experimental setup, students can experience and use of the encoder, 3-phase AC motor and PID control algorithm. Besides, this experimental setup helps students to develop their real time engineering skill and experience in departments of universities such as electrical-electronics, mechatronics, control and automation engineering.

Keywords: *PLC, PID Control, AC Motor Speed Control, Encoder, Inverter*

1. INTRODUCTION

PLC is an integrated device with programming support that assigns inputs to the output after one or more operations such as logic, data processing, counting, database, arithmetic. PLCs can be used in sequential control, motion control, process control or data management.PLC architecture includes three conceptual layers: hardware, firmware and programmable area(1-3).

PLC programming can be done in three different ways: Ladder diagram, STL (Statement List Editor), FBD (Function Block Diagram). The ladder diagram is a programming language based on electrical circuits. FBD is a graphical language used to tell signal and data flow through function blocks. STL is a programming language, which is realized by writing code, similar to the language C(4, 5).

Complex automation problems can be solved quickly and easily through PLCs. Compared to other control methods, PLCs are less damaged, more reliable, easier to maintain, more resistant the environmental conditions and have many advantages. Because of all these advantages, they are often preferred in industry.

In the Electrical and Electronic Engineering Department of the Ondokuz Mayıs University (OMU) (Samsun/ Turkey), PLC is introduced in the Introduction to Industrial Control Systems lesson. In this lesson content, there are PLC types such as Siemens S7-1200, ABB500, Delta, Mitsubishi. This study was carried out using Siemens S7-1200. This experimental setup was carried out as a project assignment in the advanced PLC lesson at the OMU Institute of Science Electrical and Electronic Engineering graduate program. For the last two semesters, it has been used as an experimental setup in the Electrical and Electronic Engineering undergraduate laboratory.

PID control is a control method commonly used in motor speed adjustment or other control systems(6, 7). In this study, PID control was performed using PLC and the motor speed was adjusted to desired speed.

The purpose of this study is to provide an experimental setup for undergraduate and graduate students to learn the use of PID block using PLC. In addition, students performing this experiment have an idea to solve other control problems.

2. PID CONTROL

PID control is a control method comprising proportional, integral and derivative elements. Each element has a coefficient and these coefficients are processed the certain mathematical operations with the error signal. The coefficient of the proportional element is multiplied by the error signal, the coefficient of the integral element is multiplied by the integral of the error signal ,and the coefficient of the derivative element is multiplied by the derivative of the error signal. Each result is collected and the result is the control signal(8, 9). The error signal is equal to the difference between the set point and the input. The equation that expresses all of this is as follows:

$$u(t) = K_p e(t) + K_i \int e(t)dt + K_d \frac{d}{dt} e(t) \qquad (\mathbf{1})$$

2.1. Properties of Proportional, Integral and Derivative Elements

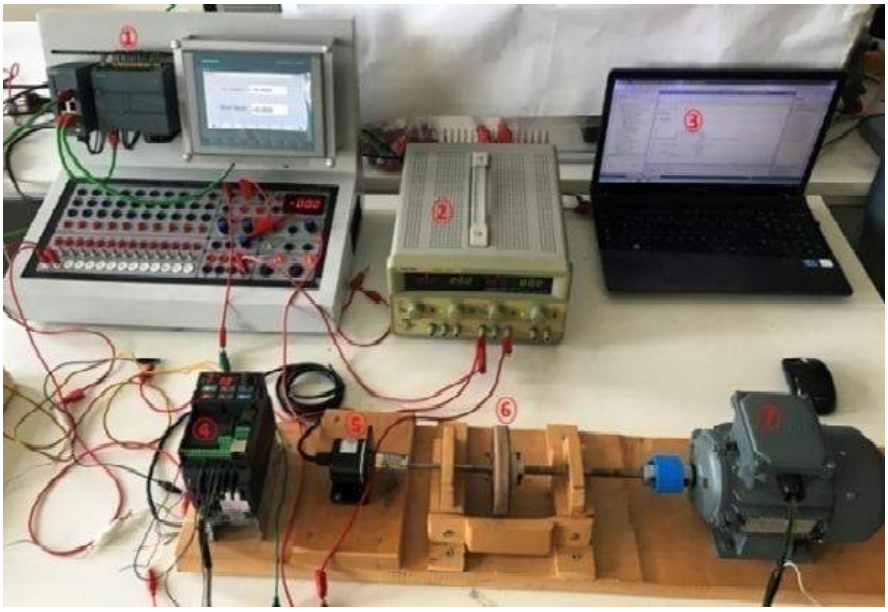
Each PID element acts differently to the operation of the control system. The proportional element reduces the rise time. The integral element greatly decrease the steady-state error. The derivative element provides reduction of overshoot(10). In Table 1, it is shown the effect of each of the PID parameters on the system(11).

Table 1: Effects of PID Parameters

PID Parameters	Rise Time	Overshoot	Settling Time	Steady-State Error
Proportional	Decrease	Increase	Small Increase	Decrease
Integral	Small Decrease	Increase	Increase	Large Decrease
Derivative	Minor Change	Decrease	Decrease	Minor Change

3. THE EXPERIMENTAL SETUP

Figure 1: The Experimental Setup



The experimental setup for this study is shown in Figure 1. This experimental setup consists of seven parts.

Part 1 is PLC experiment set. On this experiment set; there are communication module, PLC (Siemens S7-1200), HMI (KTP 700 Basic PN), digital inputs, LEDs indicating digital output, relays, analog input and output, 20-pulse encoder, 24 V supply and ground connections and voltmeter.

Part 2 is the DC power supply. 24 V supply of the encoder is provided here.

Part 3 is the computer platform. PLC program is written in computer platform and loaded to PLC through ethernet cable.

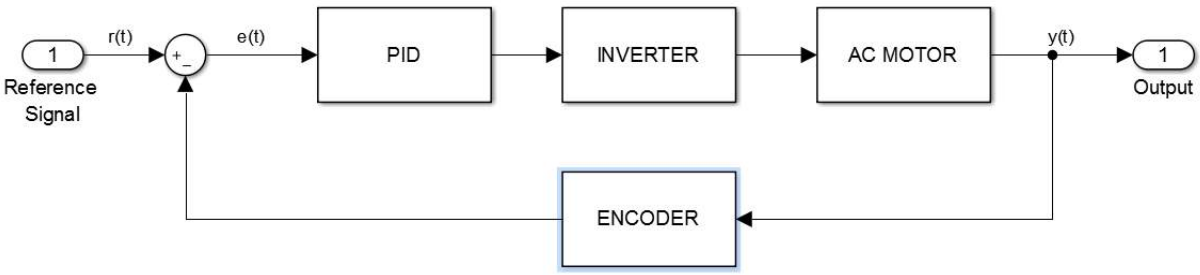
Part 4 is the inverter. 0-10 V voltage is received from the analog output of the PLC and this voltage is transmitted to the inverter. According to the this voltage information sent to it, the inverter drives the motor by sending energy to the motor at the required frequency.

Part 5 is the encoder. The encoder connected to the motor shaft generates a certain number of pulses per turn. The motor speed is calculated by evaluating the number of pulses produced by the PLC.

Part 6 is the part to be applied to the disturbance.

Part 7 is the AC motor to be controlled.

Figure 2: The Experimental Setup Control Block Diagram



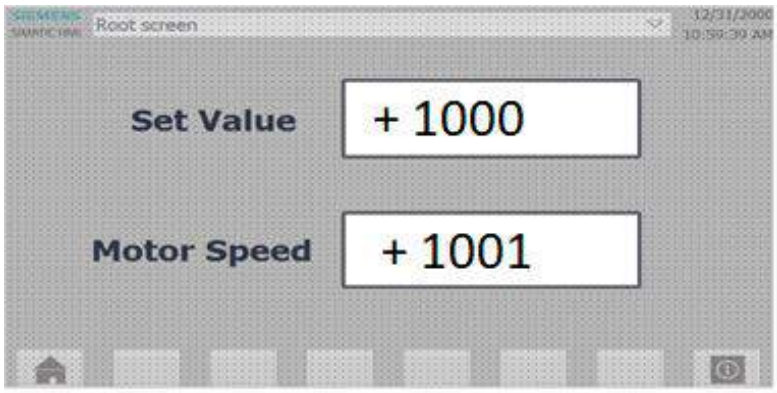
3.1. Programmable Logic Controller (PLC) and Human-Machine Interface (HMI)

In this study, Siemens S7-1200 1214C DC/DC/DC(12) type PLC is used. Here DC/DC/DC refers to the operation of the PLC. The first DC indicates that the PLC is supplied with 24 V DC voltage. The second DC indicates that the input signals are 24 V DC voltage. The third DC indicates that the PLC has a transistor output.

In the PLC used in this study, there are 6 high-speed counters (HSC), 2 analog inputs, 14 digital inputs and 10 digital outputs. Furthermore, an analog output board is added, giving 1 analog output.

In order to enter the set point and see the motor speed, a touch screen called HMI is designed. The indicators to be used are taken from the elements tab and the necessary addresses are defined for each. As a result, the design in Figure 3 has emerged.

Figure 3: HMI Design



3.2. Inverter

Devices that drive the AC motor at different speeds by changing the frequency of energy from the grid are called inverters. The inverter used in this study(13) is shown in Figure 4. The inverter used has a single phase supply, so the inputs L1 and L2 are used when feeding. The inverter output from the U,V,W terminals is connected to the AC motor. The analog output from the PLC is connected to the AVI terminal and the common end of the analog output is connected to the ACM terminal. All of these connections are shown in Figure 5.

Figure 4: Used Inverter

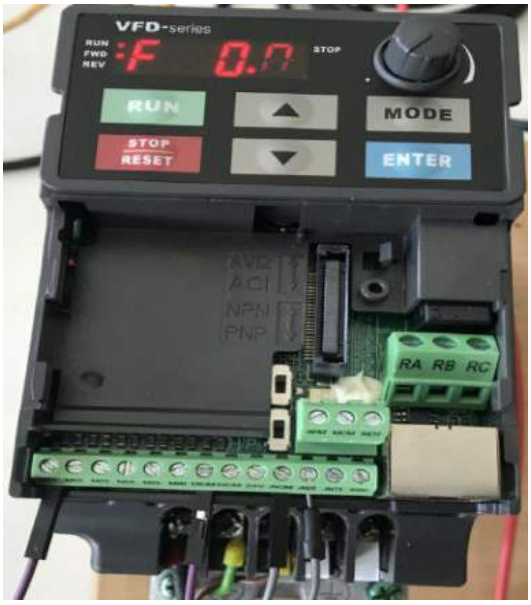
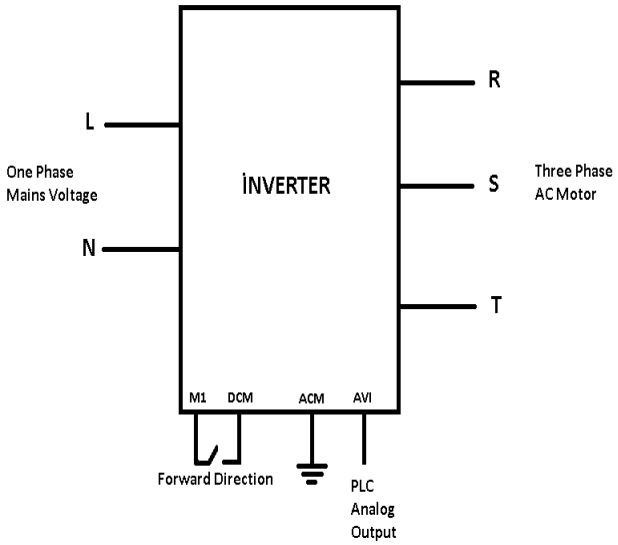


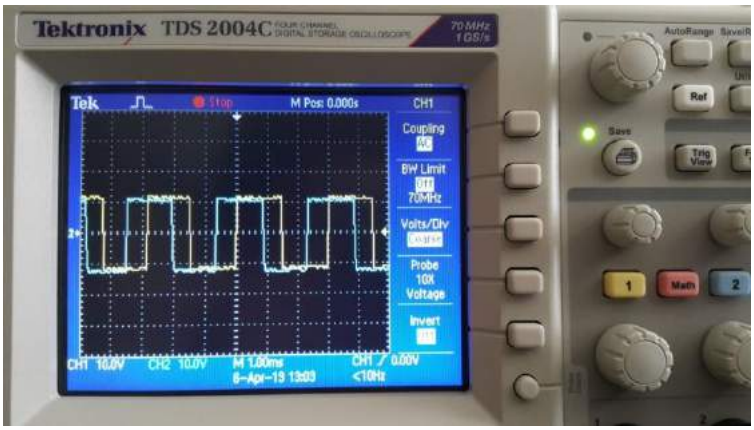
Figure 5: Inverter Connections



3.3. Encoder

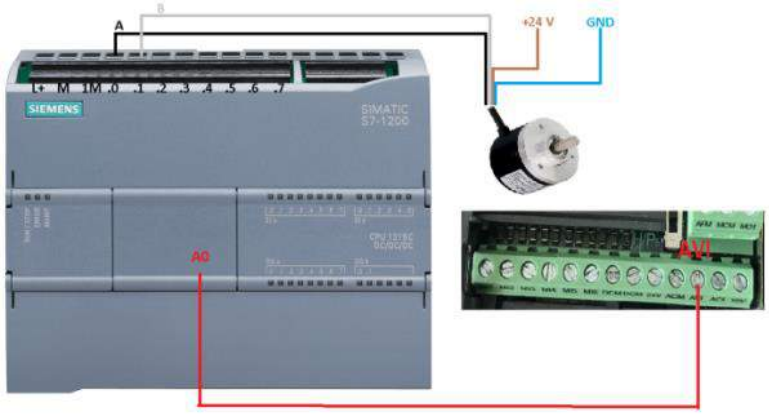
In this study, incremental rotary encoder(14) is used and it produces 2500 pulses per turn. The incremental encoder means that when the power is cut off, the information inside it will be reset. The rotary encoder means that it will produce a certain number of pulses when the shaft is turned. Rotary encoders produce pulses from two separate outputs called phase A and phase B. These pulses produced from phase A and B have a phase difference of 90 degrees. In order to observe these pulses and phase difference, A and B phases of the encoder were examined through an oscilloscope and the imagine in Figure 6 was obtained. In this figure, the pulses and phase difference are clearly seen.

Figure 6: Oscilloscope image of phases A and B



The connection of the encoder with the PLC is shown in Figure 7. The brown cable on the encoder is connected to the 24 V supply. The blue cable is connected to the ground. The black cable refers to phase A and it is connected to the I0.0 input of the PLC. The white cable refers to phase B and it is connected to the I0.1 input of the PLC.

Figure 7: Connections of PLC to Encoder and Inverter

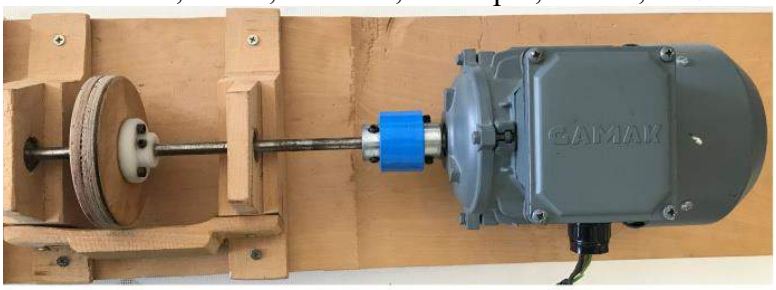


3.4. AC Motor

The AC Motor used in this study(15) and the disturbance disc are shown in Figure 8.The characteristics of this AC motor are as follows:

Figure 8: AC Motor and Disturbance Disc

Δ/Y 220/380 V, 50 Hz, 0.25 kW, 2840 rpm, 0.70 A, cos**Ø=0.78**



3.5. PLC Program

3.5.1. Main Block Program

Figure 9: Main Block Network 1

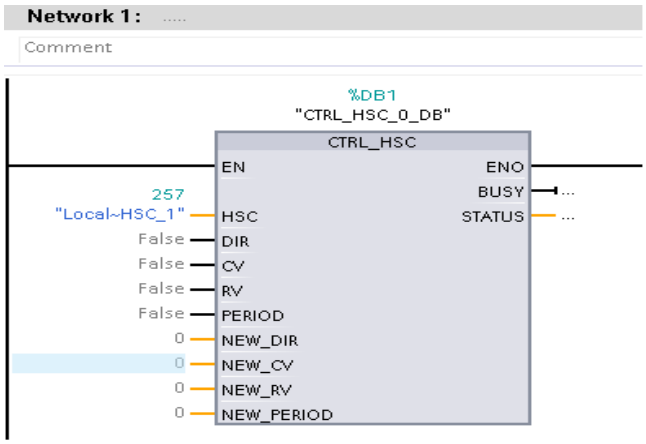


Figure 10: Main Block Network 2

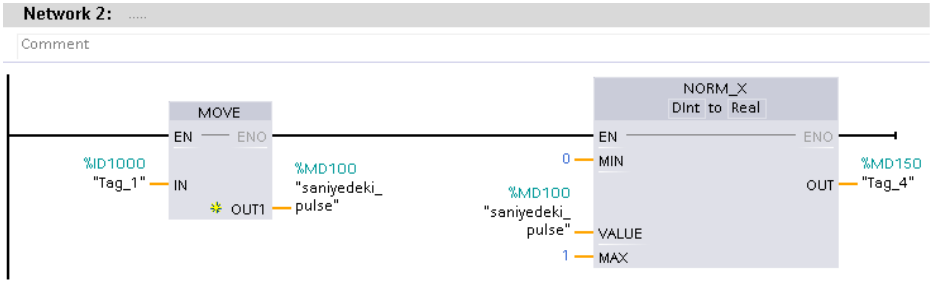
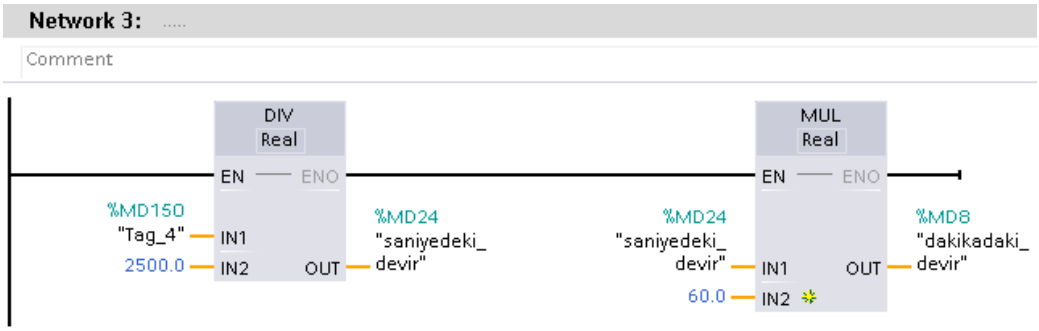


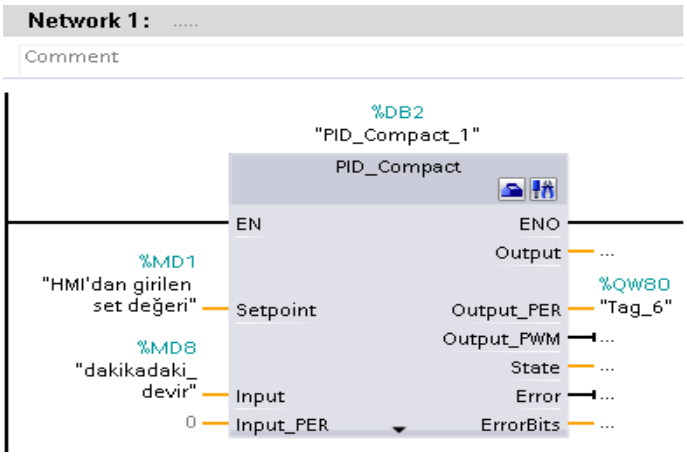
Figure 11: Main Block Network 3



The main block program consists of 3 networks and is shown in Figure 9-10-11. The network 1 shown in Figure 9 is a High Speed Counter (HSC) block. The counting of the pulses taken from the encoder is done here. In the network 2 shown in Figure **10**, the information HSC reads assigned to an address and converted to a real number. Information indicating the number of pulses per second read from ID1000 address by HSC block is assigned to MD100 address through the MOVE block. In order for speed measurement to be done correctly, the information at MD100 address is converted to real number and assigned to the MD150 address through the NORM_X block. In the network 3 shown in Figure 11, the information indicating the number of pulses per second defined at MD150 address is converted to rpm as a result of certain mathematical operation. The information at MD150 address is divided by 2500 (the number of pulses produced by encoder per turn) through DIV block. As a result of this operation, revolutions per second is obtained. Then this information is multiplied by 60 to obtain revolutions per minute (rpm) through MUL block and the operation result is assigned at MD8 address. Thus the motor speed is measured and read from MD8.

3.5.2. Cyclic Interrupt Program

Figure 12: PID Block



The PID block is not written into the main block. It is written into the cyclic interrupt created separately from the main block. After the PID block has been added, the motor speed information stored into the MD8 address is written to the input of the PID block. Set point information that is defined MD1 address when designing HMI is written to "Setpoint" section of PID block. For PID output, the QW80 address is written to "Output_PER" section of PID block. This address is the address of the analog output board. The PID block is seen in Figure **12**.

3.5.3. PID Settings

Click "Configurations" on the PID block to make PID settings. The pop-up window is the "Controller Type" tab, where "speed" is selected. Then "Input" and "Output_PER (Analog)" are selected in the "Input / output parameters" tab.If "Enable manual entry" is selected in the "PID parameters" tab, PID parameters can be entered manually.when the motor speed limiting is desired, lower and upper speed limits can be selected from the "Process value limits" tab. In this study, PID parameters was selected Kp=0.02, Ki=3, Kd=0.

Table 2: Some PLC Addresses and Their Equivalents

PLC Address	Its Equivalent
Fixed Addresses	
ID1000	HSC1 counting address
QW80	Analog output address
I0.0	HSC1 digital input (phase A)
I0.1	HSC1 digital input (phase B)
User-Selected Addresses	
MD1	Set point entered from HMI
MD8	Revolutions per minute (rpm)
MD24	Revolutions per second
MD100	Pulses per second (integer)
MD150	Pulses per second (real number)
Total Number of Addresses Used	**9**

3.6. Experimental Results

Figure 13: Operation of the motor at 1000-1200-1300 rpm

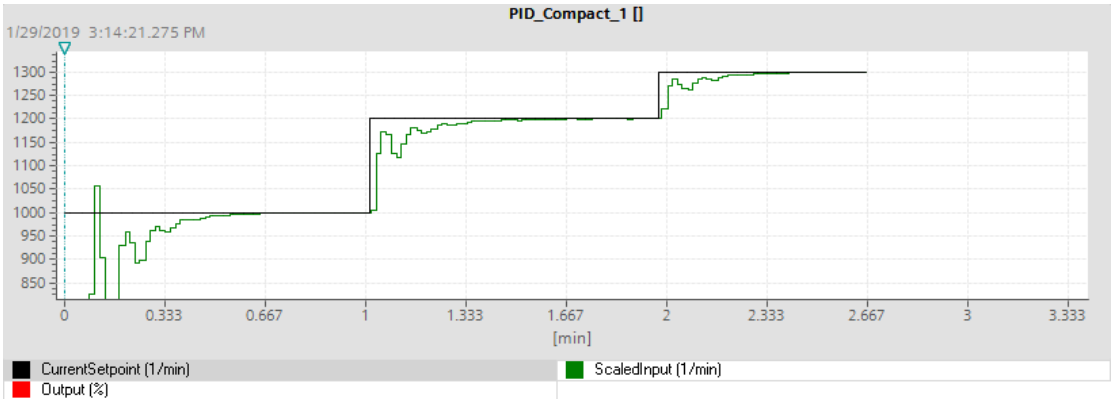
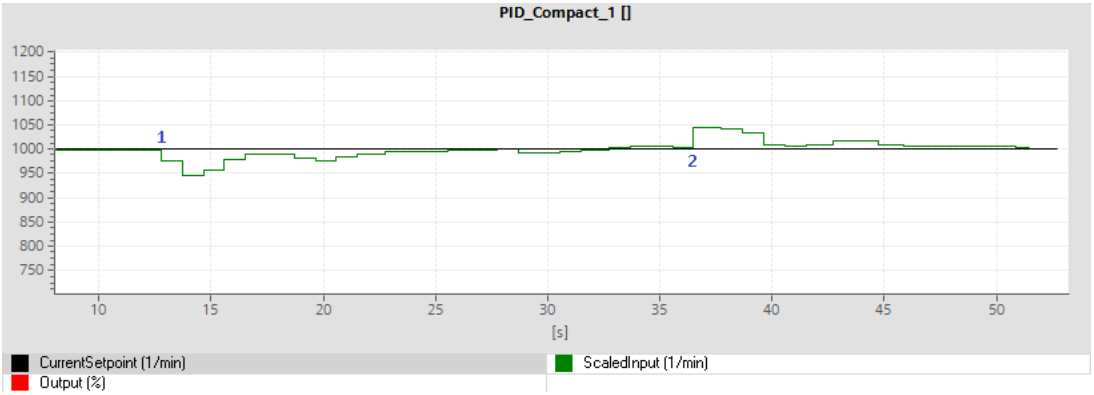


Figure 14: Graph of Disturbance

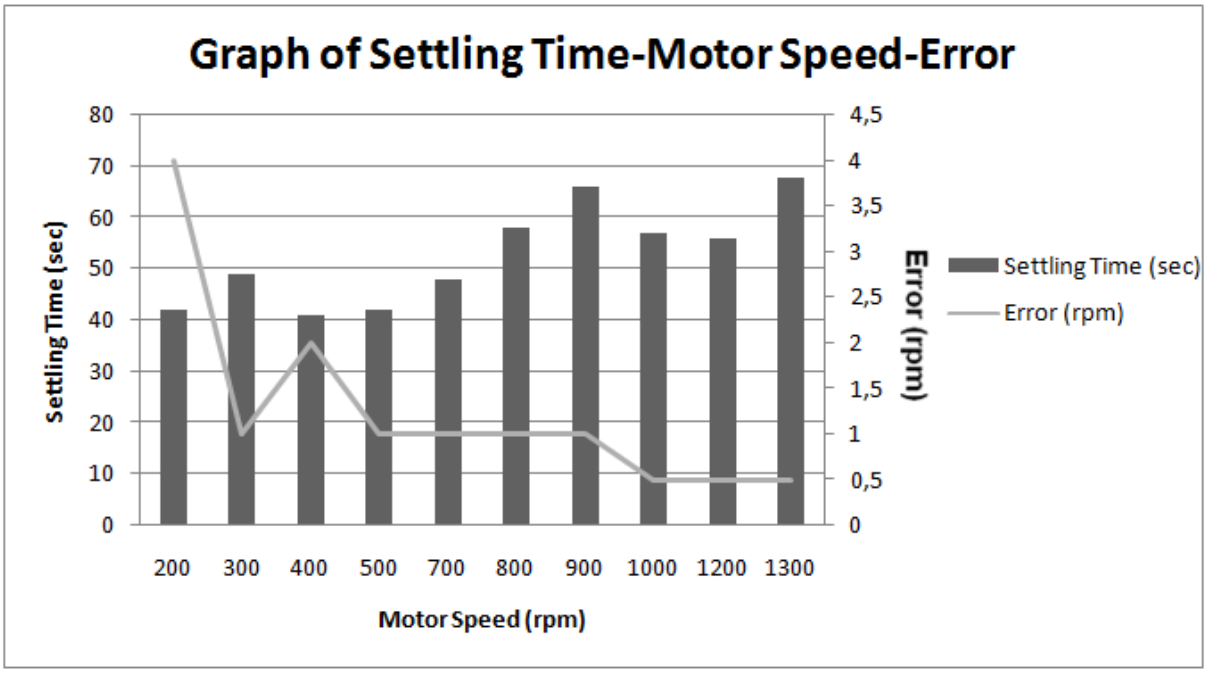


The AC motor was driven at 1000-1200-1300 rpm and graph shown in Figure 13 was obtained. In this graph, when the motor is first started or set point is changed, it is seen that the motor speed has reached the set point, after it has fluctuated below the set point for a period of time. Subsequently, the disturbance was applied while the motor was rotating at 1000 rpm. As a result of this process obtained graph is shown in Figure 14. The moment when the disturbance is applied in the graph is "1" and the moment when the disturbance is removed in the graph is "2". It was found that when the disturbance was applied, the motor speed decreased and the voltage at the analog output of the PLC increased. Then, the motor speed has reached the set point again. When the disturbance is removed, the motor speed has reached the set point again after exceeding the set point for a moment. In addition, some data obtained by driving the motor at different speeds were recorded. These data are shown in Table 3 Figure 15 shows how the settling time and error change for some motor speed values. As seen in the graph, when the motor speed increased, the error decreases, but the settling time increases.

Table 3: Some data obtained by motor speeds

Motor Speed (rpm)	Settling Time (s)	Error (rpm)	Analog Output Without Disturbance (V)	Analog Output With Disturbance (V)
200	42	4	0.75	0.93
300	49	1	1.08	1.35
400	41	2	1.40	1.58
500	42	1	1.73	1.94
700	48	1	2.40	2.52
800	58	1	2.74	2.90
900	66	1	3.07	3.29
1000	57	0.5	3.40	3.58
1200	56	0.5	4.06	4.25
1300	68	0.5	4.40	4.60

Figure 15: Graph of Settling Time-Motor Speed-Error



In this study, encoders of two different brands were tested. Firstly, 600 pulse encoder was preferred due to its low cost. However, the pulses produced by this encoder are 5 V in PLC, not 24 V. Therefore, the counting with the HSC inputs of the PLC could not be performed. This problem has been fixed by stabilizing the encoder outputs to 24 V over the buffer. Secondly, Autonics brand 2500 pulse encoder was tested. Since there was no voltage drop problem in this encoder, the study was performed with this encoder.

4. OBSERVATIONS AND RESPONSES

This experiment was applied to 29 students in the fourth year of Electrical-Electronics Engineering in Ondokuz Mayis University (Samsun/Turkey) in 2019. These students are divided into 6 groups. Firstly, software (PLC ladder diagram) and hardware (inverter, AC motor, encoder) parts of AC motor speed control test are explained in detail. Then, the experimental setup for the AC motor speed control was established and the working mechanism was shown to the students. During the application phase, the students were able to assimilate the subject with the question-answer method. Each student group conducted the experiment under the guidance of instructor.

Most group have successfully completed the experiment. At the end of the experiment, students' observations and responses were recorded using the interview form. The students were asked 4 questions, "strongly agree", "agree", "disagree", "strongly disagree".

According to the Table 4, 100% of students found this project useful and educational. The reason why they find it useful and educational is that the issue involves a direct industrial practice. Students have firstly tested speed control of AC motor with PLC. The speed control of the AC motor with PLC through the HMI display has aroused the curiosity and excitement of the students.

100% of the students stated that they understand how PLC works. The students experienced the theoretical knowledge they received in the lessons. They have been informed about PLC power connections, input and output units, inverter, encoder and AC motor connections and their working principles. This practice is important for learning where and how

to use the information. At the same time, it was observed that the self-confidence of the students who could apply the knowledge they learned increased.

93.1% of the students stated that they had learned to use encoder and inverter with PLC. As a result of interviews with the some students, it was seen that the students learned to PLC programming, use PID block, read encoder, drive inverter, control AC motor and obtain control signal. According to the results of the study, 96,55% of the students stated that they understand the speed control of the AC motor by using PLC.

Table 4: Evaluation of observations and responses

	IV	**III**	**II**	**I**
1- I found this project useful and educational	%62.52	%34.48	%0	%0
2- I understand how the PLC works.	%27.59	%72.41	%0	%0
3- I learned the use of inverter and encoder as well as PLC.	%31.03	%62.07	%6.9	%0
4- I understand how to control the speed of an asynchronous motor using PLC.	%37.93	%58.62	%3.45	%0
IV: I strongly agree III: I agree II: I disagree I: I strongly disagree				

5. CONCLUSION

In factories, industrial control systems are used in many fields such as pressure, temperature, motor speed control etc. PLC is the most preferred among them. Therefore, PLC courses are taught in different engineering departments of universities. In addition to theoretical knowledge, it should be shown in industrial applications in PLC education. For this reason, in this study, the AC motor speed control experimental setup is designed. Encoder as an input sensor, inverter as the actuator, PLC as the controller are used. Through this experimental setup, the students assigned the encoder as the input of the PLC, the inverter was assigned as the output of the PLC and programmed. They have also learned to use the PID block in the PLC and can use the PID block in other industrial control applications such as pressure and temperature. Thanks to this study, the students experienced the operation of an industrial control system in real time.

After students have learned the PLC, they can take this study as a finishing project and they can make some changes on it and use it as an experimental setup in their own laboratories. For instance; tachometer instead of encoder, other model PLCs instead of Siemens S7-1200, DC motor instead of AC motor, DC motor driver (LD298 or H-Bridge Driver) instead of inverter.

This experimental setup can be used in the Control Laboratories of the departments of Electrical-Electronic, Mechatronics, Control and Automation Engineering.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **189-200**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.019
Research Article

IMPLEMENTATION OF BIO-GAS RESOURCES TO DECREASE ENERGY CONSUMPTION OF VILLAGE INSTITUTES; A CASE STUDY OF HASANOĞLAN VILLAGE INSTITUTE[1]

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Received: 5 July 2019; Accepted: 24 July 2019

ABSTRACT

Village institutes have been one of the most effective institutions in raising the country's education level since the Republic period. Increasing the quality of education in these schools is also directly related to the support of energy resources. In this study, the increase in rural building stocks is forcing the use of renewable energy sources such as biofuels to maximize the energy requirement from bio-sources. The aim of this study is to apply bio-fossil resources in a village institute to reduce energy consumption. Hasanoglan Village Institute, which is located in Ankara, has been chosen as a case study. In this study, the potential of bio-gas use is presented.

Keywords: *Renewable energy, Village institutes, Bio-gas, Bio-mass*

[1] *Bu çalışma 2-3 Mayıs 2019 tarihlerinde Çanakkale/TÜRKİYE'de gerçekleşen **"4. Uluslararası Rating Academy Kongresi: Köy Enstitüleri ve Eğitimde Yeni Arayışlar"** temalı kongrede sunulmuş aynı isimli bildirinin gözden geçirilmiş halidir.*

1. INTRODUCTION

Organic wastes exist in the environment naturally and are generally used for various methods such as production of pyrolysis and biogas without efficient transformation and polluting the environment, improper storage, incineration or inefficient use. As a result of these processes, organic waste cannot be completely degraded and becomes a threat to the environment, ecosystem and human health although it has an important place in the national economy. Bio-gas, can be offered as new generation energy resource, is one of the less polluting gas than other gases. Bio-gas is an organic waste and a mixture of methane and carbon dioxide as a result of anaerobic fermentation and produced by the bacterial decomposition with colorless, odorless, bright blue flame burning. Ratio of produced bio-gas varies according to the composition of the organic waste used, the temperature and pH of the environment. Generally, 60-80% of methane gas (CH_4), 20-46% of carbon dioxide (CO_2), 0-2% of hydrogen sulfide, small amounts of nitrogen (N_2), water vapor and hydrogen (H_2) exist in the structure. Bio-gas is a clean energy source which is obtained from anaerobic treatment with suitable bacteria from some specially grown plants, domestic wastes, agricultural and all kinds of organic waste (Bilgin, 2003; Ekinci, 2007, Koçer *et al.*, 2006).

In Turkey, first studies on bio-gas was conducted in Eskisehir region in 1960 with the help of the Fertilizer Research Institute of Soil and Water Research Institute (Koçer *et al.*, 2006). Between the years of 1980 and 1986, Central Soil Water Research Institute (Village Services in Ankara Research Institute) continued researches on bio-gas production from cattle, sheep and chicken fertilizers in Ankara region (Bilgin, 2003). Nowadays, Directorate General of Renewable Energy was established a report under the management of the Ministry of Energy and Natural Resources (Directorate General of Renewable Energy, 2013). According to a report in 2013, two companies which processes the organic wastes from cattles, sheep and chicken exist in Turkey whilst thirty-four companies use wastes from household and food industry. The current facilities are located in West and Central Anatolia of Turkey. Futhermore, it is planned to construct twelve facilities in the near future. The total power in the current facilities are 111.23 MW, however, total capacity will be increased to 222.99 MW with the new constructed facilities (Bio-gas Report, 2011).

In order to support such activities, the Turkish Government issued a Law on the "use of renewable energy sources for the production of electrical energy" in the Official Gazette No. 25819 on 10th May of 2005 (Official Gazette, 2006). In this law, the government gives information about the use of electricity which can be produced by alternative sources, incentives to be given and pricing. According to this law, people can sell their electricity which is produced from renewable energy sources including bio-gas. Constructed facilities for biogas production in Turkey usually aim to assess the domestic waste or municipal waste as well as the food industry, however, the number of enterprises engaged in agriculture and animal husbandry have not yet reached a sufficient level. Furthermore, it is obvious that if similar studies can be performed in schools that provides education based on technology, agriculture and animal husbandry, such as the Village Institutes, the data and resources will reach large numbers. Moreover, students who will learn bio-gas production systems will contribute greatly to the dissemination of education. The advantages of fertilizer, which constitutes an important problem in herd management, as a means of recycling, make the use of a biogas attractive.

In this research, Hasanoğlan Village Institute (currently used as Hasanoğlan Atatürk Science High School) which is located in Ankara/Turkey, is selected as a case study since there are many courses in the Hasanoğlan Village Institute, such as animal husbandry, animal husbandry, agriculture and weaving. Moreover, the environment of the Institute is still available for the purpose of courses counted above. To this aim, the purpose of this paper is to produce the bio-gas energy by revitalizing the studies and to obtain a large part of the school's energy

demand by bio-gas resources. This study also aims to increase the energy efficiency of educational buildings, as well as decreasing energy consumptions with the use of renewable energy resources.

2. METHODOLOGY

2.1. Bio-gas production

Bio-gas mainly consists of CH_4, CO_2, small amounts of H_2S, NH_3 and H_2, CO, O_2, halogenated compounds (chlorides, fluorides etc.) and silicones. Once the biogas is obtained, the energy is saturated with water vapour which is highly diluent. The first production of biogas contains many chemical components with different volumes which is shown in Table 1.

Table 1. Biogas components

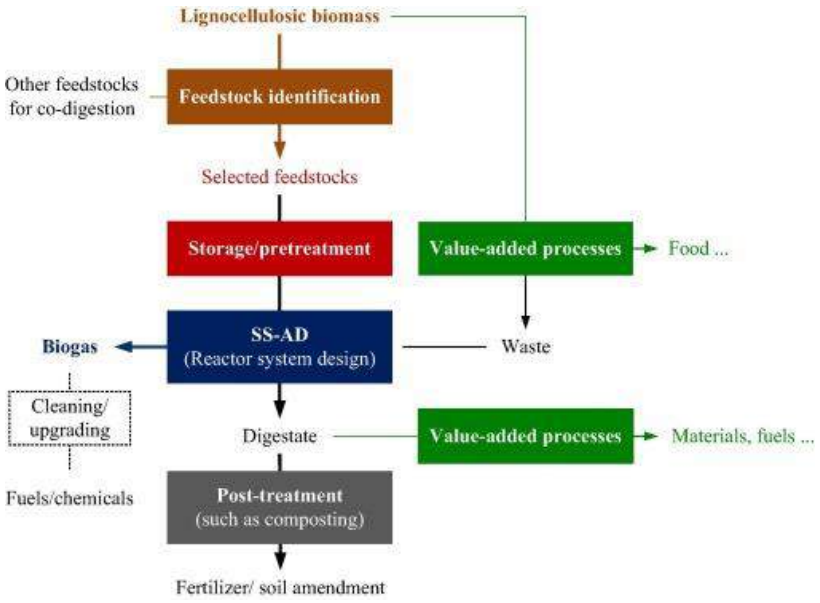
Components	Volume (%)
Methane	50-80
Carbon dioxide	20-50
Hydrogen sulfide	0,0005-0,0002
Ammonia	0,0005-0,0001
Nitrogen	0-3
Hydrogen	0-5
Water	0-1

(Painuly, 2001)

Bio-gas is a gas mixture which is lighter than air and has a density of 0.94 kg / m^3 according to air, octane number is about 110, combustion temperature is 700 ^oC, flame temperature is 870 ^oC and thermal value is 5.96 kWh/m^3 which depends mainly on CH_4 + CO_2 concentrations (Bayrakçeken, 1997). Gas composition is not stable but also varies according to the ambient temperature, water quantity, acidity (pH) and the composition of the used fertilizer.

Bio-gas can be used instead of natural gas after purification and quality improvement processes (U.S. Department of Energy, 2002). Table 2 compares the features of bio-gas and natural gas while Figure 1 depicts the solid-state anaerobic digestion (SS-AD) bio-gas production steps.

Figure 1. Overall perspectives for further research in SS-AD of lignocellulosic biomass



(Ge *et al.*, 2006)

Table 2. Comparison of bio-gas with natural gas

Features	Natural Gas	Bio-Gas
Compound (volumetric %)	95-98	55-65
Molecular weight	16.04	26.18
Density (kg/m^3)	0.82	1.21
Thermal value (MJ/m^3)	36.14	21.48

Various factors affect bio-gas production, such as raw material, capacity and location of the plant, storage and transportation of bio-gas and the transport and distribution of the manure from the plant to the field (Bilgin, 2003). Therefore, the environmental plan should be designed correctly. The organic wastes (raw material) which are used in biogas production can be examined under 3 main headings: animal wastes (livestock manure, slaughterhouse waste and wastes from processing animal products), vegetable wastes (wastes generated during the processing of various crops) and city and industrial wastes with organic content (sewage, paper-food industry waste, household waste) (Koçer *et al.*, 2006).

1 m^3 of biogas produces energy equal to 0.56 kg of fuel oil, 0.46 kg of liquefied petroleum gas and 0.62 m^3 of natural gas. Table 3 represents the thermal value of the biogas (with a metane rate of 60%) compared to other fuels (General Directorate of Electrical Power Resources Survey and Development Administration, 2008).

Table 3. Comparison of biogas with other fuels

Name of the fuel	Thermal value (kJ/kg)	Equal value of bio-gas
1 kg of lignite coal	27196	0.79 kg
1 kg of fuel-oil	38492	0.56 kg
1 kg of mixed cast gas	46024	0.46 kg
1kg of propane gas	46024	0.46 kg
Liquefied petroleum gas	46024	0.46 kg
1 kg diesel	42676	0.50 kg
1 kg natural gas	34518	0.62 kg
1 kg Soma coal	19664	1.09 kg

(General directorate of electric power resources survey and development administration, 2008)

The amount of produced bio-gas varies on the raw material used. Berglund and Börjesson (2006) concluded that the raw material in the bio-gas reactor contains high amounts of oil while another study reported that the addition of rumen content to the raw material in the reactor provides more bio-gas production (Budiyono *et al.*, 2010). Furthermore, Bilgin (2003) used fertilizers as organic wastes and reported that the produced bio-gas value varies according to the type of the animal and the size of the plant. Table 4 shows the amount of biogas that can be obtained according to the number of poultry and cattle (Bilgin, 2003).

Table 4. The amount of biogas to be obtained at the plant to be installed depending on the number of animals

Number of animals	Plant size (m^2)	Wet fertilizer need (kg)	Bio-gas production (m^3)
2500 chicken	15	200	17
50000 chicken	300	4000	340
10 cattle	10	150	5
100 cattle	100	1500	50

Storage and discharge of animal wastes are two of the most important problems of agricultural enterprises. The produced agricultural wastes can be used as fertilizer, on the one hand, the biogas production can be obtained from agricultural resources. The amount of wet manure demand in the facility should be calculated according to the capacity of the enterprise. 5-6% of live weight (average 10-20 kg / day) in bovine animals, 4-5% in sheep-goats (average 2 kg/day), 3-4% in chickens (average 0.08-0.1 kg/day) fertilizer is obtained. The average amount of manure produced in a facility is 3.6 tons / head and 0.022 tons / head per annum on average for cattle and poultry, respectively. Accordingly, biogas can be obtained from 1 ton fertilizer; 33 m^3/year for cattle and 78 m^3/year for poultry (Directorate General of Renewable Energy, 2013). The heat value of the gas obtained from bio-gas reactors is 4700-5700 kJ / m^3. For best production of bio-gas, it is required to have 7-9% solids content in in-plant fertilizer water mixture. In cases where this rate increases, the transactions for the disintegration of the raw material require additional financial expenditure.

Reactors are divided into two main groups as small and large volume bioreactors according to their volumes. Small volume bioreactors include heap type, fixed roof (Chinese type), floating indoor (India type), balloon and bag type while large volume reactors are in general, fully mixed, piston flow, lagoon type reactors and centrigas systems (Öztürk, 2005). These reactors include anaerobic contact project (ACR), anaerobic filters (AF), upstream anaerobic sludge reactors (UASB), fluid bed reactors, expandable granular sludge reactors (EGSB), acid phase reactors, internally stirred reactors (IC), hybrid reactors and full-blend digesters which can be called anaerobic lagoon digesters (Türker, 2008). According to the working principles, reactors are divided into two groups as low and high speed reactors. Low-speed reactors are lagoons, complete mix digesters, and horizontal or vertical shaped sludge reactors which have mesophilic bacteria. Fast reactors are mix digesters, contact digesters, hybrid reactors, fixed film reactors and gas production is provided by thermophilic bacteria. The evaluation of the produced energy in bio-gas plants varies according to the transport distance. If energy is produced from manure, it is reported that there is a loss of produced energy at distances of 700 km more than slaughterhouse wastes (200 km) (Berglund and Börjesson, 2016).

For bio-gas production, reactors operate at psychophilic temperature (12-20 °C), at mesophilic temperature (20-40 °C) and at thermophilic temperature (40-65 °C). Organic wastes are kept under thermophilic conditions, the destruction of weed seeds, which is a major problem in the fertilization process, occurs at a higher rate than the mesophilic conditions (20, 26). In the reactors which operate under thermophilic conditions, the heating energy is higher than the mesophilic and the reactor volume is smaller. Therefore, mesophilic temperature range (35-37 °C) is the most preferred ranges (20, 25, 27). At the hydrolysis stage and reaction stage with acidogenic bacteria, the pH of the medium is 5.2-6.3, however, pH should be between 6.7-7.5 at the stage of methane gas formation (Guo and Guo, 2010). Carbon / Nitrogen (C/N) ratio is also effective for the formation of methane gas in the reactor. Carbon is necessary for bio-gas

formation and nitrogen for the development and regeneration of anaerobic bacteria. C/N ratio in animal manure based reactors varies on the type of animal. In general, the value is between 15/1-30/ 1 (approximately average value is manure, 22 in cattle manure, 14 in poultry manure and 25 in pigeon manure). However, this value should be 10-45 at the reaction stage with hydrolysis and acidogenic bacteria and 20-30 at the stage of methane gas formation (Guo and Guo, 2010). The presence of mineral ions, heavy metals and detergents in the waste has a toxic effect by preventing the growth of micro-organisms. While heavy metals such as copper, chromium, nickel, zinc, lead in low concentration affect the bacterial growth positively, high concentrations of toxic effects can be produced in process. Detergents and disinfectants (such as soap) have also been reported to reduce methane production (Öztürk, 2005). Apart from these factors, the duration of digesters, water ratio, and the effect of inhibitor and alkalinity can also affect the bio-gas production.

Another important factor is that wastes pollutes the environmental, the earth and underground water resources. Micro-organisms consume more oxygen to de-compose organic matter in contaminated waters. The consumed amount of oxygen by micro-organisms (bio-chemical oxygen demand=BOG) is an important criteria for the determination of environmental pollution. It has been reported that BOG is higher in the wastes obtained from livestock than the daily waste produced by people (Karaman, 2006). Obviously, it is possible to reduce BOG value in animal wastes by bio-gas production. Organic wastes can be transformed into the energy by using them in reactors and fertilizer which can be used in soil. A study reported that fertilizers, which are used in agriculture, leave salt to the soil while fermented manures that passing through bio-gas reactor does not leave any residue (Alçiçek and Demiruluş, 1994). Another study showed that the weed seeds in animal fertilizers lose their germination property and the smell of manure and the destructive effect of fresh manure decrease while the fluidity increases. Methane gas can be obtained from bio-gas units and can be converted to electricity and heat energy. 500- 2000 kWh /1000 kg energy can be produced from various reactors (Ardıç and Taner, 2012). In order to ensure complete combustion in methane gas, the bio-gas should be mixed with air at a rate of 1/7. A variety of bio-gas-powered vehicles have been produced and methane gas can be purified or used directly in any of the gasoline-powered engines. By mixing the produced gas to natural gas, it is possible to reduce the current cost and bio-gas can be used during the production of chemicals in the use of fuel cells (Çanka Kılıç, 2011).

2.2. Case Study

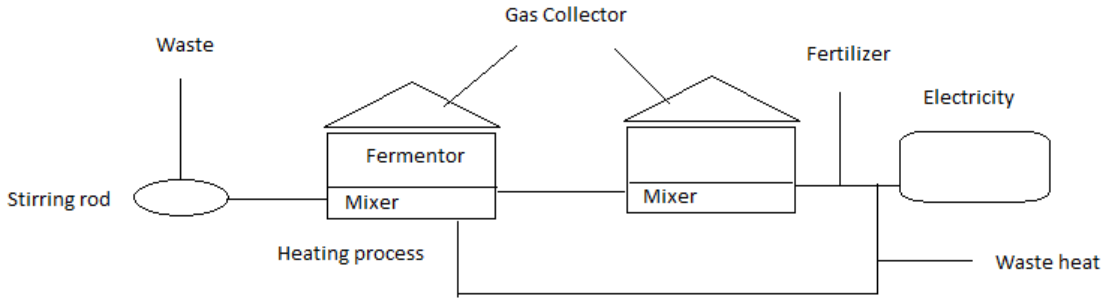
The aim of this paper is to create an environment where the energy level of living beings can be provided according to the climatic conditions. Solar, wind and underground surface waters from indirect sources, indirectly located in a gas and bio-energy systems and their data are evaluated. Hasanoğlan Village Institute which is located in Ankara is selected as a case study for the research (Figure 2).

Figuere 2. Hasanoğlan Village Institute, location (left) and building (right)

Bio-gas can be produced from agricultural wastes in the campus of Hasanoğlan Village Institute since scientific agriculture courses were given in this school in the first years of Republic. Futrhermore, raw metarial of bio-gas plant is considered to be supplied from Hasanoğlan Village where the campus is located in. Manure obtained from livestock in the village will be used for bio-gas production.

Figure 3 shows the considered bio-gas plant for the Hasanoğlan Village Institute. The case plant is taken from the reference (Kaya and Öztürk, 2012). Since the energy requirements of the Hasanoğlan Village Institute are considered to be approximately 500 m^3, the reactors are recommended according to these values. Small volume bio-reactor is chosen for the study.

Figure 3. Biogas plant and production processes used in livestock enterprises



(Öztürk, 2005)

Depending on the farm and agricultural waste capacities of the Hasanoğlan Village Institute, the amount of the produced energy may vary, however, general data is used for the study. Annual potential biogas production is obtained from Eq.1 (Kemausuor et al., 2014).

$$y_{biogas} = P_{live} \times y_{man} \times c_{ts} \times \eta_{rec} \times y_{BMP} \quad (1)$$

where y_{biogas} shows potential biogas production from manure, P_{live} is livestock population, y_{man} is produced manure, c_{ts} depicts total solids concentration in the organic fraction, η_{rec} is recoverability of the manure and finally, y_{BMP} is methane potential.

Energy capacities and electricity consumption for the purpose of heating and cooling are determined according to the data. The type of reactor in biogas production facilities varies according to the capacity, the percentage of solids, the number of steps, the operating temperature and the feeding patterns. 6-12 m^3 of family type is sufficient, while in farm type this value is between 50-150 m^3, type of village is 100-10000 m^3 (Germany, America, Denmark and Switzerland) (Bilgin, 2003). In the study, this value is estimated to vary between 12 m^3 and 150 m^3 for the Hasanoğlan Village Institute. Reactor loading was taken as 1.66 kg/m^3 /day and 170 m^3 /day gas production from 250 livestocks was assumed per ton of manure (Kaya and Ozturk, 2012). η_{rec} and c_{ts} were calculated as 0.2 and 12 gTS/100g for livestocks, respectively. A 41 m^2 floor area was selected for the bio-gas facility. Floating balloon type biogas plant was preferred since it is cost-effective, easy to design, easy to transport.

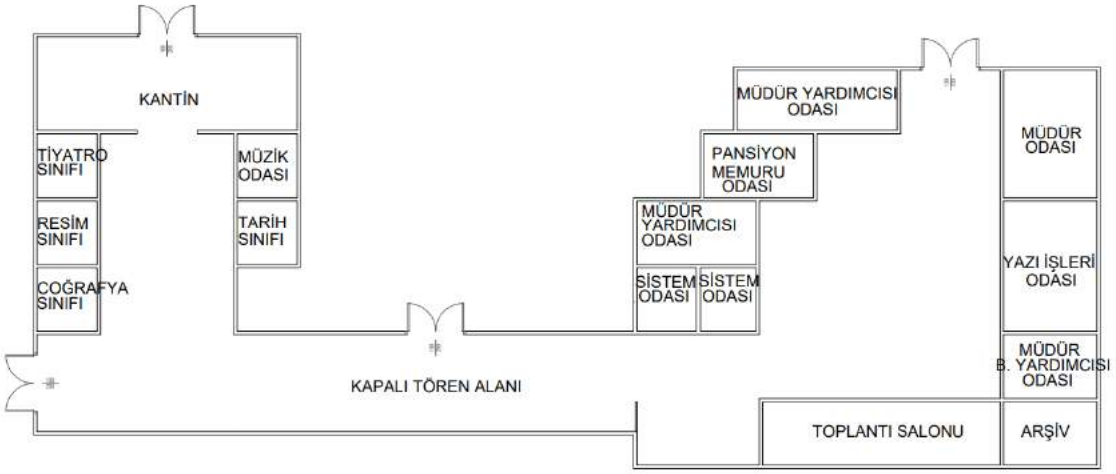
A 150 m^2 building in the campus of Hasanoğlan Village Institute was selected to compare the energy consumptions before and after implementation of bio-gas plant in the campus. Floor plans, cross-sections and side wives were all drawn in AutoCAD and dimensioning, energy and cost analyses were performed in a Building Energy Simulation (BES) tool for the building. DesignBuilder (2019) dynamic simulation software, v4.2.054, was used for modelling and simulation of the Village Institute. DesignBuilder lays on EnergyPlus simulation engine and uses FORTRAN programming language to develop simulation engine.

Moreover, the solution technique of the program is based on the Predictor-Corrector Method. DesignBuilder (2019) has inputs like lighting and HVAC systems, occupancy and equipment schedules, construction materials and allows to determine heating and cooling load of the building. In this study, the energy is supplied from proposed bio-gas plant and the energy consumption is calculated and compared with the existing model.

The pay-back period is calculated from Eq.2.

Pay-back Period: Investment Cost/ Annual Cash Savings (2)

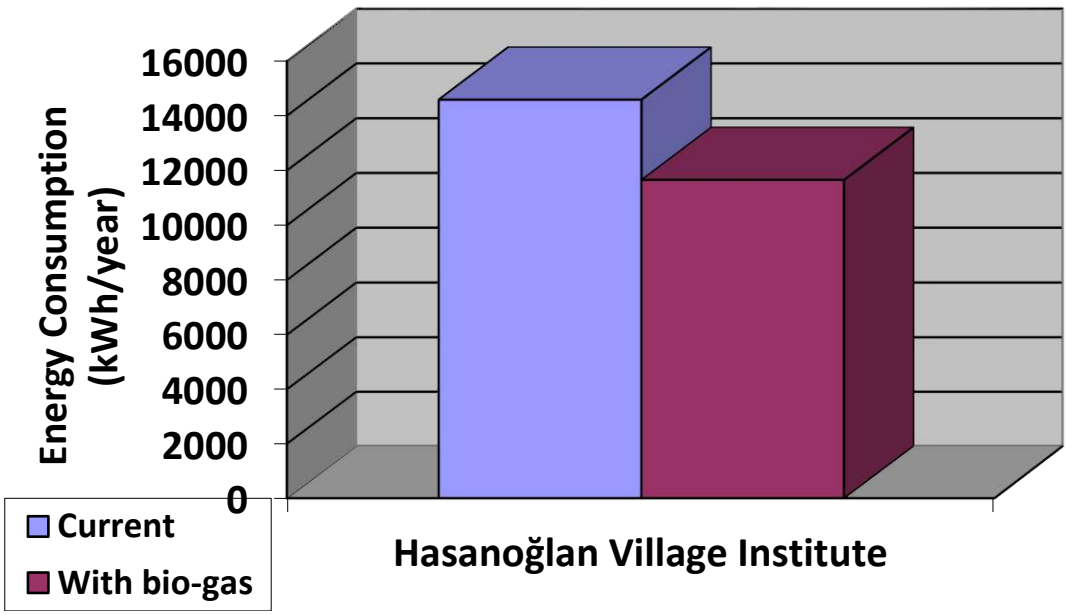
Figure 4. The plan of the case building in Hasanoğlan Village Institute



3. RESULTS

The Hasanoğlan Village Institute was modelled in a calibrated Building Energy Simulation tool, DesignBuilder (2019). The current energy consumption and the energy produced by bio-gas implementation were compared. Figure 5 compares the energy consumptions before and after implementing bio-gas production.

Figure 5. Comparison of energy consumption of Hasanoğlan Village Institute



The annual energy consumption of Hasanoğlan Village Institute is calculated as 14586 kWh/year. However, 20.1% of energy can be saved by implementing bio-gas production for the case building. Besides energy saving, wastes from organic origin can be re-used with the bio-gas production technology. Thus, the output of the bio-gas production becomes more valuable organic fertilizer since methane gas leaves from the system after bio-gas production. Furthermore, the solids of the wastes from the digester will be used to meet the demand for biogas which will increase in the future. The results show that 1 m^3 of bio-gas produces 10 kWh of energy. According to the calculations, it will be possible to produce 105000 kWh of electrical energy from 10500 m^3 of bio- gas. Knowing the electricity consumption per person is 2.562 kWh, the electricity generated from the bio-gas has the capacity to meet the daily energy need of 40984 people.

The investment cost of the bio-gas plant is calculated according to a study by Adeoti *et al.* (2000). The authors revealed that investment costs are approximately 65% of the total costs while facilities, installation, labour and land are accounted for the remaining 35%. The first costs of the construction of bio-gas plant in Hasanoğlan Village Institute is calculated as 1161.2 dollars (VAT included). The pay-back period is 3.95 years.

A comprehensive comparison is conducted in order to find which renewable energy resources is the most effective in this region. To this aim, each investment is assessed seperately for Hasanoglan Village Institute. Regarding to solar energy, ten PV panels (1.6 X 1 m, with standard 60 cells) with a total area of 16 m^2 were applied to produce electricity for the Village Institute. Considering the short total insolation hours of Ankara (2,8 hours/year), the pay-back period was calculated as 6.14 years. Another option was to add one three-bladed wind turbine to generate electricity (with 31 m height and 55kW rated power output). Although wind energy fulfills almost 79% of total energy consumption of case building, the location of Hasanoglan Village is not suitable for continous energy generation by wind energy. Renewable energy resources generally depend on climate and weather condition, however, the raw metarial of bio-gas always exist in villages.

Table 5. Comparison of bio-gas with other renewable energy resources for Hasanoğlan Village Institute

Renewable Energy Source	Implementation Type	Energy saving (%)	Investment Cost (TL)	Pay-back period (Years)
Bio-gas	Plant	20.1	1161.2	3.95
Solar energy	Solar Panel	8.1	16240	6.14
Wind energy	Wind Turbine	79.4	378855	11.24
TL: Turkish Liras, Labour charges are added to the prices, 1 $= 5.8 TL, 1£ = 7.57 TL, 1 € =6.55 TL				

As the number of people is not a value to be underestimated, the students and administrations should be aware of the capability of bio-gas production before coming to the farm, and should be informed about the necessary incentives to be given by the government and the uses and benefits of the bio-gas.

4. CONCLUSIONS

Educational structures are one of the most important equipment in the development of the country. The use of educational methods combined with theoretical sciences in education will have a major impact on the development of the new generation. Nowadays, the computer technology comes firstly to mind while life cycle in development is left in the second plan.

However, practical training for the vital return constitutes the infrastructure of the most important scientific studies. The education of teachers and participation of students in educational life are two main parts of the system. However, proper use of energy resources should be taught in order to disseminate education.

This study aimed to use renewable energy resources to decrease energy consumption of Village Institutes. Thus, additional energy and income management from agriculture and animal husbandry for the Village Institutes will be satisfied. Moreover, Village Institutes can be actively revived for education with the help of bio-gas production technology. The importance of using alternative energy instead of fossil-based energy resources can be understood. Increase of bio-gas production in Turkey will ensure a healthier environment with good converged planning and management, which will help to decrease Turkey's energy-dependence to foreign countries.

ACKNOWLEDGEMENT

The authors would like to thank administration of Hasanoğlan Village Institute and Hasanoğlan Atatürk Science High School for their valuable help in order to obtain dimensions and photographs.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **201-206**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.020
Research Article

DETERMINATION OF CR (VI) IN CREEKS DISCHARGE TO İZMIT GULF (KOCAELI, TURKEY)

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Received: 28 June 2018; Accepted: 9 July 2019

ABSTRACT

With increasing industrialization, environmental pollution has become a threat to human health. The heavy metal pollution, especially from industrial waste water, is the best example of this. Chromium holds a special position among living organisms because on its species it can be either essential or toxic. Cr (VI) even at very low concentrations is harmful and carcinogenic, while Cr(III) is a necessary microelement for cellular metabolism. Therefore, it is very important to determine the chromium metal found in the wastewater of leather, paint and iron - steel industries. Four main creeks discharges located in the important industrial area in Kocaeli Province are made to the Gulf of İzmit.

In this study, Cr (VI) was measured by the spectrophotometer S.M.3500-Cr B. Calorimetric Method sampled from four main streams Saz, Dil, Narca (Bağ) and Ambar (Ulupınar) Creeks samples and the results were found to be <0.02 mg / L. With these values it is observed that there is a visible improvement in the pollution of the creeks.

Keywords: *Creek, Water pollution, Heavy metal, Chromium (VI)*

1. INTRODUCTION

Kocaeli has been dealing with environment as the most important problem as a province which has realized its rapid industrialization and has been the problem of migration, social problems and zoning for years. Kocaeli Province; It has always been a center of attraction with its land, sea, railway transportation networks and being in the middle of metropolitan cities such as Istanbul, Bursa and Sakarya. The industrialization move that began in the 1960s brought a huge population growth in the 1970s and 1980s with it, as well as reactions from environmental problems. The 1990s and 2000s were the years when environmental technologies were implemented to meet environmental problems [1]. İzmit Bay has struggled with pollution originated from water pollution, which is one of the environmental problems, for years. Water pollutants can affect ecological life in both surface waters and ground waters.

The territory of Kocaeli Province is entirely within the Marmara basin. There is not a significant stream in the basin and the Kocaeli peninsula is divided by many brooks and streams. These waters, which are generally short and flooding, played an important role in the formation of the earth's forms in the province. Some of the streams are poured into Black Sea and others into İzmit Bay or Marmara [2].

Dilovası, an official district since 2008, is a region with industrial, agricultural and residential areas. For this reason, it is estimated that people, animals, plants and other living species living in this region with a population of 47663 are exposed to industrial pollutants. Industrial wastewater also contains heavy metals such as lead, copper, nickel, mercury, arsenic, chromium and cadmium, which are very toxic and dangerous for aquatic organisms. Many branches of industry (mining industry, energy and fuel production, fertilizer and pesticide industry, metallurgy and iron and steel industry, leather processing, photographic industry) has heavy metals containing heavy metal waste which are given directly or indirectly to the nature [3-5][6-9].

Most of the heavy metals are toxic and carcinogenic. It poses a great threat to human beings and other living things. Chromium; Two oxidation which are stated in nature are Cr (VI) and Cr (III). Cr (III) is a mineral that is useful to the human body. Cr (VI) is harmful and carcinogenic even at very small concentrations. Chromium which has a very common areas of usage like armored vehicle, blast furnace bricks, leather, paint, metallurgy, steel industry, has been accumulating in the environment and spreading to the human and aquatic ecosystem and finally creates permanent damages [10-14].

In this study, the four main creeks selected along the İzmit Bay in Kocaeli Province, Saz Creek, Dil Creek, Narca (Bağ) Creek and Ambar (Ulupınar) Creek Cr (VI) were measured. In particular, the measures taken for the Dilovası region of the İzmit Bay and the impact of the applied environmental technologies on the rivers were evaluated.

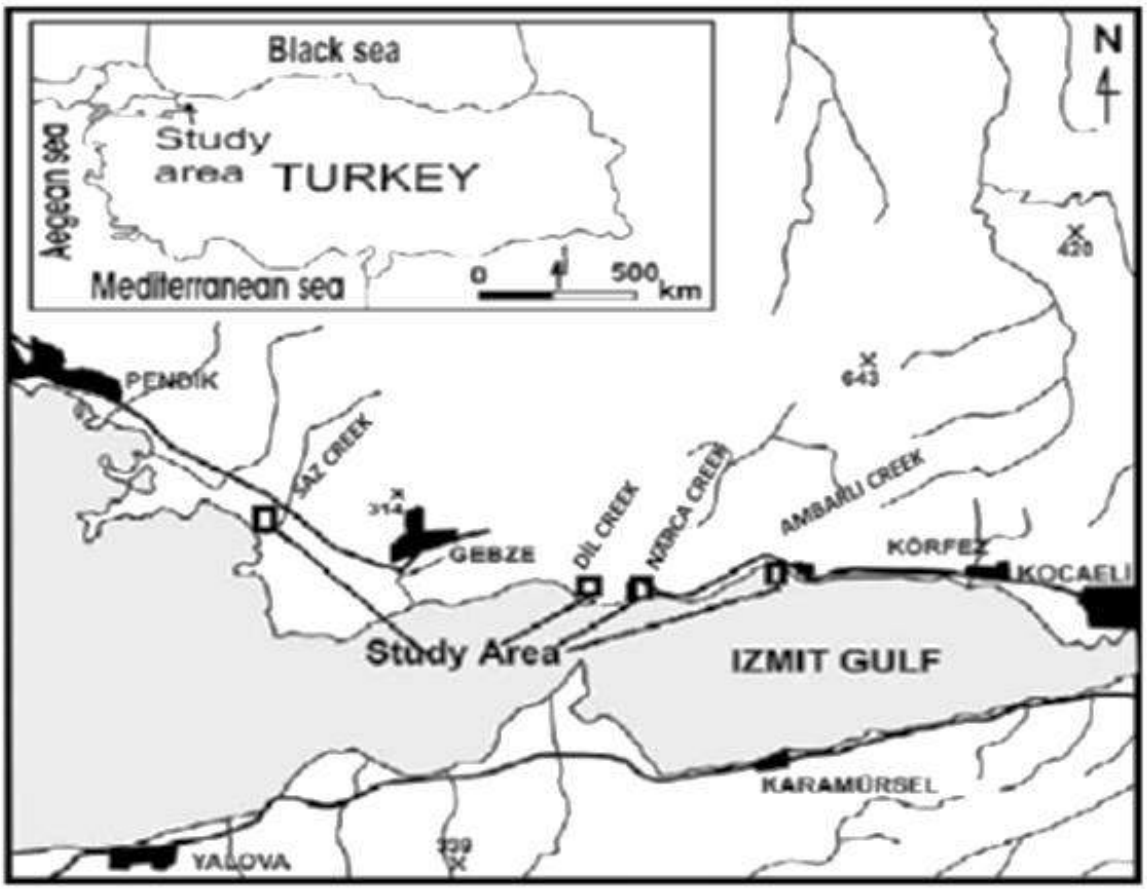
2. MATERIALS AND METODS

The study area is surrounded by the Bay of İzmit, the Marmara Sea and Istanbul, and the Black Sea in the north. The total length of the Saz Creek to the west of Dilovası is 9.75 km. Dil Creek is one of the most important rivers pouring from the north of the Bay to the Sea of Marmara and has a total length of 17 km. Narca (Bağ) Creek. It is 12 km long stream starting from Samanlı Mountains and pouring into İzmit bay. Ambar (Ulupınar) Creek is a 2,25 km long stream that flows into the Gulf of İzmit from the town of Hereke [2], (Fig. 1) .

Samples of 2L-plastic containers from each of these streams were collected according to the principles of Sampling using SM 3500 Cr (VI) B method; Cr (VI) was determined by colorimetric method using spectrophotometric (Merck Pharo 300 UV/VIS) reaction with

reaction of diphenylcarbazide in acid solution [15]. All chemicals were purchased from Merck (Germany) and they were all in analytical grade.

Fig. 1. Saz, Dil Narca, Ambarlı Creeks pouring into İzmit Bay [4].



3. RESULTS AND DISCUSSION

The sample is brought to room temperature. 100 mL of sample is taken. If the amount of suspended solids in the sample is high, it is filtered. 0.25 mL of ortho-phosphoric acid are added. With 0.2 N Sulfuric acid, pH is adjusted to 2. It is mixed well. Add 2 mL diphenylcarbazide solution. Wait for 5 -10 minutes. Read on spectrophotometer at 540 nm wavelength.

If the measured value is higher than the absorbance value in the calibration curve, the test is repeated by applying dilution. It is read on spectrophometer by remarking how many times diluted with pure water. As seen in Table 1, Cr (VI) value measured in four streams was less than 0.02 mg / L. Tests were performed in 3 replicates and averaged.

Table 1. Cr (VI) measurement results in streams

Creeks	**Parameter**	**Analysis Result**	**Unit**	**Analysis Method**
Saz Creek	Cr(VI)	<0,02	mg/L	SM 3500 Cr(VI) B
Dil Creek	Cr(VI)	<0,02	mg/L	SM 3500 Cr(VI) B
Narca Creek	Cr(VI)	<0,02	mg/L	SM 3500 Cr(VI) B
Ambarlı Creek	Cr(VI)	<0,02	mg/L	SM 3500 Cr(VI) B

In the study, which is carried out in the Dil Stream by Oktor et al [4], Cr (VI) results were found to be 0.0592 ± 0.0010 mg / L as IV. Quality Water.

Marka [6] compared all heavy metals in Dil Creek and other creeks with the Quality Criteria According to the Classes of Inland Water Resources Table for Water Pollution Control by the Regulation on Water Pollution Control in Environmental Concept Report in Kocaeli with Rehabilitation and Industrial Nuances. It is stated that the pollution given for the class is even higher than that of the pollution and even about 9 times the value of Chromium.

4. CONCLUSION

In recent years, environmental technologies have been put into use with the improvement works for İzmit Bay and Dilovasi Region. In this context, industrial facilities in Dilovası district have been assigned as DOSB Dilovası Organized Industrial Zone and all of the 200 facilities are connected to sewerage line and then the domestic wastewater of settlements is also connected to this sewerage line. In 2011, the Industrial and Domestic Wastewater Treatment Plant was established by DOSB Directorate and the wastewater that could not be connected to the treatment was brought to the facility by transportation and then discharged after the treatment [6].

The World Health Organization (WHO), the US Environmental Protection Agency (EPA) and the Turkish Standards Institute (TSE) have issued a limit value of 0.05 mg/ L for Cr (VI). In this study, the Cr (VI) value below 0.02 mg / L as II Quality Water in the samples taken from the four creeks shows that the water quality of the streams increased and the improvement studies made since 2010 are considerable development. In order to increase the water quality in both creeks and Bay Waters in Kocaeli province, new environmental technologies should be implemented and sustainability should be continued.

Acknowledgments

The author would like to thank Büşra EMİR and Hilal ŞEN for their contribution as a graduation work. The author thanks Rabia ŞAHİN for assistance in this study.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **207-214**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.021
Research Article

EFFECT OF DIFFERENT THICKNESS AND SOLUTION CONCENTRATION ON CUS THIN FILM GROWN BY SILAR METHOD

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Received: 7 July 2019; Accepted: 26 July 2019

ABSTRACT

In this study, CuS thin films were successfully coated on glass substrate at room temperature using successive ionic layer absorption and reaction (SILAR) method. Thickness and solution concentration parameters which are important in SILAR management were used to obtain CuS thin films. X-Ray diffraction spectroscopy (XRD), Scanning Electron Microscopy (SEM) / Energy Spread X-ray Spectroscopy (EDX) were used to examine the changes in thickness and solution concentration in the structure of CuS thin films. Because of the investigations, it was found that CuS thin films improved both the number of cycles and the concentration of the solution and that the crystal structure improved and the SEM / EDX results supported this result.

Keywords: *CuS, SILAR, deposition, thin film.*

1.INTRODUCTION

Copper sulfide (Cu_xS) is a p-type semiconductor with five different stable phases at room temperature, namely, chalcocite (Cu_2S), djurleite ($Cu_{1.96}S$), digenite ($Cu_{1.85}S$), anilite ($Cu_{1.75}S$) and covellite (CuS). Depending on the stoichiometric composition, the Cu_xS band gap may vary between 1.2 and 2.53 eV by Grozdanov and Naidaski in[1], Bagul et al in [2]. Moreover, this semiconductor has metal-like electrical conductivity because copper vacancies act as acceptors by Cruz-Vazquez et al in [3]. CuS thin films, electronics, optics and chemical properties are among the most important semiconductors by Chen et al in [4]. CuS thin films are widely used in many areas. We can list these fields as solar electrodes, radiation filters, organic polymers and coatings as electro-conductors. In addition to its excellent optoelectronic properties, CuS is abundant in the earth's crust, which is not dangerous, economical and environmentally friendly. Photosensors have tremendous applications in a wide range of electronic devices, circuits and systems. This proves its importance in a wide range of applications such as new generation displays, touch screens, fiber optic systems, optical scanners, automatic lighting controls and remote-control devices.

CuS thin films, which can be used in many areas, were grown using many chemical methods. These chemical methods include chemical vapor deposition by Gorai et al in [5], successive ionic layer adsorption and reaction (SILAR) method Güzeldir et al in [6], chemical bath deposition (CBD) by Kemmler et al in [7], spray pyrolysis by Sagade ve Sharma in [8]. Among these methods, SILAR method, low cost, PH, solution concentration, easy to parameters such as coating cycle

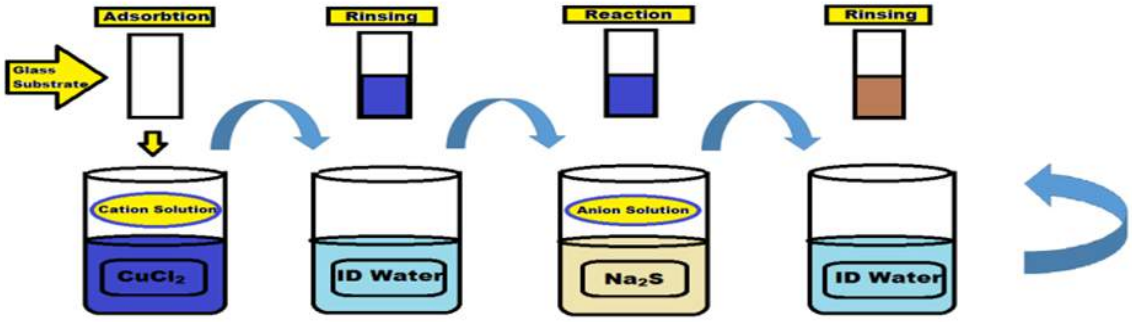
Controlled, thin film coating can also be done without distinguishing the surface type and shape. In this study, CuS thin films were grown on glass substrates using different solution concentrations and different thicknesses by SILAR method. The effect of XRD, SEM / EDX analysis, thickness and solution concentration of four different thin films on the crystal structure of the formed film was investigated on the surface.

2.MATERIAL AND METHOD

SILAR method is a very useful method for obtaining thin film according to many chemical growth methods. In SILAR method, thin film amplification is realized by changing parameters such as solution molarity, pH value, thickness and temperature. Each parameter can provide different convenience. Two solutions were prepared to obtain CuS by considering these conditions. $CuCl_2$ (pH=3) was used as the source of Cu and Na_2S (pH=12) solution was prepared as the S source. 0.1 M $CuCl_2$ solution, 0.1 M Na_2S solution was used to coating the CuS thin film. Likewise, copper chloride and sodium sulfide solutions were prepared in different molarity (0.2 M $CuCl_2$ 0.2 M Na_2S solution). Microscope glass coverslips were prepared by taking 10 x 10 x 2mm^3 size sections as a film to be thin film coated. The glass mats have passed the cleaning step before coating. It was first cleaned in dilute sulfuric acid solution with acetone and then made ready for coating by passing through pure water.

The SILAR method consists of four stages. In the first stage, the glass substrate is immersed in the solution for 20 seconds by immersing the glass substrate in a solution, so that the Cu^{+2} and Cl^{-2} ions adhere to the glass base. In the second step, the glass substrate is immersed in deionized water for 10 seconds to remove the weakly bonded Cl^{-2} ions on the substrate. In the third stage, the glass bottom of the Na_2S solution narrows for 20 seconds, and the Na^{+2} and S^{-2} ions adhere to the surface. In the fourth step, the weakly bound S^{-2} ions are immersed in deionized water for 10 seconds to leave the surface. Thus, a SILAR cycle is completed. Figure 1 shows a schematic representation of the SILAR method.

Figure 1. Schematic representation of SILAR method.



This process continues until the surface is homogeneously coated. CuS thin films are homogeneously coated after 30 SILAR cycles. CuS thin films were coated in different sizes in 30 and 40 cycles. Table 1 shows the parameters used to grow CuS thin film.

Table 1. Optimized deposition parameters for CuS thin film

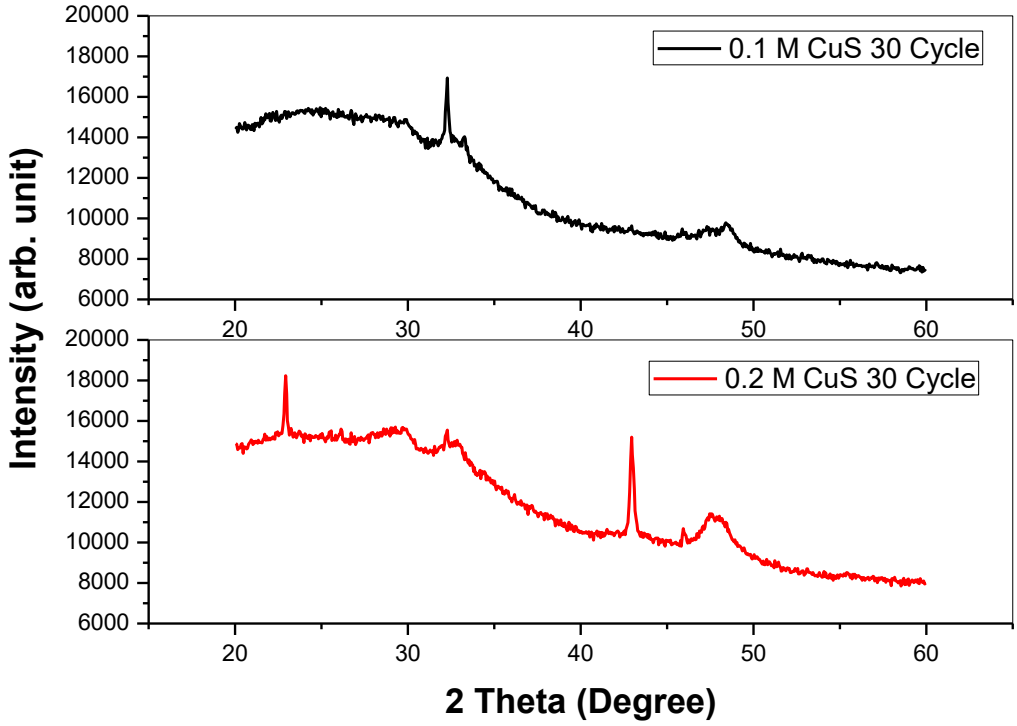
Deposition Parameters	Cationic Precursor	Anionic Precursor
Precursor	$CuCl_2$	Na_2S
Concentration (M)	0.1/0.2	0.1/0.2
pH	3	12
Immersion Time(s)	20	20
Rinsing Time (s)	10	10
Volume of Precursor (mL)	100	100
SILAR Cycle	30/40	30/40

XRD and SEM/EDX devices were used for the structural analysis of CuS thin films coated in 0.1 and 0.2 M solution and different cycle. The brands and models of XRD and SEM/EDX used for the analysis of CuS thin films are, respectively, Rigaku 2200D / Max, X-Ray Diffractometer, Zeiss Supra and Perkin-Elmer.

3.RESULTS

Figure 2 shows the XRD patterns of CuS thin films. XRD diffraction peaks were taken between 20°-60 ° (2θ). When the CuS thin film (30 cycle) was enlarged to 0.1 M, the 2θ angle showed a peak at 31.682 and 48.050, while the 0.2M CuS thin film showed peaks at 21.618, 29.110 and 42.922 in addition to these peaks. According to JCPDS-06-0464, the orientations of the peaks in these angles were obtained as 21.618, 29.110, 31.682, 42.922 and 48.050 (0 0 4), (0 1 2), (0 1 3), (0 1 6) and (1 1 0), respectively. When the CuS thin film (40 cycle) was enlarged to 0.1 M, the 2θ angle showed a peak at 29.110, 31.682 and 47.808, while the 0.2M CuS thin film showed peaks at 21.618 and 42.922 in addition to these peaks. According to JCPDS-06-0464, the orientations of the peaks in these angles were obtained as 21.618, 29.110, 31.682, 42.922 and 47.808 (0 0 4), (0 1 2), (0 1 3), (0 1 6) and (1 1 0), respectively. These planes indicated hexagonal crystal structure for CuS thin film. CuS shows that thin films have a polycrystalline structure with orientation along different planes. I can say that the crystal structure improved by increasing the precursor molarity and number of cycles.

Figure 2. XRD patterns of CuS thin films grown at 30 and 40 cycles.



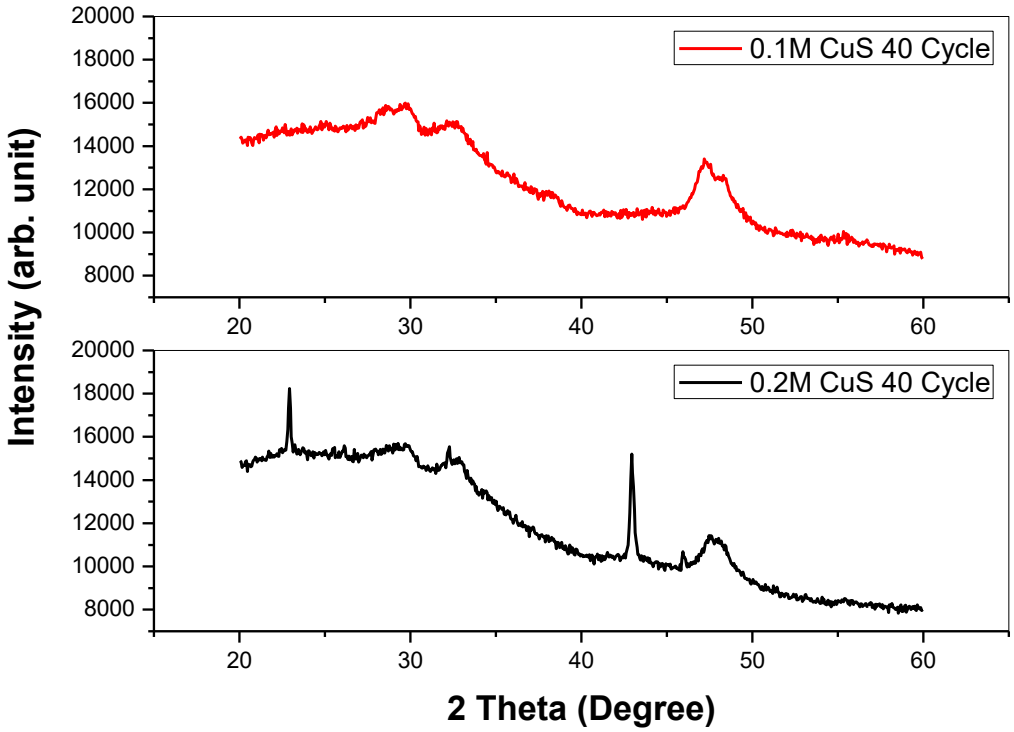
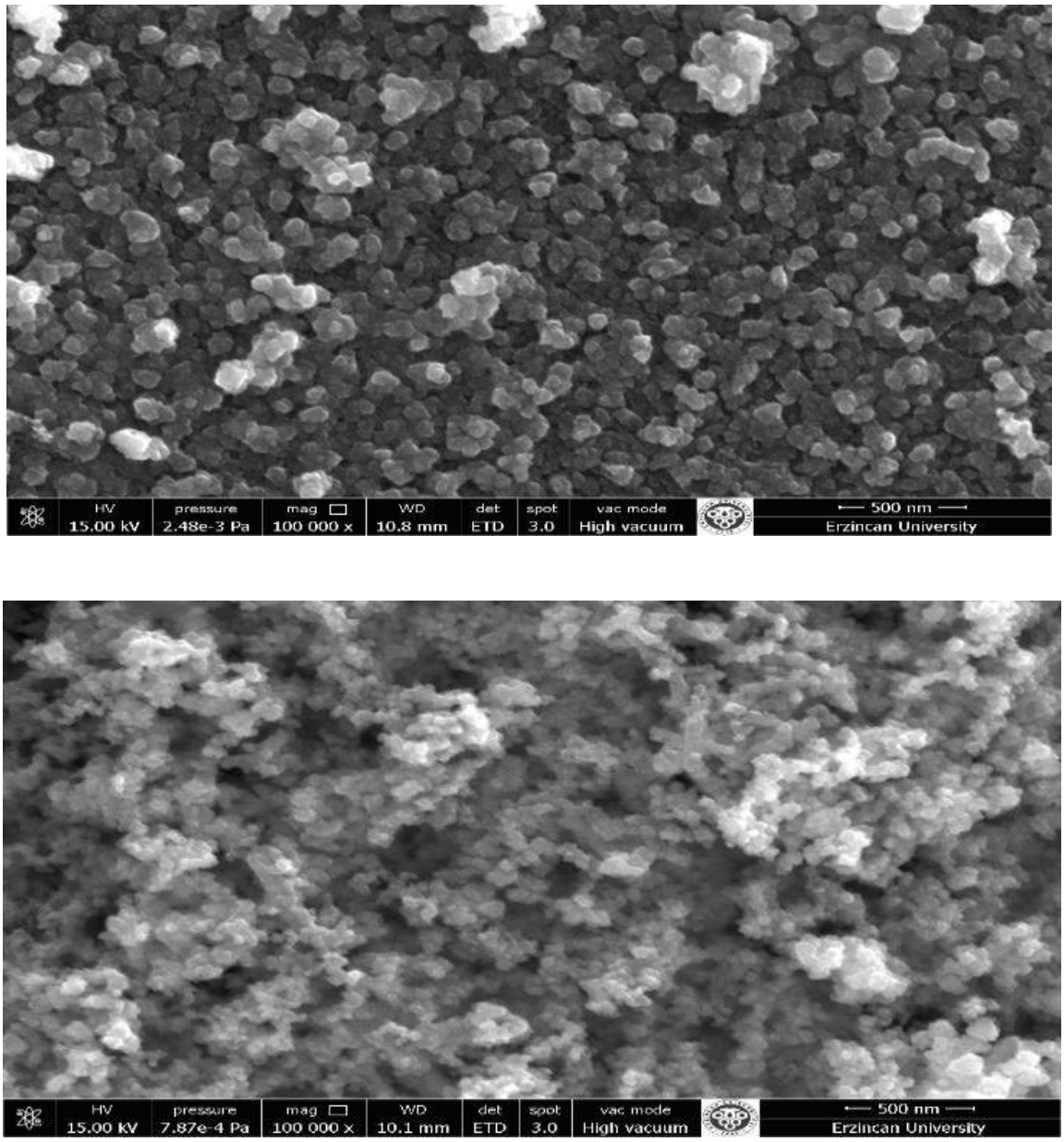


Figure 3 and 4 shows the SEM results of 0.1 M and 0.2 M CuS thin films growth 30 and 40 cycles at 100,000 magnifications. In the measurements made using scanning electron microscope, I can say that the CuS thin film is coated on the surface homogeneously. It is seen that well-crystallized grains in the first image belong to CuS film. The CuS film is dense,

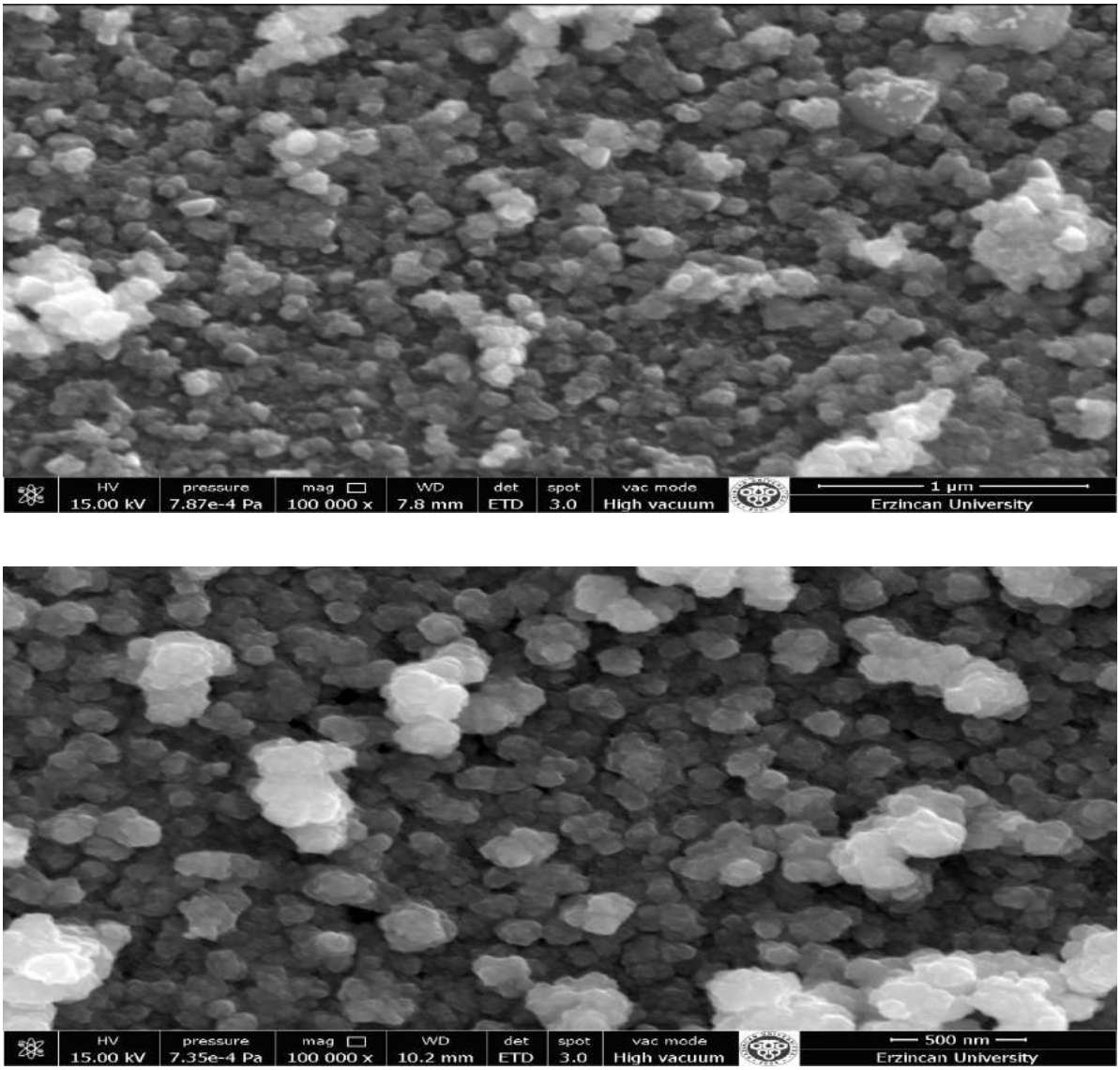
uniform and homogeneous without visible pores and covered well with glass substrate. CuS film is rough due to the formation of big grains.

Figure 3. SEM images of 100.000x magnifications of 0.1 M and 0.2 M CuS thin films grown at 30 cycles.



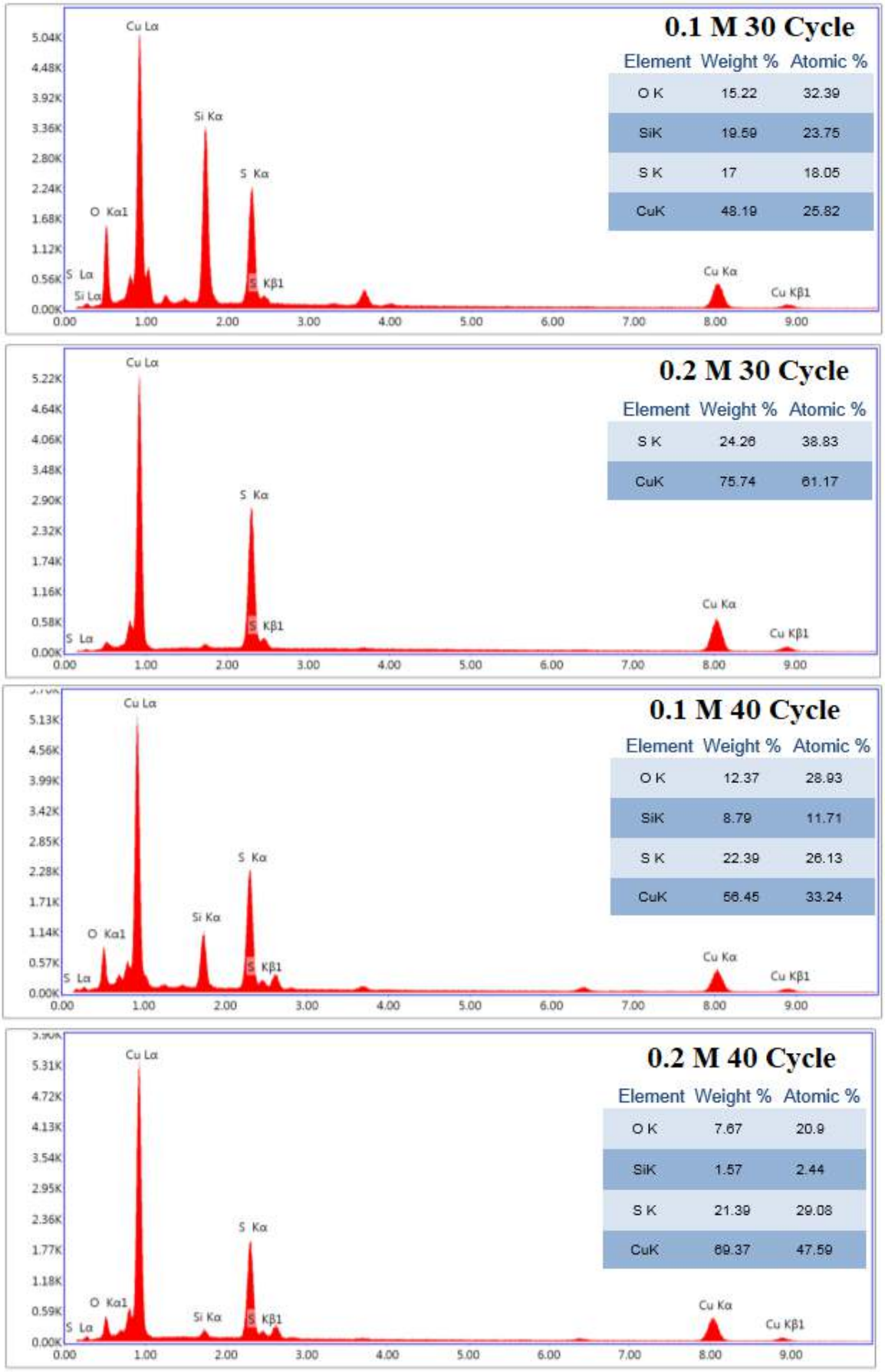
It was determined that the thin films obtained due to the increase in precursor moles had more deposition on the surfaces. In other words, it was found that there was more CuS structure on the surface of the thin film coated with 0.2 M than the 0.1 M solution. The increase in solution concentration resulted in a more compact coating of the surface structure. Different CuS thin films were obtained by applying 40 SILAR cycles by increasing the number of cycles of CuS thin films made using 30 SILAR cycles.

Figure 4. SEM images of 100.000x magnifications of 0.1 M and 0.2 M CuS thin films grown at 40 cycles.



Increasing both the solution concentration and the number of cycles of CuS thin films had a positive effect on the results. Figure 5 shows the EDX results of CuS thin films. The EDX determines the elemental distribution on the surface of CuS thin films. The Cu and S ratio increased from 48.19 to 75.74 and 17 to 24.26, respectively, by coating the CuS thin films grown at 30 cycles in 0.1 M and 0.2 M solution, respectively.

Figure 5. EDX images of 0.1 M and 0.2 M CuS thin films grown at 30 and 40 cycles.



The increase in solution concentration resulted in a more compact coating of the surface. Likewise, CuS thin films grown at 40 cycles are the same. The ratio of Cu and S shows an increase in surface dispersion depending on the concentration of the solution. Considering the number of cycles, the elemental ratio of CuS thin films grown at 30 and 40 cycles from 0.1 M increased from 48.19 to 56.45 for Cu and from 17 to 22.39 for S element. At a solution concentration of 0.2 M, this is the exact opposite. Cu and S ratio decreased with increasing number of cycles. This may be due to the inability to maintain the sample very well.

4.CONCLUSION

In this study, CuS thin films were coated on glass surface at different room temperature using SILAR method in different molarities and number of cycles. The structural properties of the CuS thin films were investigated according to the molarity and number of cycles. Thin-film enlargement processes can be used to temperature, thickness, etc. parameters were taken into consideration. This study revealed that we could obtain more homogenous and more crystalline films in a shorter time by increasing the molarity and number of cycles (thickness) in CuS thin film. We can say that SILAR method is a suitable method to enlarge the thin film of CuS.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **215-222**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.022
Research Article

EFFECTIVENESS OF NON-PHARMACOLOGICAL COMMUNITY-BASED NURSING INTERVENTIONS FOR SMOKING CESSATION IN ADULTS: STUDY PROTOCOL OF A SYSTEMATIC REVIEW

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Received: 10 July 2018; Accepted: 19 July 2019

ABSTRACT

Tobacco use is one of the common and preventable risk factors of non-communicable diseases. Although the smoking rates tends to be decreased thanks to universal policies, it still is not satisfactory, especially among the middle-aged individuals. In order to achieve success in smoking cessation activities, it is crucial to determine the most effective nursing interventions and apply them into the practice. The objective of this systematic review is to investigate the effectiveness of non-pharmacological community-based nursing interventions for smoking cessation on cessation rate, non-relapsing rate, knowledge belief and attitude related to smoking in adults living in the community. PubMed, Cochrane Library, EMBASE, PsycINFO, Cochrane Central Register of Controlled Trials (CENTRAL), EBSCO, ProQuest, Academic Search Complete, Ovid, CINAHL Plus with Full Text, MEDLINE, Web of Science, Scopus, Turkish Council of Higher Education Thesis Center, Ulakbim Turkish Medical Database and Turkiye Citation Index were searched. Databases were searched from the 1st of January 2008 to the 31st of December 2017. Languages were Turkish and English. The protocol of this systematic review was registered to PROSPERO database. The registration number is CRD42018088007. The study is ongoing. The databases were searched and 796 studies were retrieved in total. Data extraction process is ongoing. The data to be gathered from this systematic review is predicted to be a source for both primary care nurses and the other primary care professionals in terms of the effective smoking cessation method, its duration and changes in knowledge belief and attitude of individuals. The smoking cessation interventions were performed actively by primary care nurses, will facilitate to reach both local and global targets for preventing the non-communicable diseases. It is also aimed to contribute to nursing education curriculum by revealing the roles and influence of primary care nurses on smoking cessation promotion.

Keywords: *adult; community health nursing; smoking cessation; primary care.*

1. INTRODUCTION

Tobacco use is one of the most common and preventable risk factors of non-communicable diseases (WHO, 2013). Cigarette is known as the most popular tobacco products among adults (Jamal et al., 2018). Although the global prevention strategies in order to decrease the usage of tobacco and tobacco products have been effective so far, the prevalence of smoking in adults is still high (WHO, 2018). The global prevalence of tobacco use of the 15+ year-old individuals was reported as 20.2%, in 2015 (WHO, 2018). In the WHO European Region, the prevalence was decreased by 4.6% (34.5% to 29.9%) between 2005-2015 (WHO, 2018). In Turkey, the prevalence of tobacco use of the 15+ year-old individuals was stated as 27.3% in 2014 and 26.5% in 2016 (TUIK, 2017). Early adulthood (25-44 years old), male gender, lower income and education level were found to be associated with higher smoking prevalence in the literature (Asma et al., 2015; Jamal et al., 2018; WHO, 2018). In the European region, the rate of male tobacco use was higher than that of women (38.7% and 21% respectively) (WHO, 2018). Likewise, the rate of male tobacco use (40.1%) was approximately three times higher than that of women (13.3%) in Turkey (TUIK, 2017).

Although the prevalence tends to be decreased it is still not satisfactory, especially among the middle-aged individuals (WHO, 2018). It was reported that the highest smoking prevalence among the 45+ age group was in India and Bangladesh, in 2015. Approximately 29% of 45-65 year-old individuals and 10% of 65+ year elders are reported as current smokers in Turkey (Asma et al., 2015). Quitting smoking at any age has considerable impact on health status and life expectancy of individuals. In a global study, while the life expectancy of life time smokers was found to be decreased approximately 10 years, the life expectancy of individuals who stopped smoking at the ages of 40-50 or 60 was found to be increased nine-six and three years, respectively (Asma et al., 2015). The determination of the most effective smoking cessation interventions in the middle and advanced age periods is needed. It has been aimed to increase the success of smoking cessation prevalence, preventing tobacco dependence and relapses in the policies, adopted by Turkish Ministry of Health, along with the global tobacco control initiatives. According to this objective, educating primary health care providers related to smoking cessation intervention issue, monitoring smoking cessation services and widespread those in the community via technology have been targeted as essential strategies (TCSaglikBakanligi, 2015).

In order to achieve success in smoking cessation activities, it is crucial to determine the most effective interventions and apply them to the practice. In the literature, frequently used smoking cessation interventions were identified in three main topics as pharmacological, non-pharmacological and multi-modal approaches (Chen & Wu, 2015). Non-pharmacological approaches, such as cognitive behavioral therapy, motivational support, enhancing self-efficacy, counseling and specifically structured educational interventions, were proven as more effective strategies in the current literature related to smoking cessation (Byers et al., 2018; Elshatarat, Yacoub, Khraim, Saleh, & Afaneh, 2016; Hughes & Naud, 2016; Moura, Menezes, Mariano, Silva, & Sousa, 2011). In a meta-analysis, non-pharmacological and multi-modal approaches were found more effective than pharmacological treatment in smoking cessation in adults (Chen & Wu, 2015). The main philosophy of health promotion is to teach healthy lifestyle behaviors to individuals and to support them maintaining these behaviors. In this context individuals should be empowered to take health self-responsibility, particularly via improving the effectiveness of primary health care services in smoking cessation (Elshatarat et al., 2016; Nichter, Carkoglu, Nichter, Ozcan, & Uysal, 2018). Self-efficacy is known as a remarkable feature for smoking cessation. Verbal persuasion performed by health care providers for individuals who quitted smoking was stated to have a positive impact on their self-efficacy. The higher self-efficacy level was identified as the more successful the smoking

cessation interventions and the more helpful for preventing the relapses (Elshatarat et al., 2016). In line with the literature, it can be said that especially the primary health care providers should role actively in smoking cessation strategies.

Nurses, the most crowded health care professionals across the globe, are known to have remarkable roles on smoking cessation issue both in the preventive services and in the hospital settings (Byers et al., 2018; Nichter et al., 2018; Sarna, Bialous, Chan, Hollen, & O'Connell, 2013). It was stated in the literature that, although it was not statistically significant, nurse-led smoking cessation interventions were as effective as physician-led interventions in the primary care settings (Byers et al., 2018). In a meta-analysis, the smoking cessation interventions performed by nurses at the hospital settings were found to be more effective than those at the primary care services (Rice, Hartmann-Boyce, & Stead, 2013). In the update of the same meta-analysis, the researchers stated that nurse-led smoking cessation interventions performed at both primary care and hospital settings increased the cessation success of the current smokers (Rice, Heath, Livingstone-Banks, & Hartmann-Boyce, 2017). However, improvement of preventive health care behaviors when individuals faced with health problems is not an efficient approach, according to the contemporary preventive health care (Byers et al., 2018; Rice et al., 2017). It is also a cost-effective approach that providing preventive healthcare services both in the first appointment points of those services and in the places of individuals own.

There were numerous studies evaluated the effectiveness of smoking cessation interventions in the literature (Chen & Wu, 2015; Rice et al., 2013; Rice et al., 2017; Zbikowski, Magnusson, Pockey, Tindle, & Weaver, 2012). Nevertheless, there have no systematic reviews specifically indicate the effectiveness of smoking cessation interventions performed by nurses in the primary care settings. It is thought that nurse-performed smoking cessation interventions in the primary care settings will facilitate to reach the targets both at local and global levels for preventing the non-communicable diseases. There is a need to review the studies with high level of evidence evaluating the effectiveness of nursing interventions performed at the primary care settings.

The objective of this study is to investigate the effectiveness of non-pharmacological community-based nursing interventions for smoking cessation on cessation rate, non-relapsing rate and knowledge, belief and attitude related to smoking in adults living in the community. In this context, this review will aim to address the following questions:

1. Are the non-pharmacological community-based smoking cessation interventions, conducted by nurses in adults living in the community, effective for smoking cessation rate?
2. Are the non-pharmacological community-based smoking cessation interventions, conducted by nurses in adults living in the community, effective to non-relapse?
3. Are the non-pharmacological community-based smoking cessation interventions, conducted by nurses in adults living in the community, effective to change knowledge, belief and attitudes related to smoking positively?
4. Depending on the type of the smoking cessation interventions, is there any difference in quitting smoking rate, non-relapse rate, knowledge belief and attitude changes related to smoking?
5. According to the implication time of the smoking cessation interventions, is there any difference in quitting smoking rate, non-relapse rate, knowledge belief and attitude changes related to smoking?

2. METHODS

2.1. Study design and population

Our study will investigate the effectiveness of non-pharmacological community-based nursing interventions for smoking cessation in adults living in the community in this systematic review. This protocol was prepared according to PRISMA-P guidelines (Shamseer et al., 2015).

2.2. Types of interventions

The effectiveness of non-pharmacological smoking cessation interventions performed by nurses in adults as individually or group in the context of preventive health care services will be assessed.

2.3. Types of outcomes

"Smoking cessation rate" and "non-relapse rate" are the primary outcomes will be evaluated. Secondary outcomes are "changes in knowledge, belief and attitude" of the participants.

2.4. Types of study to be included

This review will be comprised of randomized controlled studies and non-randomized studies, including semi-randomized trials, controlled before and after studies and interrupted time series.

Inclusion criteria are as follows:

1. Healthy adults living in the community.
2. Turkish and English studies (research articles, reports and dissertations) published in both refereed and non-refereed journals and electronic journals between January, 2008 and December 2017.
3. Grey literature (specifically Master's and PhD Theses)
4. Studies including community-based non-pharmacological nursing interventions for smoking cessation
5. Studies with appropriate research method (randomized controlled studies, non-randomized studies)
6. Studies in which the quitting smoking rate was calculated
7. Studies in which the relapses were followed-up
8. Studies in which the duration of smoking cessation interventions carried out by nurses were identified
9. Quantitative studies to be evaluated as "moderate" and "strong" quality via the related quality assessment tool

2.5. Literature search strategy

PubMed, Cochrane Library, EMBASE, PsycINFO, Cochrane Central Register of Controlled Trials (CENTRAL), EBSCO, ProQuest, Academic Search Complete, Ovid, CINAHL Plus with Full Text, MEDLINE, Web of Science, Scopus, Turkish Council of Higher Education Thesis Center, Ulakbim Turkish Medical Database and Turkiye Citation Index were searched. Databases were searched from the 1st of January 2008 to the 31st of December 2017. Languages were Turkish and English.

The following search terms and keywords were used: nicotine (cigarette, tobacco), smoking cessation (quit smoking, tobacco cessation), program (strategy, intervention), health promotion, nursing intervention/s, non-pharmacological interventions, middle aged, adult, community health nursing, tobacco control, randomized controlled study, controlled clinical trials, non-randomized study etc. and different combinations of their Turkish synonyms. MeSH (Medical Subject Headings) terms were taken into consideration in the selection of keywords. The literature searches were conducted as a three-stage approach. Firstly; all the words which were in the titles, abstracts and keywords of the studies, associated with the research question, with the initial keywords were identified. Secondly; included databases were searched in depth via the all identified keywords and terms with various combinations. This stage was conducted under the instructions and counselling of the expert librarians. Thirdly; the reference lists of the identified studies were searched for the purpose of identifying the new studies which were not found in the first and second searching stages. Manuel searches were performed in every stage of the searching process.

2.6. Data extraction

Initially, the studies obtained by screening will be listed according to the title, abstract and first author's name by two researchers from the review group. Secondly, the listed studies which meet the inclusion criteria will be specified by the two independent researchers who have worked on the related research topic. Lastly, the full texts of the eligible studies will be downloaded after the duplicated ones are discarded. The EndNote-X8 program will be used to check the duplications.

All the included studies will be noted down on a code table which consists of the aim, study design, sample size, intervention and control groups, type of the intervention, type of the control, duration of the intervention, statistical methods, effect size, findings and quality of the studies.

2.7. Risk of bias (quality) assessment

Quality assessment (risk of bias assessment) will be conducted by two independent reviewers for each eligible study via The Quality Assessment Tool for Quantitative Studies (QATQS).

The QATQS was developed in the context of Effective Public Health Practice Project in Canada.(Thomas, Ciliska, Dobbins, & Micucci, 2004) The tool assesses the quality of different designs of quantitative public health studies, related to family health, sexual health, and prevention from chronic diseases, injuries, and substance use. It consists of eight parts, which are; "bias of selection", "study design", "confounder", "blinding", "data collection method", "exclusion from and withdrawal from the study", "integrity of intervention" and "analysis". Each part, except for the last two ("integrity of intervention" and "analysis"), is scored three Likert type as strong (1), moderate (2), and poor (3). Once all the parts have been scored, a general scoring is performed based on the QATQS assessment dictionary. A methodologically strong study has zero "poor" score, a moderately reliable study has one "poor" score and a methodologically unreliable study has two or more "poor" scores in general assessment. It was validated into Turkish by Ergin and Akın (2018). The content validity was found as .99.(Ergin & Akın, 2018)

2.8. Strategy for the data synthesis

The studies assessed and agreed to be included in this review will be grouped on a standardized form which composed of study design, sample size, interventions and outcomes. The missing information will be requested from the authors of the selected studies.

2.9. Ethical Approval

Before the data collection, ethics committee approval was obtained from Ethics Commission of the university (10.10.2017-08).

3. RESULTS

The study is ongoing. The databases were searched and 796 studies were retrieved in total (Academic Search Complete-Ulakbim-CINAHL+with full text:6, CENTRAL:299, OVID/EBSCO-MEDLINE:30, PROQUEST:50, PSYCINFO:3, PUBMED:259, SCOPUS-EMBASE:128, WoS:21, the rest had zero study). The quality assessment process was completed. Data extraction is ongoing.

4. DISCUSSION AND CONCLUSION

The effectiveness of non-pharmacological smoking cessation interventions performed by nurses in the primary care settings will be assessed in light with the parameters stated above in this systematic review. The data gathered from this systematic review is predicted to be a source for both primary care nurses and the other primary care professionals in terms of the effective smoking cessation method, its duration and changes in knowledge belief and attitude of individuals. Knowledge and recommendations to the literature associated with the research question will be presented via this study. Furthermore, it is aimed to contribute to nursing education curriculum by revealing the roles and influence of primary care nurses on smoking cessation promotion.

Acknowledgement

This is the protocol of a PhD. thesis with the same topic, which was registered to the International Prospective Register of Systematic Reviews (PROSPERO) on 07.02.2018. PROSPERO 2018 CRD42018088007. Available from: http://www.crd.york.ac.uk/PROSPERO/display_record.php?ID=CRD42018088007. We would like to thank all the members of the thesis jury for their time, support and effort.

Conflict of interest

No conflict of interest has been declared by the authors.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **223-228**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.023
Research Article

THE ROLE OF REGULARLY EXERCISE IN OVERCOMING INFERTILITY BARRIERS[1]

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Received: 10 July 2018; Accepted: 19 July 2019

ABSTRACT

Infertility is seen worldwide in developing countries and affects 30% of couples. Infertility causes depression, anxiety, social isolation, sexual dysfunction and decreased quality of life. In the treatment of infertility; besides medical treatment, significant advances have been obtained from the eastern medical strategies. Regular exercise programs, physical fitness are given to individuals. In addition, it makes them feel good about themselves physically and spiritually. It has been shown that exercise has a significant impact on health, and that regular exercise supports healthy body weight, good circulation, positive mental health, good digestion, a healthy body and helps reproduction. Complementary and alternative medicine, acupuncture and finally regular exercise are shown to be able to eliminate infertility problems. In this study, we aimed to explain the effects of exercise on male and female infertility and to create awareness.

Keywords: *Infertility, Assisted reproductive techniques (IVF), Exercise*

[1] *Bu çalışma 2-3 Mayıs 2019 tarihlerinde Çanakkale/TÜRKİYE'de gerçekleşen **"4. Uluslararası Rating Academy Kongresi: Köy Enstitüleri ve Eğitimde Yeni Arayışlar"** temalı kongrede sunulmuş aynı isimli bildirinin gözden geçirilmiş halidir.*

1. INTRODUCTION

1.1. Infertility

Infertility is defined as being unable to conceive despite regular and unprotected sexual intercourse for one year. While pregnancy occurs in 80-85% of couples during this period and pregnancy cannot be achieved in 15% (Duanif, 1992). In women, a decrease in fertility is observed depending on age, so if patients over 35 years of age do not develop pregnancy within 6 months, they are diagnosed with infertility and the treatment process begins. If the patient is older than 40 years and has a history of pelvic surgery, oligoamenorrhea, chemo-radiotherapy, male subfertility, and suspected utero-tubo-peritoneal disease, treatment should be started immediately without waiting for 6 months (ESHRE/ASRM, 2004). The number of infertile couples has increased due to stressful living conditions, unnatural nutrition and smoking habits. One in every 6-7 couples married today does not have children and has to seek medical help. However infertility can be caused by male and female reasons, pregnancy may not be obtained even though there is no significant problem in both cases. Examinations that should be included in the evaluation of basic infertility; Semen analysis determined according to WHO criteria,Tests that detect ovulation include evaluation of ovarian reserve by ultrasonographic antral follicle count and estrogen (E2) level measurement, clomiphene citrate test and hysterosalpingography (HSG) (The Practice Committee of the American Society for Reproductive Medicine, 2006). Infertility occurs in 40% of couples in men, 40% in women, 10% in men and women, and 10% in unknown causes. Therefore, both infertile couples should understand the problem and discuss it among themselves. Male infertility is due to many causes Sperm production disorders, blockages in sperm ducts, presence of antibodies to sperm, testicular trauma, hormonal disorders, anatomical problems, varicocele, past diseases, infections and certain drugs may cause infertility (Kumar, 2015). Regardless of the cause, infertility is not easy to overcome. Many infertile men feel incomplete and unhappy. Some people think have lost manhood. These feelings are normal and the way to overcome them is to communicate with other people. If we look at the cause of female infertility; endometriosis, polycystic ovary syndrome and unexplained infertility are the leading causes of infertility. Infertile couples should support each other to overcome these problems. It should be remembered that 90% of the causes of infertility can be treated and there are many treatment options.

The formation of highly reactive but unstable free radicals that are formed physiologically in the organism and their removal by antioxidant mechanisms are always in balance. Oxidative stress (OS) is the disruption of this balance in favor of free radicals (Aruoma, 1998). Stress is the body's response to various internal and external stimuli. Stress can cause physiological changes in the human body; In muscle system; tension, cramps, fatigue, also in the cardiovascular system; increases palpitation and blood pressure. This results in free radicals. Free radicals in physiological doses have important effects on ovulation, folliculogenesis, oocyte maturation, implantation and embryo development. If we look at the cause of female infertility; Endometriosis, polycystic ovary syndrome and unexplained infertility pathogenesis have been shown to be advanced free radical production. Therefore, there are studies proving that the addition of antioxidant agents to the culture media in patients who are planned for *in vitro* ertilization or oral or intravenous administration of antioxidant agents to patients in this group may increase fertility success and assisted reproductive techniques in patients. Many new techniques have been developed to minimize oocyte, sperm and embryo damage to increase pregnancy outcomes. The most commonly used ones are in vitro fertilization (IVF) and embryo transfer and intracytoplasmic sperm injection (ICSI) procedure. Oxidative stress is an important factor in the success of IVF. Oocyte and granulosa cells work in correlation with each other. Granulosa cells are useful for oocyte development-maturation, fertilization; they produce

antioxidants to protect the oocyte from apoptosis, which is enhanced by oxidative stress. Oocytes develop around the follicular fluid. Follicular fluid affects oocyte quality, ability to interact with sperm, implantation and embryonic development of the embryo. In the absence of antioxidants in follicular fluid; Causes an increase in ROS (Reactive Oxygen Species) levels (Revelli, 2009, Jana, 2010).

1.2. Exercise

Physical activity is any body movement that is generated by skeletal muscles and leads to energy consumption (Kozanoğlu, 2007). Exercise, physical activity, produced as a result of contraction of skeletal muscles, which requires physical expenditure above the basal level of physical movements. Exercise is considered a subclass of physical activity. The aim of the exercise is to set the oxygen distribution and metabolic processes, improve strength, endurance, reduce body fat, and improve muscle and joint movements. However, exercise has a great effect on living systems. It should be done in a programmed way when exercising alone. When the effects of exercise are considered in terms of health, it is working muscles, keeping the heart's pumping ability in balance, regulating heart rate and blood pressure. For many animals, mobility is the foundation of life. For people, exercise; the meaning of life for a while means a way of life, sometimes entertainment, and sometimes treatment (Ji, 1999). Being active and exercising have protective effects on all body functions and health. It is a well known fact that regular physical exercise reduces the risk of cardiovascular disease, cancer, osteoporosis and diabetes (Hara, 1997). Accompanying effects of complex mechanisms; reduction in adipose tissue; changes in lipid and hormone profile; adaptation of receptor and transport proteins; and changes in antioxidant defenseit has contains.

1.3. Effect of Exercise on Infertility

It has been proven that exercise has a significant impact on health, regular exercise provides a healthy body weight, good circulation, positive mental health, good digestion and support for a healthy body and helps reproduction ([a]Eliakim, 2010). Exercise has been shown to help weight control and contribute to the body with stress-hunting hormones (Eliakim, 2006). Proper diet and exercise are extremely important for optimal reproductive function. Physically fit men tend to have healthy sperm, but excessive exercise (especially in combination with the use of illegal bodybuilding steroids and other drugs) can reduce testosterone production and sperm count ([b]Elaikim, 2010). The male reproductive system consists of the hypothalamus-pituitary unit and testes. The testes are responsible for the production of sperm and androgens, especially testosterone (Eliakim, 2009). Androgens are also responsible for the development of secondary masculinity, muscle and bone development, red blood cells, sex drive, and other behavioral aspects. The effect, severity and duration of physical activity on the male reproductive axis depends on the activity, fitness level of the individual and his nutritional status (La Gerche, 2008). In the experimental study on rats, intense exercise is practiced and known as athlete's nutrition the changes in testicular structure and serum testesterone levels were compared with the branched-chain amino acid (BCAA) amino acid supplementation. Sperm motility and serum testosterone levels were significantly increased in the exercise group after eight weeks of exercise and BCAA supplementation. In addition, sperm lipid peroxidation was decreased but there was no be seen difference between the groups in the seminiferous tubule diameters and meiotic index. It is estimated that amino acid supplementation can have a synergistic effect in endurance exercises, not intense exercise (Bahadorani, 2019).

Short and intensive aerobic and anaerobic exercise usually increases serum testosterone levels exercise serum testosterone reduction may rarely be associated with low libido and low sperm production (Milani, 2015). In addition, low testosterone levels have been reported to play an important role in many places such as decreased muscle development, decreased repair of

muscle damage and weakened post-exercise muscle rehabilitation as it is associated with exercise. On the other hand, a decrease in low testosterone level has been found to have a negative effect on bone density mood and behavior. Surprisingly, changes in testosterone levels, their effects on performance and health are rarely evaluated in medically well-controlled elite athletes (Arce, 1993).

Clinical findings suggest that oxidant-antioxidant imbalance, which is the underlying cause of many diseases, also plays an important role in male infertility. 24-week resistance exercise and the seminal plasma oxidative stress status, inflammatory markers and DNA integrity were evaluated in the study conducted in 1228 patients in the analysis of oxidative stress and inflammatory markers were found to reduce the oxidative stress and increased reproductive performance (Hajizadeh, 2018).

Regular exercise in women leads to a more regular menstrual cycle and may increase the frequency of ovulation. As ovulation becomes more frequent, the chances of becoming pregnant increase. Polycystic ovary syndrome (PCOS) is a complex condition associated with infertility. In women with PCOS, the menstrual cycle is irregular and oocyte excretion by ovulation is rare. Regular exercise for PCOS and overweight women can increase ovulation temperature, which leads to a more regular menstrual cycle. As ovulation becomes more frequent, the chances of becoming pregnant increase. While studies have shown that exercise increases female fertility, it is important to note that many high-intensity exercises can reduce fertility and the chance of having a baby with IVF. Therefore, it is a good idea to avoid doing very high intensity exercise while you are requesting a baby (ESHRE/ASRM, 2003).

Regular exercise programs, as well as individuals to gain physical fitness it also makes him feel good physically and spiritually. Exercise increases ovarian function and chances of conception by increasing insulin sensitivity (Lewis, 1997). After adjustments to body mass index, intensive exercise program by 5% every week can reduce the risk of ovulatory infertility.

This shows that there is evidence that physical activity can protect ovarian functions independent of body mass index (Lehmann, 1997). In a study conducted with obese and infertile women; weight loss, improvement of physical fitness and psychological well-being increased ovulation and pregnancy rates. It is thought that moderate exercise and a well-adjusted diet will positively affect fertility as well as overall health benefits (Meeker, 2007). Studies have shown that exercise reduces blood sugar, adds elasticity and strength to muscles, reduces stress, and it is stated that exercise should be started before becoming pregnant (Chavarro, 2008). Scientific studies have shown that exercise increases the chance of pregnancy by increasing insulin sensitivity and regulating ovarian function. In a study conducted in the USA, it was found that women who exercise more than 4 hours a week had more negative IVF results in in vitro fertilized patients, and it was suggested that exercise should not exceed 4 hours a week in couples with infertility problems. In order to increase the chances of pregnancy in infertility, a moderate 30 minute exercise 5 days a week is sufficient for adults (Frisch, 2002). As a result exercise to moderate weight strengthens antioxidant defense mechanisms in both circulation and tissues. Thus, oxidative stress factors that affect gamet cells in the reproductive organs are removed and cell damage is prevented. As a result, in order to overcome infertility problems, exercise should be an integral part of our lives.

2. RESULTS

As a result, overweight in both men and women can directly affect oocyte and sperm quality and reduce fertility. Regular moderate exercise can help women and men to lose weight or stay in a healthy weight range, thereby improving sperm quality in men and regulating ovulation in women, ensuring good quality oocyte excretion. In addition, the rate of couples treated with assisted reproductive techniques such as IVF can increase considerably. However,

it is recommended that couples avoid long-term and high-intensity exercises, especially during periods of intention to have children and during IVF treatment. Consequently; exercise is supported by clinical and experimental studies that provide a healthy mental and physical health as well as an alternative solution for having children in infertile individuals who cannot have children.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **229-236**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.024
Research Article

MULTI-CHANNEL MARINE SEISMIC SURVEY AND PRELIMINARY RESULTS OFF-SHORE KARABURUN RIDGE (WESTERN SIGACIK GULF-AEGEAN SEA)

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Received: 4 April 2019; Accepted: 25 June 2019

ABSTRACT

Sıgacık Gulf is located south of Izmir (West Anatolia), the third crowded city of Turkey. The gulf is restricted by two important ridges on land from west to east, Karaburun Ridge and Seferihisar Ridge, respectively. Recent geological and geophysical studies suggested that these ridges are dominated by active strike-slip faults both on land and off-shore. This manuscript presents the results of the high resolution multi-channel seismic reflection survey which carried out onboard K. Piri Reis, research vessel of Dokuz Eylül University, off-shore Karaburun Ridge (Aegean Sea) and surroundings in August-2005. Two main seismic units, lower unit and upper unit, were determined on seismic sections besides the active faults, buried faults and buried folds.

Keywords: *Multi-channel seismic reflection, Karaburun Ridge, active faults*

1. INTRODUCTION

Western Anatolia is considered under N–S extension in response to westward motion of Anatolian block due to the collision with the Arabian Plate [2, 6] (inner map in Figure 1). As a result of this N-S extension, the Aegean region is defined by a number of E-W trending graben system and both normal and strike-slip movements exist together, which makes the area tectonically quite complex [2, 3, 9, 10].

Major tectonic structures [7, 8], focal mechanism of previous earthquakes and the main shocks of the 2005 earthquake series are shown in Figure 1. It is evident from the focal mechanisms of the events that strike-slip movements in the Gulf of Sığacık and surroundings are predominant tectonic regime [1, 11, 12].

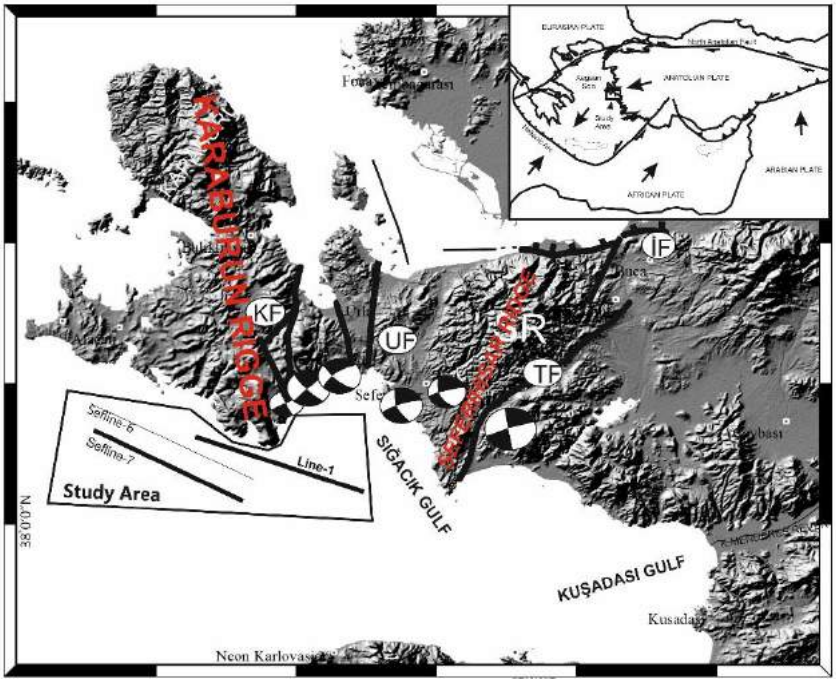
Two significant ridges on land are observed, Karaburun and Seferihisar Ridges. Karaburun Ridge is mainly formed by Late Paleozoic to Mesozoic units of Sakarya continent, while Seferihisar Ridge consists of Cretaceous flysch and melange associations [4, 5]. [7, 8] suggested a positive flower structure in Sığacık Gulf and surroundings.

Urla Fault (UF), Karaburun Fault (KF), Izmir Fault (IF) and Tuzla Fault (TF) are the most important structural formations of the land area (Figure 1). The Tuzla Fault is the most prominent fault zone in the area, and can be traced for about 40 km from the Buca area in the north down to the Kuşadası Gulf, and consists of closely spaced subparallel faults extending from NNE to SSW [5]. Its displacement, however, is controversial, especially offshore Seferihisar area. Genç et al. [5] named this fault as Orhanlı Fault Zone and suggested an oblique displacement with sinistral strike-slip and dip-slip components at SE border of Seferihisar Ridge on land. On the other hand, using geomorphologic data, Emre et al. [4] suggested a dextral movement along the Tuzla Fault. Using multi-channel seismic data, Ocakoğlu et al. [7, 8] suggested that Karaburun Fault and Tuzla Fault have an active reverse fault characteristics related to Karaburun and Seferihisar Ridges, respectively. Urla Fault exhibits a strike-slip characteristic both on land and offshore Sığacık [7].

The study area is located off the western coast of Turkey; comprising off-shore Karaburun Ridge and surroundings (Figure 1) (western Sığacık Gulf). In the past, Sığacık Gulf and surroundings have shown significant seismic activity. Previous seismic reflection studies show that the study area is widely deformed by N-S to NE-SW trending active strike-slip faults, reverse faults and some E-W trending normal faults which are, in place to place, cut by strike-slip faults [7, 8].

The earthquake series occurred between 17 and 20 October 2005 in the Sığacık Gulf describes the activity of strike-slip faults in the region. Together with active faulting, some hot spots attributable to geothermal vents are common in the region, which shows that the study area is in an unstable tectonic condition [1].

Figure 1. Map of the study area and surroundings with seismic profiles, active faults [7, 8], and focal mechanism of strong earthquakes [1, 11, 12]. Heavy lines are the seismic sections displayed in the article (Sefline-7 and Line-1). UF: Urla Fault, KF: Karaburun Fault, IF: Izmir Fault, TF: Tuzla Fault. Inner map shows regional tectonics of Anatolian micro-plate.



2. SEISMIC DATA ACQUISITION AND PROCESSING

During the cruise, the high-resolution multi-channel seismic reflection profiles were collected using a 48-channel SeaMUX 300m long digital seismic streamer with a 6.25m group interval, an NTRS-2 seismograph and the Macha gun controller of Dokuz Eylul University Institute of Marine Sciences and Technology (DEU-IMST). The source was a 105/105 in^3 generator injector (GI) air gun fired every 12.5 m. The resultant 12-fold data were recorded digitally for 2 seconds at 1 ms sample rate. The seismic data were processed in the seismic laboratory of Institute of Marine Sciences and Technology (SeisLab), at Dokuz Eylul University, using the ProMAX software. The processed data were imported into the industry seismic reflection interpretation software "The Kingdom Suite''. The detailed outline of the high resolution multi-channel seismic reflection system including seismic data processing and seismic data interpretation software and hardware are shown in Figure 2.

The following data processing stages were carried out: Raw Data Input, Geometry Load, Band-pass Filter (12-200 Hz), F-K Filter, CDP sort, Velocity Analysis, NMO correction, 12 Fold Stack, Kirchhoff Time Migration, Automatic Gain Control and SEG-Y Out. The recording parameters used during the survey are shown in Table 1.

Figure 2. Outline of the high resolution multi-channel seismic reflection system of Dokuz Eylul University Institute of Marine Sciences and Technology (DEU-IMST).

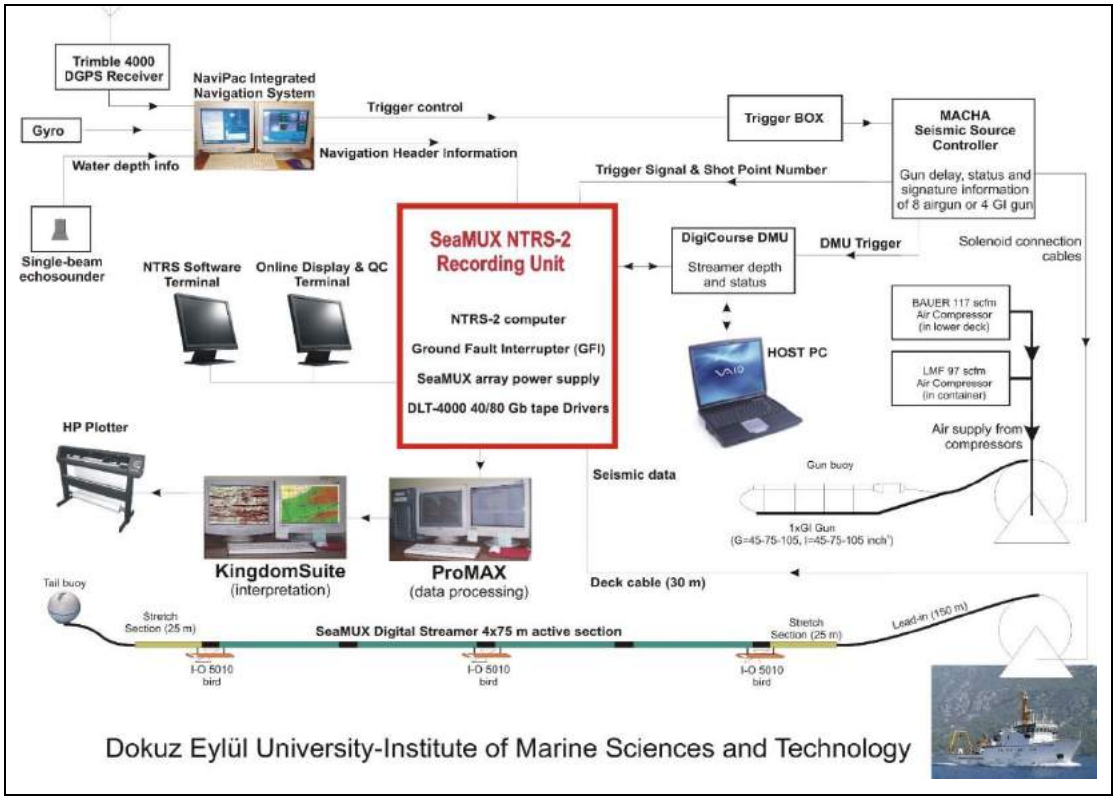


Table 1. Data acquisition parameters used during the survey.

Number of Channels	48
Streamer Length (m)	300
Near Offset (m)	40
Far Offset (m)	340
Shot Interval (m)	12.5
Group Interval (m)	6.25
Sampling (ms)	1
Record Length (s)	2
Maximum Fold	12
Source	GI Gun (105+105 $inch^3$)

3. RESULTS

Two fundamental seismic units are observed on seismic sections (an upper and a lower unit) separated by a distinct unconformity surface indicated as UN on the interpreted seismic sections. The upper seismic unit member most likely formed by basin deposits which onlap the lower member, and has parallel to sub-parallel reflectors deformed by many near-vertical faults. The lower seismic member is defined as an acoustic basement. Because of the correlation with the seismic sections of Ocakoğlu et al. [7, 8], it is hereby interpreted that the lower and upper units represent Miocene and older rocks, and Plio-Quaternary deposits, respectively.

The faults in this study, observed from seismic sections, are considered as active and buried faults due to they cut the layers until the seafloor or not, respectively. It is observed that

the study area is deformed generally by active and buried strike-slip faults and some of them have also normal component.

3.1. Karaburun Ridge Area

In the western study area (Figure 1) although we observe some active and buried faults, the density of them is lower than the eastern study area (Figure 3 and Figure 4). This area is the western part of the offshore continuation of Karaburun Ridge and Plio-Quaternary sediments are imaged as parallel to sub parallel reflectors without major deformation. That depth of the unconformity surface (UN) is almost constant at 1.300s and shows almost no apparent relief (see Sefline7 in Figure 3).

The effect of active and buried fault zones off-shore Karaburun Fault Zone (Figure 1) is illustrated in Sefline1 (Figure 4). These faults are located at the central part of the section consisting of very dense near-vertical faults. What is important for this seismic line is that we observe some small scale folds both inside of the central fault zone and also at SE part of the line. Especially at the top of fault zone, there is an erosional area on the seabed, and just below this erosional area, fault planes unusually change their slip angles (compare the fault plane inclinations of the faults at SE and NW side of the seabed erosion zone). According to these observations, we conclude that there may be some indications of local compressional tectonics in the offshore Karaburun Ridge.

Figure 3. Sefline7 seismic line (a) and its interpretation (b) This section shows the active and buried faults in the western part of-shore Karaburun Ridge.

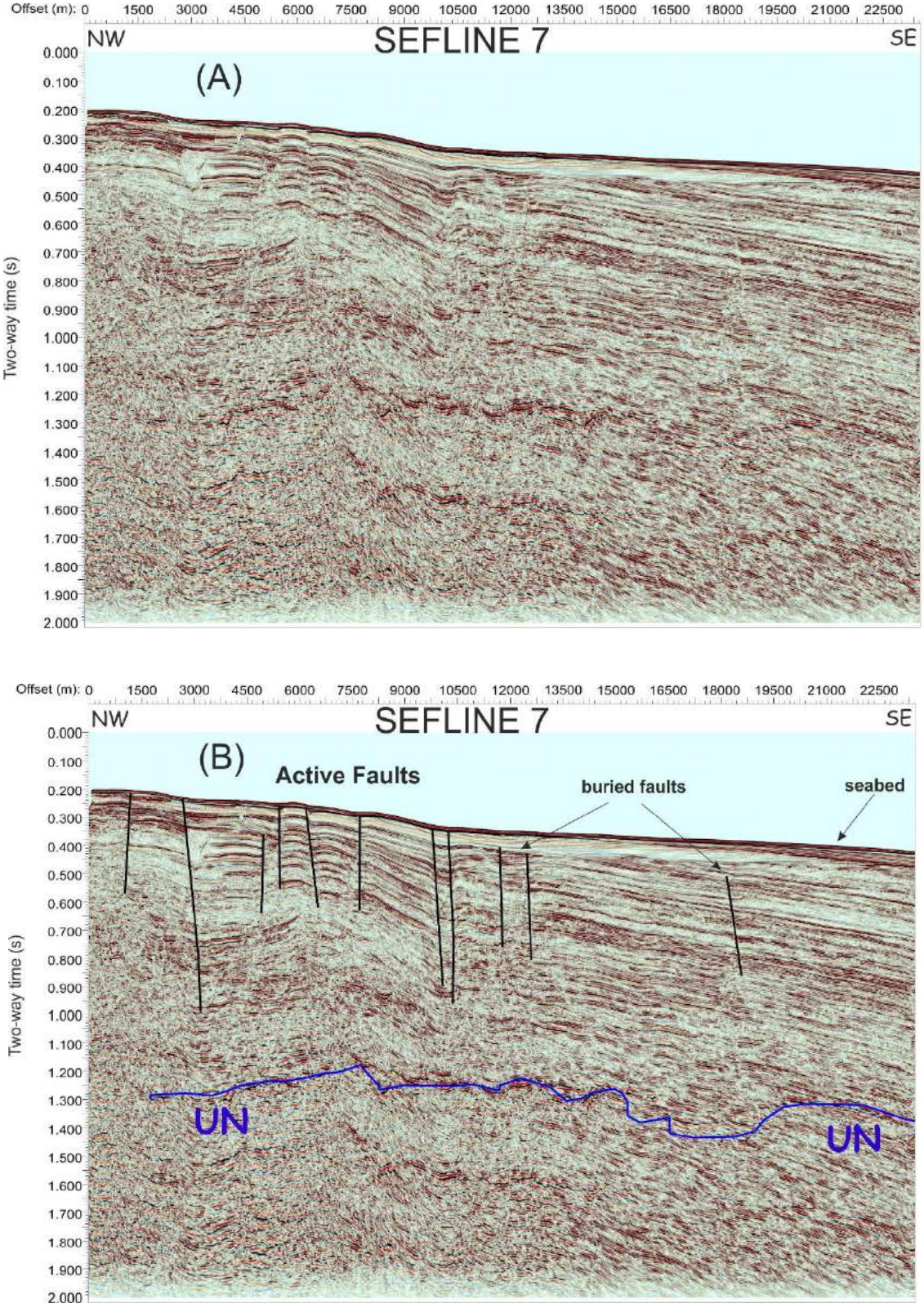
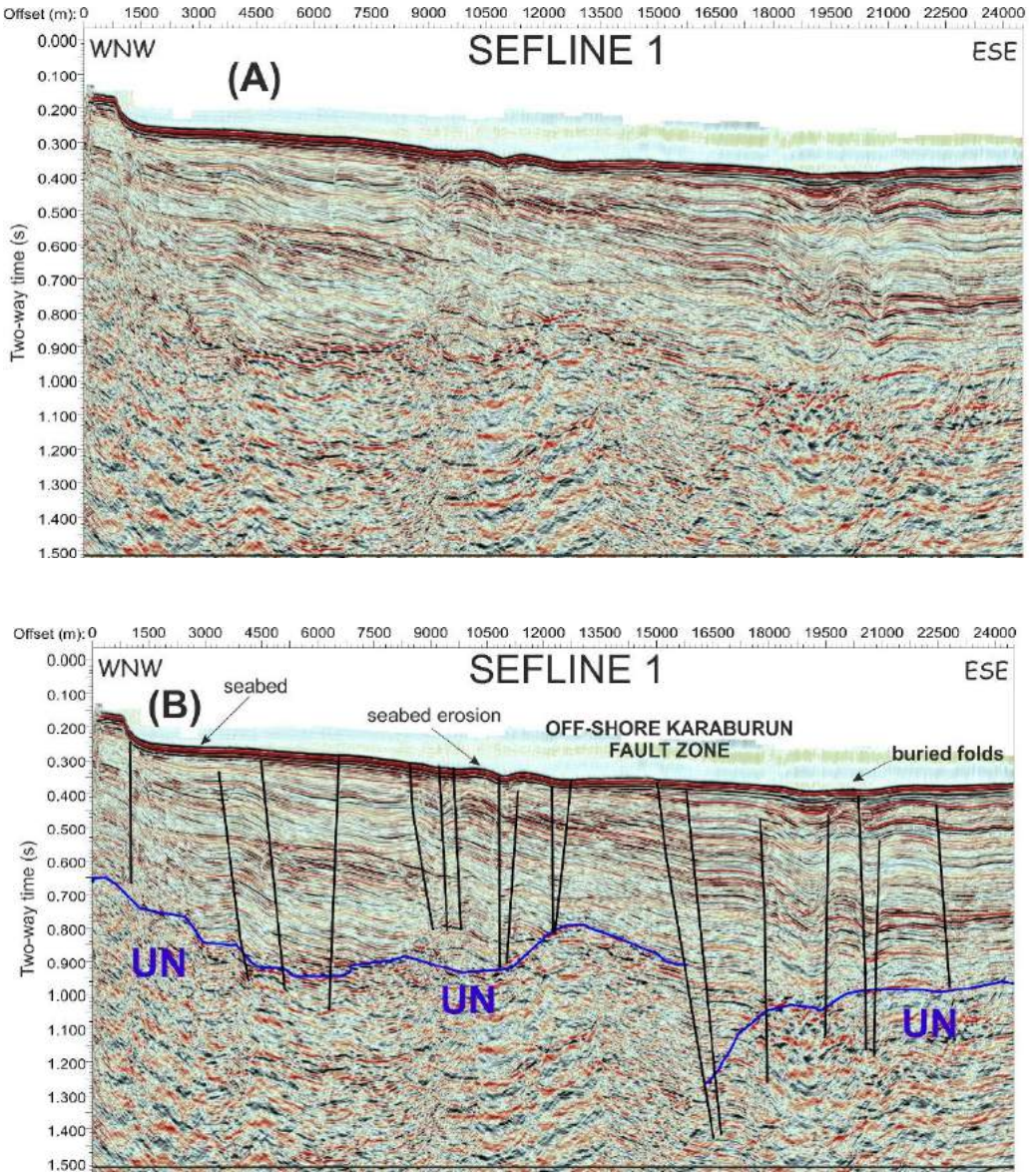


Figure 4. Seismic section Sefline1 (a) and its interpretation (b) The section shows the active and buried faults off-shore Karaburun Ridge.



4. CONCLUSIONS

A high resolution multi-channel seismic survey was carried out off-shore Karaburun Ridge and surrounding areas. The seismic data collected and interpreted in this manuscript supply high resolution and quality images to demonstrate the active tectonic and related stratigraphy. This study allows us to recognize of the unconformity and discontinuity between the layers, buried faults and folds, and investigation of the deposition shape of the upper and lower units. Two main seismic units, lower unit and upper unit, were determined on seismic sections. The study area and surroundings is under the effects of some active faults, some of which have normal component.

Acknowledgements

We thank the SeisLab team, captain and crew of the R/V Koca Piri Reis research vessel of Dokuz Eylul University-Institute of Marine Sciences and Technology for their labor during data acquisition. We thank the ProMax (Halliburton) for the data processing software. We thank the IHS for Kingdom Seismic and geological interpretation software.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **237-244**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.025
Research Article

EFFECTS OF BLACKBERRY AND BLACKTHORN FRUIT EXTRACTS ON PROTEIN AND PEROXIDASE ACTIVITY IN PEPPER

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Received: 26 April 2018; Accepted: 28 June 2019

ABSTRACT

In this research, blackthorn (Prunus spinosa L.) and blackberry (Rubus sanctus Schreb.) fruits have been extracted with water, ethanol, ethanol/water solvents. Fruit extracts were sprayed on the leaves of grossum and conoides varieties of Capsicum annuum L.. 24 and 48 hours after extract applications, healthy leaf of ten weeks old seedlings were harvested for protein and peroxidase analyses. Changing in total protein levels and peroxidase activity were measured spectrophotometrically. The highest total protein level increase was in the application of ethanolic extract of R. sanctus to grossum variety when we compare with control group. This increasing 24 and 48 hours after application were determined as 154% and 144% respectively. After the applications of R. sanctus fruit extract to the grossum and conoides varieties, peroxidase (POX) [EC 1.11.1.7] activity changing have been found better than P. spinosa extract application. After the both fruit extract applications, increasing in the POX activity of conoides variety have been found better than the grossum variety. 24 and 48 hours after application of ethanolic R. sanctus extract to conoides variety, POX activity increasing have been found respectively as 76% and 94%. In conclusion, it was shown that P. spinosa and R. sanctus fruit extracts have been stimulated the plant defense system in grossum and conoides varieties of C. annuum at different levels within the scope of total protein amount and peroxidase activity according to the control group.

Keywords: *Prunus spinosa, Rubus sanctus, Total protein, Peroxidase, Capsicum annuum.*

1. INTRODUCTION

Turkey has a rich natural biodiversity which has a great amount of medicinal and aromatic plant species. Nowadays, their usage aren't limited with medicine, food, bewerage, cosmetic industry and veterinary medicine. Organic farming and in phytoremedition as bioaccumulator are the potential usage fields of these plants (Bağdat, 2006). In addition, there are studies that use the extracts prepared from plants as a stimulant for plant defense. For example, the studies of Goupil et al. (2012), was shown that both leaf infiltration and a foliar spray of the red grape extract on tobacco leaves induced defence gene expression: The PR1 and PR2 target genes were upregulated locally and systemically in tobacco plants following grape marc extract treatment. The grape extract elicited an array of plant defence responses making this natural compound a potential phytosanitary product with a challenging issue. Kulaksız (2016), determined that different concentrations and exposure time of *Aloe vera* gels has been stimulated the plant defense system in different ratios. In this study, it has been found that low concentration *Aloe vera* gel increases the peroxidase activity in grossum varieties of *Capsicum annuum*. In the study of Dinç and Akı (2015), shown that the application of ethanolic and methanolic extracts of *Echinacea angustifolia* to *Solanum lycopersicon* seedlings decreased the amount of total protein in the *Solanum lycopersicum* seedlings and increased peroxidase activity. It was determined these effects vary depending on the extraction concentration and time. In the study of Yıldız and Akı (2018), it was shown that *Prunus spinosa* and *Rubus sanctus* leaf raw extracts were able to stimulate plant defense system at different levels.

2. MATERIAL AND METHODS

2.1. Material

In this research, the *C. annuum* seeds have been used as a plant material. Seeds were purchased from Küçük Çiftlik Company. Wild Blackberry (*R. sanctus*) fruits were collected from Terzioğlu Campus of Çanakkale Onsekiz Mart University. Blackthorn (*P. spinosa*) fruits were collected from Sarıcaeli Village of Çanakkale.

2.2. Methods

2.2.1. Growing of Pepper Seedlings

The seeds of *Capsicum annuum* varieties (conoides and grossum) were germinated in violes (capacity 45) containing a mixture of 1/3 perlite-peat under controlled conditions. The seedlings were grown in controlled plant growth chamber at 24±2°C and 60% humidity, under 16/8 hours long day photoperiod. All of the trials were replicated three times. 10 weeks old seedlings have been used for the experiments.

2.2.2. Prepearing of Fruit Extracts

For the extraction process, fresh fruits of *R. sanctus* and *P. spinosa*, were used. The fruits were shredded with hand blender. Very small pieces of *P. spinosa* and *R. sanctus* fruits were weighed 25 g each and final volume of 50 mL of water, ethanol/water and ethanol solvents were prepared. The prepared solutions have been shake at 130 rpm for 6 hours in the room temperature. Then all of the solvents were evaporated in the water bath at 60°C for 5 hours. The resulted powders of the fruit extracts were weighed 2 g each and stored at -20°C until the application.

2.2.3. Dissolution of Extracts with DMSO

2 g of fruit extracts were taken and stock solution was prepared with 20 mL of dimethyl sulfoxide (DMSO). The stock solution was diluted with distilled water and an application concentration of 10 mg/mL was prepared.

2.2.4. Application of the Fruit Extracts to C. annuum varieties

The stock solutions were diluted with distilled water as 0.01 g/mL (10mL of stock/90mL of distilled water) for application. Diluted stock solutions were sprayed on leaves of 10-week-old "conoides" and "grossum" varieties of *C. annuum* seedlings. Control groups were sprayed with distilled water.

2.2.6. Analysis Procedure

2.2.6.1. Homogenization of Harvested Leaves

After of the application 24 and 48 hours, the healthy leaves of pepper seedlings were harvested. These leaves were homogenized with 5mL 0.05M cold sodium acetate buffer (pH: 6.5) for one minute. Then these homogenants were centrifuged 13000 rpm at +4°C for 15 minutes. After the centrifugation, the supernatant were used for determination of total protein analysis and peroxidase (POX) activity.

2.2.6.2. Total Protein Level and Peroxidase Activity Analyses

The total protein amount in the homogenates was determined by spectrophotometric analysis according to Bradford (1976)'s method using bovine serum albumin (BSA) as a standard. Peroxidase (POX) activity changes in homogenants were determined by spectrophotometric analysis according to the method of Kanner and Kinsella (1983).

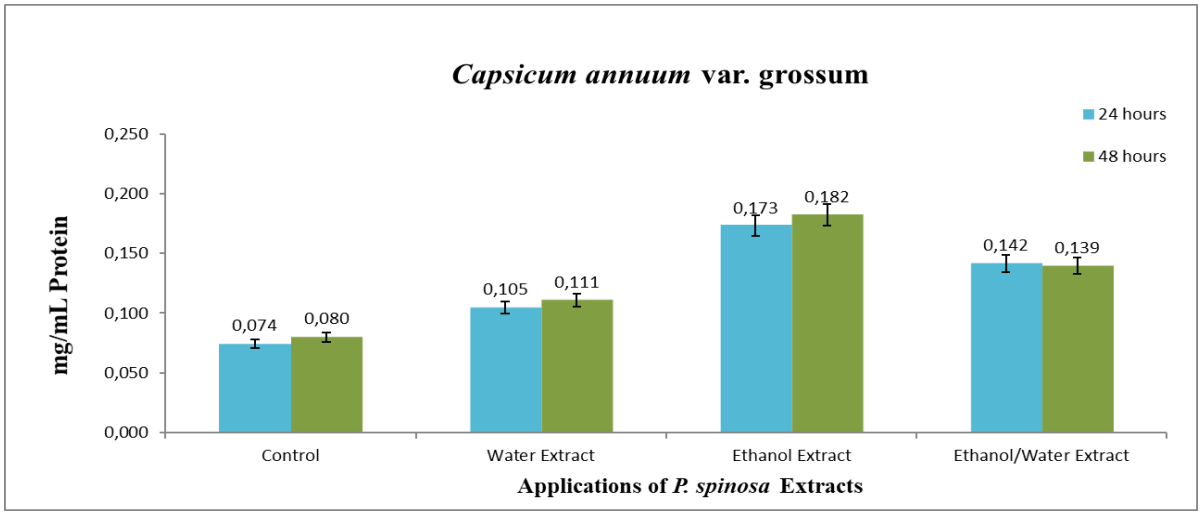
3. RESULTS AND DISCUSSION

3.1. Protein Results

When compared with the control group, it was determined that all plant extracts of this research caused an increasing in the total amount of protein. The highest increase in the total protein amount have been found in both varieties of *C. annuum* ethanolic extract application of both fruits.

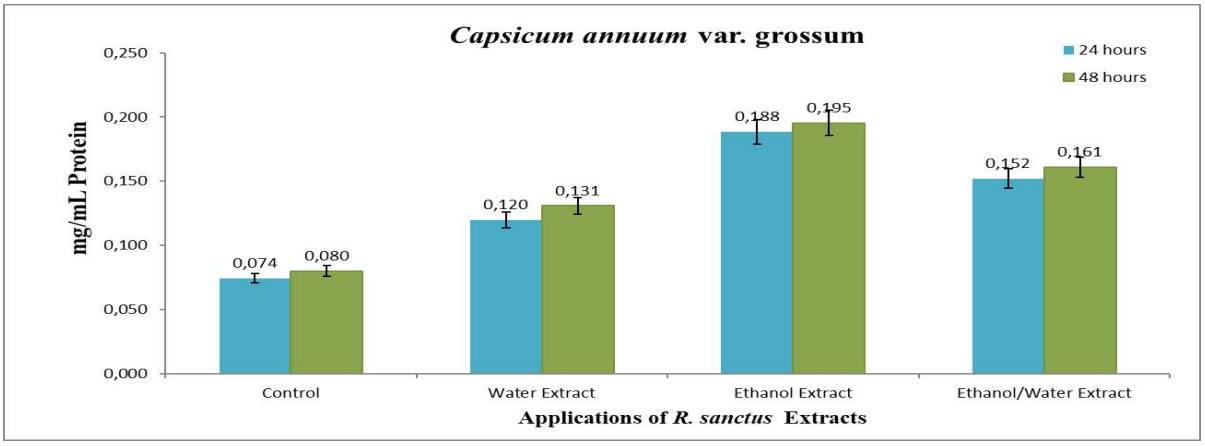
24 and 48 hours after application of ethanolic *P. spinosa* extract to grossum variety, total protein levels increasing have been found respectively as 134% and 127,5%.

Fig. 1 Effects of *P. spinosa* Extracts on Total Protein Amount in *C. annuum* var. grossum



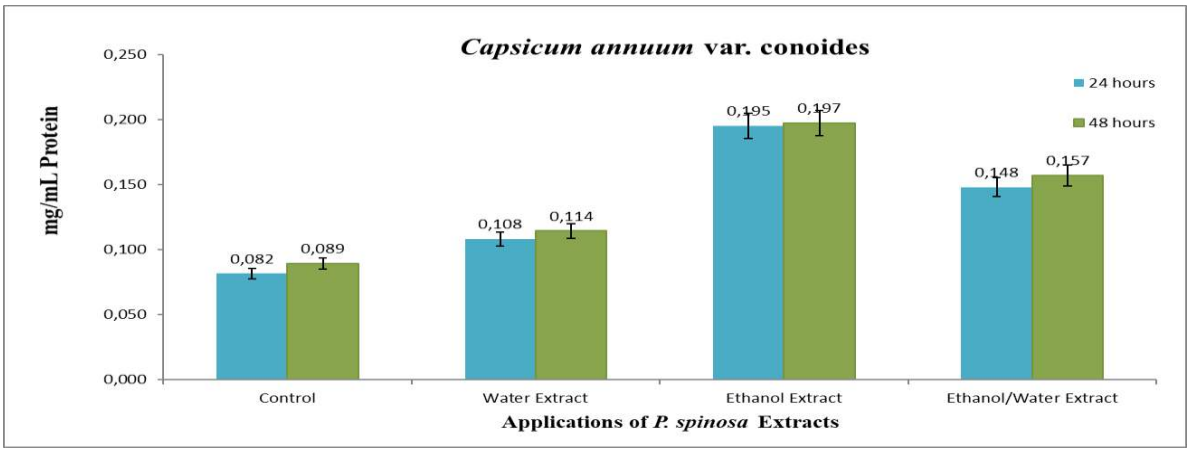
The highest total protein level increase was in the application of ethanolic extract *of R. sanctus* to grossum variety when we compare with control group. This increasing 24 and 48 hours after application were determined as 154% and 144% respectively.

Fig. 2 Effects of *R. sanctus* Extracts on Total Protein Amount in *C. annuum* var. grossum



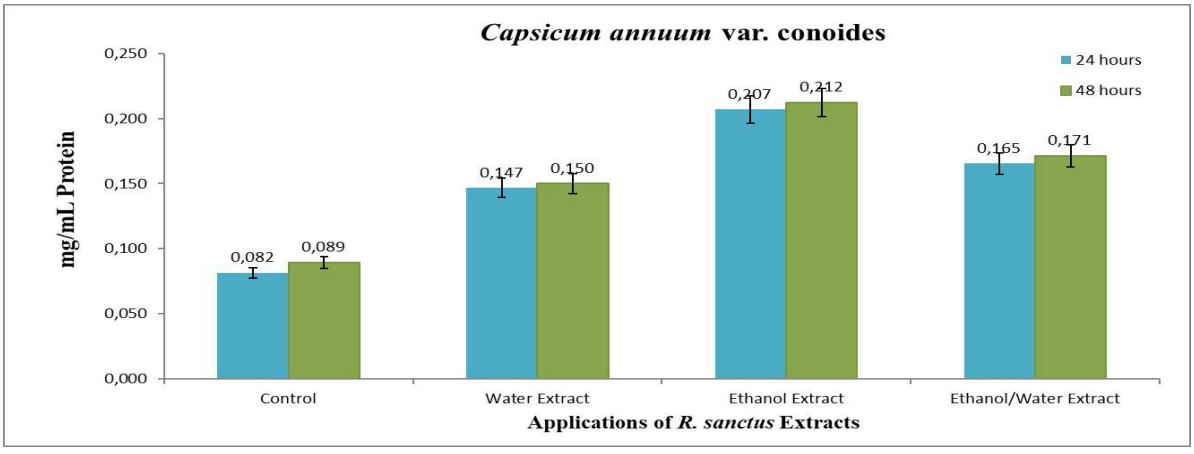
24 and 48 hours after application of ethanolic *P. spinosa* extract to conoides variety, total protein levels increasing have been found respectively as 138% and 121%.

Fig. 3 Effects of *P. spinosa* Extracts on Total Protein Amount in *C. annuum* var. conoides



24 and 48 hours after application of ethanolic *R. sanctus* extract to conoides variety, total protein levels increasing have been found respectively as 152% and 138%.

Fig. 4 Effects of *R. sanctus* Extracts on Total Protein Amount in *C. annuum* var. conoides



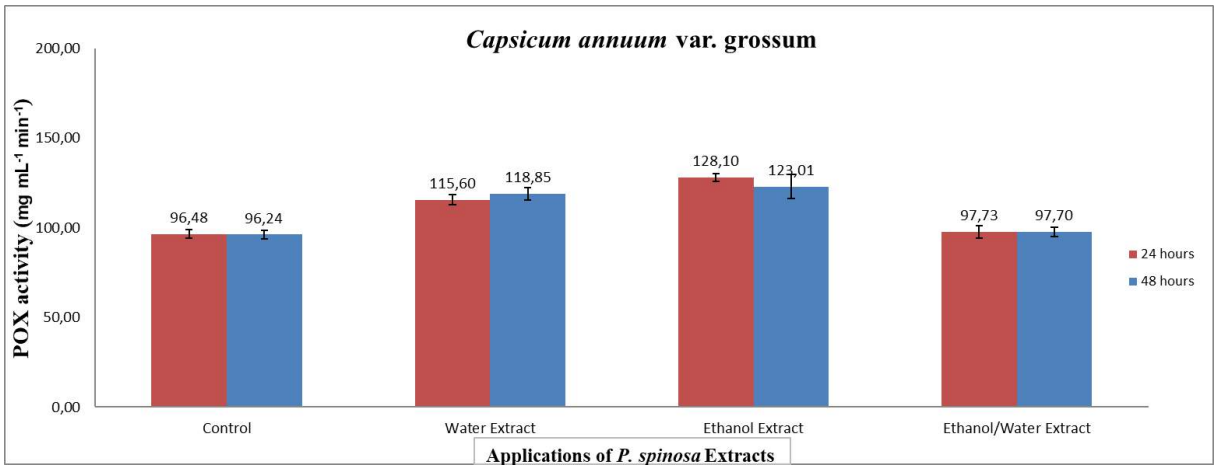
As a result, application of *Rubus sanctus* fruit extracts increased the total protein amount of *Capsicum annuum* seedlings compared to the application of *Prunus spinosa* fruit extract. There weren't significant difference between the varieties in terms of a total protein of the seedlings.

3.2. Peroxidase Results

All extracts were found to increase peroxidase (POX) [EC 1.11.1.7] activity in pepper seedlings. The extract that increased the maximum POX activity of the pepper seedlings was ethanol extracts.

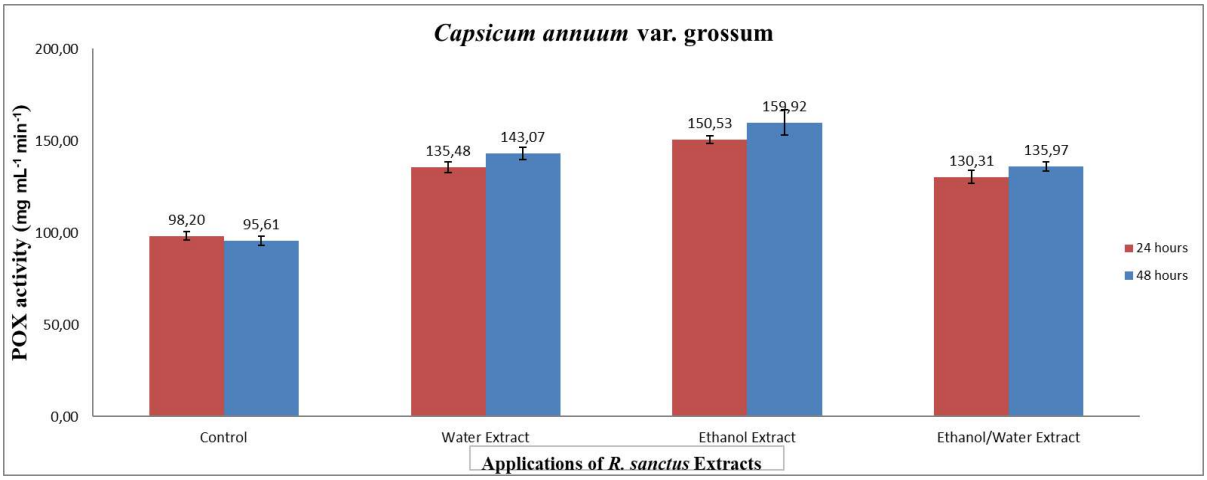
24 and 48 hours after application of ethanolic *P. spinosa* extract to grossum variety, POX activity increasing have been found respectively as 33% and 28%.

Fig. 5 Effects of *P. spinosa* Extracts on POX activities in *C. annuum* var. grossum



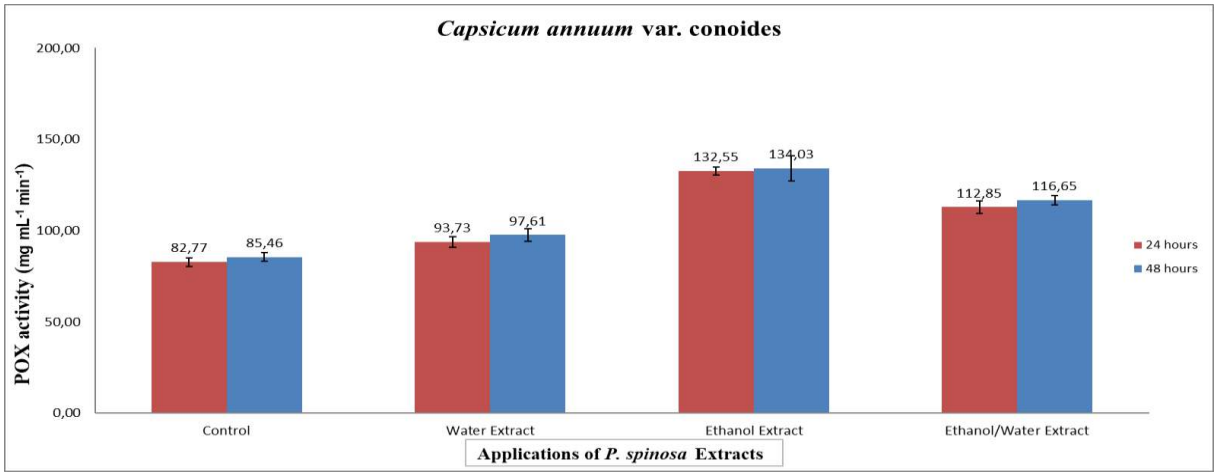
24 and 48 hours after application of ethanolic *R. sanctus* extract to grossum variety, POX activity increasing have been found respectively as 53% and 67%.

Fig. 6 Effects of *R. sanctus* Extracts on POX activities in *C. annuum* var. grossum



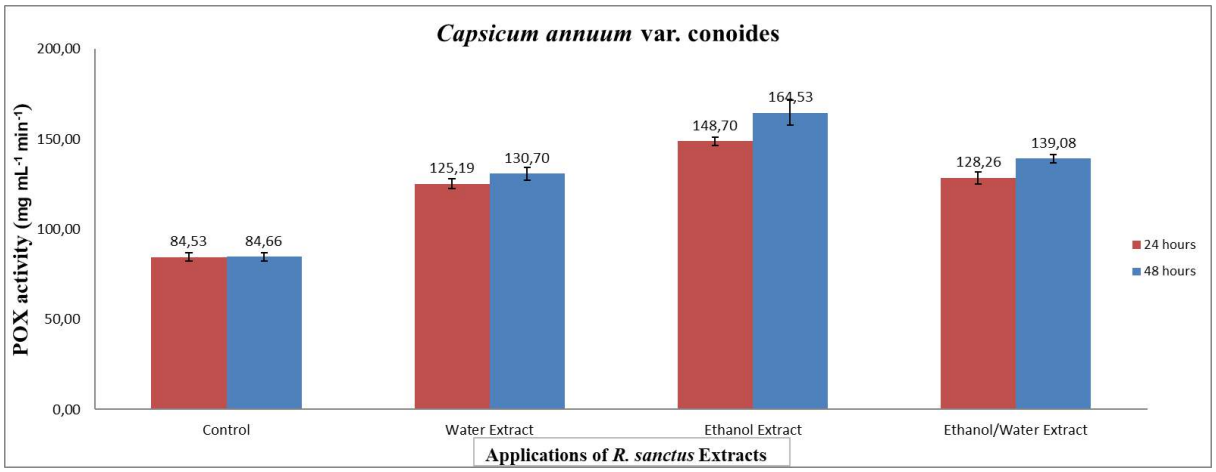
24 and 48 hours after application of ethanolic *P. spinosa* extract to conoides variety, POX activity increasing have been found respectively as 60% and 57%.

Fig. 7 Effects of *P. spinosa* Extracts on POX activities in *C. annuum* var. conoides



After the applications of *R. sanctus* fruit extract to the grossum and conoides varieties, POX activity changing have been found better than *P. spinosa* extract application. After the both fruit extract applications, increasing in the POX activity of conoides variety have been found better than the grossum variety. 24 and 48 hours after application of ethanolic *R. sanctus* extract to conoides variety, POX activity increasing have been found respectively as 76% and 94%.

Fig. 8 Effects of *R. sanctus* extracts on POX activities in *C. annuum* var. conoides



3.3. Discussion

In the research of Demiraslan and Akı (2015), in which some plant activators were applied to *Capsicum annuum* seedlings, plant activators were reported to increase total protein and peroxidase activity in *Capsicum annuum* seedlings.

In our research, *P. spinosa* and *R. sanctus* fruit extracts, like plant activators, were shown that the plant increased both total protein and POX activity at the same time.

Both *Aloe vera* and *Echinacea angustifolia* extracts showed increase in the POX activity in the application plants but the extracts showed decrease in the amounts of total protein in the application plants (Dinç,2016; Kulaksız,2016).

There are a study that was determined effect of *P. spinosa* and *R. sanctus* leaf extracts on the total protein amount and POX activity in *C. annuum* seedlings (Yıldız and Akı, 2018). When we compare this research with fruit application research, it was seen the fruit extracts, increase the total protein amount of *C. annuum* seedlings more than the leaf extracts.

4. CONCLUSION

Pesticides are widely used in agricultural production, which protect plants from diseases, insects or weeds (Kannan et al., 1997). Although pesticides are developed through very strict regulation processes to function with reasonable certainty and minimal impact on human health and the environment, serious concerns have been raised about health risks resulting from occupational exposure and from residues in food and drinking water (Damalas and Eleftherohorinos, 2011). Natural plant activators are important because of the potential to reduce or no use of pesticides. Natural plant activators are important in this context. It was determined that fruit extracts which prepared from the *R. sanctus* and *P. spinosa* plants could stimulate the defense system of the pepper plant. The results in this research are consistent with the results of the previous research results that plant extracts can be used as natural plant activators. In this research, promising results have been obtained that *P. spinosa* and *R. sanctus* fruits contents could be used as plant activator developmental studies. However, more scientific research is needed to evaluate that these fruit extracts can be used as plant activators.

Acknowledgments

This research is a part of Cahit YILDIZ's Master of Science Thesis project which supported financially by Çanakkale Onsekiz Mart University Scientific Research Projects Coordination Unit by FYL-2018-2484 project code.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **245-252**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.026
Research Article

REMOVAL OF THORIUM (IV) ION BY USING MODIFIED CYSTOSEIRA BARBATA

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Received: 16 July 2019; Accepted: 25 July 2019

ABSTRACT

In this work, it was tried to remove Th (IV) radioactive ions in aqueous solution by using modified Cystoseira barbata. pH, contact time, concentration effects and temperature were investigated. It was observed that the amount of the removal was not affected by pH change. Adsorption isotherm models were applied and the maximum qm value was found to be 116.95 mgg-1 at 250C.

Keywords: *Th, biosorption, Cystoseira barbata*

1. INTRODUCTION

Water pollution from industrial wastes and environmental activities is increasing (Caparkaya and Cavas., 2008; El Jamal and Ncibi, 2012). One of the sources of water pollution is heavy metals. Heavy metals are toxic and have acquired fame among environmental contaminants (Moghaddam et al., 2013). Thorium is one of the most hazardous heavy metals for industrial applications and the environment (Khani et al., 2006; Riazi et al., 2016). It is used as a nuclear fuel at power plants and its compounds are used in the field of science of technology. (Riazi et al., 2014). If Th spreads through the environment, it can reach humans through the food chain and can cause damage in various organs of the human body. Therefore, it has become important to remove Th ions in aqueous solution in recent years (Aytas et al., 2014; Keshtkar et al., 2015; Riazi et al., 2016). Many techniques are used in order to remove Th ions which include precipitation, solvent extraction and adsorption. Of these techniques, the adsorption technique is widely preferred for it is simple, easily feasible and cost-effective (Kratochvil and Volesky, 1998; Pavasant et al., 2006; Zhou et al., 2016; Huang et al., 2018). Algae have been found to be potentional biosorbents (McMullan et al., 2001; Abd-El Kareem and Taha, 2012) for their functional groups (Ariff et al., 1999; Davis at al., 2003; Lodeiro et al., 2006; Vieira and Volesky, 2010). Especially brown algaes have been great adsorption capacities among other algaes, because of alginates (Malik et al., 1999; Schiewer and Wong, 2000). In recent years, many successful separation operations have been carried out for radionuclides. There are many studies conducted on removal of Th ion from aqueous solution (Yang and Volesky, 1999; Picardo et al., 2006; Ghasemi et al., 2011; Cecal et al., 2012; Keshtkar and Hassani, 2014; Riazi et al., 2016; Kaynar and Sabikoglu, 2018). Factors such as, temperature, pH, contact time were affected the adsorption capacities (Vijayaraghavan and Yun, 2008). In addition, in some studies, it has been seen that pre-concentration with different chemicals increases the adsorption capacity (Bai et al., 2010).

In this study, it attempted to remove Th ion in the aqueous solution by using *Cystoseira barbata*, one of the brown algae, pre-concentrated with HNO_3. Studies on pH effect, time, concentration, temperature and desorption were conducted.

2. MATERIAL AND METHODS

2.1. Preparation of the adsorbent

The adsorbent was the alga *C. barbata* (Stackhouse) C. Agardh was collected from the Dardanos Campus of Canakkale Onsekiz Mart University. The biomass was washed at distilled water and dried in an oven at 60°C until constant weight was reached. The biomass was chemically modified by 0.1 M HNO_3.

Pre-treatment with HNO_3

A sample of 2.5 g of dries biomass was treated with 25 ml of 0.1 M HNO_3. The mixture was shaken for 3 hour on a shaker at 250 rpm at room temperature. The biomass was then filtered off, followed by washing with deionized and it was then dried in an oven at 60˚C for 24h. This was a modification of the pre-treatment performed by Rubin et al, 2005.

2.2. Reagent and equipment

In this study all chemicals were used analytical grade (Merck). Distilled water was used to prepare all solutions. Stock solution of Th (IV) (1000 ppm) were prepared by Th $(NO_3)_4$. The concentration of Th (IV) ion in the filtered samples was measured with Rayleigh Vis-7220G spectrophotometer at 667 nm. The pH adjustments were performed using 0.1 M HCl or 0.1 M NaOH. Samples were filtered with a Millipore Millex-HV hydrophilic PVDF 0.45 μm syringe filter. A Wise Bath WSB-30 model shaker was used for the experiments. The Fourier Transform

infrared spectroscopy (FTIR) analysis was completed using a Perkin Elmer Spectrum BX-11 Model FTIR spectrophotometer.

2.3. Batch biosorption studies

Five pH values (2, 3, 5, 7 and 9) were tested in the trials. Accordingly, 100 mg biomass was put into the Falcon tubes filled with 10 ppm 10 ml. Th (IV) ion solutions at different pH values. The tubes were shaken at room temperature for 60 min at 250 rpm. After adsorption step supernatant is taken out by a syringe.

The adsorbance of value of the supernatant was measured with the spectrophotometer and the amount of adsorbed Th (IV) ion solution was calculated. The percentage of Th (IV) ion removal (R) from the aqueous solution was calculated as follows:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} * 100 \quad \textbf{(Eq. 1)}$$

Where C_o is the initial Th (IV) concentration (mgL^{-1}) and C_e is the adsorbed Th (IV) concentration (mgL^{-1})

For determination of pH experiments, different time intervals (10, 25, 45, 60, 80, 100, 150, 200, 300 and 400 min) were applied in room temperature at 250 rpm. The amount of radioactive ion uptake, q_t (mgg^{-1}), at each interval was calculated using the following equation:

$$q_t = \frac{(C_o - C_e)}{M} * V \quad \textbf{(Eq. 2)}$$

Where C_o is the initial Th (IV) ion concentration (mgL^{-1}), C_e is the concentration of Th (IV) ion concentration at a given time (mgL^{-1}), V is the volume of radioactive solution (L) and M is the mass of biosorbent (g) (dry weight).

The batch adsorption technique was used for sorption. 100 mg *C. barbata* was put into a falcon tubes and treated with 10 mL of Th(IV) solution at different concentration (5-10-20-50-100-150-200-300-350-400-450 and 500 mgL^{-1}). The Falcon tubes were shaken at 250 rpm at 25ºC and 45ºC. Then samples were filtered with a syringe filter and the adsorbed amount of Th(IV) ions were measured using spectrophotometer.

The equilibrium data at different temperatures were analyzed with Langmuir and Freundlich isotherms. The Langmuir model was shown below (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{q_m a_L} + \frac{C_e}{q_m} \quad \textbf{(Eq. 3)}$$

Where q_e, (mgg^{-1}) is the amount of Th(IV) ions, C_e (mgL^{-1}) is the equilibrium concentration of the Th (IV) ions, q_m (mgg^{-1}) is the maximum adsorption capacity and a_L is the Langmuir constant related to the energy of adsorption.

A linear form of the Freundlich equation is shown below (Freundlich, 1906):

$$log q_e = log K_f + 1/ n_f \, log C_e \quad \textbf{(Eq. 4)}$$

Where K_f (mgg^{-1}) is related to adsorption capacity and n_f is an empirical parameter that varies with degree of heterogeneity.

3. RESULTS AND DISCUSSION

3.1. Determination of optimum pH

pH is one of the most important effects that have an impact upon the biosorption. In order to examine pH that affects biosorption, pH trials at different values were undertaken. Results are given in Figure 1. It was observed that Th adsorption % values remained unaffected by pH change. When looking at overall pH values subject to the study, it was ascertained that pH does not have much effect and adsorption over 96.5% was observed.

3.2. Determination of Optimum Contact Time

During equilibrium trials, trials were conducted for different times with a view to examining the effect of the time. Results are given in Figure 2. According to results obtained, it was observed that the system reached equilibrium in the first 100 minutes.

Figure 1. Effect of pH on the biosorption of Th (IV)

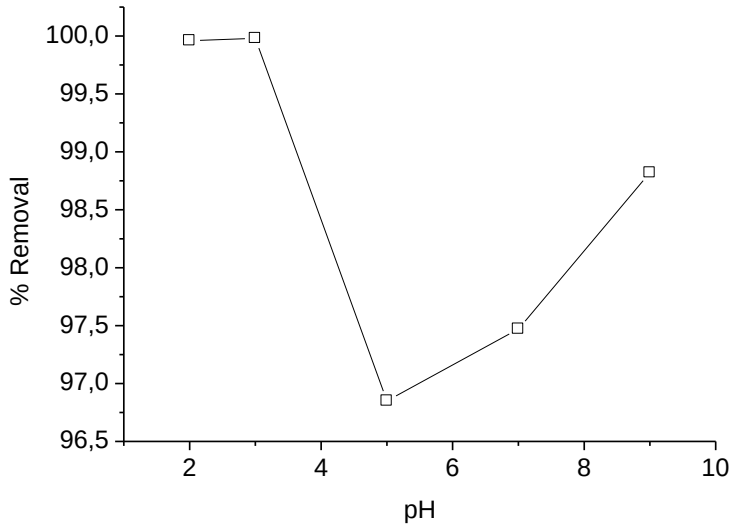
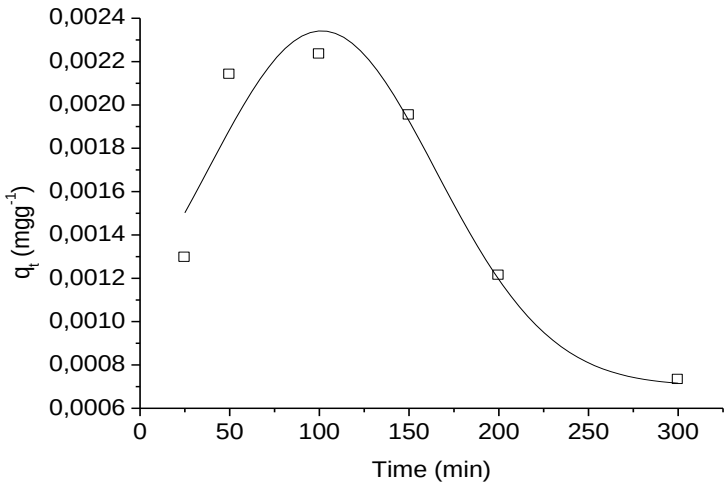


Figure 2. Effect of contact time on the biosorption of Th (IV)



3.3. Adsorption isotherms

Isotherm studies were conducted on Th (IV) ions at different temperatures. Table 1 shows Langmuir and Freundlich isotherm parameters. It was observed that, at 25^0C, Langmuir isotherm model adapted better. At 25^0C, de q_m value was 116.96 mgg^{-1} and 92.94 mgg^{-1} at 45^0C. According to results, it was observed that q_m value decreased as the temperature increased.

Table 1. Langmuir and Freundlich isotherm models of *C. barbata* for Th (IV) ion at different temperatures

		Langmuir isotherm models			Freundlich isotherm models		
	Temperature (°C)	q_m(mgg^{-1})	a_L	R_L^2	n_f	K_f(mgg^{-1})	R_F^2
0.1 M HNO_3 *C. barbata*	25	116.96	21.08	0.9537	1.13	1.893	0.9009
0.1 M HNO_3 *C. barbata*	45	92.94	27.20	0.9108	0.49	106.836	0.9182

Table 2 shows maximum Th (IV) ion adsorption capacities of different adsorbents. According to results, it was established that modification of *C. barbata* caused an increase in adsorption capacity (q_{max}). It was observed that the modified *C. barbata* has a high q_m value.

Table 2. Maximum Th (IV) ion adsorption capacities of different adsorbents

Biyomas	q_{max}(mg/g)	Referance
Rhizopus arrhizus	238.1	Abbasizadeh et al.,(2013)
Cystoseiraindica	169.49	Keshar and Hassani (2014)
Aspergillus niger	22	Tsezos and Volesky (1981)
Cystoseira indica (pretreated $CaCl_2$)	195.7	Riazi et al., 2014
Cystoseira barbata	39.45	Ozudogru (2019)
Cystoseira barbata (with modified)	116.96 (25°C) 92.94 (45°C)	This study

3.4. Desorption study

For desorption studies of Th (IV) ion, trials were conducted with different times and different eluents. Results obtained are given in Table 3. 1 M HNO_3 was found to be the best chemical for 30 minutes (99.60%). It was found to be 93.34% at 10 minutes for 0.5 M HNO_3.

Table 3. Desorption of Th (IV) ion by different eluents

Biomass 0.1 M HNO_3 *C. barbata*	Eluent	Time (min.)	% Removal of Th (IV) ions
	0.5 M HNO_3	30	62.20
	1 M HNO_3	30	99.60
	0.5 M HNO_3	20	74.56
	1 M HNO_3	20	96.96
	0.5 M HNO_3	10	93.34
	1 M HNO_3	10	94.82

4. CONCLUSION

In the present study, it was attempted to remove Th (IV) ion in the aqueous solution by using modified *Cystoseira barbata*. At each pH studied, it was observed that the biosorption capacity was over 96%. Concentration trials were conducted at 2 different temperatures and the highest adsorption capacity was found to be 116.96 mgg^{-1} at 25^0C. For recovery of the Th (IV) ion charged, it was ascertained that the most effective chemical was 1 M HNO_3 (99.60%) at 30 minutes. Desorption studies showed that Th (IV) ion charged can be recovered. To conclude, modified *C. barbata*, a natural and environmentally friendly adsorbent, can be used for removal of Th (IV) ion in aqueous solution.

Acknowledgements

This study has been funded by Canakkale Onsekiz Mart University research foundation BAP (Project no: FBA-2016-968). I would like to thank Melek MERDİVAN and Tolga GÖKSAN for their help.

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Journal of Scientific Perspectives

Volume **3,** Issue **3,** Year **2019**, pp. **253-260**
E - ISSN: **2587-3008**
URL: http://ratingacademy.com.tr/ojs/index.php/jsp
DOİ: https://doi.org/10.26900/jsp.3.027
Research Article

AQUA PRODUCTS AND EDUCATION[1]

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Received: 5 July 2019; Accepted: 17 July 2019

ABSTRACT

While the fishing adventure started with the ancestor training in the coastal areas with the same methods, it is necessary to teach this work in the coastal areas and to understand that the education is taken correctly. That's why schools open. Fishing life begins with high school education in some places for younger generations. Then it continues with the department names such as fishery, aqua products opened in universities. The first trainers gave this to themselves by mastering this work.

As educational institutions grow, this work will be done in a professional way and quality work areas will be opened for future generations.

From past to present, fisheries and aquaculture departments provide dozens of higher education opportunities. The most important reason for the sustainability of aquaculture, which constitutes a large part of our country's exports in recent years, is to increase the training activities in the same speed. Residual ancestral methods are replaced by new and more useful methods, and aquaculture is provided to support fishing activities. This makes a significant contribution to our country and of course the nature we live in.

Keywords: *Education, Aqua Products, Fishery*

[1]*Bu çalışma 2-3 Mayıs 2019 tarihlerinde Çanakkale/TÜRKİYE'de gerçekleşen* ***"4. Uluslararası Rating Academy Kongresi: Köy Enstitüleri ve Eğitimde Yeni Arayışlar"*** *temalı kongrede sunulmuş aynı isimli bildirinin gözden geçirilmiş halidir.*

1. INTRODUCTION

Education is the most important experience in every field of human life. The first education starts in the family and will learn by imitating everything. While the fishing adventure that started from ancestral training continues in the coastal areas with the same methods, it is necessary to teach this work in the inner parts and to understand that the training is taken correctly. That is why schools are opened. Fishing life starts with high school education in some places for younger generations. Then, it continues with the department names such as fishery and aquaculture. The first tutorials gave them years of mastery. As educational institutions increase, this work will be done professionally and quality workspaces will be opened for future generations. From past to present, fishing and aquaculture departments provide dozens of higher education opportunities.

Especially, the most important reason for sustainable aquaculture, which constitutes a high proportion of our country's exports in recent years, is to develop and increase the training activities at the same speed. New and more useful methods are now being replaced by ancestral methods, and aquaculture is carried out to support fishing activities. This makes a significant contribution to our country and of course to the nature we live in. Fisheries, fisheries high schools, which provide education at the secondary level, guide young people who have no marine experience. During this training, the love of water and sea is imbued and technicians equipped with theoretical and practical methods are trained in many fields from active use of water to production and protection control of aquatic organisms.

After the proclamation of the republic as the first higher education program within the framework of the Darülfunun Scientific Zoo (zoology) within the framework of fishing education and French Prof. Dr. Raymond Hovasse. Since Hovasse is the place of migration in fish migration movements, Balta Port Zoology Station is established in the Bosphorus with the idea that the researches will be conducted more easily and healthily [1, 2]. This institute is an example of the most important Hydrobiology Research Institute. After the university reform in 1933, the transition from Darülfünun to the University was made. During this period, Professor of Zoology from Switzerland. Dr. André Naville is on duty shortly. Fahire Battalgil, an associate professor in 1938, a professor in 1944 and the first researcher of inland waters in Turkey, gave it to her [3]. In the period of Ataturk (1937), have come to Istanbul that Curt Kosswig was appointed as the director of the Zoo Institute at the Faculty of Science at Istanbul University. Kosswig focuses on field studies [3, 4]. The marine laboratory in Balta Port has been allocated to these works to establish the scientific principles of fisheries in our country. In the light of these positive developments, Kosswig's initiative and with the support of Rector Prof. Dr. Nazım Terzioğlu, a Hydrobiology Research Institute was established in 1951 for the first time in our country. Prof. Dr. Remzi Geldiay took an active role in Ege University Faculty of Science in 1955 and contributed to the development of zoology. In 1964, Remzi Geldiay initiated the establishment of a Hydrobiology Research Center in Izmir under the Chair of General Zoology. Remzi Geldiay biological oceanography and ichthyology have been become Turkey's most productive academic group in marine biology and limnology [3]. In 1962, within the framework of the 10-year dam's agreement with the State Hydraulic Works of Turkey (DSI), a large number of researches were carried out, especially in the fishery of the dam lakes. In 1978, as a result of the intensive efforts of Fethi Akşıray, "Sapanca Inland-Aquaculture Production, Research and Application Unit" was put into operation in Sakarya province, Sapanca district, Kurtköy to realize the artificial production of carp and trout. In 1970, the State Planning Organization (DPT) and the United Nations Food and Agriculture Organization (FAO) in utilizing the structures of cooperation and agreement on the location of Hydrobiology Research Institute "Turkey Fisheries Development Department" were established and it has created Turkish personnel structure of the institute members [5]. 1975 years since the existence

of environmental problems in Turkey's seas have also begun to make itself felt. Studies have been conducted on pollution in the Marmara Sea and especially in the Gulf of Izmit.

Istanbul University Faculty of Science the Department of Zoology only provides training on hydrobiology and fishery biology. "Benthic invertebrates", "Turkey systematics of marine bony fishes" have started giving courses. In the 1965 academic year, oceanography was opened for the first time and this training was given by world-famous oceanographer Richard Fleming. In the 1970s, the Fisheries Department was established under the Ministry of Agriculture. Agricultural engineers with agricultural training are assigned in this branch. In 1971, the Law coded 1380 on Fisheries entered into force to allow the authorities to co-exist. In 1974, the Department of Fisheries was established within the Faculty of Agriculture of Ankara University and the Department of Fisheries and Game Animals was opened at the Faculty of Veterinary Medicine of Ankara University. Training on fish breeding has started to be provided on both chairs. In 1978, the "Fisheries Department" was opened in the Faculty of Agriculture. The department of the veterinary faculty was closed with the opening of the aquaculture departments. In line with the report given by İsmet Baran, who is the dean of the Faculty of Veterinary Medicine of Istanbul University in 1980, the foundations of today's Fisheries Faculties were laid legally with the law numbered 2547. Firstly, Fisheries and Fisheries Faculties were established in İstanbul, İzmir, Isparta, Elazığ and Trabzon [4, 6].

A total of 25 programs have been identified at the undergraduate level that provides training on aqua products/fisheries. The students who get the required scores from the entrance exams of the universities established by TC.OSYM (Republic of Turkey. Presidency of Measurement, Selection and Placement Center) are settled in the departments in our country. Students who successfully graduate from the departments start to work in the private sector and government institutions as engineers or technical personnel. A person who willing to establish its own business continues to contribute to the production of seafood.

As can be seen, aquaculture, which started with ancestral methods in the developing and changing time, has been replaced by the education of fisheries by gradually renewing itself and strengthening with higher education.

This area, which was started under the name of aquaculture in our country and later tried to be reinforced with the departments like fishing technology and the living things in it, finds its place with different names from abroad. Both in European countries and the U.S. of America and other countries of the world, "Marine Biology, Fisheries Technology or Fisheries Faculty is manifested by names as such [7, 8]. Although training objectives and topics have similarities varied widely, education has been some differences in Turkey. The only faculty named "fisheries" in the world is in Turkey. Content is too comprehensive, thus it does not match with the faculties of other countries causing some problems in student exchange.

2. MATERIALS AND METHODS

The data used in the study were compiled by using domestic and international scientific and non-scientific publications "[9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]".

3. RESULTS AND DISCUSSION

Work preparing when taken into account the information obtained starting from researching the proclamation of the republic to aquaculture and fisheries issues in Turkey were given importance since and has been supported in the field of education by opening and colleges in several cities of the country on behalf of sustaining it. Besides, scholarships are granted by YÖK (Higher Education Council) in various amounts under the support of recruiting students to these schools.

However, it has been seen that in addition to these supports, the opportunities of graduating students to find a job have been ignored. This has made these sections less preferred or not preferred at all. Although there are opportunities to work in state and private sector institutions, the lack of sufficient staff quota in the state institutions has reduced the selectability of departments due to the desire of private sector organizations to employ cheap personnel. In addition to this, since the field has been included in the veterinary and agricultural faculties in the past, job opportunities have been restricted especially by the private sector, as the authorities and responsibilities have been shared with these two other fields.

To grant the rights of the fisheries and fishery technology fields, the fisheries directorate opened under the Ministry of Agriculture and Forestry was supported, but individuals who graduated from this field were supported but could not increase their eligibility in education due to unauthorized powers and responsibilities.

Unemployment due to such limited powers and responsibilities has reduced the likelihood of the fishery and fishery technology departments to be preferred day by day.

In 2013, the number of quotas for 25 programs was 665 and 145 in 2015. In 2017, the number of the quota was reduced to 18 and 7 departments faced closure. Already for 18 sections, the number of quotas is 325 people. The latest status of the fisheries and fishery technology sections are as summarized in Table 3.1 [4, 13].

Table 3.1. Quotas in Fisheries Faculties and Fisheries Technology Engineering

Universities	**Quotas**				
	2013	**2014**	**2015**	**2016**	**2017**
Aqua Products Faculty					
1-Fisheries Faculty of Istanbul Unv. (Aqua Science Engineering)	52	41	40	52	52
2- Fisheries Faculty of Ege Ünv. (İzmir)	52	31	30	41	52
3- Fisheries Faculty of İzmir Kâtip Çelebi Ünv.	26	26	X	11	11
4- Fisheries Faculty of Akdeniz Ünv. (Antalya)	26	11	10	16	26
5- Fisheries Faculty of Mersin Unv.	26	11	X	11	11
6- Fisheries Faculty of R.T. Erdoğan Ünv. (Rize)	26	11	X	11	11
7- Fisheries Faculty of Kastamonu Ünv.	26	11	X	X	X
8- Fisheries Faculty of Süleyman Demirel Unv. (Isparta)	26	11	X	11	11
9- Fisheries Faculty of Fırat Ünv. (Elazığ)	26	11	40	11	11
10- Fisheries Faculty of İnönü Ünv. (Malatya)	-	11	X	X	X
11- Fisheries Faculty of Çukurova Ünv. (Adana)	26	11	X	11	11
12- Fisheries Faculty of Muğla Sıtkı Koçman Ünv.	26	11	X	11	16
13- Fisheries Faculty of Yüzüncü Yıl Ünv. (Van)	26	11	X	X	X
14- Fisheries Faculty of Atatürk Ünv. (Erzurum)	26	11	X	X	11
15- Fisheries Faculty of Tunceli Ünv.	26	11	X	X	X
16- Fisheries Faculty of Sinop Ünv.	26	11	X	11	11
Sum of Quotas	442	241	120	197	234
Aqua Products Engineering of Agriculture Faculty Department					
1-Agriculture Faculty of Gaziosmanpaşa Unv. (Tokat)	26	-	X	X	X
2- Agriculture Faculty of Bingöl Ünv.	26	-	X	X	X
3- Agriculture Faculty of Adnan Menderes Ünv. (Aydın)	26	11	X	X	X
4- Agriculture Faculty of Ankara Ünv	41	26	25	26	26
Agriculture Faculty of Ankara Unv. (English)	-	21	X	11	21
5- Agriculture Faculty of Kahramanmaraş Unv.	-	-	X	X	X
Sum of Quotas	119	58	25	37	47
Marine Sciences and Technology Faculties					
1-Marine Sciences and Technology Faculty of 18 Mart Ünv. (Çanakkale)	26	11	X	X	11
2-Marine Sciences and Technology Faculty of İskenderun Tech.Unv.	26	11	X	X	11
3- Marine Sciences and Technology Faculty of M.K. Ünv. (Hatay)	X	X	X	X	X
Sum of Quotas	52	22	0	0	22
Fisheries Technology Engineering Program					
1-Karadeniz Tech. Unv. (Trabzon) Sürmene Marine Science Faculty	26	11	X	11	11
2- Ordu Unv. Fatsa Marine Science Faculty	26	11	X	X	11
Sum of Quotas	52	22	0	11	22
General Sum of Quotas	665	343	145	245	325

As can be seen, it is thought that some universities may prefer the departments by changing their names, but although they are supported by scholarships and scholarships, their eligibility is not increased. Uncontrolled new programs, the first time has given excessive and

then the problem of quota due to lack of choice, tried to be preferred, name changes, programs closed for not receiving students, the rapidly increasing number of faculties and departments, considering the causes and consequences of Fisheries and Fisheries Sciences It shows that parts are no longer preferred as before.

It should be understood that the reasons why these departments cannot be preferred are the low employment opportunities if they graduate. To increase this, the department should be given the authority and responsibilities it deserves, and then base salaries should be made by the state in the employment of the graduates and the job descriptions of the graduates in these fields in the private sector should be made clear. Besides, before the new departments and faculties are opened, the employment conditions of the graduates should be considered and the instructor needs of the existing faculties and colleges should be provided in a way to make the training equipped.

This is because the departments abroad tell their graduates where they will find a job and how they will be employed. Besides, since graduates are referred to as "marine biologists or fishery technology" graduates, they can select jobs that are suitable for their fields and adapt to working conditions more easily. Even if this name confusion is solved, hierarchical pressure and unacceptability will continue to make it difficult for the graduates of aquaculture and fishery technology because of the intertwined occupational branches in our country.

If you want to exemplify this as follows; A person who graduated from aquaculture and specializes in fish diseases is not authorized to treat fish health. The reason is the lack of a veterinary surgeon. However, during the education life, only the aquaculture engineer who is confronted with aquaculture and is familiar with all the disease problems in aquaculture areas and leads to the solution of the problems has to do the treatment authority with the medication written by the veterinarian at the desk even if he is an expert. How can this be resolved? Because fish is an animal and animal health is said to be concerned with veterinarians, seafood engineers who have made high specializations in seafood diseases are ignored.

This does not include a difficult solution. A student who is a graduate of fisheries or fishery technology departments who wants to specialize in their diseases is required to receive specialization courses under a special department opened in the name of aquatic diseases in veterinary faculties and to be authorized only for aquatic organisms their authority and responsibility. Thus, the engineers who are strong in the field of aquaculture will create more efficient production areas when working with the people who specialize in aquatic health and leave minimum pollution load to the environment.

The area of employment will be expanded if a student trained in the field of the fishery is provided with opportunities that start on fishing vessels and then take the distant route. The graduates of aquaculture and fishery technology who are deployed with the requirement of compulsory employment in registered fishing vessel fleets and landing points will have more employment areas.

Of course, in the creation of these areas of employment without being attracted to the favorability of the average quota of more than 40 students in the future if the quarry that may arise in the future will be prevented.

While making such arrangements in education, support programs prepared by the directorate within the Ministry of Agriculture and Forestry should also support employment. As can be seen, the preferability of this field can be increased with the small touches to be made in the field of education and the supports to be made through the ministry.

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