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Prof. Dr. Özer Çınar

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On behalf of the organizing committee, we are pleased to announce that the 3th International Conference on Environmental Science and Technology (ICOEST-2017) is held from October 19 to 23, 2017 in Budapest. ICOEST 2017 provides an ideal academic platform for researchers to present the latest research findings and describe emerging technologies, and directions in Environmental Science and Technology. The conference seeks to contribute to presenting novel research results in all aspects of Environmental Science and Technology. The conference aims to bring together leading academic scientists, researchers and research scholars to exchange and share their experiences and research results about all aspects of Environmental Science and Technology. It also provides the premier interdisciplinary forum for scientists, engineers, and practitioners to present their latest research results, ideas, developments, and applications in all areas of Environmental Science and Technology. The conference will bring together leading academic scientists, researchers and scholars in the domain of interest from around the world.

ICOEST 2017 is the oncoming event of the successful conference series focusing on Environmental Science and Technology. The scientific program focuses on current advances in the research, production and use of Environmental Engineering and Sciences with particular focus on their role in maintaining academic level in Science and Technology and elevating the science level such as: Water and waste water treatment, sludge handling and management, Solid waste and management, Surface water quality monitoring, Noise pollution and control, Air pollution and control, Ecology and ecosystem management, Environmental data analysis and modeling, Environmental education, Environmental planning, management and policies for cities and regions, Green energy and sustainability, Water resources and river basin management. The conference's goals are to provide a scientific forum for all international prestige scholars around the world and enable the interactive exchange of state-of-the-art knowledge. The conference will focus on evidence-based benefits proven in environmental science and engineering experiments.

Best regards,

Prof. Dr.Özer ÇINAR

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Cost Evaluation of Aqueous Solutions Containing of Anionic Surfactant by US Process Treatability

Eylem TOPKAYA^{1}, Ayla ARSLAN¹, Sevil VELI¹*

Abstract

In this study, treatability of LINEAR alkyl benzene sulphonic acid (LABSA) from anionic surfactants were made by ultrasound method from advanced oxidation processes and cost analysis. Treatment of LABSA were evaluated by detergent removals. The removal efficiency and cost effects were investigated for concentration (5-20 mg/L), pH (5-10), reaction time (0-120 min), amplitude (Am=60-80%) and energy consumption parameters. The highest removal efficiency was found 76% for 20 mg/L LABSA concentration, pH=5.5, 90 min reaction time, 80% amplitude and consumption of 0.105 kWh energy. As a result of the cost analysis; in the same experiment conditions for 60 min reaction duration time by 0.065 kWh energy consumption 75% recovery yield was obtained and the unit cost of the treatment was determined as 0.168 Euro/gLABSA.

Keywords: *Anionic surfactant, Cost, Treatment, Ultrasound method.*

1. INTRODUCTION

Surfactants are come from two groups of molecules as hydrophobic and hydrophilic and grouped taking into account the chemical structure of the hydrophilic group contains [1]. They are separated to 4 groups as anionic, cationic, non-ionic and amphoteric according to the hydrophilic part load. Surfactants are a wide group of chemicals that play an important and a big role in different applications as cleaning, food, textile, metallurgy, pharmacy, medicine, painting and polishing, mining and many more [2].

Anionic surfactants are known as products containing of one or more functional groups ionized in water to produce organic ions. Linear alkyl benzene sulphonic acid (LABSA) is the most commonly used anionic surfactant. Many detergents are contain large amounts of anionic surfactants. LABSA is the most important raw materials using in detergent manufacturing industries [2].

Due to the production volume, these substances enter high correlating group of chemicals with the environment [2]. These substances have limited biological treatability in domestic and industrial wastewater treatment plants and they reach the receiving environments by abandoning the conventional wastewater treatment plants without structural modification [3]. They have shown accumulation at different concentrations in the surface waters, bottom sediments and soil and composed of a hazard in terms of health and environment. For this reason, wastewater containing these substances needs to be treatment efficiently before being delivered to receiving media [4], [5]. Advanced oxidation processes (AOPs) as alternative chemical treatment technologies for these pollutant treatments are envisaged and given weight to work this direction in recent times [6]- [9].

*¹Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/ Kocaeli, Turkey.
eylem.topkaya@kocaeli.edu.tr

¹ Kocaeli University, Department of Environmental Engineering, ataberk@kocaeli.edu.tr; sevilv@kocaeli.edu.tr

Advanced Oxidation Processes (AOPs) are based on the free radicals reaction, primarily the hydroxyl radical (HO•) which is usually very high oxidation potential for difficult decomposition, inert or toxic pollutants [6], [10]. In these methods, the toxicity of the target pollutant is eliminated with partial oxidation and/or the pollutant is converted into biologically more easily decomposable oxidation intermediates, in some cases the pollutant is oxidized up to oxidation end products such as CO₂ and H₂O [7], [11], [12]. Recently, ultrasonic (US) processes and applicability of AOP methods have begun to gain importance [13]- [16].

The ultrasound process is a chemical oxidation method provided by ultrasonic waves. The reactions performed by US processes are sonochemical reactions. This process is used electric energy generating devices to spread the sound waves to the

environment. Ultrasound waves spreading in the medium they give rise to cavitation in water while moving. Cavitation is an event of bubbles build, grow and burst by energizing very large quantities, due to the pressure changes in the liquid medium

formed by sound waves [17], [18]. In the ultrasound process, the sound waves given to aquatic environment at a suitable temperature and pressure are caused formation of radicals such as $H\cdot$, $HO\cdot$, $HO_2\cdot$, H_2O_2 in the liquid by changing the physical and chemical composition of water. These radicals provide to converting into such as CO_2 , N_2 , NO_3 , $COOH$ stable end products or less harmful compounds of the toxic and organic compounds in wastewater [19], [20]. Although chemicals are not used in these processes, these are preferred because of they are efficient.

In this experimental study, works were made for determining the best treatment and cost under different conditions by using US process which is sonochemical AOP for aqueous solutions containing of LABSA from anionic surfactants. The efficiency of the processes were determined by observing the change of the detergent concentration parameter.

2. MATERIALS AND METHODS

2.1. Materials and samples

The raw material of LABSA ($CH_3(CH_2)_{11}C_6H_4SO_3H$) was supplied from a detergent factory. The pH of the solution was adjusted using 1N NaOH or 1N H_2SO_4 , other the experiments were carried out as such at the original solution pH.

2.2. US System

SONOPULS HD 3400 model (brand of BANDELIN) probe type ultrasonic device was used for ultrasonic process (frequency of 20 kHz, maximum power of 400 W). US device probe (VS200T probe), which is 25 mm in diameter, 130 mm in length, 82 μm in amplitude and 20 kHz in frequency, is a titanium probe. The capacity of the device is 100-2500 mL. The probe of the ultrasonic device was immersed into the water as it would be exactly in the middle of the reactor and 3 cm from the bottom of the reactor. The lateral wall of the reactor was filled with cooling water in order to keep the solution temperature at $(25\pm 2)^\circ C$. The system was established into the sound-proof cabinet partly preventive to the noises.

2.3. Analysis

US experiments were performed with 1L LABSA solution. A digital pH-meter (HACH, HQd) was also used for pH measurement and 1N H_2SO_4 or 1N NaOH were used to adjust the pH. Concentration of surfactant was measured by using the methylene blue anionic surfactant (MBAS) analysis, according to the standard methods for the examination of water and wastewater [21]. Concentration of LABSA was calculated from the absorbance read at 652 nm. In US probe applications, the experiments were made pulse off application for preventing temperature control and probe heating.

3. RESULTS and DISCUSSION

3.1. The Effect of pH on Yields

In this study, LABSA which is an anionic surfactant was examined with treatment by US process from over the detergent removal efficiency for different concentration 10-20 mg/L and different range of pH (5-10) (Figure1).

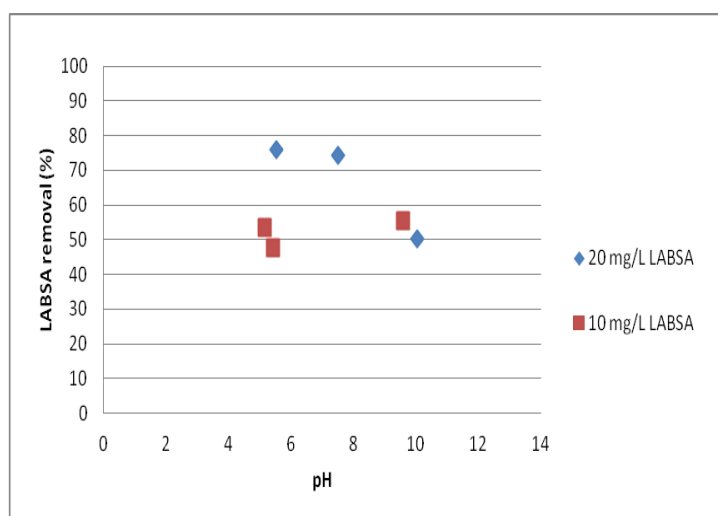


Figure 1. Effect of pH on LABSA removal efficiency ($t = 90$ min)

According to Figure 1; a yield of 76% was obtained at pH = 5.5, 20 mg / L LABSA concentration and 90 min reaction time. The LABSA removal yield was remained between 50-55 % at alkaline conditions above pH =7.5. LABSA removal efficiencies were found to be better at acidic pH. The maximum removal efficiency has been seen generally under acidic conditions at the US processes working in the literature [13], [22].

3.2. Effect of Anionic Surfactant Concentration on Yields

The experiments were made at 5-10-20 mg/L concentration range, at different pH(5-10) and 90 min reaction time to determine the effect of LABSA concentration on yield (Figure 2).

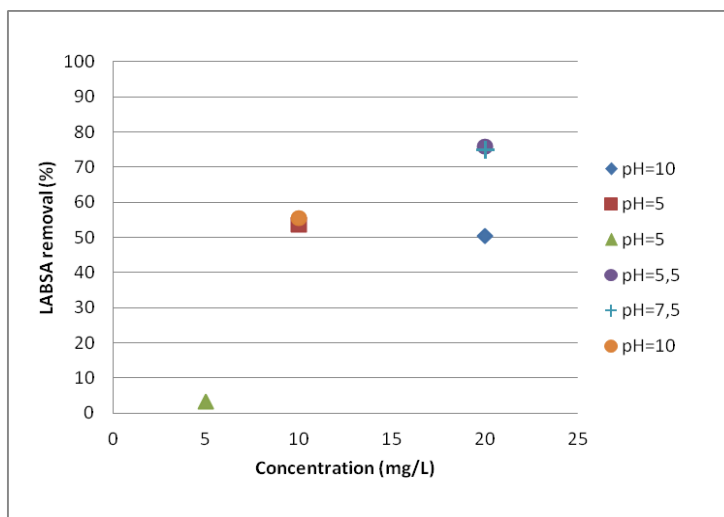


Figure 2. Effect of initial LABSA concentration on yield (t=90 min)

As can be seen from Figure 2, when the amount of concentration was decreased, removal efficiency was decreased too. According to the best removal efficiency (76%), initial LABSA concentration was determined to 20 mg/L.

3.3. Effect of the Reaction Time on Yields

After the initial LABSA concentration was determined to 20 mg/L, studies were made under 30-120 min reaction conditions to determine the effect of time (Figure 3).

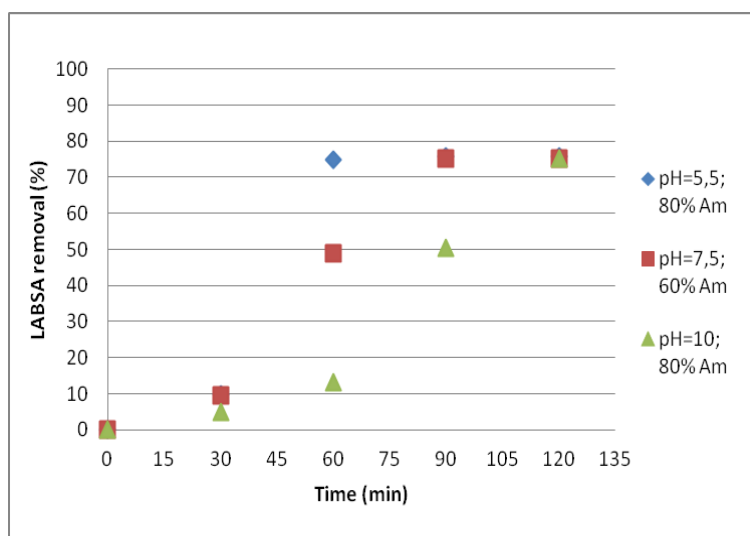


Figure 3. Effect of reaction time on LABSA removal efficiency (Co= 20 mg/L LABSA)

According to Figure 3, after from 60 min at pH = 5.5 at 20 mg / L LABSA concentration, there was no increase or decrease in recovery efficiency, but the yield was fixed at 75-76%. At pH = 7.5 the yield was increased when the reaction time increased to 90 min, and after 90 min the removal efficiency was fixed at 75%. At pH = 10, when the yield increased the reaction time increased too.

3.4. Effect of the Amplitude (Am) on Yields

LABSA removal efficiencies were investigated at different ultrasonic amplitudes (Am=60-80%) with the ultrasound process, when the amplitude amount increased the removal efficiencies also increased and the removal efficiency was maximum in less time for 80% amplitude. The solution environment was mixed in a good way with increasing the amplitude value of the US instrument, and contributed to the acceleration of the sono-sorption process. The effects of amplitude on LABSA removal efficiency was shown in Figure 4.

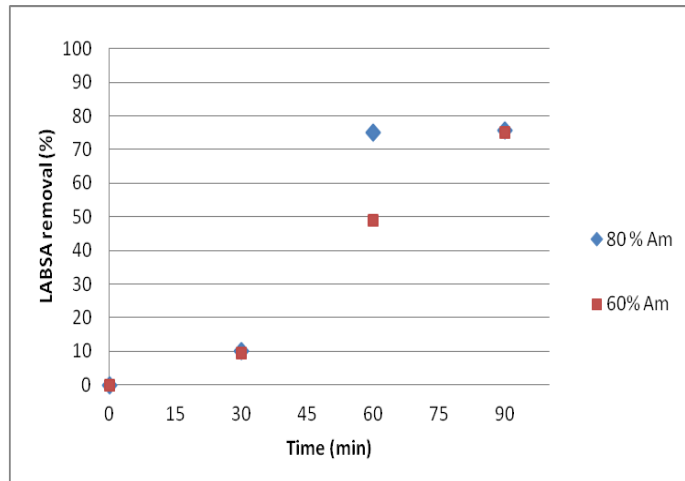


Figure 4. Effects of amplitude on LABSA removal efficiency ($C_0=20$ mg/L LABSA, pH=5,5)

As seen in Figure 4, when the amplitude value was 80 %, LABSA removal efficiency was determined as 75 % in the 60th minute. When the Amplitude value was 60%, removal efficiency 75% was reached at the longer reactions time (90 min).

In similar studies with US processes show that, the removal efficiencies also increased when the amplitudes increased [23], [24].

3.5. Effect of Energy Consumption the US Process

Energy consumption becomes for operation of the US process. The energy consumption reading from device is in kJ units. The effect of consumed energy on yield is indicated in Figure 5, according to the study results doing the 90 min reaction time, at 10-20 mg/L LABSA concentration, 60-80% Am values and range of pH=5-6.

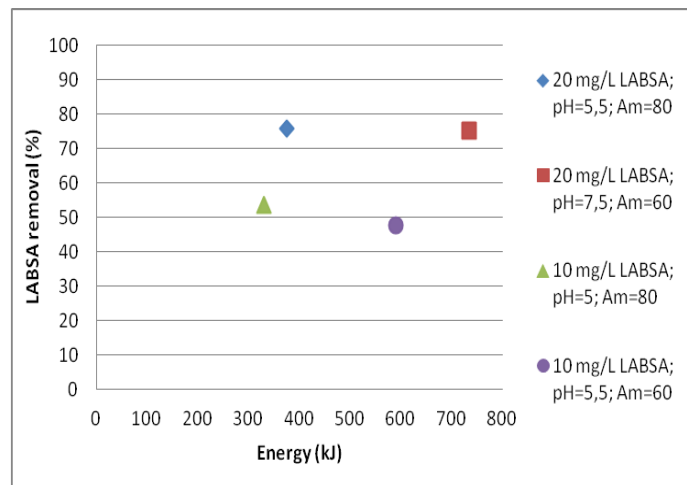


Figure 5. Effect of energy consumption on LABSA removal efficiency (t=90 min)

According to Figure 5; more recovery efficiencies have been achieved by consuming less energy at high (20 mg / L LABSA) and low concentration (10 mg / L LABSA) and high Am (80%) values, 375,997 kJ (76% removal yield) and 331,121 kJ (54% removal yield), respectively.

3.6. Evaluation in Terms of Cost

In this work, studies were made for the purification of LABSA with US process experiments to do at different concentrations, pHs, amplitudes and reaction times. Calculations have been made according to the US process consumed energy (kJ) in kWh and to the amount of consumed chemical for pH adjustment. The unit cost of the treatment is calculated in Table 1 to determine the suitability of the results of these studies in terms of cost.

Table 1. US process operating costs calculated for different experimental conditions

LABSA conc. (mg/L)	pH	Am (%)	Time (min)	LABSA removal (%)	US Energy consumption (kJ)	US Energy consumption (kWh)	US Energy consumption (Euro)	pH adjustment (Euro)	Total (Euro)	Euro / g LABSA
20	5.5	80	30	10	179.627	0.04994	0.0026	0	0.0026	0.130
20	5.5	80	60	75	232.047	0.06451	0.0034	0	0.0034	0.168
20	5.5	80	60	75	240.050	0.06673	0.0035	0	0.0035	0.173
20	5.5	80	90	76	375.997	0.10453	0.0054	0	0.0054	0.272
20	5.5	80	120	76	484.912	0.13481	0.0070	0	0.0070	0.350
20	10	80	60	13	281.086	0.07814	0.0041	0.000259	0.0043	0.216
20	10	80	90	50	441.474	0.12273	0.0064	0	0.0064	0.319
20	10	80	120	75	569.649	0.15836	0.0082	0	0.0082	0.411
5	5	80	90	3	344.191	0.09569	0.0050	0	0.0050	0.994
10	5	80	60	51	216.119	0.06008	0.0031	0	0.0031	0.312
10	5	80	90	54	331.121	0.09205	0.0048	0	0.0048	0.478
10	5.5	60	30	8	239.579	0.06660	0.0035	0.000037	0.0035	0.350
10	5.5	60	60	11	448.761	0.12476	0.0065	0	0.0065	0.648
10	5.5	60	90	48	590.689	0.16421	0.0085	0	0.0085	0.853
10	10	60	30	34	227.599	0.06327	0.0033	0.000603	0.0039	0.389
10	10	60	60	37	525.873	0.14619	0.0076	0	0.0076	0.760
10	10	60	90	55	784.46	0.21808	0.0113	0	0.0113	1.133
20	7.5	60	60	74	605.956	0.16846	0.0088	0.000076	0.0088	0.441
20	7.5	60	90	74	918.891	0.25545	0.0133	0	0.0133	0.664
20	5	60	30	10	214.302	0.05958	0.0031	0.000051	0.0031	0.157
20	5	60	60	49	424.45	0.11800	0.0061	0	0.0061	0.307
20	5	60	90	75	733.936	0.20403	0.0106	0	0.0106	0.530
20	5	60	120	75	1116.203	0.31030	0.0161	0	0.0161	0.806

According to Table 1, the highest LABSA removal efficiency was determined to 76% with asidic conditions, at 20 mg/L LABSA concentration, 80% Am, 90 min reaction time and 0.105 kWh energy consumption. The unit cost of this study was calculated as 0.272 Euro/g LABSA.

In the same conditions as 60 min reaction time removal efficiency was obtained to 75% by consuming 0.065 kWh energy. The unit treatment cost was calculated as 0.168 Euro/g LABSA. According to these results, the optimum treatment cost for this study was determined as 0.168 Euro/g LABSA because of the duration of the reaction prolongation didn't seriously changed of the yield and caused more energy consumption.

4. CONCLUSION

In this study, Treatability of water containing anionic surfactant by US advanced oxidation process was investigated in detergent removal efficiency and evaluated in terms of cost. In experiments of the 1L LABSA aqueous solution at different concentrations and different US amplitudes; the highest LABSA removal efficiency was obtained to 76% at $A_m = 80\%$, 20 mg/L concentration of LABSA and 90 min reaction time. As the prolongation of treatment times increases energy consumption, this situation affects the cost values negatively. For this reason, 60 min reaction time removal efficiency was obtained to 75% for in the same condition, this treatment was evaluated in terms of cost and the unit cost value was determined as 0.168 Euro/g LABSA. In this context, it can be said that the US process method is a feasible method for the treatment of detergent raw material and also in terms of cost.

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BIOGRAPHY

Eylem TOPKAYA; completed her undergraduate degree in 2004-2009 at Uludag University, Department of Environmental Engineering. She completed her master's degree in 2011-2014 at Gebze High Institute of Technology (GYTE), Institute of Natural and Applied Sciences, Department of Environmental Engineering. She has started her PhD education in 2014 at Kocaeli University, Institute of Natural and Applied Sciences, Department of Environmental Engineering and she is still in progress.

The effects of cadmium doses on plant characteristics of CAB-6P (*Prunus cerasus* L.)

Murat SAHIN¹, Lutfi PIRLAK², Ahmet ESITKEN³, Fatma Nur DEVECI⁴

Abstract

Cadmium (Cd) is among the rare elements found in nature that are not necessary for plants. Cd is considered to be an important contaminant because its half-life is long and it is toxic at very low doses. Cadmium is found in all agricultural soils, with varying amounts (mostly in low quantities). However, uptake of Cd is easier by plants in low pH soils.

The study was carried out in the growing room and greenhouse in 2016 and CAB-6P (*Prunus cerasus* L.) cherry rootstock was used as plant material. Plants produced with seed were kept in a growth chamber until 50 cm length was reached. As a growing medium, a mixture of peat/perlite (2/1 v/v) was used. Plants reaching 50 cm were transferred to the greenhouse in 5 liter pots. As from June 25, 150, 300, 450 and 600 μM cadmium have been applied to each plant once a month. The study design was planned as 3 replications and each repetition had one plant. As of November the plants have been dismantled. The data obtained were assessed at the $P \leq 0.05$ level in the IBM SPSS (20.0) package statistical program with one-way variance analysis (ANOVA) and subjected to the Duncan Multiple Comparison Test.

The treatments that have the greatest negative effect on plant characteristics are as follows: trunk diameter (450 μM : 9.29 mm), root collar diameter (600 μM : 10.59 mm), plant height (600 μM : 64.67 cm), stem fresh weight (600 μM : 64.20 g), stem dry weight (600 μM : 17.73 g), root length (600 μM : 28.00 cm), root volume (600 μM : 83.00 cm^3), root fresh weight (600 μM : 78.28 g), root dry weight (600 μM : 25.25 g), leaf area (600 μM : 25.48 cm^2), leaf-relative water content (600 μM : 76.14 %), stomatal conductance (600 μM : 207.43 $\text{mol m}^{-2}\text{s}^{-1}$) and chlorophyll content (600 μM : 53.52 $\mu\text{g}/\text{cm}^2$).

According to the results obtained from recent study, Cd treatments reduced plant growth. Even the lowest cadmium dose has significant negative effects on plant characteristics.

Key Words: Cadmium, cherry rootstock, heavy metal, plant characteristics.

1. INTRODUCTION

The elements are divided into two main groups, metal and non-metals [1]. The main difference between metal and non-metals is the difference in electron acceptance requirements in the reactions they enter. While metals tend to give electrons in reactions, non-metals tend to get nonetheless.

In the case of negative effects of metals on plants, 'heavy metal' phrase is used. The main reason for this is that metals (the density is over 5 grams) such as zinc [Zn (7.1 g/cm^3)], chromium [Cr (7.2 g/cm^3)], cadmium [Cd (8.6 g/cm^3)], nickel [Ni (8.7 g/cm^3)], copper [Cu (8.9 g/cm^3)], lead [Pb (11.4 g/cm^3)] and mercury [Hg (13.5 g/cm^3)] are harmful for plants. However, it can also show similar damages by metals such as aluminium [Al (2.75 g/cm^3)]. Some metals such as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and cobalt (Co) are micronutrient elements necessary for plant and animal development. Whether or not a micro-nutrient is present, a certain amount of all metals are harmful for living beings [2].

In order to prevent heavy metal welded soil pollution; pollutants such as city and industrial wastes must be mixed into the soil after purification. Besides, precautions such as planting of the plants that store heavy metals in the areas where the pollutants are concentrated and contaminated soils are the foreground. However, in areas where heavy metals are contaminated or are in danger of contamination, it is necessary to select species and varieties with high resistance to heavy metals in such areas in order to be able to do agriculture [2].

The uptake of the metal can vary depending on the plant species and cultivar. Properties such as root cation exchange capacity and root surface area of plants can affect metal uptake. Plants can affect metal uptake by changing the pH of the rhizosphere

with the substances secreted from their roots (malat, citrat, musilaj) ([3], [4], [5]). It is assumed that Cd^{2+} ions enter plant roots through Ca^{2+} channels via Fe^{2+} , Zn^{2+} and Mn^{2+} transporters [6]. This idea is derived from the fact that an Arabidopsis mutant, which cannot express the IRT1 gene that provides Fe^{2+} ion transport, cannot accumulate Mn^{2+} , Zn^{2+} , and Cd^{2+} ions in the low iron conditions ([7], [8]). In addition, high amounts of zinc and cadmium in the roots of mutants with this gene overexpression support this idea [9]. There is also evidence that plants receive Cd^{2+} from their roots via NRAMP pumps [10] and their leaves via stomata [11].

The plants carry the metals they receive with their roots to trunk and leaves by xylems. However, the transport differs according to plant species and metals. Although cadmium is transported in the xylem in ionic form [12], there are ideas that organic acids also play a role in transport [13]. Cadmium is deposited in the vacuoles of the stem cells after entering the plant roots and charged in xylem with binders such as phytochelatins, glutathione and sulfur donor ligands. After that, the cadmium ion is stored in different parts of the plants (seeds, mesophyll tissues, cell wall etc.) in varying amounts depending on the cadmium tolerance ([14], [15]). Studies on the presence of metal transport in the phloem have shown that Cd has a partial transport in the applied leaves [16]. However, studies carried out with Cd, Cu and Zn have indicated that the transport does not extend from the leaves to the roots. This is attributed to the fact that living cells that constitute the phloem prevent metal transport through ions and molecules that can bind metals [13].

In higher plants, Glutathione [17], Selenium Binding Protein [18], Ergotoine [19], Phytochelatins [20], Metallothioneins [21], Ko-Enzyme-M, Tripanotiones and Mythiols [6] are cadmium binders. It has been reported that these bind the cadmium ions to cell structures more or less. In addition, it should also be noted that some physiological events involving these substances that bind cadmium are affected adversely [6]. Studies have shown that plants accumulate these metals in extracellular carbohydrates and cell walls when exposed to high concentrations of metals (Cr, Co, Ni, Zn, Cu, Mo, Cd and Pb) ([22], [23]).

Excessive exposure to metals causes many changes in plants. Some of the damage caused by these changes is visible and measurable (morphological changes), while the detection of the majority requires complex biochemical analyzes. The first and most obvious effect of metal damage is found in the roots because of the metal-containing environment ([24], [25]). Roots exposed to excessive metal doses may be seen to be shorter than normal plant roots, decrease in the number of hairy root, increase or decrease in the number of side roots. In addition, lignification in roots and some structural changes in epidermis and hypodermis have been identified. As the plant continues to be exposed to excess metal doses, the effect begins to show up in the tree trunk and the plant height is also affected. At the same time, fresh and dry weight reduction is observed in plants and plant growth slows down ([26], [24], [27]). In addition, depending on the type and density of the metal, changes in leaf formations, area reduction in leaves, chlorosis and necrotic spot formation can be seen [2]. The reduction of water and ion uptake by plants under cadmium stress is the most important cause to prevent root growth and development. In addition, due to the closure of stomata in plants under cadmium stress, transpiration reduces water loss and prevents cadmium uptake and transport [28].

2. MATERIALS and METHODS

The study was carried out in the growing room and greenhouse belonging to the Department of Horticulture of the Faculty of Agriculture of the Selcuk University in 2016. In this study effects of cadmium treatments on CAB-6P (*Prunus cerasus* L.) cherry rootstocks were investigated. As from June 25 cadmium have been applied to each plant once a month. The study design was planned as 3 replications and each repetition had one plant. The treatments are; control, 150 μ M Cd, 300 μ M Cd, 450 μ M Cd and 600 μ M Cd doses.

Plants produced with seed were kept in a 2 liter pots at a temperature of 27,5°C / 22,5°C (day/night) and 14/10 (day/night) day length in a growth chamber until a certain length (50 cm) was reached. As a growing medium, a mixture of peat/perlite (2/1 v/v) was used. When plants reach 50 cm length, they were transferred to the greenhouse in 9-liter pots and necessary cultural processes were carried out during the adaptation period. As of November the plants have been dismantled. Plant trunk diameter (5 cm above ground), root collar diameter (just above first lateral root), plant height (from ground to top), stem fresh and dry weight (just above first lateral branch to top), root length (from first lateral root to tip of longest root), root volume (all of root from first lateral root), root fresh and dry weight (all of root from first lateral root), leaf area (surface of leaf), leaf-relative water content (difference of fresh and dry leaf weight), leaf chlorophyll amount (measured with Konica-minolta chlorophyll meter spad- 502 plus) and stomatal conductance (measured with SC-1 leaf porometer) were investigated. The data obtained were assessed at the $P \leq 0.05$ level in the IBM SPSS (20.0) package statistical program with one-way variance analysis (ANOVA) and subjected to the Duncan Multiple Comparison Test.

3. RESULT AND DISCUSSION

3.1. Trunk (TD; mm) and Root Collar Diameter (RCD; mm)

Plant trunk diameter (TD) and root collar diameter (RCD) are severely affected by the environmental factors to which the plant is exposed. Although TD and RCD are not the first affected plant parts, they are severely affected by long-term factors (positive or negative). Cd is also one of the factors that adversely affect TD and RCD in the long-term. In the study conducted, although TD and RCD were affected in the negative way by cadmium, the effect on the TD in particular is not significant in terms of statistical significance. The effect of Cd treatment on the trunk diameter was negative in parallel with the dose increase. However, the effect on the trunk diameter of Cd treatments was limited due to the low doses and the limited period. As expected, the maximum loss was seen in 600 μ M Cd treatment. In a study done by Elobeid et al. [25] (0 and 50 μ M Cd treatment, with

nutrient solution), TD began to decrease 15th day after Cd treatment. After the 20th day the difference was obviously increased and TD of the plants to which Cd was applied decreased. The results obtained from the recent study are similar to those obtained from the above study.

Considering the RCD, the negative effect of Cd treatments is more apparent than TD. This may be cause the root collar is in contact with the soil containing Cd. The most damaging treatment, as in TD, is 600 μM Cd treatment. However, 450 and 300 μM Cd treatments take place same statistic group with 600 μM Cd treatment. The RCD of *Achnatherum inebrians* plants grown in silt-clay soils applied with 0, 50, 100 and 200 μM Cd by watering with Hoagland solution (1 month) was significantly reduced [29]. In addition, the RCD of Radish (*Raphanus sativus* L.) plants grown at 0, 100 and 150 mg kg^{-1} Cd applied to the soil decreased in two growing season [27]. The results of these two studies are similar to results of the current study. As can be seen, according to the current study with previous studies, Cd treatments reduce RCD of plants. It is noted in previous studies that the causes of TD and RCD reductions are Cd treatments. According to this, Cd: 1. reduces synthesis of cell-wall components and changes the polysaccharide metabolism [30], 2. interfere water and nutrient uptake and photosynthesis [31] and 3. decrease cell turgor potential and cell wall elasticity that lead to formation of small cells and intercellular space areas [32].

Table 1. Effects of Cadmium treatments on Trunk Diameter (TD), Root Collar Diameter (RCD), Plant Height (PH), Stem Fresh Weight (SFW) and Stem Dry Weight (SDW).

	TD (mm)	RCD (mm)	PH (cm)	SFW (g)	SDW (g)
Control	9,81 ^a	12,96 ^a	80,67 ^a	84,22 ^a	30,90 ^a
150 μM Cd	9,80 ^a	12,71 ^a	77,67 ^b	79,98 ^b	28,41 ^b
300 μM Cd	9,69 ^a	11,17 ^b	71,33 ^c	76,87 ^c	23,29 ^c
450 μM Cd	9,29 ^a	10,64 ^b	66,17 ^d	70,89 ^d	19,35 ^d
600 μM Cd	9,52 ^a	10,59 ^b	64,67 ^d	64,20 ^e	17,73 ^e

3.2. Plant Height (PH; cm)

The plant height is at the top of the properties that are affected positively or negatively by environmental factors. In particular, stress factors that damage plants such as heavy metals have a negative effect on plant height. In the present study, the plant height was shortened in parallel with the increasing Cd doses. Plants applied 150 μM Cd were found 3 cm shorter than control, whereas plants applied 600 μM Cd were found 16 cm shorter than control. This reduction is considerably higher for 300, 450, and 600 μM Cd treatments when the reduction in PH is limited in 150 μM Cd treatments. When previous studies were examined, it was seen that Cd treatments decreased plant height. In some studies, the results were examined on a daily basis at the end of the treatment and changes in plant height were observed with time. According a study done in the sunflower by Azevedo et al. [24], on 3rd day after Cd supplementation, all treatments (0, 5, 50, and 500 μM) were equal in length, but on 8th day differences began. On the 8th and 15th days of the 500 μM Cd treatment, the plant size remained the same and on the 21st day the plants died. In another study, the difference between Cd treatments (0 and 50 μM) began to appear on day 7th, became more pronounced on 12th, and doubled on 24th day [25]. The studies done in the hydroponic environment, the results were obtained as end of the experiment and similar results were obtained with the above studies. According to Ouzounidou et al. [33] (0, 265, 530 and 1000 μM Cd), 265 μM Cd was significantly reduced plant height compared to the control. In other treatments, despite the reduction in plant height, the greatest difference was observed between control and 265 μM Cd doses. Farooqi et al. [34] conducted 6 different (0, 10, 30, 50, 70 and 90 $\mu\text{mol/L}$) Cd treatments in *Abizia lebeck* (L.) Benth. According to the study, the most severe reduction was observed in the treatment of 90 $\mu\text{mol/L}$ although the plant length shortened from 10 $\mu\text{mol/L}$ Cd treatment. As can see above, the current study is compatible with previous studies. According to the results obtained from experiments carried out in different growing environments, Cd treatments have negative effects on plant height. However, the growth media can affect the minimum Cd dose that causes damage.

3.3. Stem Fresh (SFW; g) and Dry Weight (SDW; g)

The leaves of plants are organs most affected by environmental factors due to their high water content and susceptibility. The first effects of the factors on the plants are usually seen on the leaves. Changes in weights of leaves and fresh shoots cause changes in SFW and SDW. Heavy metals such as Cd slow down the growth of plants (leaves and fresh shoots in short-term and trunk in long-term) by preventing water and mineral intake from the soil. In the current study, this negative effect of Cd doses is obvious.

When the effects of Cd treatments on SFW are examined, the negative effects of all Cd treatments are clearly visible. As doses of Cd increase, SFW's decrease. SFW value of plants treated with 600 μM Cd was 64.20 g, while the value of the control plants was 84.22 g. In a study of the effects of Cd treatments on SFW, 0, 5, 50 and 500 μM Cd were applied to the plants. The results were examined on the 3rd, 8th, 15th and 21st days and the SFW's of the plants on the 3rd day were similar. On the 8th day, the fresh weights of the control and 5 μM treatments were greatly increased, whereas the fresh weights of the 50 and 500 μM treatments did not increase much. On the 15th day, the change was similar, and plants that eventually underwent 500 μM Cd at 21st day died [24]. Caffei et al. [35] used 0, 5, 10, 20 and 50 μM Cd doses in a study conducted on tomato. While the fresh weights of the control plants were above 3 g, they fell below 2.5 g at 5 μM Cd dose and below 1 g at 50 μM Cd dose. Farouk et al. [27] used 0, 100, and 150 μM Cd doses in a study on Radish plant. The experiment was repeated for 2 years and the SFW

obtained from 150 μM Cd treatment in the first year was below the control and above the 100 μM Cd dose. However, in the second year the highest value was obtained from control and the lowest value was obtained in the 150 μM Cd treatment.

When SDW is examined, Cd treatments are seen to lead to a dry matter reduction of up to 50%. In particular, the reduction in the amount of dry matter in 300 and 450 μM Cd treatments is noteworthy. Compared to other treatments, the amount of dry matter is proportionally reduced by 300 and 450 μM Cd treatments a considerable amount. At the same time, the proportional decrease in 600 μM Cd treatment is relatively low. When considered together with the leaf area in Table 3, it can be assumed that the cause of this decrease is caused by the decrease in leaf size and number. The effects of Cd treatments on SDW were investigated by Azevedo et al. [24]. The negative effect of the treatment of 500 μM Cd from the 3rd day has begun to appear. Over the following days the negative effects of 50 μM and finally 5 μM Cd treatment were well established. On the 21st day, 500 μM Cd applied plants died. Similarly, SDW, in the study conducted by Caffei et al. [35], which is above 0.25 g in control plants, fell below 0.2 g in 5 μM Cd treatment. For 10 and 20 μM Cd treatments, the SDW decreased to 0.1 g, while for the 50 μM Cd treatment it decreased to under 0.1 g. In another study conducted by Farouk et al. [27] on radish plant (2-year experiment), SDW decreased significantly in 100 and 150 μM Cd treatments. 150 μM Cd treatment reduced SDW by almost 50%. Cd treatments have negative effects on dry weight as well as fresh weight. In fact, the negative effect on dry weight is more than fresh weight. Azevedo et al. [24], Zhang et al. [29], Farouk et al. [27] and the results obtained from the current study support this idea, but Rai et al. [36] do not support.

3.4. Root length (RL; cm)

Because the roots are in the soil, they are face-to-face with soil stress factors. Since it is also in the soil, Cd damages to the roots firstly. After Cd damage, because the roots are less able to be produced and functioned, other parts of the plants cannot grow and develop sufficiently. In the present study, average plant root lengths as a result of Cd treatments decreased as expected. The root lengths of the control plants are 35 cm while the root lengths are lower in Cd treatments. However, although the root length decreased significantly in 150 μM Cd treatment, the decrease in 300 and 450 μM Cd treatments was slower. In 600 μM Cd treatment, root length was 28 cm. According to these results, even low cadmium doses can cause considerable damage to plant roots. Considering only the root length, the effect of high cadmium doses may be considered to be low. However, taking into account the other root characteristics in Table 2, it is understood that increasing doses cause significant damage. Rai et al. [36] conducted experiment using 0, 20, 50 and 100 ppm Cd on *Phyllanthus amarus* Schum. and Thonn. seedlings of the plant were used. Researchers reported that 20 ppm Cd (5.12 cm) dose resulted in decrease in root length, but 50 ppm Cd (3.99 cm) treatment to cause the most decrease (control: 5.51 cm) comparatively. At the same time, 100 ppm Cd treatment (3.48 cm) has provided the lowest root length value. Zhang et al. [29], 0, 50, 100 and 200 μM Cd doses were used on *Achnatherum inebrians* plant. Accordingly, 50 μM Cd treatment caused a slight increase in root length compared to control. However, in 100 μM Cd treatment root length decreased by almost 50%. In the case of 200 μM Cd, root length decreased to less than 50% of control. Farooqi et al. [27] used 0, 10, 30, 50, 70 and 90 $\mu\text{mol/L}$ Cd doses in a study of *Albizia lebeck* (L.) Benth. According to the study, the statistically significant difference in root length was observed from 10 $\mu\text{mol/L}$ Cd treatment. Treatment of 30, 50 and 70 $\mu\text{mol/L}$ Cd continued to reduce root length. In 90 $\mu\text{mol/L}$ Cd treatment, the root length decreased dramatically. As seen in the results of previous studies, Cd treatments have a negative effect on root length. However, low doses of Cd may increase root length. From this aspect, the results of the present study and the results of the previous studies support each other.

3.5. Root Volume (RV; cm^3)

Cd has also adverse effect on root volume as well as root length. It leads to decrease of root mass as an obstacle to root length and lateral root growth. In the study done, the adverse effect of Cd treatments on root volume is clearly visible. The root volume of the control plants was 128.67 cm^3 while the root volume was found to be 119.00 cm^3 in 150 μM Cd treatment. However, the greatest volume reduction occurred between 150 μM (119.00 cm^3) and 300 μM (99.33 cm^3) Cd treatments. While there is no statistically difference in the root lengths of these treatments at this level, the difference in root volume may be related to the amount or length of lateral root. Finally, root volume reduction caused by 450 (93.67 cm^3) and 600 μM (83.00 cm^3) Cd treatments remained relatively low. As seen above, RV is susceptible to Cd like other root features. In parallel with the dose increase, RV decreases.

Table 2. Effects of Cadmium treatments on Root Length (RL), Root Volume (RV), Root Fresh Weight (RFW) and Root Dry Weight (RDW).

	RL (cm)	RV (cm^3)	RFW (g)	RDW (g)
Control	35,00 ^a	128,67 ^a	153,61 ^a	48,45 ^a
150 μM Cd	29,83 ^b	119,00 ^b	121,17 ^b	37,30 ^b
300 μM Cd	29,33 ^b	99,33 ^c	103,40 ^c	32,81 ^c
450 μM Cd	29,17 ^{bc}	93,67 ^d	80,49 ^d	25,41 ^d
600 μM Cd	28,00 ^c	83,00 ^e	78,28 ^d	25,25 ^d

3.6. Root Fresh (RFW; g) and Root Dry Weight (RDW; g)

RFW and RDW are susceptible to Cd stress like other root features. This is due to the decrease in root growth with the increase in the amount of Cd. Accordingly, the root fresh weight is decreasing in weight, parallel to the dose increase. According to the data obtained from the present study, increasing doses of Cd decrease the RFW. The most dramatic decrease is seen in 150 μM

(121.17 g) Cd treatment. With increasing doses, the rate of decrease in RFW is decreasing. Ultimately, the reduction in RFW with 600 μM Cd treatment is quite low. 450 (80.49 g) and 600 μM (78.28 g) Cd treatments are statistically in the same group. Azevedo et al. [24], 50 μM Cd is statistically insignificant although RFW is increased on 3th day after treatment. Cd treatments caused RFW decline on the 8th and 15th days. On the 21st day, 500 μM Cd applied plants were completely dead. The RFW of 50 μM Cd applied plants were less than 50% of the control treatment. Caffei et al. [35] reported that 5 μM Cd treatment increased RFW in a study conducted on tomato. However, 10 and 20 μM Cd treatments were found to cause a slight decrease. In addition, RFW of plants treated with 50 μM Cd decreased by almost 40%.

According to the results obtained from recent study, both characteristics were similarly affected by Cd treatments. However, the treatment of 600 μM Cd in particular has more influence on RFW. Accordingly, the mean root dry weight of the control plants was 48.45 g, whereas at 150 μM Cd treatment the RDW decreased to 37.30 g. The most weight loss occurred with treatment of 150 μM Cd. While the weight loss caused by 300 (32.81 g) and 450 μM (25.41 g) Cd treatments was lower, the weight loss of the 600 μM (25.25 g) Cd treatment was similar to the 450 μM Cd treatment. According to these results, it can be said that the effects of 450 μM to 600 μM Cd treatments on root dry weight are similar. According to Azevedo et al. [24], Cd treatments cause reductions in RDW as well as in RFW. However, 5 μM Cd treatment was similar to control (8th day) and close results (15th day) unlike the effect in RFW. Similarly, Caffei et al. [35] also obtained similar results with RFW and the declining graph drawn by 10, 20 and 50 μM Cd treatments was linear. As can be seen, Cd treatments lead to reduced root fresh and dry weight. Similar results with previous and recent studies suggest that Cd has negative effects on root characteristics. However, it has been reported by researchers that low Cd doses have positive effects on roots.

3.7. Leaf Area (LA; cm^2)

The leaf area, which differs according to the plant species and cultivars, is one of the plant parts (another one is roots) which first affected by the factors harmful to the plants. Also in the present study, leaf area decreased by increasing doses of Cd. Decrease in leaf area reduced in a balanced manner parallel to the increase of Cd doses. The mean leaf area was 40.73 cm^2 in control plants, while this average was 25.48 cm^2 in 600 μM Cd treatment. According to a study on tomato done by Chaffei et al. [35], high Cd doses reduced leaf surface area while lower doses were increased. This positive effect of 5 μM Cd was very limited. LA of 10 μM Cd treatment was less than 70% compared to the control. Ultimately, the LA obtained from 50 μM Cd treatment was almost 40% of control LA. Haag-Kerwer et al. [37] conducted a study on *Brassica juncea* in which 2 different Cd doses (0 and 25 μM) were used. Leaf areas were measured at 0, 24, 48, 72 and 96 hours. Accordingly, plants treated with 25 μM Cd after 48 hours showed a significant decrease in LA. At the end of 72 and 96 hours, the LA of 25 μM Cd treatment was lower than the control. As seen in previous studies, higher cadmium doses reduce LA while lower doses increase. The high doses of Cd used in the present study have reduced LA's of plants.

3.8. Leaf-Relative Water Content (L-RWC; %)

Reducing the water content of the leaves is one of the obvious effect of stress factors. This effect may be caused by environmental stress factors such as drought, heat, as well as by soil stress factors affecting root development and function. Cd is among the stress factors that inhibit the transpiration of water to the leaves by reducing root development and preventing roots from functioning. The above-mentioned effects are also seen in the present study. The mean L-RWC of the control plants was 90.44%, while these ratios decreased with increasing Cd doses. So, it decreased to 84.08% at 150 μM Cd treatment. Along with the dose increase, the water content of the leaves has also decreased. However, L-RWC was similar in 300 (82.87%) and 450 μM (82.00%) Cd treatments, and these two treatments were statistically in the same group. In contrast to this, L-RWC was significantly reduced at 600 μM Cd and was 66.14%. Zhang et al. [38] reported that Cd treatment decreased L-RWC in a study conducted by applying 0, 50, 100 and 200 μM CdCl₂ for 4 weeks on *Achnatherum inebrians*. Accordingly, L-RWC reduction from 50 μM Cd treatment began and L-RWC fell below 80% in 200 μM Cd treatment. Farouk et al. [27] conducted a two-year study in the Radish plant, Cd treatments (0, 100 and 150 mg/kg soil DW) reduced L-RWC both years. While, the L-RWC ratios of control plants were higher than 80% in both years, L-RWC ratios of 100 (first year: 71.85%, second year: 75.61%) and 150 (first year: 66.12%, second year: 66.36%) mg/kg Cd treatments were significantly reduced. It has also been determined in the present study that Cd treatments reduce L-RWC. In this respect, there is no contradiction between the previous studies and the present study.

Table 3. Effects of Cadmium treatments on Leaf Area (LA), Leaf-Relative Water Content (L-RWC), Stomatal Conductance (SC) and Leaf Chlorophyll Content (Chl-C)

	LA (cm^2)	L-RWC (%)	SC ($\text{mmol m}^{-2}\text{s}^{-1}$)	LCC ($\mu\text{g}/\text{cm}^2$)
Control	40,73 ^a	90,44 ^a	243,20 ^a	59,39 ^a
150 μM Cd	36,86 ^b	84,08 ^b	243,93 ^a	56,49 ^b
300 μM Cd	32,87 ^c	82,87 ^c	239,81 ^a	56,72 ^b
450 μM Cd	29,15 ^d	82,00 ^d	224,35 ^b	54,82 ^c
600 μM Cd	25,48 ^e	76,14 ^e	207,43 ^c	53,52 ^d

3.9. Stomatal Conductance (SC; $\text{mol m}^{-2}\text{s}^{-1}$)

Stomatal conductivity is high under optimum conditions, while under other conditions it is low. Stomatal conductance is reduced when the air temperature increases, water is reduced in the soil, or roots fail to function. This is also the case for heavy metal stresses such as Cd. Cd reduces stoma conduction by preventing root growth and functioning of roots. This is similar to the study done. However, with the 150 ($243.93 \text{ mmol m}^{-2}\text{s}^{-1}$) and 300 μM ($239.81 \text{ mmol m}^{-2}\text{s}^{-1}$) Cd treatments, the results obtained from the control treatment are similar. The results are statistically similar, although these doses of Cd have reduced stomatal conductance. However, the average stomatal conductance obtained from the control plants is $243.20 \text{ mmol m}^{-2}\text{s}^{-1}$, while the stomatal conductance is low at 450 μM ($224.35 \text{ mmol m}^{-2}\text{s}^{-1}$) and 600 μM ($207.43 \text{ mmol m}^{-2}\text{s}^{-1}$) Cd treatments. Haag-Kerver et al. [37] conducted a study in *Brassica juncea* using 25 μM CdNO₃. According to the researchers, although the transpiration rates were similar after 5 hours of treatment, the transpiration rates of Cd applied plants reduced when measurements were made after 48 and 96 hours. On the other hand, in a study conducted by Chaffei et al. [35], 0, 5, 10, 20 and 50 μM Cd doses were used. Accordingly, from 5 μM Cd treatment, transpiration was reduced (almost 30%). However, there was a partial increase in 10 μM Cd treatment compared to 5 μM Cd treatment. Subsequently, in 20 and 50 μM Cd treatments, transpiration decreased below 60% relative to the control. According to another study which conducted by Sandalio et al. [39] used 0, 10, 20, 30, 40 and 50 μM Cd doses in a study on pea plant. According to the researchers, statistically significant reduction was observed in 10 μM Cd ($2.14 \text{ mM H}_2\text{O m}^{-2}\text{s}^{-1}$) treatment compared to the control ($2.52 \text{ mM H}_2\text{O m}^{-2}\text{s}^{-1}$). In 50 μM Cd treatment, the transpiration was significantly reduced with $1.42 \text{ mM H}_2\text{O m}^{-2}\text{s}^{-1}$. The results obtained from the current study (even though the Cd doses are higher) are higher than the above studies. This may be due to the fact that the above studies have been carried out in the hydroponic, although the recent study has been carried out in the peat and perlite mixture.

3.10. Leaf Chlorophyll Content (LCC; $\mu\text{g}/\text{cm}^2$)

Chlorophyll is a molecule that allows plants to photosynthesize and is produced as a result of a synthesis where Iron (Fe) joined. In the case of iron deficiency, chlorophyll production slows down. As mentioned above, increasing the amount of Cd in the soil reduces the Fe content. Leaf chlorophyll content obtained from the study done supports this idea. The LCC obtained from the Cd treatments are lower than the control treatment. Furthermore, as the doses of Cd increase, the decrease in chlorophyll content is exacerbated. The mean LCC of control plants was $59.39 \mu\text{g}/\text{cm}^2$, while at 150 mM Cd treatment the LCC decreased to $56.49 \mu\text{g}/\text{cm}^2$. In 300 mM ($56.72 \mu\text{g}/\text{cm}^2$) Cd treatment, LCC is in the same statistical group with 150 mM Cd treatment. However, it was higher than the LLC 150 mM Cd treatment in the 300 mM Cd treatment. At 450 mM ($54.82 \mu\text{g}/\text{cm}^2$) Cd treatment, LCC continued to decrease and eventually reached the lowest level at 600 mM ($53.52 \mu\text{g}/\text{cm}^2$) Cd treatment. Sandalio et al. [39] used 0, 10, 20, 30, 40 and 50 μM CdCl₂ doses in the study of *Pisum sativum* L.. According to the data obtained from study, the LCC of the control plants was thereabout $110 \mu\text{g}\cdot\text{mg}^{-1}$. This value decreased with 10 μM Cd treatment and decreased to about $60 \mu\text{g}\cdot\text{mg}^{-1}$ at 50 μM Cd treatment. In a study conducted by Ewais [26] on *Cyperus difformis*, *Chenopodium ambrosioides* and *Digitaria sanguinalis* species, cadmium was used in doses of 0, 5, 10 and 20 $\text{mg}\cdot\text{kg}^{-1}$. In all three species, LCC values began to decrease after 5 $\text{mg}\cdot\text{kg}^{-1}$ Cd treatment. In the case of 20 $\text{mg}\cdot\text{kg}^{-1}$ Cd, the decline in all three species was close to 30%. Farouk et al. [27] investigated chlorophyll content in the study of Cd (0, 100 and 150 $\text{mg}\cdot\text{kg}^{-1}$ soil DW) in Radish plant. The chlorophyll amounts were also reduced in all three species during both experiment years. However, the reduction rate in the second experiment year is lower than the first year. In 150 $\text{mg}\cdot\text{kg}^{-1}$ Cd treatment, LCC loss approached 30% in both years. As can be seen in previous studies, low cadmium doses caused high loss of LCC may be related to the age of the plants used and the growing medium used. The fact that the plants used in this study are older and the media used is different may explain low LCC loss.

4. CONCLUSION

In this study, the effects of 5 different Cd doses (0, 150, 300, 450 and 600 μM) on CAB-6P cherry rootstocks were investigated. According to the results obtained, Cd damages especially roots and leaves from low doses. Damage of Cd on relatively stronger trunk and tap-root are less. According to previous studies, Cd caused significant losses from low doses. At the same time, at very low doses, Cd has a positive effect on certain plant characteristics. However, the fact that these studies were usually carried out in hydroponic media may have caused Cd to be damaged at low doses. In plant growing medias such as soil, the minimum amount required for the occurrence of Cd damage may increase. The reason for this is the buffering feature of medias such as soil. As a result, Cd is among the heavy metals that can cause considerable damage to plants. It would be useful to select the species and varieties that are resistant to Cd containing soil.

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Removal of Linear Alkyl Benzene Sulphonic Acid by Sonication Process

Ayla ARSLAN¹, Eylem TOPKAYA^{1*}, Sevil VELI¹, Deniz BINGOL²

Abstract

In this study, treatability of linear alkyl benzene sulphonic acid (LABSA) from aqueous solutions were investigated by sonication process. The effects of initial LABSA concentration, pH and reaction time which are process independent variables were investigated on the yield. Removal of LABSA was followed by absorbance analysis. The system optimization was made with experimental design by using the surface response method in this study. It was determined that the independent variable that most affects LABSA removal was the reaction time. The reaction time and initial pH value of the solution showed a positive effect on the removal yield. The initial LABSA concentration had a negative effect, and as the concentration increased, the yield decreased. The predicted maximum absorbance removal was 68% at the optimum conditions of pH 9.6, initial LABSA concentration of 10 mg/L and reaction time of 78 min. Only 11% of total variability can't be explained by this model.

Keywords: Anionic surfactant, Linear alkyl benzene sulphonic acid, Optimization, Response surface methodology, Ultrasonic degradation.

1. INTRODUCTION

Linear Alkyl Benzene Sulphonic Acid (LABSA) is an anionic surfactant. LABSA is one of the most important raw materials used in the detergent industry. It is used as the main surfactant in production processes like washing and dishwashers' powder detergents, detergent gels, liquid soaps, cleaning powders, liquid and oily soaps etc. today as well as dishwashing detergents [1].

Biological treatability of surfactants and degradation products are limited in domestic and industrial wastewater treatment plants. Moreover, the degradation products are become partly more toxic and refractory qualified from themselves [2]. These substances are shown accumulation at different concentrations in shallow water, bottom sediments and soil [3]. This accumulations are creating a growing danger in terms of health and environment, the wastewater of containing these substances must be treated effectively before being delivered to the receiving medium [4]. In the treatment of these pollutants, advanced oxidation processes (AOP) are anticipated as alternative chemical treatment technologies [5]-[8].

AOP is a method based on the formation of hydroxyl radicals (OH•), which can convert toxic and persistent organic substances into harmless end products such as CO₂ and H₂O [9]. OH• radicals are strong, non-selective chemical oxidants and can be produced by photochemical and chemical means [7].

* ¹Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/ Kocaeli, Turkey.
eylem.topkaya@kocaeli.edu.tr

¹ Kocaeli University, Department of Environmental Engineering: ataberk@kocaeli.edu.tr ; sevilv@kocaeli.edu.tr

² Kocaeli University, Department of Chemistry; deniz.bingol@kocaeli.edu.tr

The sonication process is improved chemical oxidation processes with supported by sound. In this process; creating of hydroxyl radicals are intended by ultrasonic waves cavitation effect. In this process microbubbles are formed, grew and then disappeared. Reactive free radicals are consisted of during the extinction phase. These radicals are provided conversion of toxic and organic compounds in wastewaters to stable final products or less harmful compounds [10]-[13]. Ultrasonic (US) method is preferred in recent times due to its simplicity in application and its not forming unwanted by-products (toxic etc.) [14]-[16].

In this study, sonication process was used to investigate the treatability of linear alkyl benzene sulphonic acid (LABSA) through the absorbance parameter and optimized by the surface response method.

2. MATERIALS and METHOD

2.1. Materials

The Linear Alkyl Benzene Sulphonic Acid (LABSA-C₁₈H₂₉SO₂OH) used in the study was obtained from HAYAT Chemical Company. The chemical formula of the LABSA used is given in Figure 1. LABSA aqueous solutions were used in the experiments. 1N H₂SO₄ or 1N NaOH solutions were used to adjust the pH.

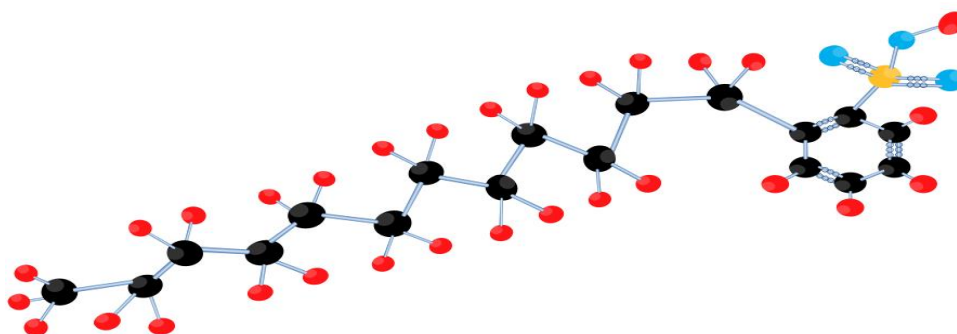
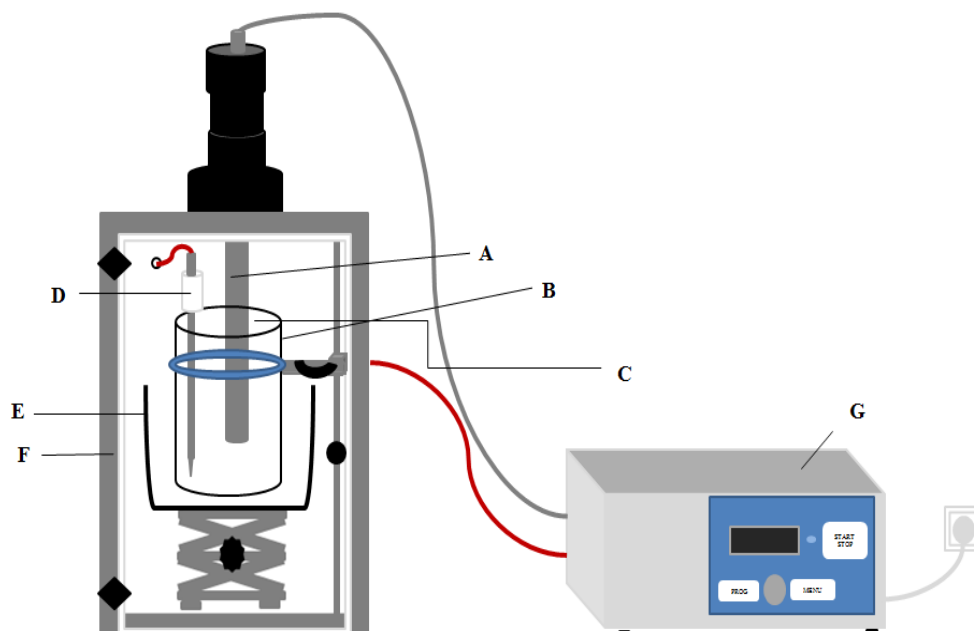


Figure 1. LABSA chemical formula

2.2. US System

The probe type ultrasonic device was used for oxidation studies by SONOPULS HD 3400 model (BANDELIN brand), 20 kHz frekans, 400 W maximum power. The ultrasonic probe is where ultrasound energy is converted to electrical energy or vice versa. The capacity of the US device is 100-2500 mL. The temperature was kept constant (25 ± 2 °C) with cooling water during the experiment. The US device was established in a noise-proof partly preventive cabinet. The US device is as shown in Figure 2.



A: Ultrasonic probe nib; B: Glass reactor; C: Sampling point; D: Temperature meter; E: Cold water container; F: Sound holding cabin; G: Ultrasonic monitor.

Figure 2. Ultrasonic System

2.3. Analysis

The experiments were performed with 1 L LABSA solution. HACH, HQd brand digital pH-meter was used for pH measurement. HACH DR 5000 spectrophotometer was used to measure the absorbance by scanning in the wavelength range of 200 to 700 nm. The absorbance of LABSA was measured at $\lambda_{max}=278$ nm. All experiments were made in pulse off application to preventing temperature control and probe heating in US probe applications.

2.4. Experimental Design Technique

Response Surface Methodology (RSM), is an empirical modeling technique, designed to graphically evaluate the relationship between different experimental variables and the responses. The most commonly used designs to determine response surfaces are the full and fractional factorial designs and the more complex central composite, Box–Behnken, Doehlert and mixture designs. Central composite designs (CCD) presented by Box and Wilson are a second-order multivariate design technique based on three-level factorial design used for evaluation of a dependent variable as functions of independent variables. It allows the determination of both linear and quadratic models. The CCD is a better alternative to the full factorial three-level design since it demands a smaller number of experiments while providing comparable results [17], [18]. For the RSM, a second-order polynomial model (Eq. (1)) is usually performed to estimate the effects of various factors on a response based on experimental results from CCD.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where y is the predicted response, xi is a coded variable, and the β_0 is the constant, the β_i is linear coefficient, the β_{ii} is quadratic coefficient and the β_{ij} is the interactive coefficient [19].

3. RESULTS and DISCUSSION

In the studies carried out by the sonication process, the system efficiency was evaluated by observing absorbance removals. The maximum absorbance was observed at 278 nm in an absorbance spectral scan. Degradation of the LABSA was followed by checking its absorbance value at 278 nm. Response Surface Methodology was optimized based on the central composite design. The data used in experimental design:

Variables:

pH (4-11)

The reaction time (30-90 min)

The initial LABSA concentration (8-20 mg / L)

Outputs:

Percent of Absorbance Removal

3.1. Experimental

The conditions for 20 experiments containing different combinations of factors and the average results obtained are given in Table 1.

Table 1. Central composite designs matrix

Run	pH	LABSA (mg/L)	t (min)	Absorbance Removal (%)
1	5.4	10	42	32
2	9.6	10	42	42
3	5.4	18	42	8
4	9.6	18	42	11
5	5.4	10	78	64
6	9.6	10	78	68
7	5.4	18	78	14
8	9.6	18	78	13
9	4	14	60	18

10	11	14	60	34
11	7.5	8	60	47
12	7.5	20	60	32
13	7.5	14	30	12
14	7.5	14	90	32
15	7.5	14	60	22
16	7.5	14	60	33
17	7.5	14	60	18
18	7.5	14	60	20
19	7.5	14	60	21
20	7.5	14	60	22

The ANOVA table of the model obtained from the central composite design is given in Table 2.

Table 2. ANOVA for Absorbance Removal (%)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	4317.65	479.74	4.82	0.011
Linear	3	3373.94	1124.65	11.30	0.001
pH	1	134.82	134.82	1.36	0.271
LABSA	1	2512.22	2512.22	25.25	0.001
t	1	726.91	726.91	7.31	0.022
Square	3	600.71	200.24	2.01	0.176
pH*pH	1	36.33	36.33	0.37	0.559
LABSA*LABSA	1	583.05	583.05	5.86	0.036
t*t	1	0.43	0.43	0.00	0.949
2-Way Interaction	3	343.00	114.33	1.15	0.376
pH*LABSA	1	18.00	18.00	0.18	0.680
pH*t	1	12.50	12.50	0.13	0.730
LABSA*t	1	312.50	312.50	3.14	0.107
Error	10	994.90	99.49		
Lack-of-Fit	5	855.56	171.11	6.14	0.034
Pure Error	5	139.33	27.87		
Total	19	5312.55			

Almost all major factors with a probability of less than 0.05 and their interactions are significant at 95% confidence level.

Since $P > 0.05$, the effects on the system at 95% confidence level of these interactions are statistically insignificant. For this reason, these interactions must be removed from the model.

Standard deviation and determination coefficients of the reduced model obtained with significant coefficients are as follows:

$$S = 5.0288 \quad R\text{-sq} = 91.21\% \quad R\text{-sq(adj)} = 88.87\% \quad R\text{-sq(pred)} = 83.23\%$$

Only 11% of total variability cannot be explained by this model.

The regression equation of the model obtained with the coded coefficients is given in the following equation:

$$\text{Absorbance removal (\%)} = 23.92 + 3.14 \text{ pH} - 13.56 \text{ LABSA} + 7.30 \text{ t} + 6.20 \text{ LABSA*LABSA}$$

According to the above equation, the initial LABSA concentration had the greatest but negative effect on LABSA removal, followed by reaction time. Removal performance was least affected by pH.

Response surfaces are used to determine an optimum. In addition, it is a good way to graphically illustrate the relation between different experimental variables and the responses. To be able to determine an optimum it is necessary that the polynomial function contains quadratic terms. The three-dimensional response surface plots and contour plots are shown in Figure 3 and Figure 4, respectively.

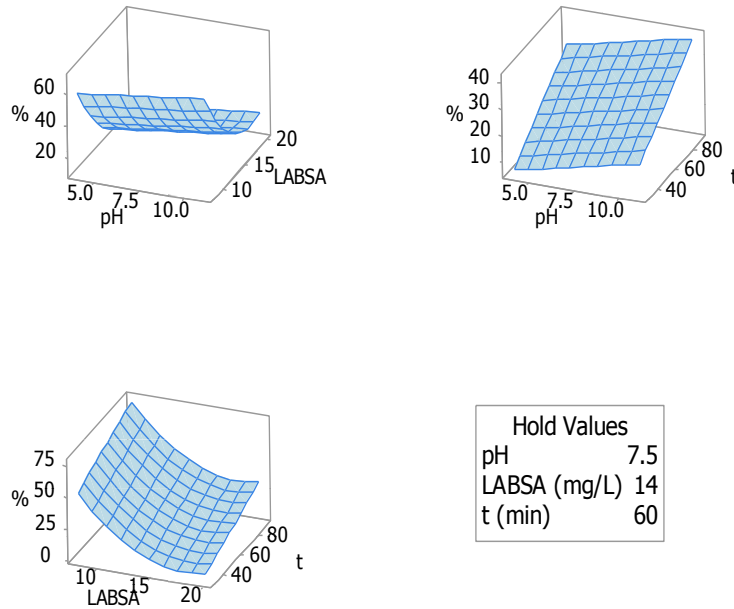


Figure 3. Response surface plots for the absorbance removal

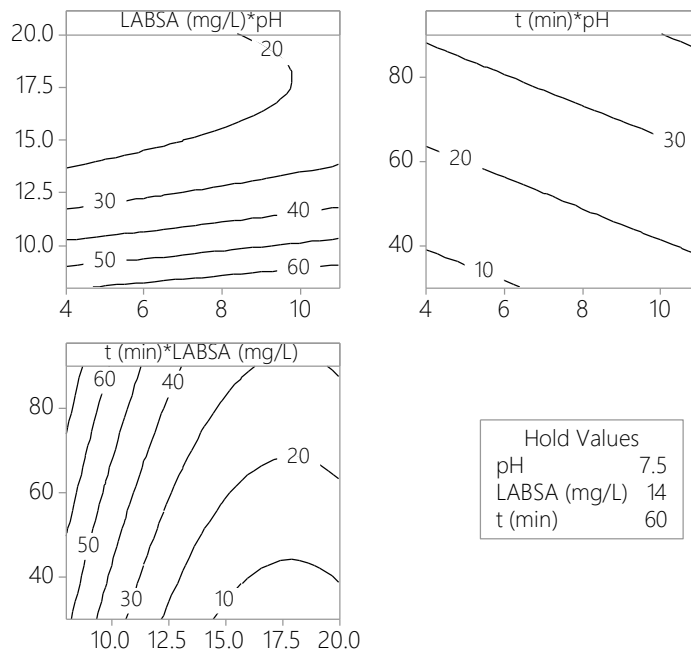


Figure 4. Contour plots for the absorbance removal

3.2. Application of the RSM results to the real wastewater

In this study, wastewater sample was taken from the detergent plant where LABSA was supplied. pH value of wastewater was 9.6; the maximum absorbance value was measured as 3.725 at 366 nm wavelength. The effects of process components were revealed by RSM in LABSA degradation. Taking these results into consideration, sonication treatment was applied to wastewater at three different pH values. The results of experiments carried out with wastewater are as indicated in Table 3.

Table 3. Results of wastewater studies

pH	Time (min)	Absorbance values after sonication (abs) (366 nm)	Absorbance Removal (%)
5.3	0	3.386	-
	30	2.961	13
	60	2.134	37
	90	2.278	33
7.5	0	3.377	-
	30	2.819	17
	60	2.818	17
	90	2.821	16
9.6	0	3.725	-
	30	3.089	17
	60	2.992	20
	90	2.078	44

According to Table 3; The US process was more effective under basic conditions for industrial wastewater and the absorbance removal was achieved up to 44%. Treatment of sonication process will be more economical at the original pH value of the wastewater.

4. CONCLUSION

LABSA removal was investigated by sonication process from aqueous solutions. In the experimental design, the system optimization was made of using the surface response method. The initial LABSA concentration, pH and reaction time, which were process independent variables, effects on the removal efficiency were investigated.

In the study carried out with the sonication process; a maximum absorbance removal of 68% was achieved at pH of 9.6, initial LABSA concentration of 10 mg / L and reaction time of 78 min.

When LABSA removal was followed by the absorbance parameter, it was determined that the independent variable most affecting the yield was the reaction time. The reaction time and the solution initial pH value were showed a positive effect on the recovery efficiency. The initial LABSA concentration had a negative effect. As the initial LABSA concentration increased, the yield decreased. According to the model; for pH 9.6, initial LABSA concentration 10 mg / L, and reaction time of 78 min the maximum absorbance removal was estimated to be 68%. Only 11% of total variability can't be explained by this model.

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BIOGRAPHY

Eylem TOPKAYA; completed her undergraduate degree in 2004-2009 at Uludag University, Department of Environmental Engineering. She completed her master's degree in 2011-2014 at Gebze High Institute of Technology (GYTE), Institute of Natural and Applied Sciences, Department of Environmental Engineering. She has started her PhD education in 2014 at Kocaeli University, Institute of Natural and Applied Sciences, Department of Environmental Engineering and she is still in progress.

Biodiesel Production from Microalgae

Veli Gokhan DEMIR^{1*}, Hakan Serhad SOYHAN¹

Abstract

Depletion of fossil fuel reserves, increasing energy demand and serious environmental concerns makes renewable energy such as biofuels more importance. In recent years, biodiesel, the methyl or ethyl esters of fatty acids, gained a significant position as an environmentally friendly substitute of conventional diesel fuel. Generally, biodiesel is produced through transesterification method between vegetable oil and alcohol in the presence of catalyst efficiently. However, the major obstacle of large-scale commercialization of biodiesel production is its high cost related to high feedstock prices especially in the countries that import most of the consuming food-grade oils such as Turkey. On the other hand, microalgae have gained attention as an alternative biodiesel feedstock because of their fast growing nature and high adaptability to the existing environment. The aim of this study is to investigate "microalgae" as an alternative biodiesel feedstock to vegetable oils. In this regard, the processes and used technologies existing in from microalgae to biodiesel formation; including microalgae production, harvesting, and conversion methods, are reviewed. It is found that using microalgae in biodiesel production in Turkey can be helpful to make it self-sufficient for energy demands.

Keywords: Biodiesel, Feedstock, Microalgae, Transesterification.

1. INTRODUCTION

The world energy consumption has increased rapidly and will continue to increase due to an annual projected population increase of about 1%. Fluctuations of oil prices have worsen the situation and further decreased oil supply due to political pressure. It is estimated that the seriousness of the depletion of oil and other fossil fuels along with the climate change effects will be felt by the beginning of 2030–2050 [1], stressing the need for alternative fuels. As a result, a large amount of money is being invested on the research and development of alternate energy resources, such as solar, wind, hydro and biofuels. Solar, wind, and hydro energy can be used to produce electricity, but the only alternative to liquid transportation fuel is liquid biofuel [2].

With the need to reduce carbon emissions, and the dwindling reserves of crude oil, liquid fuels derived from plant material – biofuels – are an attractive source of energy. Moreover, in comparison with other forms of renewable energy such as wind, tidal, and solar, liquid biofuels allow solar energy to be stored, and also to be used directly in existing engines and transport infrastructure. Currently, bio-ethanol from, for example, corn starch, sugar cane or sugar beet, and biodiesel from oil crops such as palm and oilseed rape, are the most widely available forms of biofuel [3].

Biodiesel is made from biomass oils, mostly from vegetable oils. Biodiesel appears to be an attractive energy resource for several reasons. For example: biodiesel appears to have several favourable environmental properties resulting in no net increased release of carbon dioxide and very low sulphur content [4, 5]. The release of sulphur content and carbon monoxide would be cut down by 30% and 10%, respectively, by using biodiesel as energy source. Using biodiesel as energy source, the gas generated during combustion could be reduced, and the decrease in carbon monoxide is owing to the relatively high oxygen content in biodiesel. Moreover, biodiesel contains no aromatic compounds and other chemical substances which are harmful to the environment. Recent investigation has indicated that the use of biodiesel can decrease 90% of air toxicity and 95% of cancers compared to common diesel source [6]. Also, biodiesel is better than diesel fuel in terms of flash point and biodegradability. On the other hand, biodiesel appears to have significant economic potential because as a non-renewable fuel that fossil fuel prices will increase inescapability further in the future [7].

Alcoholysis or transesterification of triglycerides has emerged as the most common method for biodiesel production with obtaining accepted fuel qualities. This process consists of three sequential reversible reactions: the triglyceride (TG) in the oil is converted to di-glyceride (DG), then to mono-glyceride (MG) and finally to glycerol with alkyl esters (biodiesel) formed in each step [8]. Conventional biodiesel mainly comes from soybean and vegetable oils, palm oil, sunflower oil, rapeseed oil as well as restaurant waste oil [7]. The number of carbon in the carbon chain of the diesel oil molecular is about 15, which is similar to that of the plant oil with 14–18 carbons. The structural characteristic of biodiesel determines that biodiesel is a feasible substitute for conventional energy. Nevertheless, the production cost is generally high for biodiesel. The price of

^{1*} Corresponding author: Balikesir University, Department of Mechanical Engineering, 10100, Balikesir, Turkey.
veligokhandemir@balikesir.edu.tr

biodiesel is approximately twofold that of the conventional diesel at present. The production cost of biodiesel consists of two main components, namely, the cost of raw materials (fats and oil) and the cost of processing. The cost of raw materials accounts for 60% to 75% of the total cost of the biodiesel fuel therefore, the major bottleneck limiting the development of the biodiesel industry is supply and price of feedstocks [9, 10].

Since vegetable oils may also be used for human consumption, it can lead to an increase in price of food-grade oils, causing the cost of biodiesel to increase and preventing its usage, even if it has advantages comparing with diesel fuel. In order to not compete with edible vegetable oils, the low-cost and profitable biodiesel should be produced from low-cost feedstocks such as non-edible oils, used frying oils, animal fats, soap-stocks, and greases. Among alternative biodiesel feedstocks; microalgae, the promising source of biodiesel, can grow in fresh water or marine environments, without using arable land and competing with food production. Some microalgae have high biomass and oil productivity [9]. Moreover, microalgae are present in all existing earth ecosystems and they can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structures [11].

In this study, it is focused on the microalgae, the significant and promising source of biodiesel production especially for Turkey which imports nearly all of its oil supplies. The paper presents a critical review on the prospects of microalgae for biodiesel production via transesterification method.

2. BIODIESEL

2.1. Biodiesel Production

According to the International Energy Agency (IEA) report [12] and Shahid and Jamal [13], the world will need 50% more energy in 2030 than today, of which 45% will be accounted for by China and India. In the past 30 years, the transportation sector has experienced a steady growth especially due to the increasing numbers of cars around the world. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035. Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy, of which 80% is road transport. It is believed that this sector is currently responsible for nearly 60% of world oil demand and will be the strongest growing energy demand sector in the future [14].

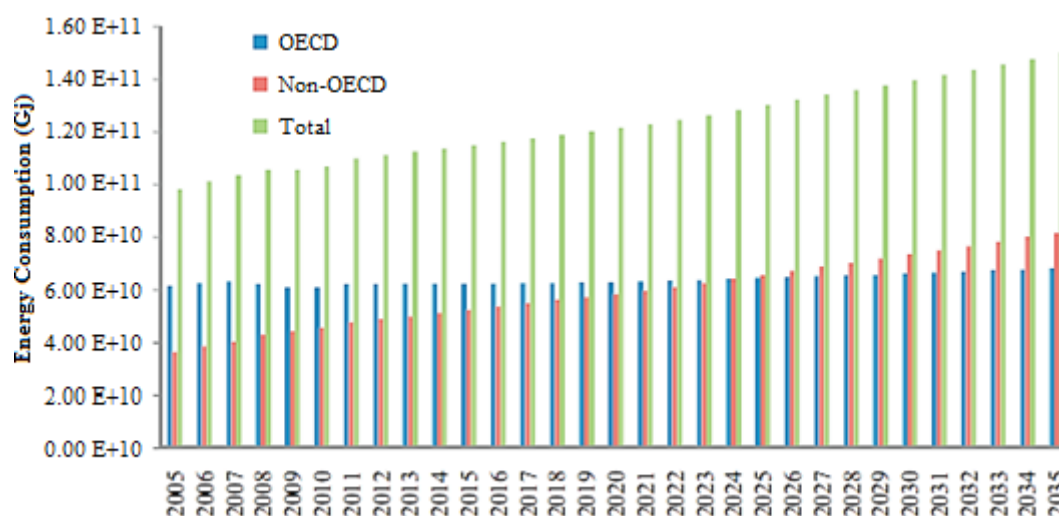


Figure 1. 1. Total world, OECD and non-OECD transportation sector energy consumption (GJ) between 2005-2035 [14]

Biodiesel can be considered as a possible substitute of conventional diesel, is biodegradable, non-toxic, renewable and has reduced emission of CO, SO₂, particulate matter, volatile organic compounds and unburned hydrocarbons as compared to conventional diesel. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification. The concerns of the harmful effects of fossil fuels to environment and rising energy demand of the world while fossil fuel reserves are running out, biodiesel seems to be a realistic fuel for future; it has become more attractive recently because of its environmental benefits [15].

Global biodiesel production is expected to reach 41.4 Bln L by 2025 corresponding to a 33% increase from the 2015 level. The European Union is expected to be the major producer of biodiesel. Other significant players are the United States, Brazil, Argentina and Indonesia. Policy rather than market forces will continue to influence production patterns in almost all countries [16].

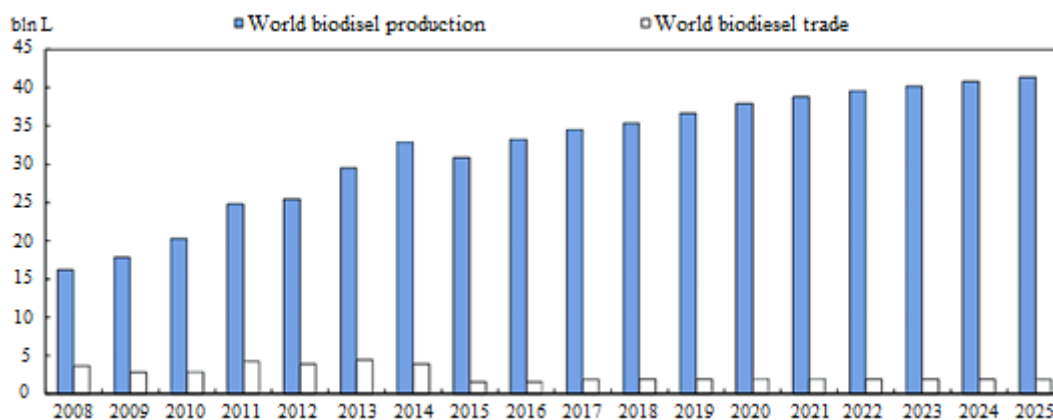


Figure 2. World biodiesel production and trade [16]

2.2. Why Microalgae?

It is projected that the growth in production and consumption of liquid biofuels will continue, but their impacts towards meeting the overall energy demands in the transport sector will remain limited due to: competition with food and fibre production for the use of arable land, regionally constrained market structures, lack of well managed agricultural practices in emerging economies, high water and fertilizer requirements, and a need for conservation of bio-diversity [17]. There are several reports on biodiesel production from edible oils; thus, its competition with food consumption has been a global concern. About 6.6 Tg (34%) of edible oil was estimated for worldwide biodiesel production from 2004 to 2007, and biodiesel is projected to account for more than a third of the expected growth in edible oil use from 2005 to 2017. Consequently, employing waste and nonedible oils in biodiesel production would eliminate the competition with food consumption; it will also allow for compliance with ecological and ethical requirements for biofuel. Algae are currently considered to be one of the most promising alternative sources of non-edible oils for biodiesel [18].

2.3. Biodiesel Production Methods

Globally, there are many efforts to develop and improve vegetable oil properties in order to approximate the properties of diesel fuels. It has been remarked that high viscosity, low volatility and polyunsaturated characters are the mostly associated problems with crude vegetable oils. These problems can be overcome by four methods; pyrolysis, dilution with hydrocarbons blending, Micro emulsion, and transesterification [14]. Transesterification is regarded as the best and most common method among other approaches due to its low cost and simplicity. Transesterification is a well-established chemical reaction in which a primary alcohol reacts with the triglycerides of fatty acids (oils) in presence of a catalyst to form glycerol and esters (biodiesel) [15].

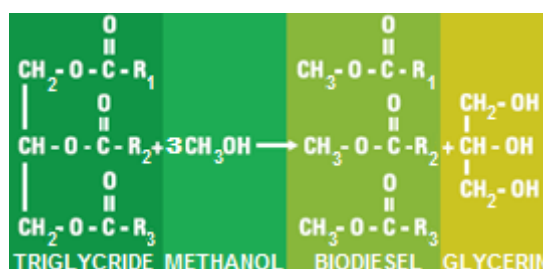


Figure 3. Transesterification reaction scheme

3. MICROALGAE

The algal organisms are photosynthetic macroalgae or microalgae growing in aquatic environments. Algae are simple organisms that are mainly aquatic and microscopic. Microalgae are unicellular photosynthetic micro-organisms, living in saline or freshwater environments that convert sunlight, water and carbon dioxide to algal biomass [19]. They are categorized into four main classes: diatoms, green algae, blue-green algae and golden algae. There are two main species of algae: filamentous and phytoplankton algae. These two species, in particular phytoplankton, increase in numbers rapidly to form algae blooms. Many species exhibit rapid growth and high productivity, and many microalgal species can be induced to accumulate substantial quantities of lipids, often greater than 60% of their dry biomass [20]. Microalgae are very efficient solar energy converters and they can produce a great variety of metabolites.

Microalgae are known as third generation feedstock used in biodiesel production. Algae cultivation has been developed for decades with the initial purpose of providing food supplements and animal feeds. During the energy crisis in 1970s, the U.S. National Renewable Energy Laboratory's (US NREL, formerly SERI) Aquatic Species Program (ASP) started to utilize algae biofuels as alternative energy sources. Although the high cost of algae biofuels during that time put a halt to the program in 1996, extensive amount of data on cultivation, harvesting, extraction, and transesterification of algae published throughout the period of ASP serves as foundations for modern studies of algae biofuels [2]. Main steps of microalgae based biodiesel production are illustrated in Figure 4.

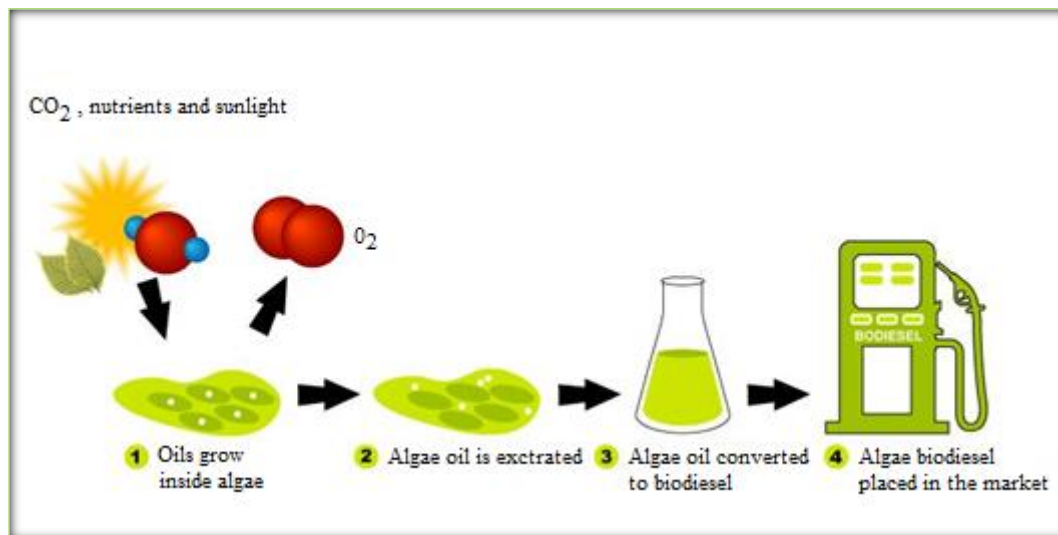


Figure 4. Main steps of microalgae based biodiesel production

Microalgae have been suggested as potential candidates for fuel production because of a number of advantages including higher photosynthetic efficiency, higher biomass production and higher growth rate compared to other energy crops. Main advantages and disadvantages of microalgae using in biodiesel production can be listed as following [7]:

Advantages:

- Fatty acid constitutions similar to common vegetable oils,
- Under certain condition it may be as high as 85% of the dry weight,
- Short-time growth cycle,
- Composition is relative single in microalgae.

Disadvantages:

- Most algal lipids have lower fuel value than diesel fuel,
- The cost of cultivation is higher compared to common crop oils currently.

In Table 1, biodiesel productivities from common seed plants and microalgae are compared. It can be seen how microalgae show a clear advantage in terms of land use because of their higher biomass productivity and oil yield. It should be also noted that although the oil contents are similar between seed plants and microalgae there are significant variations in the overall biomass productivity and resulting oil yield and biodiesel productivity with a clear advantage for microalgae [21].

Table 1. Comparison between plants and microalgae biodiesel properties [11]

Plant sources	% seed oil content (wt in biomass)	Oil yield (L oil/ha year)	Land use (m ² year/kg biodiesel)	Biodiesel productivities (kg biodiesel/ha year)
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Corn	44	172	66	152
Hemp	33	363	31	321
Soybean	18	636	18	562
Jatropha	28	741	15	656
Camelina	42	915	12	809
Canola	41	974	12	862
Sunflower	40	1070	11	946
Castor	48	1307	9	1156
Palm Oil	36	5366	2	4747
Microalgae (low oil content)	30	58700	0.2	51927
Microalgae (medium oil content)	50	97800	0.1	86515
Microalgae (high oil content)	70	136900	0.1	121104

3.1. Microalgal Biotechnology for Lipids Production

Oil levels of 20–50% are common in microalgae. The whole technical process in the production of biodiesel from microalgae has been well investigated in recent years. The entire production process ranging from the cultivation of high-lipid microalgae to the production of biodiesel from the microalgal oils has also been explored. In the laboratory conditions, the ideal oil content could reach 56–60% of total dry biomass by genetic engineering or heterotrophic culture techniques. These technological advances suggest that the industrial production of biodiesel from microalgal oils may be feasible in the near future. The main methods for lipids production using microalgae are [7]:

- a) Biosynthesis of lipids/fatty acids in microalgae
 - The elongation and desaturation of carbon chain of fatty acids
 - The formation of acetyl coenzyme A (acetyl-coA) in cytoplasm
 - The biosynthesis of triglycerides in microalgae
- b) Phototrophic cultivation of microalgae for lipids production
- c) Heterotrophic cultivation of microalgae for lipids production
- d) Genetic engineering for lipids production

3.2. Microalgae Cultivation Technology

Industrial reactors for algal culture are at present known as open pond and photobioreactor systems. Photobioreactors are different types of tanks or closed systems in which algae are cultivated. Open pond systems are shallow ponds in which algae are cultivated. Nutrients can be provided through runoff water from nearby land areas or by channeling the water from sewage/water treatment plants. Technical and biological limitations of these open systems have given rise to the development of enclosed photoreactors. Microalgae cultivation using sunlight energy can be carried out in open or covered ponds or closed photobioreactors, based on tubular, flat plate or other designs. A few open systems are presented for which particularly reliable results are available. Emphasis is then put on closed systems, which have been considered as capital intensive and are justified only when a fine chemical is to be produced. Microalgae production in closed photobioreactors is highly expensive. Closed systems are much more expensive than ponds. However, the closed systems require much less light and agricultural land to grow the algae. High oil species of microalgae cultured in growth optimized conditions of photobioreactors have the potential to yield 19,000–57,000 liters of microalgal oil per acre per year. The yield of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils [22].

3.2.1. Open Pond Systems

Open ponds are natural waters (lakes, lagoons, ponds), artificial ponds or containers. Many different designs have been suggested for pond construction but generally four major pond design have been developed and operated at a large-scale (Figure 5) [21]:

- a) Unstirred ponds (lakes and natural ponds),
- b) Inclined ponds,
- c) Central pivot ponds,
- d) Raceway ponds.

One of the major advantages of open ponds is that they are easier to construct and operate than most closed systems. However, major limitations in open ponds include poor light utilization by the cells, evaporative losses, diffusion of CO₂ to the atmosphere, contamination and requirement of large areas of land [23].

Open pond cultivation systems are considered to be the most economical culture systems for large-scale microalgal cultivation. However, the productivity of open pond microalgae cultivation systems is strongly correlated to the location of the pond, the layout of the pond system, microalgae species and weather conditions. The calculation-based results showed that climate conditions such as temperature changes and solar irradiation play very important roles in open race-way ponds [24].



Figure 5. Different designed open pond systems [21]

3.2.2. Photobioreactors (PRB)

Algae can be harvested using a device called photobioreactors, this is also known as a PBR. The PBR is a self-contained system with a controllable environment. It allows the supply of light, nutrients, carbon dioxide, air, and temperature can be regulated. Using a PBR can prevent or at least minimise contamination (from other algae species and bugs), and allows easier cultivation of one algae strain. It also offers better control over a range of other growing conditions. In addition to this a, closed system such as the PBR reduces evaporative water losses, and has lower carbon dioxide losses which all-in-all means higher cell concentrations. In other words there are more grams of algae produced per litre of water [23].

Closed systems can be classified as horizontal tubular photobioreactors; stirred photobioreactors; airlift and bubble column photobioreactors represented in Figure 6. The main factors affecting PBR cultivation are known as temperature, pH, light, carbon uptake, oxygen generated, mixing rates, and nutrient uptake. The advantages and disadvantages of the respective PBRs are summarized in Table 2. [24].

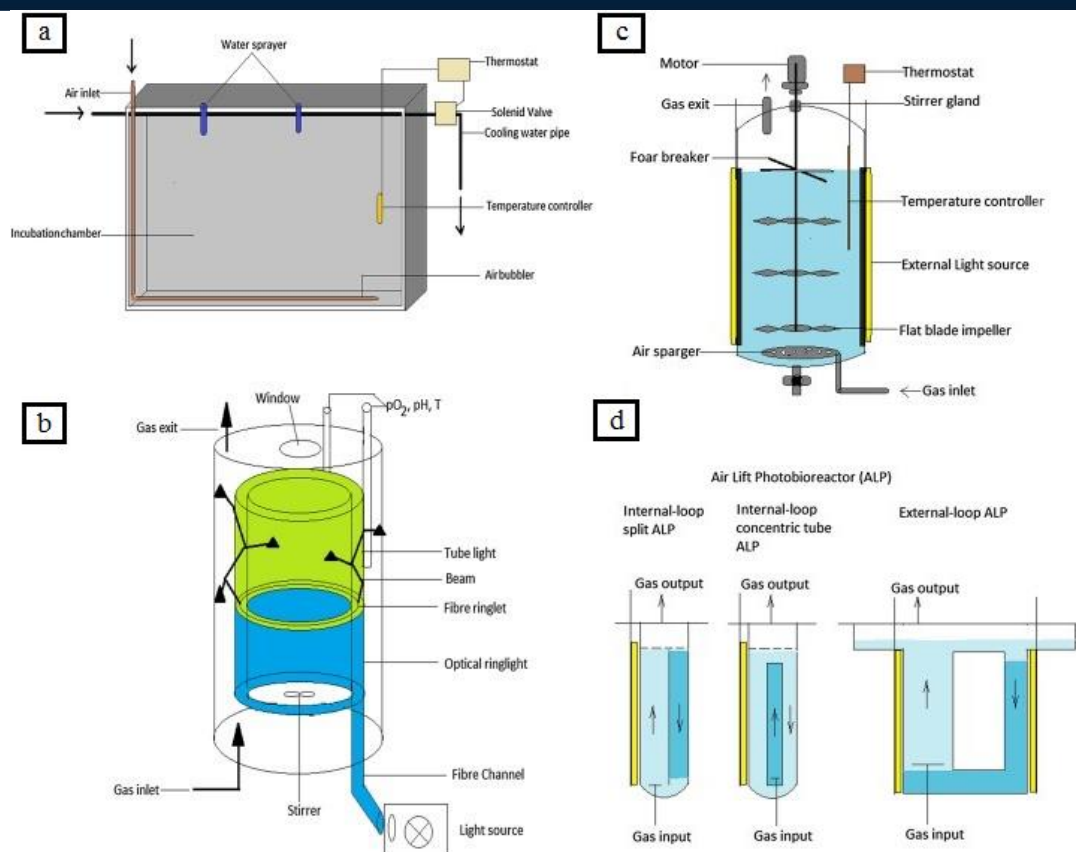


Figure 6. Diagrammatic representation of the different types of photobioreactors used for microalgal cultivation [24]

Table 2: Advantages and disadvantages of different PBRs [24]

Type of photobioreactor (PBR)	Advantages	Disadvantages
Horizontal tubular PBR	The shape is itself an advantage for their orientation towards sunlight which results in high light conversion efficiency	High concentration of dissolved O ₂ causes photo bleaching and reduces photosynthesis efficiency High energy consumption
Stirred PBR	Most conventional reactor, agitation is provided with the help of impellers CO ₂ enriched air bubbled through the bottom	Lack of internal light Low surface area to volume ratio and mechanical agitation limits its use
Airlift PBR	High mass transfer, good mixing achieved Good for immobilization of algae	Due to its complexity there is difficulty in scaling up
Bubble column PBR	Low capital cost, high surface area to volume ratio, lack of moving parts Satisfactory heat and mass transfer, efficient release of O ₂	At gas flow rate less than $\leq 0.01 \text{ m s}^{-1}$ circulation flow pattern do not exist because of the lack of back mixing Lack of internal light

Among the different PBRs available for microalgal biomass production, the airlift reactor seems the most suitable reactor for flue gas CO₂ sequestration. High gas transfer, uniform mixing, low hydrodynamic stress, and ease of control are the characteristic advantages of this reactor. But, none of these configurations present in the bioreactor can effectively control all the various parameters that are required for utmost microalgal growth, metabolic activity, and bio-fixation of CO₂ particularly at large scale production process [24].

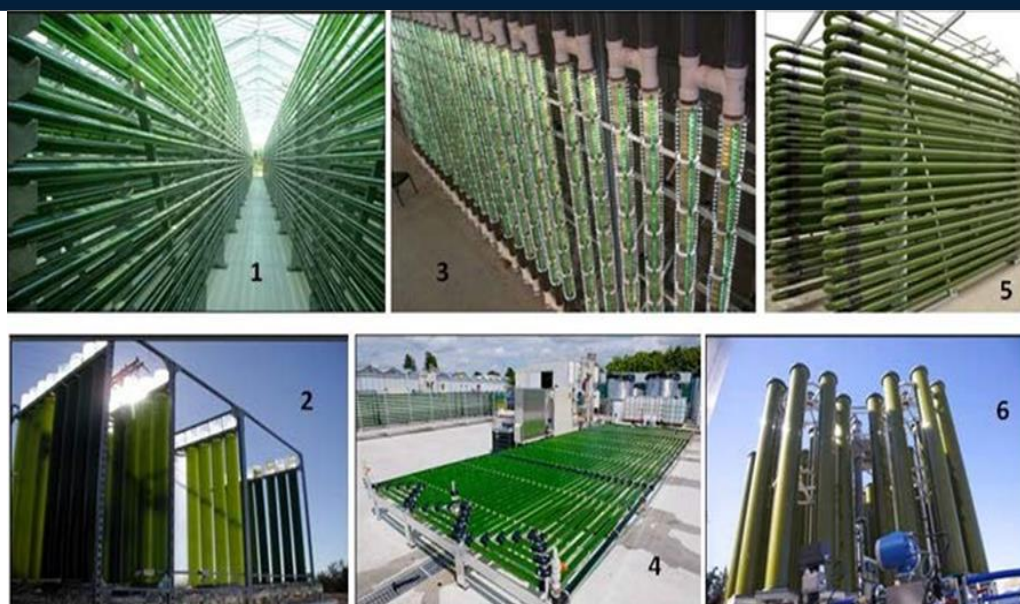


Figure 7. Different closed photobioreactors for production of microalgae in the world [25]

3.3. Microalgal Industry

The area of microalgae biotechnology is rapidly developing, attracting funding and investment worldwide. Examples shown in Table 3 indicate the range of products from large-scale microalgae cultivation and include a description of the different cultivation methods, sectors and location. Large-scale cultivation facilities for the production of nutritional supplements are predominant as these are economically feasible due to the high value end product (e.g. pigments and nutrients). Over 80% of the world's green algae producers are currently located in Taiwan, with Inner Mongolia in China and Israel being the top three producers of *Dunaliella* worldwide. The use of large-scale microalgae cultivation for wastewater treatment is being developed in some regions and this is discussed in more detail later. There is funding from governments in the US, EU, Brazil, China, India, Canada and other countries worldwide in both universities and commercial facilities. Many petro-based companies including Exxon, Shell, BP, Statoil, ENAP, Chevron are investing in biofuel R&D for production of methanol, ethanol, bio-butanol, biodiesel, and bio-crude as well as bio-based chemicals [26].

Table 3. Some examples of industries investing in large scale microalgae cultivation [26]

Algae Types	Cultivation	Industry/Product	Location	Link
Cyanobacteria	Closed (PBR)	Biofuel (Ethanol, biodiesel)	USA (Florida)	www.algenolbiofuels.com
Unknown	Closed (Heterotrophic)	Biofuel (Biodiesel)	Brazil	solazyme.com
Unknown	Closed (Heterotrophic)	Biofuel (Jet fuel)	USA (New Mexico)	www.sapphireenergy.com
Chlorella	Closed (PBR)	Nutraceutical (Dietary supplement)	Germany	www.algomed.de
Haematococcus	Open (Raceway)	Nutraceutical (Astaxanthin)	Israel	www.algatech.com
Haematococcus /Spirulina	Open (Raceway)	Nutraceutical (Dietary supplement)	USA (California)	www.earthrise.com
Haematococcus	Closed (PBR)	Nutraceutical (Astaxanthin)	Sweden	www.bioreal.se
Spirulina	Open (Raceway)	Nutraceutical (Dietary supplement)	USA (California)	www.earthrise.com
Spirulina/Chlorella	Open (Centre Pivot Ponds)	Nutraceutical (Dietary supplement)	Taiwan	www.wilson-groups.com

Dunaillella	Closed (PBR)	Nutraceutical caretone)	(β- Israel	nikken-miho.com
Unknown	Open (Biofilm)	Wastewater treatment	USA (Florida)	www.aquafiber.com

3.4. Algae Oil Extraction

According to ASTM standards, biodiesel produced from microalga feedstock shows similar affection to standard biodiesel. Downstream process leads with harvesting, dewatering, extraction of algal oil and ends with transesterification of lipid constituents into biodiesel. It is arduous to explain processing due to its specificity as well as dependency on the required product. After harvesting of algal biomass, next step is drying and extraction of oil. Selection of methods for drying and extraction purpose needs to be of special concern due to some valuable products such as proteins, carbohydrates etc. containing algal species are also formed. Extraction of algal oil from biomass can be done by mechanically, chemically or combination of the two. Mechanical extraction is a conventional method which includes bead mill, press, high press homogenization, ultrasonic, autoclave and microwave assisted oil extraction. Non mechanical methods are solvent extraction, supercritical fluid extraction and osmotic shock. In case of extraction carried out chemically, it involves solvents such as hexane, ethanol, chloroform, diethyl ether etc. One of the major detriments during solvent extraction is denaturing of by-products. It also comprises risk of explosion and decontamination of the final product. Methods used for cell disruption are based on cell wall of algal species as well as required product. Mechanical methods used for biomass extraction elect to overcome the possibility of contamination that occurs in case of chemical extraction. If approximately 80%(w/w) lipid content is obtained from algal species, then the method is regarded as better and appropriate [27].

3.5. Biodiesel Production Methods Using Microalgae

Biodiesel production from algae is generally done by one of three methods. The first is a two-step protocol in which algae oil is extracted with organic solvent and then converted to biodiesel using a catalyst, such as an acid, a base, an enzyme or heterogeneous ones. The second method directly produces biodiesel from algae biomass using an acid catalyst at atmospheric pressure and ambient temperature. The third method is one-step conversion to biodiesel at high pressure and high temperature in the absence of a catalyst. Each method has innate advantages and disadvantages. Method 2 requires high concentrations of sulphuric acid since moisture in the biomass is a limiting factor for conversion efficiency. In contrast, moisture can be ignored under the subcritical or supercritical conditions of method 3; however, side reactions happen at subcritical or supercritical conditions that produce organic acids and heterocyclic nitrogen compounds from the degradation of proteins and carbohydrates. These contaminants lower the quality of biodiesel or interfere with the purification process. From an economics and energy cost point-of-view, oil extraction directly from wet algal slurry is thought to be preferable. Biodiesel is produced from algal oils by transesterification and has similar properties as petro-diesel [9].

3.6. Economic Overview of Microalgal Biodiesel Production

The cost of building a biodiesel plant depends upon factors like feedstock, location of the plant, plant capacity, plant design and equipment. When biodiesel is produced from Soya or rapeseed oil the cost of biodiesel production increases because the cost of feedstock is the largest expense [24].

Therefore, use of non-edible feedstock like jatropha oil reduces the cost incurred on feedstock to a considerable amount. The economic analysis of Jatropha biodiesel revealed the cost of production of jatropha ethyl ester to be 0.40 € per liter [28] whereas, the cost of production of biodiesel from palm oil is 0.57 € per liter [22].

Although the use of non-edible oil for biodiesel production reduces the cost of production yet, there are major drawbacks which prevent the industry to flourish. A jatropha plant takes 2–3 years to grow and produce seeds. Under such circumstances, the various advantages of microalgae over other terrestrial crops make them an interesting perspective for the future. Medipally [29] claims that when the influential factors like irradiation, mixing, media constituents are well optimized then the production cost could be reduced to 0.68 € per kg. At these price microalgae could become a promising feedstock for biofuel production.

4. BIODIESEL IN TURKEY

4.1. Requirement of Biodiesel

Turkey which is not a producer of gas and oil, supplies 96% of its gas demand and 90% of its oil demand by imports. Because the dependency on importation is so high, energy security and continuity of energy supply have vital importance for Turkey [30].

The 2020 projection related to the Blue Book published by the Ministry of Energy in 2011 is shown in Table 4. It is predicted from the table that in a decade, the energy need would increase at a rate of 157% for the industry sector; it would increase at a rate of 64.7% for the residential sector; and it would increase at a rate of 122% for the transportation sector [31].

Table 4. Energy projection of Turkey (Ttoe) [31]

Year	Industrial	Housing	Transport	Total final energy	Total primary
20	49,270	32,650	22,370	111,705	142,861
20	52,056	34,500	23,700	117,950	150,890
20	54,766	36,450	25,100	124,300	160,211
20	57,633	38,507	26,541	130,968	170,154
20	60,991	40,400	28,000	137,996	178,455
20	64,842	42,150	29,480	145,403	187,923
20	69,144	43,900	31,000	153,310	198,911
20	73,795	45,700	32,500	161,610	210,236
20	78,732	47,549	34,039	170,292	222,424

According to the data from Turkish Statistics Institute (TUIK), while the number of diesel-powered vehicles in 2015 (9,576,896) is about three times higher than in 2004 (3,346,355), there is no significant increase is observed in the number of gasoline vehicles (from 5,569,192 to 5,977,352). It is expected that the requirement of diesel fuel in Turkey will be increased dramatically in future especially in transportation sector [32]. For this case, alternative fuels for transportation are essential to supply requirements.

On the other hand, when Kyoto Protocol, Turkey's "Intended Nationally Determined Contributions (INDCs)" report and the energy demand in Turkey are taken into account, utilization of biofuels instead of petroleum based fossil fuels became prominent [33].

It is clear that with the increasing energy demand and environmental concerns of Turkey, renewable biofuel biodiesel is getting more importance day by day.

4.2. Biodiesel Feedstocks in Turkey

The conventional feedstocks for biodiesel production are vegetable oils and fats, such as rapeseed, soybean, sunflower, coconut and palm oil. Among them, vegetable oils are the most common used ones as biodiesel raw materials. Depending upon environmental condition, the sources of biodiesel vary from country to country like soybean for North America, sunflower and rapeseed for Europe, palm for Southeast Asia, coconut for tropic and sub-tropic area etc. [34].

Although Turkey is an agricultural country, vegetable oil production is not sufficient compared to the consumption rates. The production and importation of crude vegetable oil are shown in Figure 8 [35]. According to the data (TUIK), importation rates of crude vegetable oil is pretty higher than production rates. In the circumstances, biodiesel production from vegetable oil is not realistic for Turkey, hence new generation biodiesel feedstocks like microalgae must be cultivated and used to supply needed biodiesel raw material without affecting food prices such as edible vegetable oils.

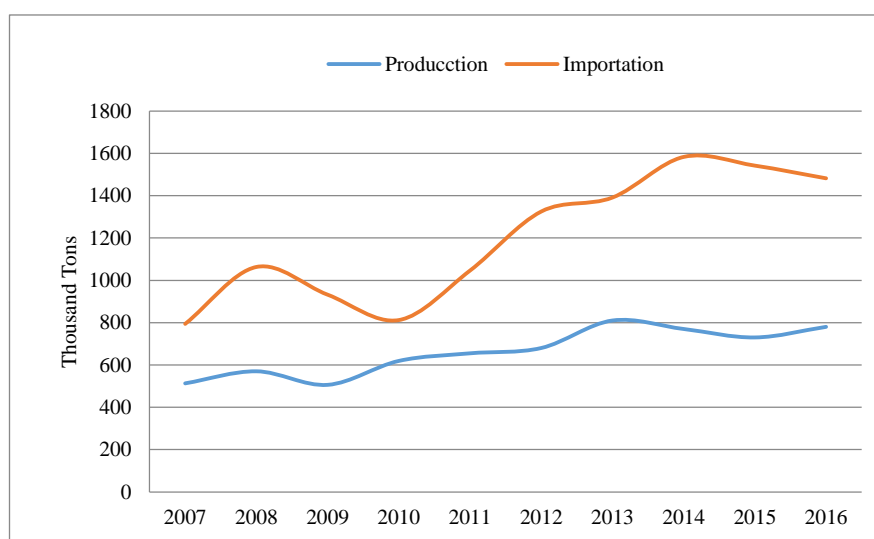


Figure 8. Crude vegetable oil production and importation of Turkey [35]

5. CONCLUSION

Because of the superior advantages over the petroleum diesel fuel, the use of biodiesel and biodiesel/diesel blends in internal combustion engines has attracted much attention in recent years. However, high costs of oleaginous materials are the major problem hindering commercial production and being widespread of biodiesel fuel. In addition, using conventional feedstocks such as vegetable oils in biodiesel production compromise production of food or another products derived from crops. In this case, microalgae are getting promising biodiesel feedstock since microalgae can be easily cultivated even in harsh conditions, including salty and sewage receiving areas without causing any negative impacts on food security, global food markets, water scarcity, and deforestation. Therefore, in the countries such as Turkey where oil crops, waste cooking oil and animal fat cannot realistically satisfy the demand of biodiesel feedstock, the investigations and government aids must be focused on large scale microalgal biomass cultivation, and development of microalgae-based technologies to minimise technical and economic constraints.

BIOGRAPHY

Veli Gokhan DEMIR graduated from mechanical engineering at Sakarya University in 2008. He has a master degree in mechanical engineering from Balikesir University and he has been a Ph.D. student since 2011. In his Ph.D. work, he has investigated about production of biofuels and their combustion efficiencies. His main research interests are in the field of energy efficiency improvement, biomass energy utilization, and combustion in engines. Currently, he is a research assistant in mechanical engineering at University of Balikesir.

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Wastewater Treatment by Floating Macrophytes (*Salvinia Natans*) Under Algerian Semi-Arid Climate

Laabassi AYACHE^{1*}, *Harzallah DAOUD*², *Boudehane ASMA*¹, *Fercha AZZEDINE*³

Abstract

Macrophyte pond has developed strongly in the field of wastewater treatment for irrigation in rural areas and small communities. Their association allows, in some cases, to increase the hydraulic capacity while maintaining the highest level of quality.

*The present work is devoted to the treatment of domestic wastewater under climatic conditions of Algeria (semi-arid) through a system using two tanks planted with *Salvinia natans*.*

The performance study and treatment efficiency of the system overall shows that the latter provides a significant removal of nitrogen pollution: total Kjeldahl nitrogen NTK (85.2%), Ammonium $\text{NH}_4^+\text{-N}$ (79%), Nitrite $\text{NO}_2^-\text{-N}$ (40%) also, a major meaningful reduction of biochemical oxygen demand BOD_5 was observed at the output of the system (96.9 %). As BOD_5 , the chemical oxygen demand (COD) removal was higher than 95 % at the exit of the two tanks.

A moderately low yield of phosphate-phosphorus ($\text{PO}_4^{3-}\text{-P}$) was achieved with values not exceeding 37 %. In general, the quality of treated effluent meets the Algerian standard of discharge and which allows us to select a suitable species in constructed wetland treatment systems under semi-arid climate.

Keywords: *Nutrient removal, *Salvinia natans*, semi-arid climate, Wastewater treatment*

1. INTRODUCTION

In most countries of the world, there has been growing and irreversible interest of the public for the protection of the environment. In Algeria, for instance, the water pollution problem is quite serious and therefore, purification techniques including constructed wetlands (CWs) using macrophytes are currently widely used for treatment of wastewater. CWs become an interesting alternative for the treatment of wastewater, seen the great benefits that they exhibit, they are less expensive to build and operate, are constructed directly on the wastewater discharge site, require little mechanized equipment and ultimately are less sensitive to changes in pollutant loads [1].

The main functions of CWs include surface water storage, holding and recycling nutrients, providing wildlife habitats, stabilizing shorelines, controlling and buffering storm related flooding, recharging groundwater, providing treatment for pollutants in water [2]. Furthermore, CWs can effectively remove organic matter, suspended solids, metals, and excess nutrients (such as nitrogen, phosphorus, etc.) through various processes including filtration, sedimentation, biological and microbiological adsorption, and assimilation [3].

^a Corresponding author: Department of Ecology and Environment, Faculty of Natural and Life Sciences, University of Batna2, Algeria. laabassiyache@gmail.com

Department of Ecology and Environment, Faculty of Natural and Life Sciences, University of Batna2, Algeria.
biologie-ecologie@hotmail.fr

² Laboratory of applied microbiology. Faculty of Natural and Life Sciences, University of Sétif 1, 19000 Algeria.

harzaldaoud@yahoo.co.uk

³ Department of Agronomy, Faculty of Natural and Life Sciences, University of Abbas Laghrour Khenchela Algeria.

ferchazzed@yahoo.fr

Macrophyte-based wetland systems (MBWS) are reported to be effective for the treatment of primary, secondary and tertiary urban wastewater, domestic, stormwater, agricultural and industrial wastewater [4, 2, 5], however, the challenge is to maximize efficiency the lowest possible cost [6]. The choice of plants is an important issue in the filters planted with macrophytes because they have to survive the potential toxic effects of sewage and their variability. The use of local plants with economic and environmental interests in the sewage system makes them more exciting.

Aquatic plants, emergent or free floating, acquire more and more importance in the world especially in countries with hot climates where the photosynthetic efficiency is important. The produced biomass is valued using biomethanation or by incorporation in animal nutrition [7]. Floating or emergent aquatic plants, such as water hyacinth (*Eichhornia crassipes* (Mart) Solms), water lettuce (*Pistia stratiotes* L.), *Salvinia natans* (L.), cattail (*Typha latifolia* L.), bulrush (*Scirpus validus* L.), are able to treat wastewater with high purification yields [8, 9, 10].

2. MATERIALS AND METHODS

2.1. Experimental device and methods

The experiment was carried out under semi-arid conditions at the town of Merouana (35°37'43''N, 05°54'42''E) located 500 km East of Algiers (Fig. 1), which has a semi-arid to arid Mediterranean climate with an average rainfall of about 240mm per year and an average temperature of about 5 to 38°C. The experimental device used for the present study depicted in Figure 2. Three biofiltration unit, comprised two tanks of 75 liters capacity (50 cm(L) x 50 cm(W) x 60 cm(H)). The tanks are filled to 5 cm in depth and 30 cm with respectively gravel (5-10mm) and soil with silty clay-sandy texture (31% clay, 20% silt and 49% sand). The tanks were planted with *S. natans* (36.5 g per tank).

The systems supplied by raw domestic wastewater (25 liters/day) acquired from Merouana municipal sewage treatment works, and Table 1 summarizes its physicochemical characteristics. Tanks inclined at 10° to the surface such that water can be directly downstream, and fitted with a drain at the bottom for percolating water collection (effluent). Wastewater passes from a tank to another through a 4-cm (outside diameter) perforated PVC pipe. The experiment lasted eight months from April to November 2015.

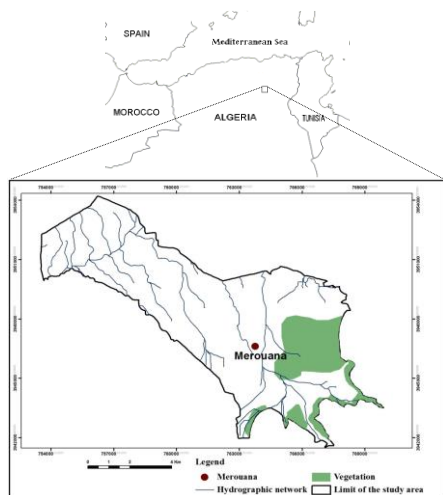


Figure 1. Location map of analyzed area.

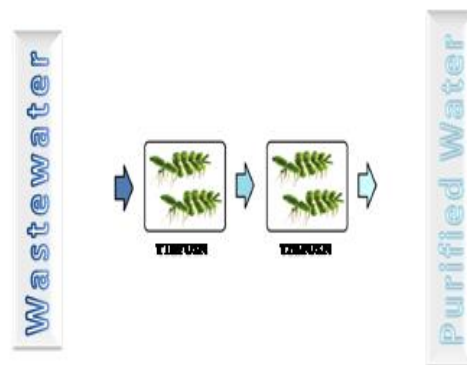


Figure 2. Macrophyte-biofiltration system used for wastewater treatment. T1 BFUSN, T2 BFUSN (Tanks 1 and 2 of second biofiltration unit planted with *Salvinia natans*).

2.2. Wastewater quality monitoring and statistical analyses

The CWs placed in operation in April 2015. Their removal efficiency and treatment performance evaluated in eight sampling campaigns, which took place in the eight-month period from April to November 2014.

Wastewater samples (influent and effluent) were collected and stored in glass bottles, transported to the laboratory and analyzed immediately for biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), nitrate-nitrogen (NO₃-N), nitrite-nitrogen (NO₂-N), ammonium-nitrogen (NH₄-N) and phosphate-phosphorus (PO₄-P) according to French standard methods [11]. In addition, measurement of temperature (T) and pH had done using a portable instrument (ProfiLine pH 3110, WTW). We used at least five repetitions of each sample to achieve sufficient accuracy.

Treatment efficiency of chemical parameters was calculated as the percentage of removal for N and P as follows:

Removal efficiency (%) = $\left(\frac{C_i - C_e}{C_i}\right) \times 100$, where C_i and C_e are the influent and effluent concentrations in mg/L.

Data analyzed using one-way ANOVA and least significant difference tests (LSD at $\alpha = 0.05$) to find differences among means of the different physicochemical parameters of wastewater before and after treatment. Statistical analyses carried out using STATGRAPHICS Centurion XV (Manugistics, Rockville, MD, USA)

3. RESULTS AND DISCUSSION

Constructed wetlands (CWs) using macrophytes are currently widely used for treatment of wastewater. In order to investigate whether the CWs using emergent macrophytes (EM) and floating macrophytes (FM) were effective for the treatment of domestic wastewater, we carried out the present study the aquatic plant species, namely *S. natans* an FM

Overall, our results indicate that the biofiltration system (FM) is highly effective in the treatment of domestic wastewater (Tables 1, 2 and Fig. 3a-i).

3.1. Mean physicochemical parameter variation

Table 1 summarizes results of the measured physicochemical proprieties of wastewater before and after biofiltration treatment. Figure 3, however, displays the seasonal variation of all these parameters throughout the eight-month period of experience. In contrast to the mean values of the wastewater temperature, which showed only slight spatial variations along the biofiltration unit and generally ranged from 18.2 to 24.6°C depending on the season (Fig. 3a), all the studied parameters were showed a significant variation after wastewater biofiltration (Table 1).

As revealed by Figure 3b, the mean pH value of input water used in this study was 7.2 and ranged from 7 to 7.5. However, at the outlet of biofiltration units, the pH values were ranging from 7.1 to 8.3. This decrease in pH values was statistically significant ($P < 0.01$).

In contrast to the slight decrease observed in the mean values of wastewater temperature at the outlet the biofiltration unit, can be explained by the fact that water surface was fully hedged by *S.natans* (Fig. 3a and Table 1), the mean values of pH were significantly increased (Table 1). Similar results observed in previous studies [12- 13]. Both decrease in temperature and increase in pH can be explained by the algal growth observed at the surface of each tank since foliar cover may preserves the tank surface against summer drying and offer shade to bacteria and the fact that algae can absorb CO₂ faster than it can be replaced by bacterial respiration [12].

3.2. Pollutant removal efficiency

Table 2 presents the variation of mean removal efficiency along the various biofiltration unit for all the pollutants. Overall, we calculate the removal for each constituent based on its concentrations at the inlet and outlet of the biofiltration unit. As displayed by Table 2, with the exception of nitrate (NO₃-N), the biofiltration system exhibited high percentages of removal efficiency of nitrogen from wastewater namely in term of NH₄-N, and TKN.

Regarding nitrogen pollution, our results indicate high average removal efficiencies of the biofiltration system, particularly for ammonium (NH₄-N) and TKN. Consistent with this, in aquatic ecosystems, the decrease in NH₄-N content was usually explained by the transformation of NH₄-N into NO₃-N (the so-called nitrification), which is favored by aerobic conditions, plus a subsequent denitrification [14]. Another possible way is volatilization as NH₃, which is inducible by the increase of pH [15]. Under natural growth conditions, NH₄-N is probably the main N source preferred for most aquatic macrophytes as revealed by results of numerous studies [16-17].

Table 1. Physicochemical parameter and pollutant concentration statistics

		INLET	OUTLET	F	LSD5%
			BFUSN		
pH	Mean	7.18 ^(c)	7.41 ^(bc)	5.50**	0.29
	SD	0.17	0.23		
	Min	7.0	7.1		
	Max	7.5	7.75		
T °C	Mean	21.13 ^(a)	19.94 ^(ab)	1.63 ^{n.s}	n.s
	SD	2.25	2.10		
	Min	18.2	17.3		
	Max	24.6	23.3		
NH₄-N	Mean	64.36 ^(a)	13.38 ^(bc)	264.3* **	5.51
	SD	8.46	2.29		
	Min	51.84	10.42		
	Max	76.18	16.46		
NO₃-N	Mean	2.43 ^(b)	3.61 ^(b)	25.77* **	10.11
	SD	0.93	2.32		
	Min	1.4	1.0		
	Max	3.9	6.9		
NO₂-N	Mean	0.128 ^(a)	0.083 ^(ab)	3.73*	0.056
	SD	0.05	0.06		
	Min	0.08	0.02		
	Max	0.20	0.22		
TKN	Mean	102.4 ^(a)	15.84 ^(b)	97.43* **	86.52
	SD	22.81	11.01		
	Min	69.6	6.40		
	Max	131.3	40.1		
PO₄-P	Mean	10.95 ^(a)	6.86 ^(b)	10.66* **	3.85
	SD	1.47	1.90		
	Min	8.9	5.1		
	Max	13.2	11.1		
BOD₅	Mean	311.3 ^(a)	8.31 ^(b)	43.7** *	302.07
	SD	129.7	3.65		
	Min	112.4	4.2		
	Max	466.1	15.5		
COD	Mean	981.7 ^(a)	40.56 ^(b)	209.08 ***	935.64
	SD	171.4	4.47		
	Min	683.5	33.2		
	Max	1230.1	47.1		

Table 2. Removal efficiency (%) of different nutrients for the three units

		BFUSN	F	LSD5%
NH₄-N	Mean	79.0 ^(a)	18.18***	3.45
NO₃-N	Mean	17.1 ^(a)	n.s	n.s
NO₂-N	Mean	40.0 ^(a)	n.s	n.s
TKN	Mean	85.2 ^(a)	4.32*	7.75
PO₄-N	Mean	36.9 ^(a)	n.s	n.s
BOD₅	Mean	96.9 ^(a)	n.s	n.s
COD	Mean	95.7 ^(a)	5.04*	1.25

*, **, *** indicate significant differences at P<0.05, 0.01 and 0.001 respectively. n.s, not significant. Different small letters mean significant differences (P < 0.05) among treatments.

The lower removal of $\text{NO}_3\text{-N}$ in the outlet water compared to wastewater, on some individual occasions, bear witness to the great nitrifying activity. In agreement, aquatic macrophytes have well-developed internal air spaces (aerenchyma) throughout the plant tissues that ensures the transfer of oxygen to the roots and rhizomes [18]. The oxygen that diffuses through the roots stimulates growth of nitrifying bacteria in the rhizosphere [19]. In general, the positive removal efficiencies of BFUSN can probably due to macrophytes uptake [20] and/or the process of denitrification [21].

Nitrite concentrations of the inflow and the outflow are of secondary importance for the evaluation of the overall annual nitrogen removal of the wetland [22]. In general, the low outflow concentrations ($< 1\text{mg/L}$) been brought about by nitrification of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ at aerobic plant roots, with subsequent rapid denitrification to the atmosphere in the anaerobic parts of the substrate or is immobilized by plant uptake, adsorption, and precipitation [23].

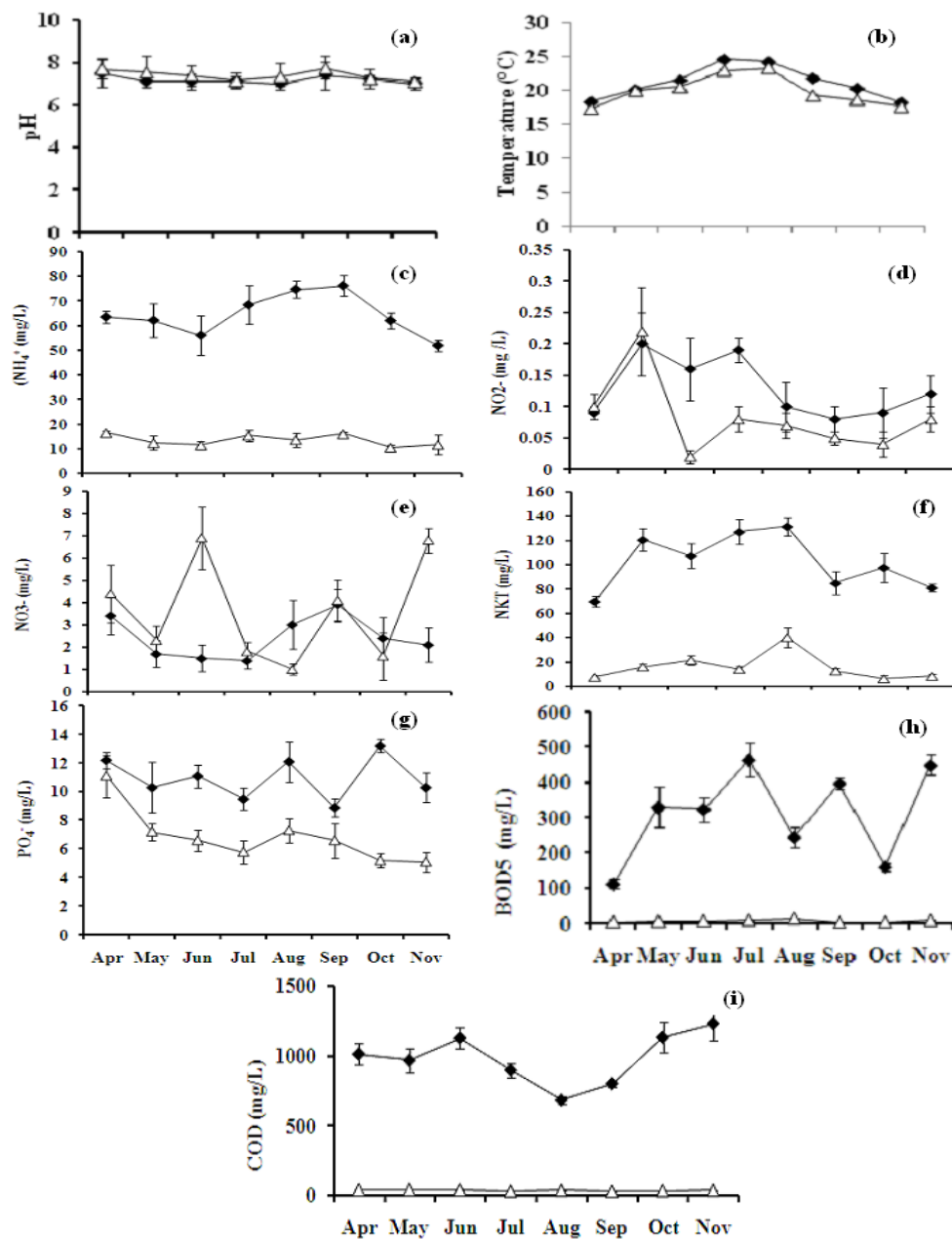


Figure 3. Time-course of change in Temperature (a), pH (b), $\text{NH}_4\text{-N}$ (c), $\text{NO}_2\text{-N}$ (d), $\text{NO}_3\text{-N}$ (e), TKN (f), $\text{PO}_4\text{-P}$ (g), BOD_5 (h), COD (i) throughout the period of study (Mean \pm SD).

The high levels of TKN removal efficiencies in all the treatments are probably due to macrophytes that play a major role in eliminating TKN through nitrification, metabolism, and storage processes [24, 25, 26]. TKN removal efficiency increases with increase in pH [27-28].

In addition, it appears from the same figure that the concentration of the main forms of nitrogen ($\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and TKN) and $\text{PO}_4\text{-P}$ as well as BOD_5 and COD in wastewater showed highly significant decreases ($P < 0.001$) after biofiltration (Table 1 and Fig. 3).

Table 2 also showed the variation in removal of orthophosphate from the wastewater in the various experimental devices. Overall, there is no significant difference in the removal efficiency of $\text{PO}_4\text{-P}$ among the biofiltration unit. The efficiencies of removal in BFUSN increase by 09-60.6% with an overall average of 36.9%. It is worth noting that even though $\text{PO}_4\text{-P}$ concentrations increased in the outlet waters on some individual occasions.

The moderately high level of phosphorus monitored as orthophosphate ($\text{PO}_4\text{-P}$) could be due to direct use of $\text{PO}_4\text{-P}$ by plants [29] or attributed to adsorption on the soil particles and precipitation reactions [30]. However, it also added that release of orthophosphate and clogging of the system could explain this low average reduction.

The average concentrations and overall efficiency elimination of BOD_5 in the influent and effluent throughout the study period displayed in Figure 3h and Table 2 respectively. The removal of BOD_5 found higher (96.9 %).

Otherwise, the higher reduction of BOD_5 can be attributed to several mechanisms (physical and biological processes) including sedimentation and filtration associated with settleable solids or filterable material, in addition to oxidation mainly by aerobic bacteria (protozoa, rotifers, etc.) attached to plant roots [31].

The load of domestic wastewater chemical oxygen demand (COD) fluctuates greatly between 683.5 mg/L and 1230.1 mg/L with a mean value of 981.7 mg/L. Thus, at the outlet of the three units follows fluctuations in domestic wastewater with significant picks (Fig. 3i). Overall, compared to domestic wastewater, the treated wastewater quality is significantly better. The removal rates of COD (95.7 %).

Like BOD_5 , COD reduction is almost entirely due to physical processes such as filtration and adsorption rather than biological processes associated with the microbial community or with the plants [32]. These findings are in agreement with some studies reported in the literature, which found better COD removal whether using floating macrophytes [33-28].

4. CONCLUSION

This work provides an opportunity to highlight the potential of floating plants (*S. natans*) to treat the domestic wastewater under semi-arid conditions. Overall, our result indicates that the biofiltration unit provide a significant removal of the organic (BOD_5 , COD) and inorganic (TKN, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$) pollutants from domestic wastewater. The effluent quality was lower than the Algerian standards related to effluent quality for agricultural reuse purposes, therefore, it is possible to reuse the treated wastewater for restricted irrigation and can be environmentally friendly. The good results given by *S. natans* (rare plant) involve its use in wastewater treatment in order to preserve this kind of plants. Finally, the use of this kind of biofiltration system for the treatment of other types of water pollution (e.g. microorganisms and heavy-metal pollution) is required.

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Estimating Willingness to Pay for Improved Domestic Water Services in Terengganu, Malaysia: A Comparison between Contingent Valuation and Choice Modelling Approaches

Mahirah KAMALUDIN¹, Kuna SANDRAN², Nor SHUHADA²

Abstract

Many environmental resources are characterized as public goods, such as water quality, biodiversity, and a stable climate. It is reasonable to question whether environmental resources are public goods in a fully pure sense. With low water quality, for example, those enjoying it may cause some degree of rivalry, when good water quality is not accessible to everyone. Unsustainable and excessive water consumption harms the environment by changing the water table and depleting ground water supplies. The objective of this study is to assess the willingness to pay of consumers in Terengganu for improvements in domestic water services. Excessive water consumption, frequent interruptions, urbanization, climate change, rapid social and economic growths are putting higher demands for quality of services and the water provider is unable to cope with the growing number of populations. Water price was last reviewed about 20 years ago and demonstrated among the lowest in Malaysia. This study has employed Contingent Valuation (CVM) and Choice Modelling (CM) methods to investigate water demand among the consumers, focusing on improvement in water services. This study found that consumers are ready and willing to pay for new proposed water prices as long as they are guaranteed with high standards in services. They are willing to pay about RM0.58 applied on the first 30m³ which is 11.53 percent higher than the current water price. Moreover, the findings have several implications for the water companies, by reducing the frequency of water interruption becomes the main concern of the consumers for a positive change in their water services. The estimated water prices can be suggested for implementation in the water industry which will support numerous upgrading projects for sustainable water supply for future generation. A sustainable water service is also helping the environmental, economic, and social sustainability of the communities with these utilities served.

Keywords: Economic Valuation; Contingent Valuation Method, Choice Modeling, willingness to pay, water service.

1. INTRODUCTION

Water is fundamental to life; however access to safe and clean drinking water is scarce nowadays. Water consumption has been growing at more than twice the rate of population increase. Moreover, many of the water systems that keep the ecosystems flourishing and feed the human population have become stressed. There is sufficient water on this planet for all but water is distributed unevenly and too much of it is wasted, polluted, and inefficiently used. In many parts of the world, the water resource is also unsustainably managed. At the global level, water providers and related authorities are facing pressure in water management. Population increases, changes in urbanization, and climate

¹ Corresponding author: School of Social and Economic Development, Universiti Malaysia Terengganu, Terengganu, Malaysia. mahirah.k@umt.edu.my

² School of Social and Economic Development, Universiti Malaysia Terengganu, Terengganu, Malaysia.

change force the providers to re-evaluate their policies and guidelines in water management. Basically good water management is tied to poverty reduction and improvement in health. Cheaper water prices may have burdened heavily on the producer's side, as it is too costly to upgrade their services. Cheap water price makes consumers take water for granted. Consumers believe that they can afford to pay the lower water price, thus they do not take any positive actions to conserve water. Lack of financial sources limits numerous projects while ignoring the consumer demand may create frustration at both sides; consumers and the producer. Previously, the events have demonstrated costly experiences because of frequent interruptions in services. Increasing water demand makes water supply insufficient to cater the whole population. Thus, new development and improvement in water services should be implemented without any delay in order to meet the increasing water demand.

The study investigates domestic water services in the state of Terengganu, Malaysia, using willingness to pay (WTP) approach. A survey was conducted to seek the value that people will place on water and their willingness to pay higher water rates for improved domestic water services. This study uses Contingent Valuation Method (CVM) and Choice Modelling (CM) methods to determine consumers' WTP and based on the WTP value obtained, the aggregate monetary benefits of improving water services for the consumers of Terengganu is estimated. The CM is able to determine marginal values and implicit prices for each attribute, which is related to the water services. This study includes a hypothetical change in the water services in the state from its current condition to improved conditions until the consumers believe it is at the acceptable level for their daily use.

1.1 Background of the Study

Sole water provider is Syarikat Air Terengganu Sdn. Bhd (SATU) operates in every district in the state. Their company's missions are to supply sufficient high quality of clean water and to improve the quality of services in order to fulfill consumer satisfaction. Their corporate visions are to support sustainable development, to concern and protect the environment, and to educate society about the importance of water conservation. Presently, water tariffs seem too cheap and the water provider is not able to generate enough revenue to cover the full cost of capital investment, operation and maintenance. In 2015, the state ranked second lowest in terms of domestic water prices in Malaysia about MYR0.52/USD0.13 applies for first 30m³. Low water prices will limit implementation of infrastructure projects to upgrade facilities and it implies a low value of water, though the sources are valuable and insufficient. There are many difficulties in pricing the water as water demonstrates as public good supply and this valuable resource does not have well defined market. Though, it is still very costly and involves high investment when it comes to supply the services to consumers. In 2012, the state was supplying water roughly 96% of the state's population. There are two main sources of water supply in Terengganu which are from river extraction and dams. About 440 million litres per day is direct extraction from river and 187 million litres per day is from storage dams in 2012 (Malaysian Water Association, 2013). SATU serves about 85.2% for domestic users and 14.8% for non-domestic users. Based on statistics from Malaysian Water Association (2013), it shows that about 99.1% in urban areas and 92.9% in rural areas get connected to water supply.

2. PREVIOUS STUDIES ON APPLICATION OF CHOICE MODELLING AND CONTINGENT VALUATION METHOD

CVM captures the estimation of WTP by asking people directly what they are willing to pay for goods or services in the future (Wedgwood and Sansom, 2003). Meanwhile, the strength of CM is that it can measure the trade-off based on the attributes that respondents are willing to make in order to decide the best preference in the selection of those attributes. The CM is able to assess the benefits transfer when environmental goods have measurable attributes, which can be estimated (Hanley et. al, 1998). The CVM and CM have been used to estimate economic values for all types of ecosystem and environmental services. These methods are broadly used in many environmental studies in order to value the quality of environmental sources.

A study conducted by Hanley et al., (1998) shows that there are many advantages of the CM method over the CVM method in estimation of economic values for conservation and claimed that the CM method is more suitable in the estimation of marginal values of the wildlife and landscape characteristics. Adamowicz et al., (1998) carried out a study to measure passive use values in an enhancement program and found that the CM method performs well compared to CVM method, and if error variance is put into consideration, the preferences over income between the two methods are insignificantly different. Jin et al., (2006) maintains that CM method has its advantages over the CVM method in the valuation of waste management programs and concluded that the CM method is better in understanding different management attributes which help to choose the solid waste management options in efficient ways. However, the CVM offers limited number of scenarios and usually involves only one or two scenarios (MacDonald et al., 2005). The CM approach concerns respondent preferences about the attributes of the scenario rather than the specific scenario (Adamowicz et al., 1998). The CVM is low in cost to implement and produces a single policy option, while the CM has the advantage since it produces a value function which can be used to estimate values with multiple policy options. The CM is preferred more than CVM because it is important to value individual attributes. The CM provides a wider

range of scenarios and organizes the experiment as a trade-off process between the attributes. Thus, it shows that CM is more cost-effective (Bennett and Blamey, 2001).

3. RESEARCH METHODOLOGY

In this study, survey was conducted on 1200 of household by using structured questionnaires designed to gather information for the CVM and CM approaches to determine willingness to pay for improved water services in Terengganu. A pre-test survey was conducted with 25 respondents in order to get realistic bid amount and to ascertain how significant the questions are. The pre-test was conducted for two times since in the first time of pre-test, the problem of yea-saying bias was occurred for CVM questions and there were not a consistent combination in attributes and their levels for CM questions. In final survey, respondents received a set of questionnaire with situations that ask how much they are willing to pay for improvements in the domestic water services. The amount that the respondents would be willing to pay depends on how strong they feel about the improvement in that program. The sampling consisted of domestic users of water supply in the state; who have registered active accounts with water provider. Besides, most of the respondents were the head of households since they are accountable for monthly water bill and we would like to know their contribution and WTP regarding to the services.

3.1 Contingent Valuation Method (CVM)

The CVM was proposed by Ciriacy Wantrup in 1947 and he believed that prevention of soil erosion will generate some extra market benefits. The one possible way to estimate these benefits is to elicit the individual's willingness to pay for these benefits through a survey method (Hanemann, 1994). In the CVM, only a price or bid is offered to respondents. The respondents are asked whether or not they would pay or accept a specific single amount for a program in question. The WTP question was, "Would you be willing to pay MYR X for an improvement in water services so that your households can enjoy high standard of services in the future?". When a respondent is asked to pay a specific amount of money or price bid due to an improvement in domestic water services in the state, there will be a probability to obtain "yes" or "no" answers. Thus, the model can be formulated following Hanemann *et al.* (1991) as follows;

$$\text{Prob} \{ \text{No} \} \Leftrightarrow \text{Prob} \{ \text{WTP}_{\max} < \text{BID} \} \Leftrightarrow G(\text{BID}; \theta) \quad (1)$$

$$\text{Prob} \{ \text{Yes} \} \Leftrightarrow \text{Prob} \{ \text{WTP}_{\max} > \text{BID} \} \Leftrightarrow 1 - G(\text{BID}; \theta) \quad (2)$$

where, BID is the proposed price bid, WTP_{\max} is the maximum willingness to pay (WTP) and $G(\text{BID}, \theta)$ is the cumulative distribution function (CDF) of WTP. This study uses CDF model to regress against the independent variables since the response variable is dichotomous, by taking 0 - 1 values (Gujarati, 2003). If the proposed price bid (BID) amount is more than the consumer's maximum willingness to pay, then they are not willing to pay for that amount. Conversely, if the bid is below their maximum willingness to pay amount, the probability of answering to that amount is "yes", showing that they will maximize utility and are willing to pay for that specific amount. The probability of the consumer willing to pay RM X is specified as follows according to Bishop and Heberlain's pioneering study, $G(\text{BID}; \theta)$ is the log-logistic cumulative density function:

$$\text{Pr}_i^Y = [1 + e^{(\alpha + \beta \text{BID})i}]^{-1} \equiv 1 - G(\text{BID}; \theta) \quad (3)$$

Then, by employing Hanemann's suggestions, the log-likelihood function for the CVM that has two parts for "yes" and "no" answers; which is given as follows:

$$\begin{aligned} \ln L^{\text{CVM}} &= \sum_{i=1}^N \{ c_i^Y \ln \text{Pr}_i^Y + c_i^N \ln \text{Pr}_i^N \} \\ &= \sum_{i=1}^N \{ c_i^Y \ln [1 - G(\text{BID}; \theta)] + c_i^N \ln G(\text{BID}; \theta) \} \end{aligned} \quad (4)$$

where c_i^Y takes a value of 1 if the i th consumer is willing to pay, answering "yes" to the initial bid and 0 otherwise, whereas c_i^N is 1 if the i th consumer states "no" and 0 if not. N is considered as consumers who participated in this study. The estimation of mean WTP can be derived based on Cameron (1988) as stated in the following equation:

$$\text{WTP} = \frac{b_0 + \sum_{i=2}^n b_i X}{-b_1} \quad (5)$$

where β_0 is the estimated constant, β_1 is the coefficient for the price bid, and β_i is a vector of coefficients for the socio-economic characteristics of the respondents.

3.2 Choice Modelling (CM)

CM is another stated preference technique that is frequently employed in estimation of values for environmental trade-offs (Bennet and Blamey, 2001). This method is based on the idea that a good can be depicted by its attributes and the levels that it takes. Respondents will be given a set of choices based on the attributes of the subject. Respondents are presented with different descriptions of the subject, differentiated in their attributes and their levels, and they are asked to rank, then rate or choose their most preferred option. The method has advantages since it offers a richer data set,

benefit transfer potential, context flexibility, strategic bias reduction and framing effect control (Do and Bennet, 2007). The results can be used to determine the amount of money that people are willing to pay to move on from *status quo* to improved situations which are defined by different combinations of attribute levels (Bennet and Blamey, 2001). The CM portrays a series of water service combinations and consists of water prices presented to respondents in order to observe their most preferred choices which they derive the greatest utility.

This study portrays the probability of consumer c choosing alternative i in the choice set. The random utility model is linked with the probability of consumer utility in choosing the best option in the choice set. The random utility model depends on characteristics of the alternatives, characteristics of the consumer who picks the choices, and the variables which are the combination of the alternatives. The model specifically demonstrates that the utility which a consumer c correlates with alternative i is stated as:

$$U_i^c = V_i^c + \varepsilon_i^c \quad (6)$$

The probability of consumer c in choosing alternative i can be indicated in parametric function as follows:

$$\text{Prob}_i^c = f(x_i^c, x_j^c; i \neq j, \beta) \quad (7)$$

Where,

Prob_i^c = Probability of consumer c in choosing alternative i

x_i^c = Parameter of observable characteristics of alternative i for consumer c

x_j^c = Parameter of observable characteristics of alternative j for consumer c .

McFadden (1974) as cited by Hanley *et al.* (1998) states that the analysis of CL model assumes that the random error terms are independently and identically distributed (IID) based on Gumbel distribution and follows extreme value Type 1. The probability of consumer c chooses the alternative i over alternative j with the presence of the random term can be written as follows:

$$\begin{aligned} \text{Prob}_i^c &= \text{Prob} \{ U_i^c > U_j^c \} && ; i \neq j \\ &= \text{Prob} \{ (V_i^c + \varepsilon_i^c) > (V_j^c + \varepsilon_j^c) \} && ; i \neq j \\ &= \text{Prob} \{ (V_i^c - V_j^c) > (\varepsilon_j^c - \varepsilon_i^c) \} && ; i \neq j \end{aligned} \quad (8)$$

It can be seen that the probability of the sum of random utility terms of alternative i is greater than the other random utility term of alternative j . This study assumes that the V_i^c shows a linear parameter and generalized specification of utility function can be shown as follows:

$$V_i^c = \beta_1 x_{i1}^c + \beta_2 x_{i2}^c + \beta_3 x_{i3}^c + \dots + \beta_n x_{in}^c \quad (9)$$

where β is vector of parameters to be estimated and x indicates a vector of all independent variables in the model.

$$\text{Prob}_i^c = \frac{\exp(\beta' \cdot v_i^c)}{\sum_j \exp(\beta' \cdot v_j^c)} \quad (10)$$

where, Prob_i^c demonstrates the probability of consumer c choosing alternative i and x_i^c and x_j^c are vectors expressing the attribute i and j . Based on Equation 9, the β coefficients indicate the taste of parameters which are attributes that directly affect utility. It can be used to estimate the marginal rate of substitution (MRS) or at which consumers are willing to trade-off between the attributes. The substitution rate can be estimated by dividing the β coefficient with another β coefficient (monetary attribute) and multiply it by -1 and the equation is as follows:

$$\rho_k^c = \frac{\beta_{\text{attribute}}}{\beta_{\text{price}}} \cdot x - 1 = - \frac{\beta_{\text{attribute}}}{\beta_{\text{price}}} \quad (11)$$

This study examines how much that households in Terengganu would be willing to pay for three key results of improvements in the services in order to measure the value that households place on water services. First, increasing water quality; second, reducing water supply disruptions; third, increasing water pressure. Better water quality, water supply and water pressure are not things that are bought and sold in the markets. Thus, specific non-market valuation techniques were used to estimate their value. The orthogonal design allowed generating 15 water service options.

Respondents were given with a number of choice card sets which described the three proposed improvements in water service policies. This study exhibits a range of impacts that these programs might have on the water quality, water disruptions and water pressure as in Table 1. The choice cards also listed the amount of money that the policy options would cost a household. Willingness to pay (WTP) can be indirectly estimated from the choices by including water price as one of the attributes in the study. The aim of this method is to increase the level of the attribute, for instance, water quality at QUAL1 (*status quo*) to improve level, QUAL2 or QUAL3.

Table 1. Water Service Attributes and their Levels

Attributes	Levels	Descriptions
Water Quality (QUAL)		Connection of water supply at homes with high quality, safe for direct human consumption, colourless, tasteless, odourless and comply with standard of drinking water quality.
QUAL1	Satisfactory	
QUAL2	Good	
QUAL3	Very Good	
Water Disruption (DIST)		Reducing the frequency of water supply disruptions at homes.
DIST1	Always	
DIST2	Sometimes	
DIST3	Never	
Water Pressure (PRES)		Condition of water pressure when the water gushes out from the tap water.
PRES1	Low	
PRES2	Moderate	
PRES3	High	
Water Price (PRICE)		Water price describes household monthly water bills charged by water provider; Syarikat Air Sdn. Bhd.
PRICE1	Current Price	
PRICE2	Low (Increases 28% from current price)	
PRICE3	Moderate (Increases 56% from current price)	
PRICE4	High (Increases 90% from current price)	

Table 2. Attributes and Expectation Sign

Attribute	Descriptions	Expectation Sign
Water quality	Connection of water supply at homes with high quality, safe for direct human consumption, colorless, tasteless, odorless and comply with standard of drinking water quality	Positive
Water disruption	Reducing the frequency of water supply disruptions at homes.	Positive
Water pressure	Condition of water pressure when the water gushes out from the tap water.	Positive
Water price	Water price refers to household monthly water bills charged by water provider; Syarikat Air Sdn. Bhd., presented as amount increase over the current bill.	Negative

4. RESULTS AND DISCUSSIONS

4.1 Socio Demographic Characteristics of the Respondents

Table 3 presents the results of the respondent demographic profiles. The majority of respondents were head of households with female (50.1%) and male (49.9%). The percentage for both genders was about the same. Majority of the respondent (34.5%) were between 41 and 50 years old where the mean for the age groups is 42 years old. The present study found that the participants mostly had university/college education (55%) as their highest education level, followed by secondary school (31%), primary school (12%) and no formal education (2%). The results are reported that average household monthly income was MYR4182.50. Household size ranged from 1 to 5 members, with a mean of 6 for the whole sample. A majority about 424 of respondents (35.3% from the sample) was government servants, respondents who are working at private sectors (20.1%), managing business (12.5%) and others (32.1%). Most of the respondents are about 94% had a job between 1 to 3 members in their family.

Table 3. Descriptive Statistics for respondents, n=1200

Demographic characteristics	Frequency	Percentage (%)	Mean	Std. deviation
Gender				
Male	599	49.9		
Female	601	50.1		
Age group (Years)				
20 – 30	207	17.4		
31 – 40	336	28		
41 – 50	413	34.5	42.13	11.42
51 – 60	185	15.4		
61 – 70	42	3.7		

> 70	17	1.6		
Education level				
University/college	662	55		
Secondary school	367	31		
Primary school	141	12		
No formal education	30	2		
Household income				
Less than RM2000	312	26		
RM2001 - RM4000	446	37		
RM4001 - RM6000	263	22	RM4182.50	RM4242.80
RM6001 - RM8000	102	9		
RM8001 - RM10,000	58	5		
More than RM10,000	19	2		
Size of household				
1 - 5	701	58.4		
6 - 10	471	39.3	6.444	3.069
> 10	28	2.4		
Head of household's occupation				
Government sector	424	35.3		
Private sector	241	20.1		
Businessman	150	12.5		
Others	385	32.1		

4.2 Determinants of Households' Willingness to pay for Water Services

4.2.2 Estimation of Contingent Valuation Method (CVM)

In CVM, this study offers 5 group different prices to different respondents. The prices are RM0.52, RM0.54, RM0.56, RM0.58 and RM0.60 in order to demonstrate diversifications in the price bids. About 97 of respondents are willing to pay RM0.60 which is the highest proposed price bid in this study. The probability of respondents state "Yes" is high when then proposed price bid is low as shown at proposed price bid RM0.52; about 149 of respondents accept the offer. According to Tietenberg (2000) the demand theory states the higher the prices of goods, the lower the quantity demanded of the goods.

Table 4. Logit Model (n=1200)

	Coefficient	t-value	Coefficient	t-value
	Preliminary Regression		Final Regression	
Constant	9.906	1.412***	9.650	1.380***
Price Bid	-17.282	2.285***	-17.192	2.278***
Income	0.000175	0.000034***	0.000179	0.000033***
Education	-0.188	0.076***	-0.185	0.067***
Job	0.040	0.064		
Home	-0.081	0.058		
Race	-0.497	0.228***	-0.485	0.226***
Household size	-0.045	0.027**	-0.043	0.027*
Age	0.011	0.006**	0.011	0.006**
Announcement	-0.406	0.144***	-0.346	0.131***
Experience	-0.086	0.130		
Report	0.111	0.139		
Consumer's awareness	0.534	0.137***	0.511	0.134***
-2 Log likelihood		1474.490		1478.085
Cox & Snell R Square		0.136		0.133
Nagelkerke R Square		0.182		0.178

Note: Significant level at 15% (*), 10% (**) and 5% (***).

The logit model presents that the log of the odds ratio is a linear function of independent variables. For this method, the data was analysed by using "Statistical Package for Social Science" (SPSS) Version 21 software. Table 4 demonstrates preliminary and final regression models to determine consumers' WTP in the study. According to these models, preliminary regression model includes all variables in first round and final regression is chosen statistically significant variables towards the dependent variable. In order to develop the best-estimated model, this study rejected the insignificant variables in preliminary regression such as job, home, experience and report water disruptions to water company. Price bid portrays a negative relationship towards consumers' WTP and significant at 5% level as $p < 0.05$ (Table 4). This shows as suggested water price increases, the probability of respondents stating "Yes" decreases. Based on Mezgebo *et al.*, (2013) the price bid (BID) has negative sign relates to economic theory; when the price rises, the willingness to pay for goods and services decreases. This study found that the respondents were concerned regarding to the amount that they were asked to pay for improving the services. Household income exhibits a positive sign with 5% significant level that shows as household income increases, consumer's WTP increases. As household income increases the probability of respondents to say "Yes" will increase too. This is because more people can afford and willing to pay for higher water bills for upgrading water services as they have ability to increase utility. The result also in line with previous studies by Carson *et al.*, (1994), Alias and Shazali (2005) and Mamat *et al.*, (2013) which also indicates a show a positive sign on income towards the WTP.

Besides, the level of education presents negative sign with WTP and significant at 5% level where the higher the level of education achievement, the lesser of consumers' willingness to pay for new increments in water price. This is because most of the households have low income and they are willing to pay but not as the suggested stated amount for improvements of water services in Terengganu. However, few studies prove this relationship is not important and does not give practical effect on willingness to pay (Ibrahim, 2012; Wang and Mullahy, 2006). Moreover, household size presents a negative relationship with WTP and significant at 0.15% level. The relation shows the more household members; then the lesser their willingness to pay for water bills as most of households from rural areas with low household income in this study. Previous studies by Mahirah and Khalid (2013) demonstrate that household size has a negative impact to WTP in which the households would reduce the WTP as their members become bigger. Age of respondents portray negative effect on WTP at 0.05 level of significant. This is because of elder people demanded more water than younger people. Normally most of elder people are more responsive to quality of the services at home. They are more involving in household chores and taking care of families' health. Besides, the result of announcement by water company regarding to the water supply disruptions bring negative impact towards households' WTP. Respondents should get a notice regarding to any disruptions of service in their area. This survey shows that most of the respondents are not been noticed about interruptions of services. Variable of "Awareness" exhibit a positive effect towards WTP and significant at 5% level. The variable explains that the respondents are alert that high expenses are needed to reduce Non Revenue Water (NRW) in water services. It can be seen that the respondents are aware that the expenses for to lessen the level of NRW are costly to be implemented. A study by Mezgebo *et al.*, (2013) states that a positive sign between households' awareness and WTP which have greater awareness about the availability of irrigation water and environment complications. Moreover, the calculated mean value based on Equation 12 is RM0.5772 applied on the first 30m³. The current water price is RM0.50m³ and it increases about 7.7%. Though the calculated mean water price is still below than national average price which is RM0.65 applied on the first 30m³.

4.2.2 Estimation of Choice Modelling (CM)

Estimation for CM was employed by using econometric software which is NLogit Version 5. A Conditional Logit model was applied in order to interpret the data collected through the CM. The dependent variable for this model was the choice of a water alternative whereas the independent variables were presented by the attributes of water services.

Table 5. Estimated Coefficients for Households' Willingness to Pay in Terengganu, Malaysia

Variables	Coefficient	t-value
Water Quality (QUAL)		
Good (QUAL2)	3.7682	7.190***
Very Good (QUAL3)	3.8076	7.573***
Water Disruption (DIST)		
Sometimes (DIST2)	4.0899	9.251***
Never (DIST3)	0.3394	3.984***
Water Pressure (PRES)		
Moderate (PRES2)	0.2881	2.100**
High (PRES3)	-2.9269	-11.384***
Water Price (PRICE)	-3.1706	-4.658***
Marginal Values of the Attributes: (β 's coefficients/- β 's price)		
Good (QUAL2)	1.18	12.636***
Very Good (QUAL3)	1.20	9.827***

Sometimes (DIST2)	1.29	9.133***
Never (DIST3)	0.11	6.556***
Moderate (PRES2)	0.09	1.932*
High (PRES3)	-0.92	-7.263***

Note: Significance level; (***)1% level, (**) 5% level, (*)10% level.

Based on Table 5, the overall coefficients and signs are as expected and present positive signs except for *High* (PRES3) in water pressure attribute. All coefficients for attribute levels are significant at the 1% level except for a *Moderate* (PRES2) water pressure which significant at 5% level. The result indicates that at highest level of the attribute (PRES3), it portrays a negative relationship towards dependent variable. Preferences of water quality attribute levels showed a similar pattern. The conditions of water quality such as colourless, tasteless and odourless are most favoured by respondents during the interview session. In terms of water disruptions, preferences in *Sometimes* and *Never* indicate that respondents prefer in lessening the frequency of water supply interruptions. For water pressure, both *Moderate* and *High* water pressure has an effects on willingness to pay for water services but in different signs. It shows that respondents more preferred *Moderate* water pressure compared to *High* water pressure. Probably due to 'High' water pressure can cause water leakage in plumbing and piping system; besides, the respondents do not expect the water services can improve to the highest level as the current situation of water pressure is too worsening. Table 5 presents an estimation of the WTP for every option for improving domestic water services. Hence, Marginal willingness to pay was used in order to estimate marginal values of the attributes for a change from current to alternative situation. It can be estimated as in Equation (11).

The result of marginal willingness to pay at level 'good to very good' for water quality attribute is at RM1.20. An improvement of services in terms of water disruptions from level of 'sometimes to never' is at RM0.11. These values illustrate how much respondents are willing to pay for any improvement in water services for each level. Meanwhile, the differences in marginal values in water pressure at level 'low to moderate' is at RM0.09 and level 'moderate to high' is at negative values RM0.92. 'Water pressure' attribute exhibits relatively low values compared to other attributes and it has a level incurred negative value. Surprisingly, most households concern about water disruptions at their homes as the attribute generates the highest willingness to pay which is RM1.29 compared than other attributes. The marginal rates of substitution of water disruption attribute in Level 2 (Sometimes) is highest which is presenting consumers are willing to pay for water disruption improvements. Though, the main problem in the service is water pressure as the demand is very high in the state has 12 water plants which is need to cater for 1.15 million of population in Terengganu. Similarly, Mahirah *et al.*, (2006) found that respondents choose to improve water interruptions to reduce the frequency of disruptions in Kelantan from moderate level to high level (less water service disruptions) as it generates the highest marginal values based on the CM model.

4. CONCLUSION

The finding demonstrates that the CM has a greater capacity to describe selected choices by consumers. The evidence from this study finds that the CVM method is described by just one variable which is the bid price and socioeconomic parameters. Conversely, the CM method is explained according to many attributes or characteristics. Hence, it is able to measure the welfare benefits of any number of different programs by varying the attribute levels for further consideration in the policy review. In CVM method we obtained only the value of the estimated WTP which is RM0.57 applied on the first 30 m³. However, in CM method we can get numerous individual marginal values based on their attribute levels which are selected by respondents. Comparing those methods will produce different results and with different aspects too. This study presents that the aspect of level of water service disruption is most concerned by the respondents since it produce the highest marginal willingness to pay among others attributes. Water provider in the state should be taken into account the efficient and equitable allocation of water to urban and rural consumers. The survey was conducted in the state shows that households are not happy with the current level of water services, particularly in terms of water pressure. Better water pricing is needed in order to implement various programs in the services. Water prices should reflect the cost of water production in order to promote market efficiency. Although the government fails to protect the consumers and sometimes it harms others, controlling the prices can avoid the pressure of price increases. If the water price is increased, it can lessen the financial burden of water companies by providing needed funds for further improvement in infrastructure, upgrade services and financial development. Revising prices can help the water companies to reduce cost somewhat but they still have to operate until the optimum production is achieved. For the time being, consumers feel that the water is too cheap and this leads to water wastage and excessive water consumption. By increasing the prices the public will be aware to conserve water and avoid water wastage. Besides, the public must be educated based on the needs, benefits, problems and responsibilities surrounding water

conservation. Without changes in water consumption in the next several years, the most precious natural resource diminishes and the world becomes less inviting and self-sustaining.

BIOGRAPHY

Mahirah is a senior lecturer at Economics Department and an associate fellowship of Institute of Oceanography and Environment (INOS), University Malaysia Terengganu, Malaysia. Her expertise is in economic valuation and environmental economics.

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Evaluation of air quality in the city of Istanbul during the years 2013 and 2015

Ayşe Emel ONAL^{1*}, Osman Faruk BAYRAMLAR¹, Elif EZIRMIK¹, Bugra Taygun GULLE¹, Fatma CANATAR¹, Dilan CALIK¹, Dilber DERYOL NACAR¹, Leyla Evin AYDIN¹, Ahmet BARAN¹, Zeynep KIRDI HARBAWI¹

Abstract

Air pollution has been the most important health issue in recent years. In this study, the aim was to evaluate the results of regular measurements of air pollutants PM10 and SO₂ concentrations in the city of Istanbul by taking the years 2013 and 2015 as a sample. The data were obtained through the website <http://www.havaizleme.gov.tr>, which was published by the Administration of Marmara Clean Air Center of Ministry of Environment and Urbanization in Turkey. For the years 2013 and 2015, the mean SO₂ concentration was 8.35±6.04 and 10.60±7.16 µg/m³. The mean PM10 concentration was 73.06±30.63 µg/m³ for 2013 and 51.57±18.84 µg/m³ for 2015. The acceptable upper limit values by WHO (World Health Organization) for daily mean SO₂ and PM10 concentrations respectively are 20 µg/m³ and 50 µg/m³. In Istanbul, SO₂ concentrations were above the upper limit values recommended by WHO but, PM10 concentrations during 2013 and 2015 were over the recommended limit values by WHO. As the particulate matter pollution is high concentrations during these two years, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

Keywords: Istanbul, Air Pollution, PM10, SO₂

1. INTRODUCTION

Air is one of the most indispensable and essential substance for human life. A human-being can survive only for up to 4 minutes without breathing air. Clean air consists of 78% nitrogen (N₂), 20% oxygen (O₂), 0.9% argon (Ar), 0.04% carbon dioxide (CO₂) and very small amounts of neon (Ne), methane (CH₄), helium (He), hydrogen (H₂), krypton (Kr). About 0.25% of the atmospheric mass is water vapor. Today, pollutants originating mainly from heating, industry and traffic disrupt air quality and so cause air pollution.

Air pollution has been the most important health issue in recent years. EPA (Environmental Protection Agency) determined 6 criteria air pollutants for outdoor air. These pollutants are particulate matter of 10 microns in diameter (PM10), carbon monoxide (CO), lead (Pb), sulfur dioxide (SO₂), nitrogen dioxide (NO₂) and ozone (O₃) (1). Nowadays, it is well-known fact that these pollutants increase the incidence of asthma and chronic obstructive pulmonary disease (2-4).

^{1*} Corresponding Author: Prof. Ayşe Emel Onal, M.D., Istanbul University, Istanbul Medical Faculty, Department of Public Health, Istanbul, Turkey, onale@istanbul.edu.tr

In addition, myocardial infarction, angina pectoris, hypertension among cardiovascular diseases, also cerebrovascular diseases and associated paralyses have increased due to air pollution (5, 6). Air pollution leads to damages in the nervous system and so causes headache and anxiety; moreover, air pollution is held responsible for the increase in some neurological diseases such as Alzheimer's and Parkinson's diseases. Air pollution has unfavorable effects on fertility and child's health, too. It gives rise to low birth weight and premature birth (7). Besides, air pollution has been held responsible for the etiology of some cancers like breast and prostate cancer, which have been increasingly incident over the recent years (8).

Air pollution affects the environment, human health and thus life negatively. Climate change, depletion of the ozone layer and acid rains stems from air pollution. For this reason, air pollution must be monitored with Air Quality Index (AQI). This

index, which was identified by Environmental Protection Agency (EPA), has been adapted and used as “National Air Quality Index” for Turkey. Air quality index is calculated for five main pollutants. These pollutants are particulate matter of 10 microns in diameter (PM10), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen dioxide (NO₂) and ozone (O₃). The Air Quality Index is calculated by using these five parameters and this index is expressed in colors: We refer the values between 0-50 green as “good”; between 51-100 yellow as “moderate”; between 101-150 orange as “sensitive”; between 151-200 red as “unhealthy”. The values between 201-300 are referred as “bad” (purple), whereas the ones between 301-500 are considered “dangerous” (brown) (9). These pollutants are measured daily at monitoring stations and their concentrations are published at the website of Turkish Ministry of Environment and Urbanization (10). But, to make comments on results and so to benefit from them in the field of health require knowing this basic information.

In Turkey, the Ministry of Environment and Urbanization have measured all the criteria air pollutants except lead (Pb) daily in each city and in each district up to today since 2005. In Istanbul, there are 31 Air Quality Monitoring Stations at 39 districts; at some districts, more than one monitoring stations exist. Yet, there are losses at some parameters for several districts. The parameters, which are obtained most regularly, are PM10 and SO₂. In this study, our aim was to evaluate the measurement results of PM10 and SO₂ concentrations, which are regularly measured pollutants in the city of Istanbul, by sampling from the years 2013 and 2015.

2.MATERIALS AND METHODS

Between the years 2013 and 2015, the air quality was audited by the Administration of Marmara Clean Air Center (MTHM). The data of Istanbul were obtained through the website <http://www.havaizleme.gov.tr>, which was published by the Administration of Marmara Clean Air Center. The acceptable upper limits by WHO (World Health Organization) for daily average, for SO₂ and PM10 respectively are 20 µg/m³ and 50 µg/m³ (11). For evaluation, the months of January, April, June and September in 2013 and 2015 were chosen since these are the months that the data were either complete or included the highest numbers of days with measurement.

Among the data of these months, the measurement results of PM10 and SO₂ were entered into SPSS 21.0 software package and then evaluated as mean, standard deviation. The monthly mean values with each other for the same year and with the other year’s equivalent monthly mean values were compared statistically. The suitability of variables for the normal distribution was examined by Kolmogorov-Smirnov Test. For the variables, which are distributed normally, Independent Samples t Test was used. For the statistical comparison of the means of more than two groups, One-Way ANOVA Test was used.

3.RESULTS AND DISCUSSION

For the years 2013 and 2015, the mean SO₂ concentration was 8,35±6,04 µg/m³ and 10,60±7,16 µg/m³. The mean PM10 concentration was 73,06±30,63 µg/m³ for 2013 and 51,57±18,84 µg/m³ for 2015. The mean concentration of PM10 was above the recommended limit values determined by WHO for both years.

For the city of Istanbul, the measurement results of mean SO₂ and PM10 concentrations in January 2013 and January 2015 was shown in Table 1, whereas the ones in April for the same years in Table 2, the ones in June for the same years in Table 3 and the ones in September for the same years in Table 4 can be seen.

Table 1- The measurement results of SO₂ and PM10 concentrations among air quality criteria pollutants in Istanbul in January 2013 and January 2015 (µg/m³).

	n	Minimum	Maximum	Mean	Std. Deviation
SO ₂ (2013)	31	2.0	28.0	7.32	5.71
PM10 (2013)	31	5.0	138.0	61.90	35.70
SO ₂ (2015)	31	6.0	51.0	16.94	9.84
PM10 (2015)	29	25.0	104.0	53.38	23.95

Table 2- The measurement results of SO₂ and PM₁₀ concentrations among air quality criteria pollutants in Istanbul in April 2013 and April 2015 (µg/m³).

	n	Minimum	Maximum	Mean	Std. Deviation
SO ₂ (2013)	30	8.0	27.0	15.10	5.02
PM ₁₀ (2013)	30	29.0	189.0	86.63	37.41
SO ₂ (2015)	30	3.0	15.0	7.43	2.76
PM ₁₀ (2015)	28	18.0	67.0	38.86	15.93

Table 3- The measurement results of SO₂ and PM₁₀ concentrations among air quality criteria pollutants in Istanbul in June 2013 and June 2015 (µg/m³).

	n	Minimum	Maximum	Mean	Std. Deviation
SO ₂ (2013)	30	1.0	16.0	7.70	4.00
PM ₁₀ (2013)	27	40.0	139.0	73.26	24.19
SO ₂ (2015)	30	5.0	23.0	12.17	3.71
PM ₁₀ (2015)	30	33.0	76.0	55.70	12.45

Table 4- The measurement results of SO₂ and PM₁₀ concentrations among air quality criteria pollutants in Istanbul in September 2013 and September 2015 (µg/m³).

	n	Minimum	Maximum	Mean	Std. Deviation
SO ₂ (2013)	30	2.0	6.0	3.30	0.84
PM ₁₀ (2013)	30	50.0	105.0	70.83	14.67
SO ₂ (2015)	27	2.0	9.0	5.11	1.34
PM ₁₀ (2015)	27	26.0	91.0	58.22	15.68

Except the mean PM₁₀ concentration during April 2015, all of its concentrations were above the upper limit values recommended by WHO; whereas the mean SO₂ concentrations were under the upper limit values recommended by WHO throughout all of these months within these two years. Among the chosen months, SO₂ concentration was detected as the highest in 2013 during April and in 2015 during January; on the other hand, PM₁₀ concentration was detected as the highest in 2013 during April and the highest in 2015 during September.

Table 5- The comparison of mean concentration of SO₂ measurements for the year 2013 during January, April, June and September by One Way ANOVA Test.

SO ₂	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2177.4	3	725.78	38.703	.000
Within Groups	2194.1	117	18.75		
Total	4371.4	120			

Table 5 shows the statistical comparison of mean concentration of SO₂ measurements during the four months observed for the year 2013 by One -Way ANOVA Test. Among the four months' means, there is a statistical significance at high level. The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by using One-Way ANOVA Test can be seen in Table 6. It was detected that the measurements of mean PM10 concentrations showed a statistical significance between different months.

Table 6- The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by One Way ANOVA Test.

PM10	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9535.6	3	3178.52	3.614	.015
Within Groups	100253.0	114	879.41		
Total	109788.6	117			

The statistical comparison of mean concentration of SO₂ measurements for the year 2015 during January, April, June and September by using One Way ANOVA Test can be seen in Table 7; there is a statistical significance at high level among the means. The statistical comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by using One Way ANOVA Test was shown in Table 8; there exists a statistical significance at high level among the means.

Table 7- The comparison of mean concentration of SO₂ measurements for the year 2015 during January, April, June and September by One Way ANOVA Test.

SO ₂	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2432.2	3	810.74	25.889	.000
Within Groups	3570.1	114	31.32		
Total	6002.3	117			

Table 8- The comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by One Way ANOVA Test.

PM 10	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6326.7	3	2108.91	6.863	.000
Within Groups	33801.2	110	307.28		
Total	40127.9	113			

Taking the results in January and September as one group called “cold seasons” and the results in April and June as another group called “hot seasons”, for SO₂ concentration, a statistical significance at high level was detected in 2013 between both seasons (t:-6.361; p:0.000); on the contrary, the same statistical difference wasn't detected for the year 2015 (t:1.239; p:0.218). For PM10 concentration, these values were calculated as (t:-2.539; p:0.012) for the year 2013 and (t:2.353; p:0.020) for the year 2015. There was a statistical significance between summer and winter seasons in terms of air pollution. In winter, the level of air pollution was more severe than summer. PM10 seemed to play an important role in air pollution. When PM10 and SO₂ results were compared according to the districts, Uskudar was ranked first among the districts with the highest mean PM10 concentration measured 89.57±64.48 µg/m³. The district of Uskudar was followed by Aksaray (62.80±28.66 µg/m³), Maslak (59.89±37.93 µg/m³) and Alibeykoy (54.68 ±28.36 µg/m³). As seen among SO₂ measurements, it was detected that mean SO₂ measurements were even above the WHO recommended limit values in Uskudar (55.91±28.19 µg/m³) and in Sultanbeyli (42.87±29.60 µg/m³); on the other hand, the mean SO₂ measurements were under the limit values in other districts.

According to European Environment Agency (EEA)'s data, 97.2% of the urban population in Turkey has been exposed to PM10 at unhealthy levels (12). Air pollution within cities is also known to have negative effects on health (13). Among different Turkish cities, there are limited number of studies indicating the status of air pollution. The annual mean PM10 concentrations recommended are 58 µg/m³ in Turkey, 40 µg/m³ in European Union (EU) and 20 µg/m³ by WHO. According to WHO's data, the annual mean PM10 concentrations between the years 2008-2015 are 85 µg/m³ for the world, 235 µg/m³ for Eastern Mediterranean countries with high income, 158 µg/m³ for Eastern Mediterranean countries with low income, 123 µg/m³ for Southeastern Asia, 119 µg/m³ for Africa and 104 µg/m³ for Western Pacific Mediterranean countries with low-middle income. This value for European countries with low-middle income is 55 µg/m³, thus the city of Istanbul is shown as “moderately polluted” on WHO's maps in terms of air quality (Air Quality Index – Yellow: Between 51-100). Eastern Mediterranean and Southeastern Anatolian cities of Turkey are demonstrated as “sensitive” (Air Quality Index – Orange: Between 101-150) (14). In this study, the levels of PM10 concentrations were found to be above the recommended limit values by WHO in Istanbul during the years 2013 and 2015. No research made in Istanbul about this subject was found during literature survey. In a doctoral thesis research conducted in Kırklareli, air pollution and meteorological parameters were detected to increase the number of hospital admissions due to cardiovascular and respiratory diseases (15). In a study conducted in Duzce, the annual mean PM10 concentration was found to be 106.42±102 µg/m³, whereas the annual mean SO₂ concentration was found to be 6.15±5.39 µg/m³ (16). Air pollution occurs due to local, regional and global problems. Therefore, it is possible to take measures with multidimensional studies. Industrial activities, increased level of traffic, destruction of forests, combustion of biomass and continuous energy production trigger climate change and as a result of this situation, natural disasters like sea level rise, floods, hurricanes, drought may emerge. In each country, a national air quality monitoring network should be established as it is in Turkey. So as to reduce air pollution, as society, we should use public transport, use energy-efficient appliances and energy-saving light bulbs, use clean energy such as wind, geothermal and solar energy and also organize public education on these issues.

4 CONCLUSIONS

In conclusion, the lower levels of air pollution during the summer months give rise to thought that the level of heating-based pollutants decrease and the traffic reduces relatively in the city of Istanbul during the summer months. As the particulate matter pollution is within high concentrations during these two years and throughout all the seasons, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

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Kinetics of Granulated Waste Tyre Pyrolysis via Thermogravimetry and Model-free Methods

Peter T. CHEROP^{1*}, Sammy L. KIAMBI¹, Paul MUSONGE¹

Abstract

There has been an increase in global consumption of waste tyres over the years. However only a portion of the total amount of waste tyres can be recycled or reused for other applications. Land-filling has been considered an alternative to address the problem of continued waste tyres accumulation, but huge space is needed for this and the reusable resources are wasted. This therefore has led to environmental and economic problem of disposal of the large mass of waste tyres. Waste tyre pyrolysis, which is the thermal decomposition in absence of oxygen, can be used to recover both energy and material. Thermogravimetric analysis (TGA) is the technique commonly used to evaluate the weight loss kinetics associated with the vaporisation of materials during pyrolysis. The purpose of this study was to establish the kinetics of thermal degradation of waste tyres by TGA and to compare the activation energies (E) obtained using two model-free methods. The experiments were carried out in a nitrogen environment and a temperature range of 20°C to 600°C at three heating rates. Results show that the pyrolysis process of the tyre crumb occurs in three stages as the various components of the tyre undergo decomposition. A mean activation energy of approximately 232 kJmol⁻¹ was obtained using the two models.

Keywords: Waste tyre, Activation energy, Thermal degradation, Model-free.

1. INTRODUCTION

The amount of waste tyres dumped all over the world is roughly 1.5 billion [1], but only 15-20 % is reused whereas the remaining percentage is simply dumped into the earth [2]. The valorisation of waste plastics and tyres plays a big role in the reduction in fossil fuel consumption and helps to address the issue of climate change [3]. Due to the high calorific value of waste tyres (33-35 MJkg⁻¹), recovery of energy is considered an alternative to recycle them [4]. Pyrolysis, which is the process of thermal degradation in absence of oxygen, can be potentially involved to recover energy from waste tyres. During pyrolysis, the organic volatile matter in the tyres is transformed into low-molecular weight products, whereas the inorganic constituents, are retained as solid residue [5].

Tyres are made up of more than 100 different substances such as rubber, steel, silica gel, carbon black etc. During tyre production, the rubbers commonly used are natural rubber (NR), butadiene rubber (BR,) and styrene-butadiene rubber (SBR). The degradation of these components occurs at different temperature ranges. The thermal degradation behaviour of waste tyres depends on the type of rubber as well as its contents [6, 7].

The study of kinetics of waste tyre pyrolysis has recently been an area of interest since understanding of kinetics of this process is important in the design and optimisation of industrial scale waste tyre recycling units. Model-free and model-fitting methods are commonly used to determine the kinetic parameters during solids decomposition [8-10].

The following expression is commonly used for thermal degradation of solids:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \quad (1)$$

where α is the degree of conversion, $k(T)$ the reaction rate constant, and $\frac{d\alpha}{dt}$ the conversion rate over time. The conversion degree, α is determined as:

^{1*}Corresponding author: Durban University of Technology, Department of Chemical Engineering, P.O Box 1334, Durban 4000, South Africa.: tumwet2@gmail.com

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (2)$$

where w_0 is the initial weight of the sample, w_t the weight of the sample at a given temperature, and w_f the final mass of the sample. $k(T)$ is expressed according to Arrhenius law as :

$$k(T) = A \cdot \exp \frac{E}{RT} \quad (3)$$

where E is the activation energy, R the gas constant, and A the pre-exponential factor. Combining equations (1) and (3) yields:

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E_a}{RT}} \cdot f(\alpha) \quad (4)$$

Equation (5) is the underlying equation used in determination of kinetic parameters in non-isothermal degradation of solid materials.

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \cdot \int_{T_0}^T e^{-\frac{E}{RT}} dT \quad (5)$$

where $g(\alpha)$ is the conversion integral function.

The Friedman (FR) method [11] is one of the iso-conversional methods used to calculate the activation energy. The expression for FR equation is:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln \left[\beta \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right] = \ln(A_\alpha) + \ln[f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (6)$$

where E_α and A_α represent the activation energy and pre-exponential factor at a specific conversion degree respectively. The slope in the plot of $\ln \left[\beta \left(\frac{d\alpha}{dT} \right)_{\alpha,i} \right]$ against $\frac{1}{T_i}$ yields the activation energy. The Kissinger-Akahira-Sunose (KAS) method [12, 13] is expressed as follows:

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{A E_a}{R g(\alpha)} \right) - \frac{E_a}{RT} \quad (7)$$

where the plot of $\ln \left(\frac{\beta}{T^2} \right)$ versus $\frac{1}{T}$ gives a straight line. The slope from this plot is then used to determine the E

The aim of this study was to establish the non-isothermal kinetics of pyrolysis of waste tyres by applying two model-free methods to the TG/DTG data in order to determine the activation energies. The models used were KAS and FR.

2. MATERIALS AND METHODS

Tyre crumb from Mathe group, South Africa was used during this study. The elemental analysis of the tyre crumb was done using vario EL cube elemental analyser, while the thermogravimetric analysis was carried out in a Differential Scanning Calorimeter – Thermo Gravimetric Analyser SDT Q600. The tyre crumb samples were heated from 20°C to 600°C at three different heating rates in nitrogen (100 mLmin⁻¹) environment to prevent oxidation of the samples. Three heating rates of 2°C, 5°C, and 10°C min⁻¹ were used to establish the behaviour of thermal degradation of the tyre crumb, while the TA Instruments software was used to extract the data that aided to plot the TG and DTG curves.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

The elemental analysis results showed that the carbon content in the tyre crumb was 83.54 wt. % while the hydrogen content was 7.55 wt.%. The contents of nitrogen and sulphur were 0.35 wt.% and 1.84 wt.% respectively whereas the oxygen content (calculated by difference) was 6.73 wt.%.

3.2. Thermal Degradation of the Tyre Crumb

The TG/DTG thermograms of the tyre crumb thermal degradation for the heating rates of 2, 5 °C, and 10 °C min⁻¹ are shown in Figures 1,2, and 3 respectively.

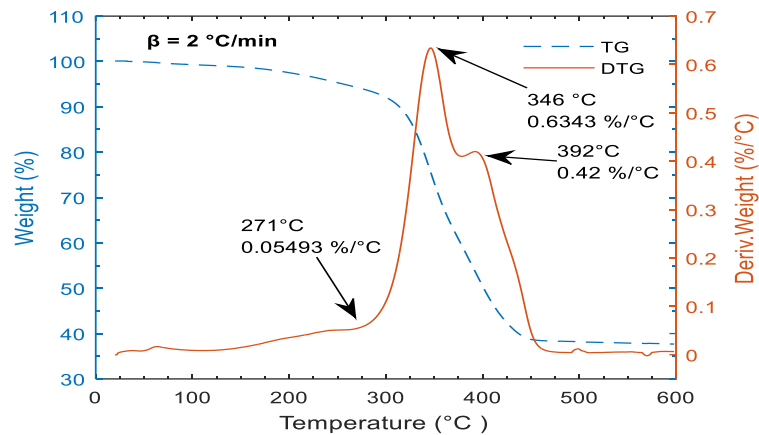


Figure 8. TG/DTG thermogram at 2 °C/min

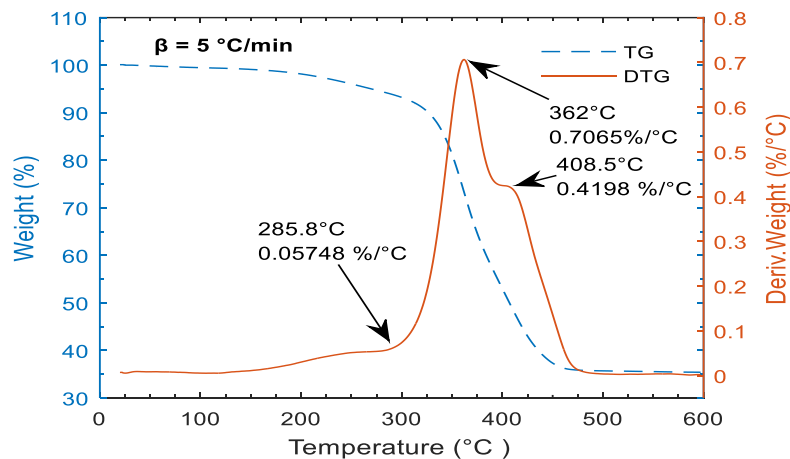


Figure 9. TG/DTG thermogram at 5 °C/min

The thermal decomposition started at about 270 °C and 285 °C and was complete at about 460 °C and 480 °C for the heating rates of 2 and 5 °C min⁻¹ respectively. At the heating rate of 10 °C min⁻¹, the decomposition started at about 290 °C and was complete at about 495 °C. There was no further weight loss above the temperature of 500 °C for the three heating rates. Three stages of decomposition are notable from the peaks seen in the DTG curves i.e. removal of lubricants and oil in the waste tyre with a mean temperature peak value of about $T_m = 285$ °C, breakdown of NR with $T_m = 367$ °C and breakdown of BR and SBR with $T_m = 411.0$ °C. The TG/DTG thermograms indicate that the temperature peaks increase as the heating rates increase during the three-stage thermal degradation process.

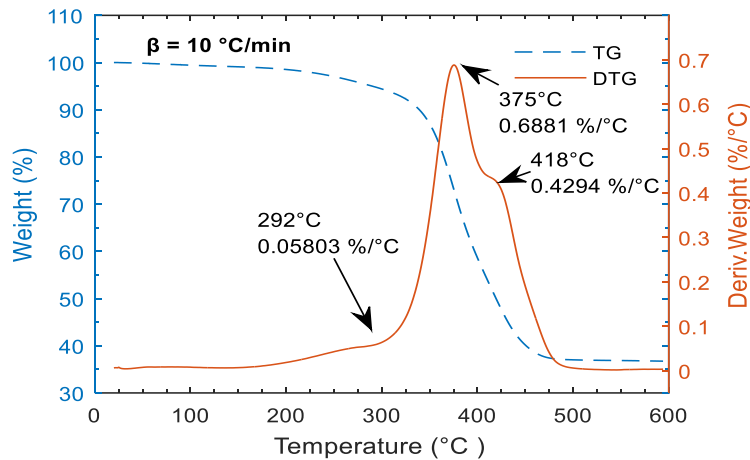


Figure 10. TG/DTG thermogram at 10 °C/min

3.3 Non-isothermal Kinetics of Tyre Degradation

The KAS and FR models were used to determine the activation energies. The two models aided to establish the relationship between the conversion degree and the activation energies. Using KAS model, the plot of $\ln\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ gave a slope of $-\frac{E}{R}$, from which the activation energy was determined while the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ was used to determine the activation energies by the FR model. The kinetic plots of tyre crumb thermal degradation using the two models are shown in Figures 4 and 5.

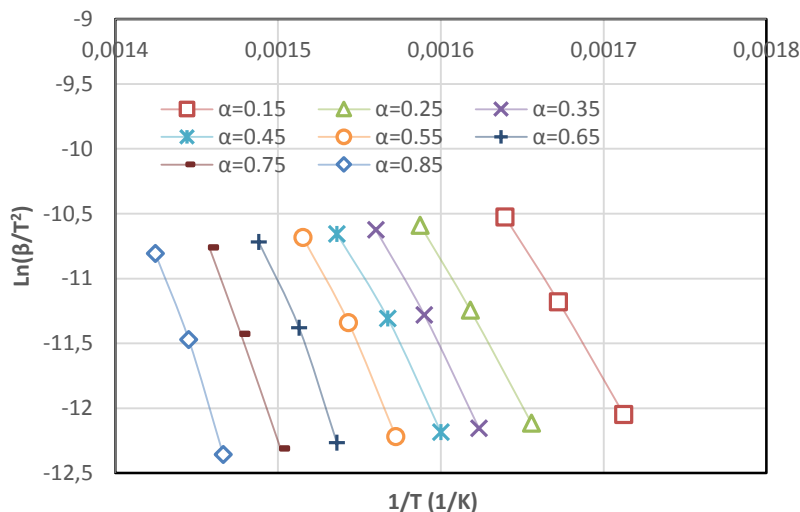


Figure 11. KAS plot at various conversion degrees

The degrees of conversion considered using the KAS and FR models ranged between 0.15 - 0.85. Figure 6 shows the variation of activation energy with conversion degree for the two models. The relationship between the activation energies obtained from KAS and FR models at same conversion degrees is shown in Figure 7. In both models, the activation energy increases with conversion degree up to $\alpha = 0.45$ where the activation energy drops (Figure 6). The trend of increasing activation energy with conversion degree then continues without any further fluctuation. The mean activation energies obtained using KAS and FR models were $231.76 \text{ kJmol}^{-1}$ and $231.92 \text{ kJmol}^{-1}$ respectively. This clearly shows that the values obtained from the two models are similar and it indicates that the models used can accurately predict the non-isothermal thermal degradation of the tyre crumb. The similarity in E values from KAS and

FR models is further justified by the linear relationship (Figure 7) between the E values from the two methods. The regression coefficient values obtained from the plots using the two models were high. The lowest R^2 values using the KAS and FR methods were 0.9895 and 0.9903 respectively while the highest values were 0.9998 and 0.9999. This indicates the thermogravimetric data fit well into the models used.

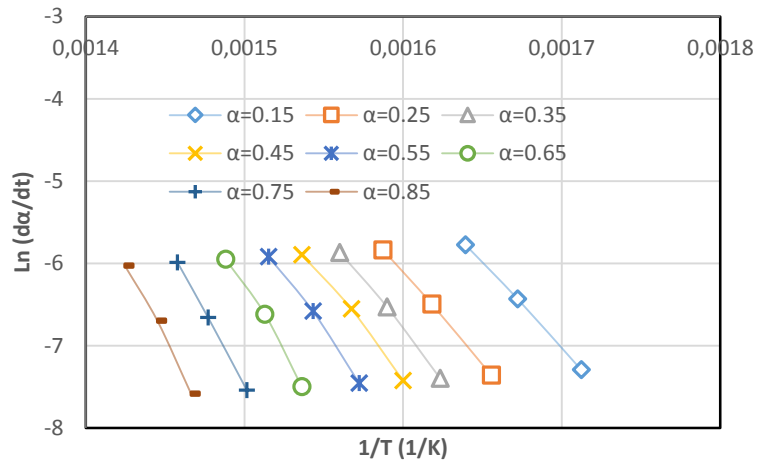


Figure 12. FR plot at various conversion degrees

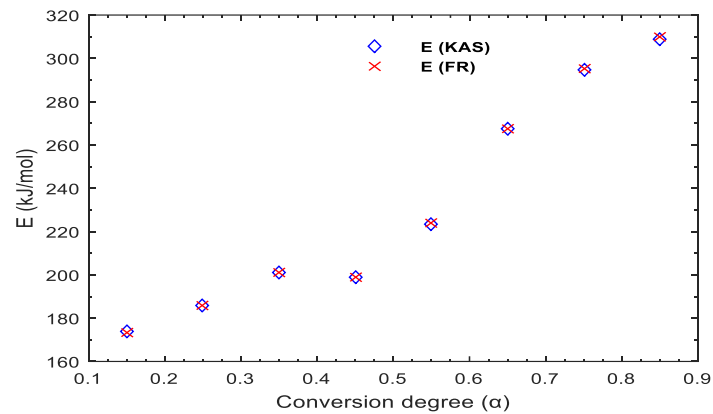


Figure 13. Activation energy versus conversion degree

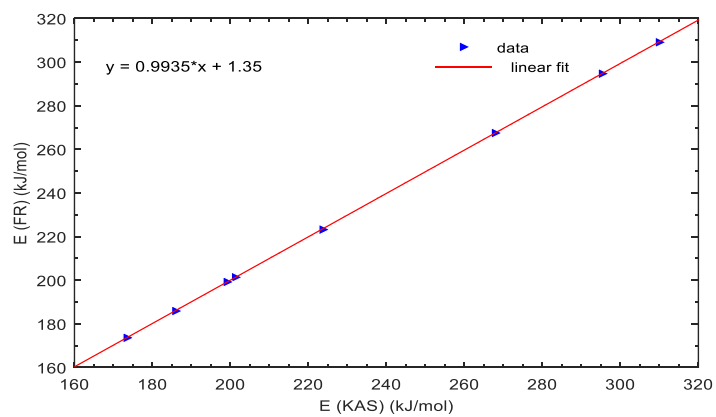


Figure 14. E_{FR} versus E_{KAS}

4. CONCLUSION

This study aimed to establish the thermal degradation process of the tyre crumb by applying two model-free methods to the thermogravimetric analysis data. The thermogravimetric analysis was carried out at heating rates of 2°C, 5°C, and 10°C min⁻¹ in presence of nitrogen. Results show that the pyrolysis process of the tyre crumb takes place in three stages as the various components of the tyre undergo decomposition. The activation energy generally increases with increasing conversion degree in the early stages of thermal degradation. There is, however, a slight drop in activation energy at $\alpha = 0.45$, after which the trend of increasing activation energy with conversion degree continues. A mean activation energy of approximately 232 kJmol⁻¹ was obtained using the KAS and FR models, an indication that the values from the two models are similar. The data obtained from this kinetic study could play a big role in the optimisation of the design of industrial scale waste tyre pyrolysis units.

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Green Chemistry Analysis of Baker's Yeast Process Wastewater Treatment with Microalgae

Dicle CELIK¹, Togayhan KUTLUK¹, Kadriye OKTOR^{2*}

Abstract

Baker's yeast production constitutes an important portion of production industry in Turkey. In many parts of the yeast production process, high quality water is used and discharged as effluent. According to water pollution control regulations, the wastewater of yeast production in food industry is characterized with respect to the given limits of chemical oxygen demand (COD), suspended solids (SS), oil, grease, pH, and color. Inert COD caused by molasses is hard to refine; therefore, advanced treatment technologies are used to achieve the regulation limits. In this study, wastewater obtained from production facilities was centrifuged under 4000 rpm for 20 minutes to get rid of SS. After SS was removed, the wastewater was diluted to different concentrations. 6 ml microalgae cultures incubated in erlenmeyer flasks. Here, organic substances of effluent had become nutritional source for microalgae. After 40 days of incubation, the grown microalgae were centrifuged under 5000 rpm for 5 minutes to get separated from the media. The COD of baker's yeast process wastewater treated with microalgae had been found to be quite lower than regulation limits. The efficiency of COD refinement had been almost 94%. This promising biological treatment had been assessed with respect to 12 principles of green chemistry to evaluate its greenness. This method satisfies 8 principles: waste prevention by no sludge formation, atom economy, safer solvents and auxiliaries, energy efficiency, renewable feedstock, reducing derivatives, bio-catalysis, and design for degradation. Since there exist no chemical synthesis, the remaining 4 green chemistry terms are not applicable.

Keywords: Baker's Yeast Wastewater, Green Chemistry, Microalgae

1. INTRODUCTION

Baker's yeast wastewater is one of the most studied topics in wastewater treatment field because of its pollutant properties. The characteristics of baker's yeast effluent are high chemical and biochemical oxygen demand (COD and BOD), acidity (pH range 4-5), recognizable odor, and dark brown color [1]. The raw material used for baker's yeast is molasses. The dark brown color of molasses is due to its melanoidin content; moreover, the wastewater has brown color and high COD because of this untreated melanoidin in the effluent [2]. For the treatment of baker's yeast wastewater, various methods and studies are being conducted, such as adsorption [3], [4], coagulation/flocculation [5], chemical oxidation [6], [7], electrocoagulation [1], [8], [9], electrochemical processes [10], membrane processes [11] – [14], ozonizing [15] – [17], advanced oxidation processes [18], ultrasound [2], [19], and so on. However, the oxygen demands of the effluent is a major problem to deal with. For example, combined biological treatment of anaerobic digestion and aerobic systems are effective for decreasing BOD beyond to limits; yet, they fail on COD resulting in inhibition of recycling used water [1].

Microalgae treatment is a recent method on wastewater treatment. These systems can be useful for treating city sewages, agricultural wastes, and industrial wastes [20] because microalgae remove coliform bacteria, reduce COD and BOD, remove nitrogen and phosphorus, and eliminate heavy metals [21]. Moreover, microalgae treatment can be a green alternative to conventional methods. Greenness of a method is becoming a selection criterion as it means being environment friendlier.

¹ Kocaeli University, Department of Chemical Engineering, 41380, Izmit/Kocaeli, Turkey.

^{2*}Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/Kocaeli, Turkey. oktor@kocaeli.edu.tr

In this study of microalgae treatment, it is aimed to research the probability of decreasing COD lower than legislative limits; which are 1200 mg/L for 2 hours composite sample and 1000 mg/L for 24 hours composite sample for yeast industry [22]. Another aim of the study is to see if microalgae use is environment friendly, or not. Assessment of this novel method with respect to 12 principles of green chemistry is a practical tool for this purpose. According to literature, the greener the method is, the more principle provided out of the 12 principles [23]. Therefore, this biotechnological process has been assessed regarding each principle of green chemistry.

2. MATERIALS AND METHODS

2.1. Experimental Setup

Microalgae culture of *Chlorella variabilis* was used in this study. A baker's yeast manufacturing facility's process effluent was collected prior to any industrial treatment for being used as a growth medium. Before incubation, wastewater was centrifuged at 4000 rpm for 20 min to remove the solid impurities, and then it was diluted with tap water to following ratios: 0%, 10%, 20%, 30%, and 40%. In Kocaeli University wastewater laboratory, COD content of the wastewater was identified by using DR2800 Hach Lange LCK 314 standard cell kit. The cell concentration and growths were determined by using Jenway 6800 UV Vis. spectrophotometer at 680 nm.

After the pretreatment for removal of suspended solids (SS), microalgae were cultured in 250 mL open flasks for 40 days at 27 °C in a 200-rpm shaking incubator INNOVA 40. The experimental setup can be seen in figure 1. The necessary illumination for microalgae was provided by a 7W 2700K LED lamp.



Figure 1. The experimental setup of microalgae treatment to baker's yeast manufacturing process wastewater.

The growth rates of *Chlorella variabilis* cultures were determined by using equation 1:

$$\mu = \frac{\ln(x_2 - x_1)}{t_2 - t_1} \quad (1)$$

where x is the cell concentration (g/L), t is the time (h). Maximum growth rate (μ_{\max}) is the growth rate obtained during the logarithmic phase of the growth plots.

2.2. Green chemistry analysis

Green chemistry is a recent environmentalist concept, which is increasingly gaining importance nowadays. Paul T. Anastas and John C. Warner proposed to use the term "Green Chemistry" first in 1991 and they developed the 12-principle in 1998 [24]. The concept of green chemistry and its 12 principles are useful guides for investigating and determining if a given method is environmentalist (green) or not. The use of the tool is analyzing the method for each one of the principle stated in Table 1 to see how many of them are ensured.

Table 5. Green chemistry's 12 principles and their brief explanations. [23]

Principle	Explanation
1. Prevention	Preventing waste is better than cleaning.
2. Atom economy	To maximize the incorporation of all reagents used into the final product
3. Less hazardous chemical synthesis	Less toxic means lower hazard at workplace and to environment.
4. Designing safer chemicals	At design stage, the chemical toxicity should be minimized.
5. Safer solvents and auxiliaries	Solvents must be replaced with less toxic alternatives.
6. Energy efficiency	Synthetic methods having equilibrium conditions at or close to T_{room} and P_{atm} .
7. Using renewable feedstocks	Renewable feedstocks should be used rather than depleting sources.
8. Reducing derivatives	Unnecessary derivatization should be minimized or avoided if possible, since they require additional reagents and generate waste.
9. Catalysis	Efficiency and yield of synthesis must be increased.
10. Designing for degradation	At the end of the useful life, items should be easily degraded.
11. Real-time analysis	In-process monitoring prior to hazardous substance formation.
12. Inherently safer chemistry	Raw materials and chemicals should be inherently safe.

3. RESULTS AND DISCUSSIONS

3.1. Experimental results and discussion

The COD content of the effluent at the outlet of the process stream was 2500 mg/L and this sample was diluted up to 40% to be incubated for 40 days at 27 °C. At the end of the incubation period, each flask content was then analyzed in terms of COD content with DR2800 Hach Lange LCK 314 standard cell kit. The experimental results and analysis shown in table 2 states that COD content was lowered drastically below the given legal limits for COD. Removal of COD up to 94% from the effluent has been a successful result in terms of wastewater treatment. Moreover, as can be seen in table 2, this result is obtained for any concentration. It can be concluded that pre-dilution is not a necessary step for microalgae treatment method.

Table 2. COD analysis results of the samples with various dilutions.

Dilution	COD (mg/L)
0%	172
10%	150
20%	173
30%	140
40%	142

When cell concentrations and growth rates are calculated, it is observed that the maxima are reached when there was no dilution. The maxima are $x_{\max} = 1.24 \text{ g/L}$ for cell concentration and $\mu_{\max} = 0.0038 \text{ h}^{-1}$ for cell growth rate. These results confirm that pre-treatment dilution is not effective for this type of system.

3.2. Green chemistry analysis results and discussion

The green chemistry analysis of this specified wastewater treatment with microalgae is performed step by step for each principle and overall findings are tabulated in table 3.

Prevention: Any advanced industrial wastewater treatment yields in formation of sludge. However, this method has no sludge formation; thence, waste prevention is achieved.

Atom Economy: All the inlet stream is used as feed of the microalgae without any side product formation. So, it can be said that all atoms are incorporated by growth of microalgae.

Less hazardous chemical synthesis: Since there exist no chemical synthesis, this principle is not applicable.

Designing safer chemicals: The wastewater treatment has no chemical design. This element is also not applicable.

Safer solvents and auxiliaries: When compared with conventional industrial treatment technologies, microalgae treatment replaces severe chemicals. Henceforth, this principle is successfully placed.

Energy efficiency: The microalgae are living things and this avails to process the wastewater treatment under mild conditions, at ambient temperature and pressure, which means the lower use of energy.

Using renewable feedstocks: Microalga itself is a renewable feedstock as it can be cultured.

Reducing derivatives: The product of microalgae treatment method is grown microalgae only. This means that there is no formation of any other compounds. This principle is fulfilled in parallel with atom economy.

Catalysis: The system uses enzymes of microalgae as its bio-catalysts.

Designing for degradation: Microalgae is a biodegradable end product of the treatment. It can be disposed, degraded or used furtherly in some other processes.

Real-time analysis: This principle is applicable for industrial applications and continuous processes. It is not applied for laboratory trials.

Inherently safer chemistry: Although the microalgae method is safer than conventional methods, it is not because of inherent safety. Replacing severe chemicals is related to 4th principle, so this last principle is not applicable since the method is not offering a new chemical.

Table 3. Results of green chemistry analysis of baker's yeast wastewater treatment with microalgae.

Principle	Analysis*
1. Prevention	+
2. Atom economy	+
3. Less hazardous chemical synthesis	N/A
4. Designing safer chemicals	N/A
5. Safer solvents and auxiliaries	+
6. Energy efficiency	+
7. Using renewable feedstocks	+
8. Reducing derivatives	+
9. Catalysis	+
10. Designing for degradation	+
11. Real-time analysis	N/A
12. Inherently safer chemistry	N/A

* "+" stands for meeting the principle, "-" stands for not meeting the principle, and "N/A" stands for not applicable principle.

4. CONCLUSIONS

Baker's yeast effluent is hardly treatable wastewater with definitive dark brown color and specific odor caused by melanoidins of molasses. Manufacturers of baker's yeast are dealing with eliminating this color and unpleasant odor for environmental reasons and public health. Current applications of this process' wastewater is combined advanced treatment technologies which includes using severe chemicals, sludge formation and microbiological treatments. Moreover, the facilities should deal with remaining sludge of wastewater treatment. In this study, it is aimed to employ a novel approach to water treatment technologies while making treatment process environment friendlier. In order to achieve this target, microalgae are cultivated to process effluent obtained from an industrial yeast manufacturer. The compounds in the effluent had become feeds of microalgae. Henceforth, the growth of microalgae had been observed as it is the biological process of water treatment in the system. Additionally, COD amount in the wastewater was measured, because it was also aimed to specifically decrease COD content below legislative limits. The result of the microalgae treatment has been promising as COD content is lowered successfully beyond limits. Meanwhile, it can be concluded from the experiment that dilution of the wastewater prior to cultivation is not necessary. Lastly, the aim to make the water treatment greener has successfully achieved. The green chemistry analysis shows that overall treatment process is environment friendly. However, it should be denoted that scale up studies should include economic feasibility searches.

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Preparation of Ionic Liquid Mediated Sol-gel Silica for the Removal of Cr(VI) Ions from Aqueous Solutions

Nilay GIZLI^{1}, Merve ARABACI²*

Abstract

In this study ionic liquid mediated sol-gel silica adsorbents are prepared and used for the removal of Cr(VI) ions from aqueous solutions. For this purpose silica based adsorbents containing ionic liquids (ILs) are synthesized by sol-gel method. Thus the high extracting ability of ILs are combined with the surface properties of silica substances. Commercial (Aliquat 336® and EMIMTf2N) and synthesized ([A336][NO3]) ionic liquids are incorporated directly by sol-gel operation. Silica based adsorbents are being initiated with silica precursor (TEOS), water, alcohol and ionic liquid hydrolysis in the presence of an acid catalysts then completed with a condensation reaction. Physicochemical and morphological characterization of prepared adsorbents have been investigated by FTIR, SEM and BET analysis. The sorption behaviors of adsorbents have been investigated by using a series of batch sorption studies. Sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption processes.

Keywords: *Adsorption, Cr(VI) Removal, Ionic Liquid, Sol-gel, ,*

1. INTRODUCTION

Chromium has a wide range of industrial application areas such as; metal plating, leather tanning, pigment and coating industries [1]. Chromium in aqueous solutions exists in a range of oxidation state from -2 to +6. Cr(VI) exhibits toxic effects for living organisms, therefore the allowable limit is kept at low concentrations. World Health Organization (WHO) has set this limit as 0.05 mg/L for the drinking waters [2]. For that reason it is very important to develop a process for selective removal of Cr(VI) ions from aqueous solutions.

Removal and extraction of dissolved heavy metal ions from aqueous media are generally accomplished by several methods including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flocculation, flotation, and electrochemical methods [3-5]. Among all these methods, adsorption is considered as the effective technique for the removal of heavy metals from aqueous solution because of advantages like the low cost, availability, profitability, ease of operation and efficiency [6, 7].

In general, the efficiency of the adsorption depends on many factors, including the surface area, pore size and distribution of it, as well as the surface chemistry of the adsorbents. The sorbents with a high specific surface area as a result of the porous character are generally needed for high adsorption efficiency [8].

Ionic liquids (ILs) are organic salts which have liquid form at room temperature. Because of this, they are recognized as Room Temperature Ionic Liquids (RTILs). The large number of possible ILs structures and their unique properties such as high thermal stability, non-flammability, negligible vapor pressure make them feasible to consider them as an opportunity to contribute to greenness in the various field in which they can be applied [9]. In addition, ILs have adjustable hydrophobicity, polarity and selectivity compared with organic solvents when used for extraction [8, 10]. ILs can be used as metal extraction reagent for separation of metal ions. There are many advantages of ILs in separation processes such as high separation efficiency and high selectivity. However, some drawbacks of ILs are found in some liquid-liquid separation processes, such as large amount used, high viscosity leading unfavorably to dissolve and

^{1*}Corresponding author: Ege University, Department of Chemical Engineering, 35100, Bornova/Izmir, Turkey. nilay.gizli@ege.edu.tr

² Ege University, Department of Chemical Engineering, 35100, Bornova/Izmir, Turkey. mmervearabaci@gmail.com

diffuse, difficulties of separation and recovery, and the low interface area [11]. To overcome these shortcomings, ILs can be incorporated onto highly porous solid supports in many different ways, such as simple impregnation, grafting, polymerization sol-gel method and encapsulation [12]. Among these, sol-gel method has an incredible attention because of the advantages such as; (i) easy and inexpensive; (ii) functional groups are readily anchored on the substrate; and (iii) it can be used for the deposition of substrates that have complex surfaces or large surface areas [13].

In this study, Ionic Liquid (IL) Mediated Sol-gel Silica adsorbents were prepared and used for the removal of Cr(VI) ions from aqueous solution. Three different types of ILs such as Aliquat 336, EMIMTf₂N and [A336][NO₃] were incorporated onto silica adsorbents by following the one-step sol-gel process. Physicochemical and morphological characterization of prepared adsorbents has been investigated by Fourier Transform Infrared Spectroscopy (FTIR) Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) Analysis. In addition, thermal behavior of prepared adsorbents was also characterized by Thermogravimetric Analysis (TGA). The sorption behaviors of adsorbents were investigated by a series of batch sorption experiments. Effect of the type of ILs on the adsorption performance was investigated as well as sorption percentages.

2. MATERIALS AND METHODS

2.1. Materials

In this study, tricaprylmethylammonium chloride (trade name Aliquat 336, (C₈H₁₇)₃CH₃NCl), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [EMIMTf₂N] and tricapryl methyl ammonium nitrate [A336][NO₃] were used as ionic liquids. [A336][Cl] and EMIMTf₂N were obtained from Sigma Aldrich, [A336][NO₃] was synthesized by anion metathesis reaction. Tetraethyl ortosilicate with the formula of Si(OC₂H₅)₄ (TEOS) was used as a precursor for obtaining SiO₂ matrix. Required concentration of chromium solution was prepared by using potassium dichromate salt, K₂Cr₂O₇. Also, 0.1M of HCl and 0.1 M of NaOH solutions were used to adjust the pH of the solution.

Chemical structures of commercial ionic liquids are shown in Figure 1.

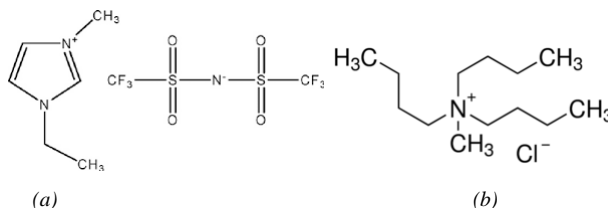
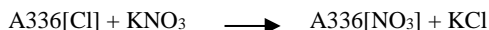


Figure 15. Chemical structures of commercial ionic liquids a) EMIMTf₂N b) Aliquat 336

2.2. Synthesis of the Task Specific Ionic Liquid

A336 [NO₃] (task specific IL) was synthesized by anion metathesis reaction of Aliquat 336 with KNO₃ solution. Reaction can be given as follows;



Ionic liquid (A336[Cl]) and 2 M of KNO₃ solutions were contacted for 1 hour by vigorous stirring. The phases were then separated by using a separating funnel followed by washing with distilled water. These steps were repeated for 4 times. Completion of the reaction was controlled by checking the Cl⁻ ion content of the ionic liquid by using AgNO₃ indicator.

2.3. Adsorbent Preparation

Sol-gel process was used for the preparation of sorbents based on nanoporous silica oxide matrices in whose interconnected network, ionic liquid got trapped. In this manner, 5 mL of TEOS as a silica precursor and 2.5 mL of EtOH were mixed in an ultrasonic media. And various amount of IL (0-14%) were added into TEOS-EtOH solution. and mixed at 40°C during 30 min. Then, 2.5 ml of aqueous HCl solution (37 wt %) was added as dropwise and the solution was mixed during further 2 hours. Then, the solution was poured into the petri dishes and left to dry at ambient conditions. Finally obtained products was ground into powders for the subsequent characterization and adsorption studies

Prepared sorbents are abbreviated according to type of IL, as given in Table 1.

Table 6. Abbreviation of prepared silica adsorbents

ID	Ionic Liquid
SG-A	Aliquat 336
SG-TS	[A336] [NO ₃]
SG-IL	[EMIMTf ₂ N]

2.4. Characterization

The structural formation of the prepared adsorbents was investigated by using a Fourier Transform Infrared spectrometer (FTIR-Pelkin Elmer Spectra 100) in the wave number range of 650-4000 cm⁻¹ to identify the functional groups. The surface morphology of adsorbents was investigated by using Scanning Electron Microscope (SEM) and qualitative element composition was analyzed using Energy Dispersive X-ray (EDX) operated in QUANTA 400 F Field Emission Spectrometer. The microscope was operated at an accelerating voltage of 20.00 kV. The particles were coated with a gold layer in order to make them conductive. Surface area and pore volume of silica adsorbents was analyzed by Brunauer–Emmett–Teller (BET) in Micromeritics Gemini V model. Thermal Gravimetric Analysis (TGA) was carried out using Perkin Elmer Diamond TG/DT model to investigate the thermal behavior of the silica particles.

2.5. Batch Sorption Studies

The adsorption of Cr (VI) ions from aqueous solutions onto the silica based adsorbents was investigated by a series of batch sorption tests to obtain the adsorption performances of adsorbents as removal percentage. For batch adsorption studies, solution varying concentration (50-700 mgL⁻¹) of Cr(VI) were equilibrated with 50 mg of adsorbents by shaking at 150 rpm using a NUVE model ST 30 water-bath shaker. After equilibration, the adsorbents were removed and the supernatants were analyzed for Cr(VI) concentration by using Atomic Absorption spectrophotometer (Varian 10+) (AAS).

The percentage of Cr(VI) removal, R(%) was calculated by using the following expression:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} * 100$$

where C₀ and C_e are the initial and equilibrium concentrations (mgL⁻¹), respectively.

The adsorption capacity of the prepared adsorbents was evaluated using the following equation:

$$q_e = \frac{(C_0 - C_e) * V}{m}$$

where q_e is the adsorption capacity (mg/g), C₀ and C_e are the initial and equilibrium concentrations (mgL⁻¹), respectively. V is the volume of Cr(VI) solution and m is the mass of dry adsorbent

3. RESULTS

3.1. Characterization

3.1.1 FTIR analysis-Physicochemical Characterization

FTIR spectrums of the prepared adsorbents are shown in Figure 2.

In the FTIR spectra of untreated silica materials (Figure 2 a), has a peak at 3258.80 cm⁻¹ wavelength which can be attributed as an indication of unreacted –OH structure. At this wavelength, –OH peaks are decreased or disappeared with the increasing in the amount of ionic liquid in the sol-gel process.

The FTIR spectrum of [A336][Cl] (Figure 1.c), the peaks around the position of 2923 cm⁻¹ can be attributed to the characteristic absorption of –CH₃ of alkyl chain and at the position of 1466 and 1378 cm⁻¹ are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1465 cm⁻¹ (Figure 2 b) is pronounced functionalization of silica particles with [A336][Cl] type ionic liquid.

Peaks appeared at 3159 and 1574 cm⁻¹ wavelengths (Figure 2 e) can be attributed as the C=N bonds of the imidazolium ring. Also, the bands around 1067 and 795 cm⁻¹ indicate the asymmetric and symmetric stretching of Si–O–Si vibration, respectively. These data are the important indications for the ionic liquid presence in SG-IL structure.

The peaks around the position of 2924 cm^{-1} can be attributed to the characteristic absorption of $-\text{CH}_3$ of alkyl chain and the bands between 1467 and 1328 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1326 cm^{-1} (Figure 2 f) is pronounced functionalization of silica particles with [A336][NO₃] type ionic liquid.

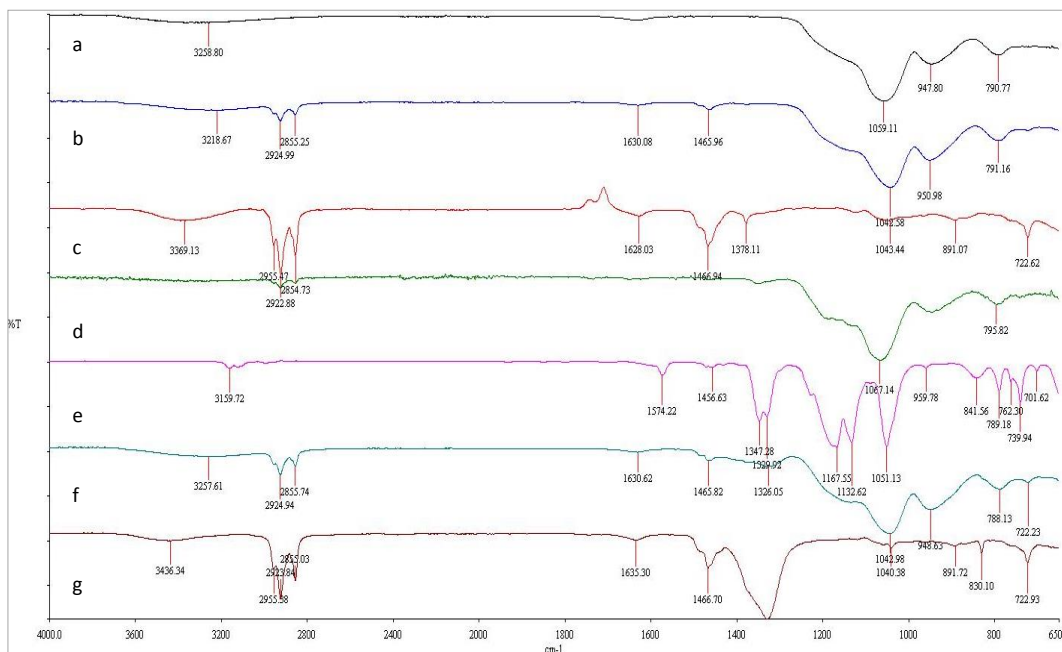


Figure 2. FTIR spectra of ionic liquid functionalized silica based adsorbents **a**) before functionalization (SG-0) **b**) adsorbent (SG-A) functionalized with [A336][Cl] **c**) ionic liquid [A336][Cl] (Aliquat 336) **d**) adsorbent (SG-IL) functionalized with EMIMTf₂N **e**) ionic liquid EMIMTf₂N **f**) functionalized with [A336][NO₃] adsorbent (SG-TS) **e**) ionic liquid [A336][NO₃]

3.1.2 BET Analysis-Surface Properties

BET surface area [m^2g^{-1}] and pore width [\AA] values of silica based and ionic liquid functionalized silica adsorbents are shown in Table 2.

Table 2 BET analysis data of prepared adsorbents

Adsorbents	Surface Area [m^2/g]				Pore Volume [cm^3/g]	Pore Size [\AA]
	BET	Langmuir	t-Plot Micropore	t-Plot External		
SG	577.0834	744.6663	148.7083	428.3751	0.307997	21.3485
SG-IL	299.7985	402.8222	-	372.4833	0.230098	30.7003
SG-TS	593.26	755.6763	-	-	0.3365	20.6932
SG-A	602.35	762.3354	-	-	0.32426	20.3324

As shown in Table 2. Silica based adsorbents functionalized with various type of ILs were characterized to be mesoporous with average pore diameter of 2 nm and BET surface area in the range of $300 - 600\text{ m}^2\text{g}^{-1}$. Pore volumes of SG-TS and SG-A are higher than SG (untreated) type adsorbents while average pore diameters of adsorbents containing TS and A type ionic liquids are lower than SG leading to higher surface area. On the other hand Surface Area of SG adsorbents decreases with modification with IL type ionic liquids. This may be attributed that the surface area is occupied by the long alkyl chain of EMIMTf₂N type ionic liquid.

3.1.3 SEM Analysis -Morphological Characterization

The morphological characteristics of SG-A, SG-TS and SG-IL were evaluated respectively, using a scanning electron microscope (SEM) as shown in Figure 3.

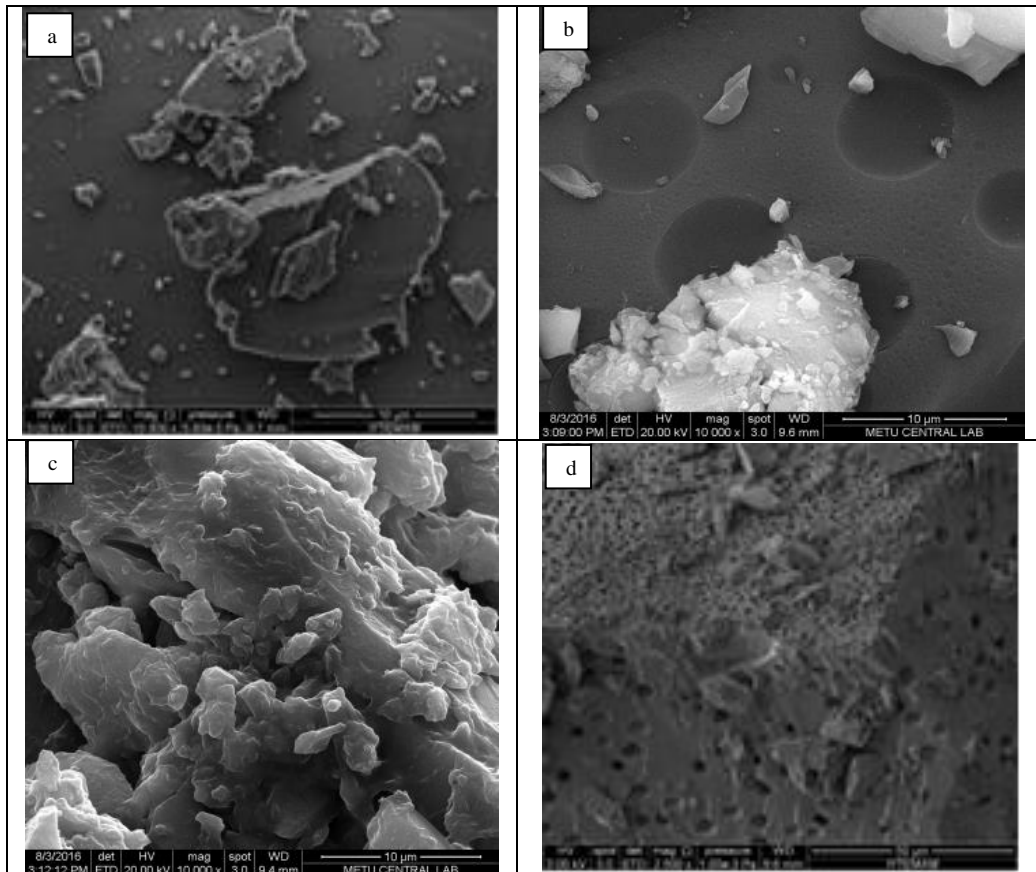


Figure3. SEM images of prepared adsorbents with the magnification rate of 10000 a) SG b) SG-A c) SG-TS d) SG-IL

In the SEM images of silica materials having none IL content, it is observed that, the surface area of SG has nonporous and nonhomogeneous structures. Unreacted alcohol and other residues are evident on the surface. Pore structure formation is observed by presence of the ionic liquid especially Aliquat 336, [A336][Cl], (SG-A) and imidazolium based IL, EMIMTF₂N, (SG-IL). From the SEM images it can be concluded that ionic liquids acted as porogens in the preparation of silica adsorbents.

3.1.4 TGA-Thermal Behavior Analysis

Thermal stability of the silica based adsorbents containing various amount of ILs ara shown in the Figure 4.

In TGA results (Figure 4),it is clearly observed that silica adsorbents without IL content (SG) is started to decompose at low temperatures around 50 °C. The adsorbents containing imidazolium based ionic liquid with the weigh percentages of 20 and 40 %, have a weight loss at the higher temperatures because of high thermal stability of IL. It can be concluded that IL increases the thermal stability of silica materials.

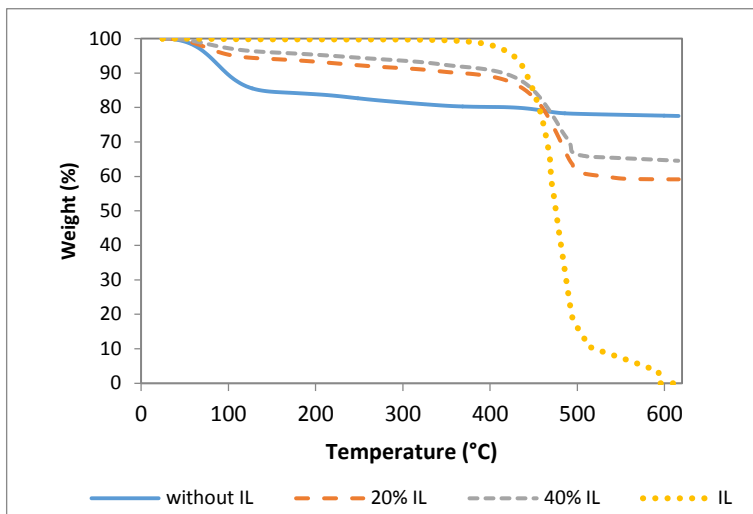


Figure 4. TGA results of SG-IL adsorbents

3.2. Effect of IL type on the sorption of Cr(VI) ions

Sorption performances of silica based adsorbents containing various amount and type of ionic liquid were evaluated as removal percentage of Cr(VI) ions from aqueous solution. Effect of ionic liquid amount were also examined by using two different ratio of ILs on the mass basis such as 0.5 and 0.7 g-IL/g-silica precursor. Results are shown in Figure 5.

It can be confirmed from Figure 5 that SG-TS and SG-A type adsorbents showed a better removal performance for Cr(VI) in comparison to untreated silica adsorbent (SG). Although the results of SG-A and SG-TS exhibited quiet similar results, SG-A can be chosen as adsorbent for the further studies. Because of the fact that SG-TS needs additional step for synthesis of ionic liquid comparing with the preparation of SG-A.

Sorption percentages of the adsorbents have been enhanced by containing Aliquat 336 type ionic liquids (SG-A) up to 99%.

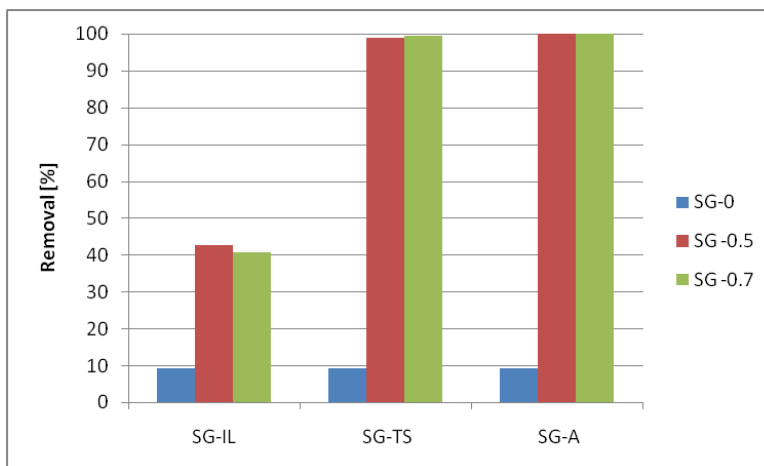


Figure 5. Removal efficiency of silica based synthesized by using various type of ionic liquids for the sorption of Cr(VI) ions.

Adsorption capacity of SG-A type adsorbents was calculated as 31.74 mg.g-1 and it is also observed that increase in IL content has no pronounced effect on the sorption performances.

4. CONCLUSIONS

In this study ionic liquid mediated sol-gel silica adsorbents are prepared for the removal of Cr(VI) ions from aqueous solutions. Physicochemical and morphological characterization of prepared adsorbents concluded that ionic liquids acted as porogens and increased the thermal stability of the silica based adsorbents.

Based upon the experimental results, Cr(VI) sorption percentages achieved with silica adsorbents containing ionic liquid were higher than that of untreated adsorbents due to synergistic effect of electrostatic interaction with IL and Cr(VI) ions. Sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption

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A modelling methodology for assessing use of datacenter waste heat in greenhouses

Marcus SANDBERG^{1*}, Mikael RISBERG², Anna-Lena LJUNG³, Damiano VARAGNOLO³, Shaojun XIONG⁴, Michael NILSSON⁵

Abstract

In Sweden, the number of datacenters establishments are steadily increasing thanks to green, stable and affordable electricity, free air cooling, advantageous energy taxes and well-developed Internet fiber infrastructures. Even though datacenters use a lot of energy, the waste heat that they create is seldom reused. A possible cause is that this waste heat is often low grade and airborne: it is therefore hard to directly inject it into a district heating system without upgrades, which require additional energy and equipment that generate extra costs. One option for reusing this heat without needs for upgrades is to employ it for heating up greenhouses. But assessing the feasibility of this approach by building physical prototypes can be costly, therefore using computer models to simulate real world conditions is an opportunity. However, there is a lack of computer modelling methodologies that can assess the possibility of using waste heat from datacenters in greenhouses in cold climates.

The objective of this paper is therefore to propose such a methodology and discuss its benefits and drawbacks in comparison with other research studies. This methodology combines computational fluid dynamics, process modelling and control engineering principles into a computer model that constitutes a decision support system to study different waste heat and greenhouse or mushroom house scenarios.

The paper validates the strategy through a case study in northern Sweden, where we assess the amount of produced waste heat by collecting temperature, relative humidity, and fan speed data for the air discharged from the datacenter.

The resulting methodology, composed by conducting measurements and computer models, calculations can then be used for other datacenter operators or greenhouse developers to judge whether it is possible or not to build greenhouses using datacenter waste heat.

Keywords: Computational Fluid Dynamics, Cooling, Datacenter, Measurements, Simulations, Waste Heat Recovery

1. INTRODUCTION

In the digital age of today, also known as digitalization, with cloud-based solutions and wide use of social media, the number of datacenters is increasing to handle the new demands on information storage. Datacenter servers consume a lot of energy and generate a lot of heat so these servers need efficient cooling solutions to not overheat. This has attracted datacenter operators to northern Europe since the opportunities for free air cooling by using the outside air are favorable. Other aspect like stable green electricity, robust digital infrastructure and reasonable energy taxes are also reasons. There are examples of research aiming to make datacenters more energy efficient such as the FIT4green project, [1], where the energy need for the automation technology was focused and the GAMES project, [2], where developing smart datacenters to decrease energy need was is focus. There are studies on how to absorb the heat during

^{1*} Corresponding author: Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering, SE-97187, Luleå, Sweden, marcus.sandberg@ltu.se

² Luleå University of Technology, Department of Engineering Sciences and Mathematics, SE-97187, Luleå, Sweden, mikael.risberg@ltu.se, anna-lena.ljung@ltu.se

³ Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, SE-90183, Umeå, Sweden, shaojun.xiong@slu.se

⁴ Luleå University of Technology, Department of Computer Science, Electrical and Space Engineering, SE-97187, Luleå, Sweden, damiانو.varagnolo@ltu.se, michael.nilsson@ltu.se

the cooling of the servers, e.g. [3], but to the authors knowledge, studies on how to use or reuse the heat from the datacenter ventilation systems are lacking.

Although newly built datacenters use technology that allow for using server heat for heating up the building there are still waste heat being let out to the free air. There is a challenge to use this waste heat that is usually low grade, up to 30-40°C although there are examples of such technology [4]. Ward et al [5] presented an approach that decentralizes the datacenters into nodes and where the waste heat from each node is used for heating adjacent buildings or facilities. We see a need of tools that help evaluating the opportunities for using datacenter waste heat in greenhouses. Therefore, we started a project in collaboration with many stakeholders within the energy, datacenter and food growing area, which is presented in this paper.

2. THEORETICAL FRAMEWORK

2.1. Process modelling

To model the heat transfer solution between the datacenter and greenhouse the process simulation software such as aspen plus, [6], can be used. Aspen plus uses basic engineering relationships and mass and heat balance to determine the outputs for the system. By varying some specific design parameters of the heat transfer solutions, correlations can be obtained that can be used for greenhouse dimensioning.

2.2. Computational fluid dynamics

With computational fluid dynamics (CFD) it is possible to numerically retrieve information about airflow and temperature inside a greenhouse [7]. The detailed knowledge provides the possibility to evaluate designs prior to construction but it is at the same time crucial that the models are set up with quality and trust in focus. The heat transfer situation of a greenhouse is complex with the joint effects of sun radiation, heat radiation, ventilation, external convection and conduction, heat transfer through the ground, condensation at the walls, leakage of air etc. The conditions inside the greenhouse are furthermore subjected to transient variations with regards to external conditions such as time of day, time of year and current weather situation. In this context, CFD can be a valuable tool in the assessment of external heat sources, e.g., the waste heat from a datacenter.

2.3. Control engineering related modelling

Solving a control problem (in terms of deciding how to steer actuators like ventilation, heating and cooling units based on current measurements from the plant) may benefit from the knowledge of mathematical models of the plant itself. If available (and with the caveats written below), models may indeed be used to forecast what will be the outcome of taking a specific control action. This means that (at least theoretically) models may enable choosing the current action as that one that leads to the "best" forecasted performance (with the metric "best" to be opportunely defined).

This paradigm is known as the predictive-control paradigm [8]. Implementing it, nonetheless, requires sufficiently lightweight mathematical models: since the control-decision problem should be taken "now", the system needs to compute forecasts of the future outcomes sufficiently fast. This means that CFD tools - typically computationally intensive - are in general not suitable for implementing predictive control schemes.

Obtaining control-oriented models can then performed in different ways: one is to derive simplified descriptions (typically in terms of ordinary differential equations) using first-principles and physical knowledge of the plant. Another one is to employ data-driven approaches, where past measurements from the plant are used to compute statistical estimates of the inputs-outputs map (an operation that is often referred to as the "identification" of the system). Notice that often these two paradigms are blended into so-called "grey-box" modelling strategies where the structure of the model is fixed using first-principles, and then the parameters of this model is then populated using measurements from the plant and opportune statistical estimation algorithms).

Using a data-driven approach typically leads to more accurate models than using just first-principles and physical knowledge. In the case described in this paper, nonetheless, the plant needs still to be built, so actual measurements are not available. Our approach to perform control-oriented modelling of our data center - greenhouse system is then to follow a hybrid approach: if a CFD model is available, then the CFD simulator can be used as a virtual plant to obtain virtual measurements. This eventually allows using classical system identification strategies to obtain a control-oriented model; this control-oriented model then is used to design a plant control algorithm, and finally this controller can be embedded into the original CFD model so to perform a virtual feedback loop.

3. METHOD

3.1. Case

The municipality of Boden in northern Sweden wanted to study the possibility to use waste heat from datacenters to heat up greenhouses. They need a new greenhouse for growing park flowers and plants but they also see a need in creating educational possibilities and activities for immigrants as well as providing space for commercial actors to

grow food or other crops. Hydro66 is a datacenter operator in Boden that was interested in participating in the study, see Figure 1.



Figure 1. The Hydro66 datacenter in Boden.

3.2. Measurements



Figure 2. Sensors for measuring temperature and humidity was mounted outside the outlet fans (left part) and on the inside of the outer wall (right part) to measure the incoming air.

Seven sensors, two measuring both temperature and relative humidity and five measuring temperature, were mounted at the Hydro66 datacenter in Boden. One of them was mounted on the inside of the outer wall, which is a wall with lot of small holes where outside air easily can come through, to measure temperature and humidity, see right hand side of Figure 2. The six other sensors were mounted as shown in the left-hand side of Figure 2. The temperature was logged from July 2016 until April 2017.

3.3. Model development

To determine the mass flow of hot air from the datacenter a process simulation model was created that is presented in Figure 3. The model consists of the air flow into the datacenter, the computer load that is represented as a heater in the middle and the airflow out from the datacenter. Also, some of the air is recirculated and mixed to create more stable condition inside. The inputs to the model is the outdoor temperature and heat load from the servers and output is the airflow out from the datacenter. In the model, the temperature out was controlled to 35°C. A correlation was then created from the results and used in the greenhouse dimensioning.

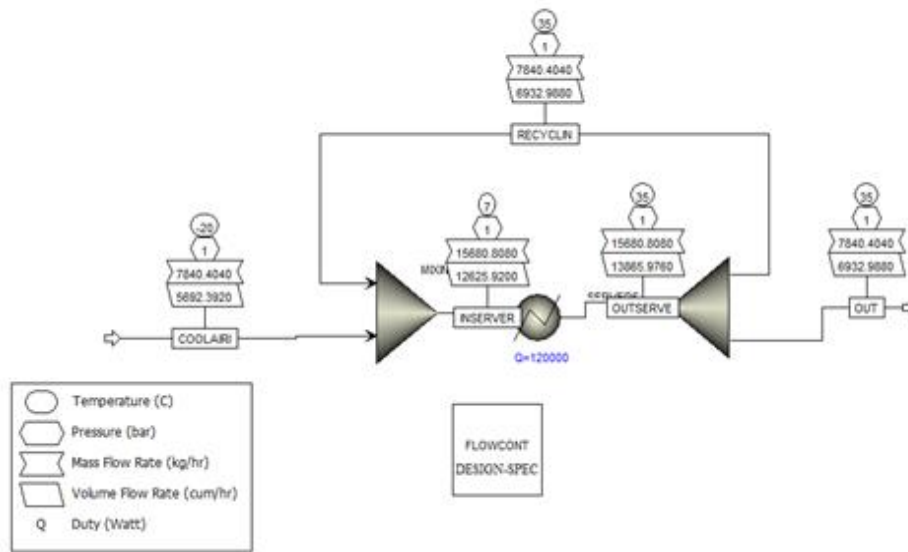


Figure 3: Process model of the datacenter used to determine mass flow of air at a specified temperature for different outdoor temperatures.

The heat transfer model presented in Figure 4 is consisting of the airflow from the datacenter that are heat exchanged with water. The heated water is then transported in a pipe to the greenhouse where used as heat. After the greenhouse, the water is then recirculated in pipe back to the heat exchanger where it is reheated. The inputs to the model is airflow from the datacenter, distance between datacenter and greenhouse and the outdoor temperature, the output is the available heat at the greenhouse. The results from the model was then converted to a correlation that are used for the greenhouse dimensioning.

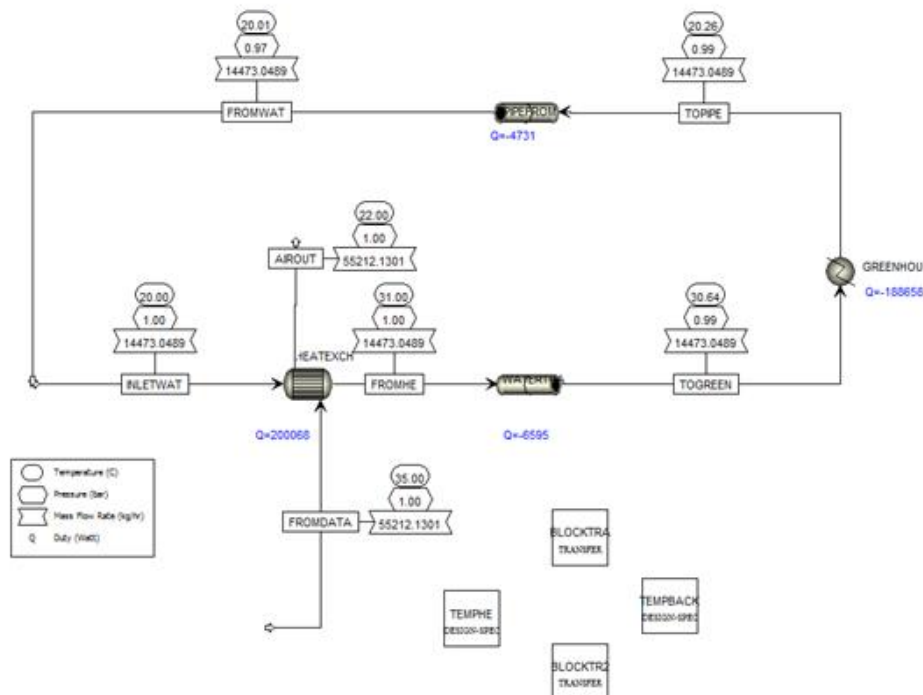


Figure 4: Process model of the heat transfer solution.

For the greenhouse dimensioning an excel spreadsheet was developed that considers the outdoor temperature based on data from the Swedish Meteorological and Hydrological Institute (SMHI), datacenter size, greenhouse building

envelope and distance between datacenter and greenhouse. In this excel spreadsheet the correlation from the process model was implemented.

4. RESULTS

4.1. General framework

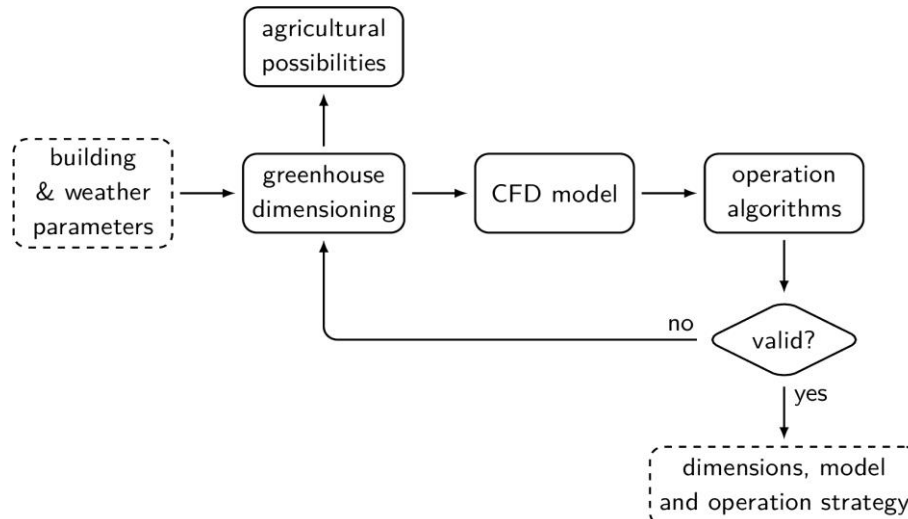


Figure 5. Proposed modelling methodology.

The methodology proposed in this paper, graphically summarized in the chart in Figure 5, is the following: starting from the requirements of having preliminary information on: the structural parameters on the datacenter (such as expected maximal power usage); the properties of the greenhouse (such as u-values of the walls); the requirements of the minimal and maximal temperature within the greenhouse; statistics on the weather conditions for the location (thus not only, e.g., daily average temperatures, but also traces of actual past evolutions so to be able to assess the extent of variations from nominal average values); and a CFD model of the datacenter.

The first step is then to perform an initial greenhouse dimensioning, considering the average weather conditions and using the first principles modeling and computations described in Section 3.3. Following this dimensioning, the designer should then: i) generate a CFD model of the greenhouse, ii) obtain the control-oriented one by performing system identification on the systems using the CFD models as virtual plants as explained in Section 2.3; iii) implement predictive control systems on top of the so-identified model; iv) eventually embed these controllers into the CFD models above. In this way, the designer obtains a complete CFD simulator of the system in closed-loop (i.e., something that simulates how the system should behave not only when the weather conditions are the nominal, but also when these change).

With this closed-loop simulator the designer can then understand if the data center - greenhouse system designed up to now can sustain the typical variations in the weather conditions. The designer can indeed understand through simulations if this system can reject weather disturbances by opportunely acting on the indoor-conditioning subsystem, and guarantee that the temperature of the greenhouse above the required one for all the colder-than-average situations collected in the traces mentioned in the first step of the methodology. The proposed methodology then works as follows: if the overall system can reject the weather disturbances as intended above, then it is meaningful to try to consider what would happen with a bigger greenhouse (i.e., change the design of the greenhouse and then re-perform the steps above). If instead the disturbances are not rejected, then it is necessary to consider a smaller greenhouse. Our proposal is then to iterate the steps above up to the moment that one finds a "big-just-enough" greenhouse.

4.2. Example

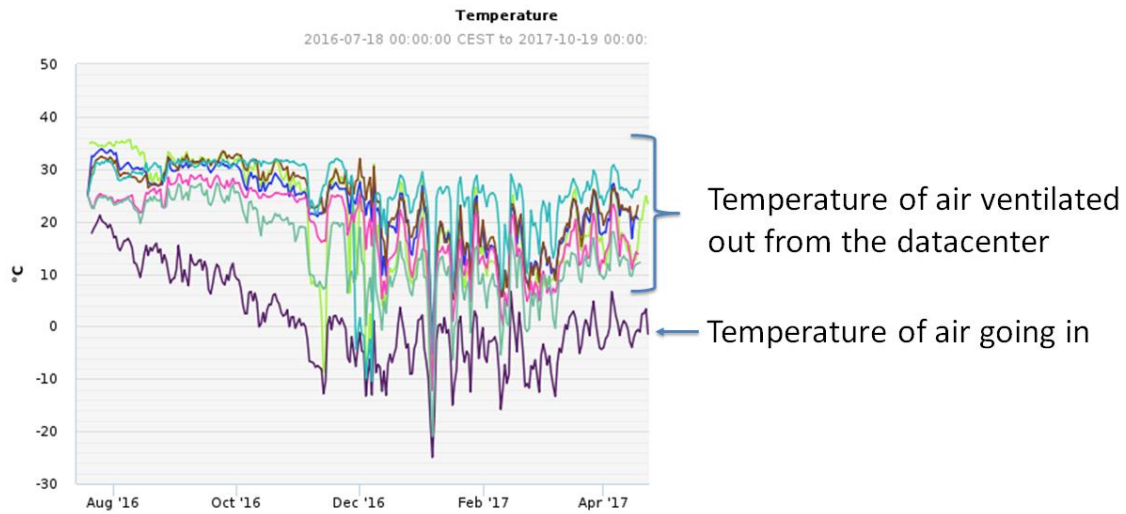


Figure 6. Measured temperature of the air ventilated out and air going into the Hydro66 datacenter.

In Figure 6 the measured temperature is presented. The temperature of the air going out is from below zero up to 35°C. When the outgoing air is below zero the ventilation fans are shut off.

In the following example, the datacenter located in Boden, not far from the Arctic circle, has a load of 1 MW and the greenhouse has a width of 12.5 m and a height of 4 m with double pane glass for the green house. In Figure 7 the results for the length of the greenhouse dependent of outdoor temperature (left) and the date (right) is presented. For a low temperature under -10 °C the data center can support a greenhouse that is 50 m long and when the temperature goes the down to -30 °C it can only support a length of 17 m. Over the year, during the winter, only a small greenhouse can be heated from the datacenter but during the summer a large greenhouse of length 300-400 m could be heated.

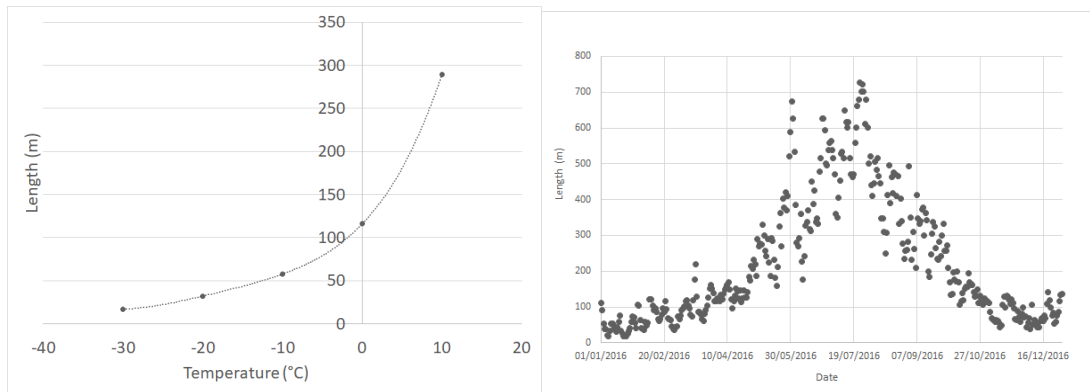


Figure 7: Example of results from the greenhouse dimensioning for a datacenter of 1 MW located in Boden, Left: Length dependent of outdoor temperature, Right: Length dependent on date.

In Figure 8 the airflow inside a suggested greenhouse is evaluated. Here it is possible to evaluate fan solutions and other ventilation related parameters.

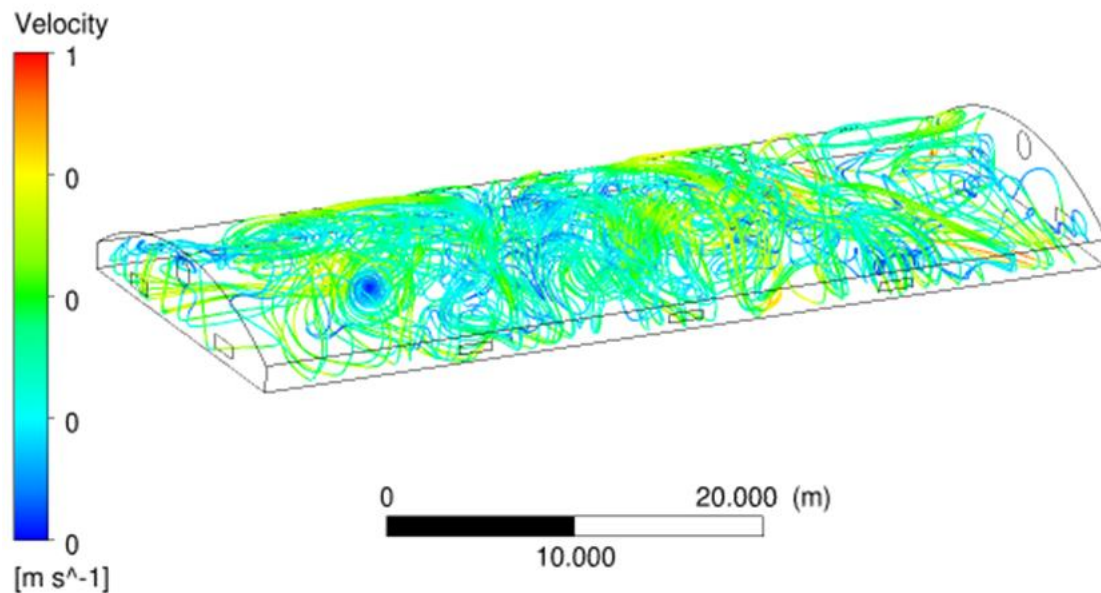


Figure 8. Computational fluid dynamics model of a suggested greenhouse.

5. DISCUSSION

During the winter only a small greenhouse can be heated from the datacenter. Therefore, if the greenhouse should be used during the coldest part of the year additional heating will be needed which for example could be district heating, pellets burner or biogas. Another option is only to use the heat to extend the growing season and not use it during the coldest months. The process modeling part have some uncertainties that needs to be addressed before the heat transfer solutions is implemented in a real system. The first one is the heat exchanger sizing after the data center. Since it's several air outlets from the datacenter one options is to have a heat exchanger connected to each outlets but this will probably end up in a very costly solution while the other options is the gather the airflows together which will be a practical problem for an existing datacenter since it is not designed according to that. The other uncertainties it how much heat that can be used in the greenhouse since currently greenhouses are not designed to use low temperature heating system and therefore more work are needed in this area.

The waste heat from the datacenter can be considered for cultivations of variable crops including vegetables, ornamental plants, berries, spices and edible mushrooms, however exact design for dedicated species is beyond this current study. The fact that the heat exiting from the datacenter is below the 35°C suggests that the target crops shall be reasonably among those species having low heat requirement for the growth. For example, the optimal air temperature during the cultivation is about 15 - 20 °C for spices (such as parsley, grass onion, basil, lemon balm etc.) and ornamental plants (such as pence, primula, geranium, etc.), and 10 - 18°C for shiitake and oyster mushrooms [9]. The exact design shall also incorporate with other inhouse climate variables such as lighting, CO² and relative air humidity. It is worth addressing that many edible mushrooms are growing on forest or crop residues and have a low demand of lighting (500 - 2000 lux, depending on strains and growth stages) as well as less requirements for fertilizers and pesticides. Cultivation of edible mushrooms has drawn more global attentions in recent years, because edible mushrooms are protein rich [10] and contain components good for human health [11]. Edible mushrooms have also been suggested as one of potentially alternative to substitute meat since meat production and associated transportation have caused considerable greenhouse gas emissions [12].

It is understood that a use of the waste heat from datacenters, i.e. a type of secondary energy source, for greenhouse cultivation shall contribute to a low CO² footprint, in general or in respect of the users. However, any implementation regarding to such a move have to consider an innovative and system solution for an optimized energy balance and cost efficiency. It could be explorable in future work, for example, an integrated cultivation of ornamental plants/vegetables that demands for light and CO² input, and edible mushrooms that prefer to darkness and emit CO². The development of a digital system enabling control and monitoring of the entire heat flow and mechanical devices from datacenter to crop growth chamber will be important and make a smart industrial integration possible.

6. CONCLUSIONS

A modelling approach using process modelling, computational fluid dynamics and control-oriented models to assess the use of waste heat from datacenter in greenhouses, have been presented. Using the models, we have shown that it is possible to run greenhouses on waste heat in the north of Sweden but you may need additional heat sources. The modelling approach could benefit from validation on real greenhouses and energy transfer solutions.

ACKNOWLEDGMENT

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Levels and Ecological Risk of Organochlorine Pesticides and PCBs in Surface Sediments and Fish along the Eastern Aegean Coast

Filiz KUCUKSEZGIN¹, Shareef K.I. MUZYED², L. Tolga GONUL¹, Idil PAZI¹

Abstract

Organochlorines were measured in fish and sediment collected from Izmir and Candarli Bays. Surface sediments with three replicates were collected and all samples were extracted in microwave extraction system. The results showed that in all samples, *p,p'*-DDE was the predominant DDT congener. Σ Cyclodienes were generally predominant contaminants. Aroclors were found in noticeably higher levels than OCPs in sediments and fish. The highest level of organochlorines was found in sediments of Nemrut which can be attributed to industrial activities. The maximum levels of Σ OCPs were found in fish collected from Gulbahce, while Aroclors were measured in Aliaga. According to selected ratios indicated no recent influxes of DDT in the sampling areas.

Keywords: Organochlorine compounds; fish; sediment; ecological risk; Izmir Bay; Candarli Bay

1. INTRODUCTION

Organochlorines (OCs) are generally hydrophobic substances, with low water solubility, frequently at the μg or ng per liter level. These organic compounds are highly concentrated by living organisms and concentrations can biomagnify along the food chain. Therefore, an investigation of the distribution of some OCs such as organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) in fish and sediment samples can provide valuable data about contamination in a marine environment. Although their production, usage and disposal have been regulated or prohibited in most of the developed countries, OCPs are still used at present in many developing countries [1]. The production and usage of OCPs and PCBs were completely banned in Turkey in the 1990s and in 1995, respectively [2]. Although the consumption of OCs was banned in Turkey, the usage of these OCs continued illegally until the 2000s.

A number of studies have been carried out on the concentrations of metals in sediments and biota [3] in Izmir Bay, however few studies were performed on organochlorines in sediment [4], [5] and no data are available from the published literatures on the organochlorine levels in fish from the sampling areas. The aims of this study were to assess the distribution patterns of OCs in sediment and fish samples from Izmir and Candarli Bays, to evaluate the potential sources of DDTs using related indices, to find possible sources as well as potential biological risk of DDTs, PCBs in the study areas.

¹Corresponding author: Dokuz Eylul University, Institute of Marine Sciences and Technology, 35340, Inciralti/Izmir, Turkey, filiz.ksezgin@deu.edu.tr

²Palestine University, Pharmacy Faculty, Gaza, Palestine, xlas4@hotmail.com

¹Institute of Marine Sciences and Technology, tolga.gonul@deu.edu.tr, idil.erden@deu.edu.tr

2. MATERIAL AND METHODS

2.1. Study Area

Fish and sediment samples were collected from Izmir and Candarli Bays located in the Eastern Aegean coast (Figure 1). Izmir Bay is one of the great natural bays of the Mediterranean. Izmir is an important industrial and commercial centre and cultural focal point. The Gediz River, which flows into the Outer Bay, is the second biggest river along the Eastern Aegean and densely populated and includes extensive agricultural lands and numerous industrial areas [3].

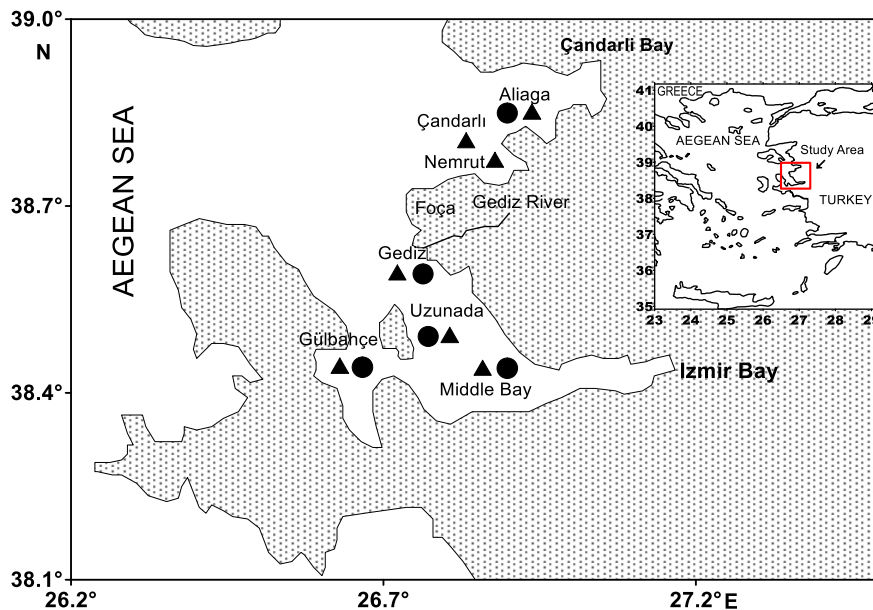


Figure 1. Biota (●) and sediment (▲) sampling sites in Izmir and Candarli Bays

Candarli Bay is a semi-enclosed bay in the Eastern Aegean. Great industry settlements located in the coastal area of Candarli, have been discharging their wastes into Bakircay River or Candarli Bay after limited treatment. Aliaga town located in the southern part of Candarli Bay, has been subjected to extensive industrial developments and is a ship dismantling area [6].

2.2. Sample Collection

Surface sediments with three replicates were collected from the seven sampling sites (Gediz, Uzunada, Gulbahce, Middle Bay, Candarli, Aliaga, Nemrut) in 2014 using a box corer sampler, wrapped in aluminum foil and stored at -20°C for subsequent analysis in order to avoid degradation. The samples were freeze-dried, hand-sieved through 250 μm for grain size correction and homogenized, then kept until chemical analysis.

Fish (*Mullus barbatus*) were collected by trawling from five sites in Izmir (Gediz, Uzunada, Gulbahce, Middle Bay) and Candarli Bays during cruises of R.V. *K.Piri Reis* in 2014. Immediately, 25-30 organisms were dissected on the research vessel from each sites and preserved at -20° . Muscle tissues were pooled and freeze-dried and then homogenized.

2.3 Analytical Procedure

10 g of each sediment sample were extracted in microwave extraction system by adding a mixture of hexane/dichloromethane and internal standards. After pre-concentration for the extracts sulfur was removed using activated elemental copper. For fractionation, sediment samples were transferred into florisil column [7]. Quantitative analysis was performed with Agilent5975C GC/MS (DB-5MS column: $30\text{m}\times 0.25\text{mm}\times 0.25\mu\text{m}$). To analyze OCs, GC/MS was programmed initially 70°C (2min held), then increase to 150°C with a velocity of $25^{\circ}\text{C min}^{-1}$ then increase to 200°C with a velocity of $3^{\circ}\text{C min}^{-1}$ and up to 280°C with a velocity of $8^{\circ}\text{C min}^{-1}$ held for 10 min.

Three subsamples of each sample (approximately 5 gr of dried fish) were extracted with a microwave digestion system using mixture of 30ml hexane/acetone. For recovery of the method, internal standards (PCB29, PCB198, endosulfan Id4, ϵ -HCH) were added. The extract was then concentrated to about 10 ml and then the extract was dried with sodium sulfate and concentrated with nitrogen down to 1 ml. To avoid the lipid interfere during GC analysis sulfuric acid was used for saponification. Florisil column was used for fractionation of OCs for 3 groups using different solvents [7].

The quality of the analytical data is assured using the reference materials of IAEA-451 and IAEA-417 for the biota and sediment samples (from IAEA, Monaco), respectively.

3. RESULTS AND DISCUSSION

3.1. Organochlorine Levels in Sediment

The concentration of OCPs, cyclodienes, DDTs, Aroclors and the selected ratios of chlorinated pesticides in sediments from Izmir and Candarli Bays were presented in Table 1.

Table 1. Total concentration of OCPs, cyclodienes, DDTs, Aroclors and the selected ratios of chlorinated pesticides in sediments from Izmir and Candarli Bays (as dry weight:dry wt)

Compounds/Locations	Gediz	Uzunada	Gulbahce	Middle Bay	Aliaga	Nemrut	Candarli
Σ OCPs (ng g ⁻¹)	1.48	3.62	1.71	1.88	6.52	29.6	3.51
Σ DDTs (ng g ⁻¹)	0.29	0.88	0.16	0.46	0.96	19.2	0.58
Σ Cyclodienes ¹ (ng g ⁻¹)	1.16	2.69	1.51	1.24	4.96	8.93	2.71
Σ Aroclors ² (ng g ⁻¹)	8.61	11.9	14.7	12.4	97.0	562	16.8
DDD/DDE (DDE+DDD)/ Σ DDT	0.27	0.31	0.17	0.29	0.45	0.196	1.89
DDT/DDE	0.050	0.045	0.13	0.059	0.032	0.033	0.15
%DDT/ Σ DDTs	3.78	3.30	9.68	4.35	2.19	2.66	4.84

² Σ Aroclors: Aroclor1254+Aroclor1260, ¹ Σ cyclodienes: heptachlor + aldrin + dieldrin + endrin

Concentrations of OCPs (sum of DDTs, HCB, lindane, heptachlor, aldrin, dieldrin, endrin) in surface sediments ranged from 1.48-29.6 ngg⁻¹ with an average value of 6.91 ngg⁻¹. The highest value was found at Nemrut site in Candarli Bay, while the lowest value of OCPs occurred at the Gediz site located in the outer part of Izmir Bay. The mean concentrations of OCPs were as following: 2.54 for *p,p'*-DDE, 1.88 for dieldrin, 0.58 for *p,p'*-DDD, 0.62 for endrin, 0.55 for heptachlor, 0.32 for HCB, 0.26 for aldrin, 0.091 *p,p'*-DDT and 0.063 ngg⁻¹ (dry wt) for lindane. Σ Cyclodienes were the predominant contaminants in all sediment samples with the exception of Nemrut site and Σ DDTs was higher than Σ Cyclodienes in this area (Table1).

Aroclors in sediments showed in noticeably higher concentrations than OCPs at both of Candarli and Izmir Bays. Aroclors are used as industrial chemicals and their probable source is industrial waste. Aroclor 1254 levels in sediments ranged from 3.35 at Gediz site to 215 at Nemrut site and Aroclor 1260 concentrations from 1.4 at Middle Bay to 347 ngg⁻¹ at Nemrut site.

p,p'-DDT is degraded to *p,p'*-DDE under aerobic and to *p,p'*-DDD under anaerobic conditions. Thus, higher or lower ratios of (*p,p'*-DDE+*p,p'*-DDD)/ Σ DDTs (sum of *p,p'*-DDT and its metabolites) indicated past or recent usage of technical DDT, respectively and the *p,p'*-DDD/*p,p'*-DDE ratios of these two metabolites provide the basic biodegradable condition of the intended environmental compartments [8].

According to results appeared in Table 1, ratios of (DDE+DDD)/ Σ DDT were in the range of 0.90-0.98 with entire values being >0.5. This infers that the degraded metabolites formed a significant proportion of total DDT compounds. The relatively slow degradation rate of DDT in the environment indicates early DDT influxes and by implication, non-existing DDT use throughout the region. Moreover, whole values of DDD/DDE ratio in Izmir Bay ranged between 0.17-0.31 and were lower than unity, indicating that the sediments was dominated by *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT. This result showed that the sediments collected from Izmir Bay were mainly under oxic conditions (Table 1).

Table 2. Assessments of potential biological risks of selected OCPs in the surface sediments of Izmir and Candarli Bays using two sediment quality guidelines (SQG)

Chemical	Range (ngg ⁻¹)	ER-L ¹	Above ER-L (%) ⁵	ER-M ²	Above ER-M (%) ⁵	TEL ³	Above TEL (%) ⁵	PEL ⁴	Above PEL (%) ⁵
p,p'-DDT	0.011-0.51	1.0	0	7	0	1.19	0	4.77	0
p,p'-DDE	0.12-15.6	2.2	14	27	0	2.07	14	374	0
p,p'-DDD	0.02-3.05	2.0	14	20	0	1.22	14	7.81	0
DDTs	0.16-19.2	1.58	14	46.1	0	3.89	14	51.7	0
Dieldrin	0.07-5.92	NA	-	NA	-	0.71	57	4.3	14
γ-HCH	0.01-0.17	NA	-	NA	-	0.32	0	0.99	0
Heptachlor	0.22-0.89	0.5	43	6	0	2.26	0	4.79	0
PCBs ⁶	8.57-562	22.7	29	180	14	21.5	29	189	14

¹ Effect range-low value, ² Effect range-median value, ³ Threshold effect level, ⁴ Probable effect level, ⁵ Percentage of samples above the corresponding levels, ⁶ Sum of Aroclor1254 and Aroclor1260. NA: Not available

As shown in Table 2, two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines [9], [10], as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines [11] were applied to evaluate the possible ecotoxicological risks of OCs in the study area. For *pp'*-DDE and *pp'*-DDD were higher than ERL values at one site (Nemrut site). Meanwhile, these compounds also exceeded the TEL value at the same site, but were significantly lower than the PEL and ERM values. The level of heptachlor was over the ERL value at 3 sites located in Nemrut, Gulbahce and Middle Bay, whereas it was still below the ERM, TEL and PEL values. This suggested that the levels of *pp'*-DDE, *pp'*-DDD and heptachlor at most sites other than Nemrut, Gulbahce, Middle Bay sites were lower than the values that may cause adverse biological risk. For DDTs, although it was not above the ERM and PEL values, 14% of total sites (Nemrut) in the study area were higher than ERL and TEL values appearing that the exposure of DDTs may cause ecological risk on the neighboring benthic organisms.

Total PCBs concentrations of the samples exceeded the ERL (ERL, 22.7 ngg⁻¹ dry wt) value at Aliaga (97.1 ngg⁻¹) and Nemrut regions (562 ngg⁻¹) which suggests that PCBs can exert toxic biological effects on aquatic organisms. On the other hand, these concentrations exceeded the ERM (ERM, 180 ngg⁻¹ dry wt), PEL (PEL, 189 ngg⁻¹ dry wt) values just only in Nemrut site. That means, based on Canadian quality guidelines, PCB concentrations at this region can cause adverse effects on aquatic biota.

3.2. Organochlorine Levels in Fish

Tables 3 shows the concentrations of organochlorines (ng g⁻¹ dry wt) and selected ratios in fish samples collected from five sites in Izmir and Candarli Bays. The maximum concentration of ΣOCPs (29.5 ngg⁻¹) was found in samples collected from Gulbahce site while the minimum concentration of ΣOCPs (5.31 ngg⁻¹) was observed in samples collected from Middle Bay of Izmir. In all samples *pp'*-DDE was the predominant DDT congener. Highest ΣDDTs levels occurred at Gulbahce region with 7.74 ngg⁻¹, while the lowest concentration was observed at Aliaga region with value of 0.93 ngg⁻¹ (Table 3).

ΣCyclodienes were the predominant contaminants in all fish samples, representing 53-89% of total OCPs. The concentrations of Σcyclodienes in the fish samples ranged between 3.84–20.7 ngg⁻¹. The mean cocentration of cyclodienes in the five sampling sites in this study was 12.6 ngg⁻¹. The highest levels of γHCH and HCB were found in Uzunada site.

Aroclor1254 concentrations ranged from 15.9 at Middle Bay to 44 ngg⁻¹ at Aliaga site. Aroclor1260 concentration ranged between 14.5 at Gediz and 95.4 ngg⁻¹ at Aliaga. The mean concentrations of Aroclor1254 and Aroclor1260 were 30.4 and 34.9 ngg⁻¹, respectively. The highest concentration of Aroclors (140 ngg⁻¹) was found in samples from Aliaga, while the lowest concentration of Aroclors (35.1 ngg⁻¹) was found in fish samples collected from the Middle Bay (Table 3).

In general, a ratio of (DDE+DDD)/ΣDDTs is more than 0.5 shows long-term biodegradation of DDT to DDE and DDD whereas a ratio of less than 0.5 may indicate recent input of DDT. The ratios of (DDE+DDD)/ΣDDTs were 0.73 to 0.88 in fish in this study (Table 3). These results indicated aged DDT pollution and showed that there has been no

recent input of technical DDT from the agricultural regions into the sampling regions. Ratios of DDD/DDE in fish less than 1 mean that *p,p'* DDT had been biotransformed to DDE under aerobic conditions in the all sampling sites.

Table 3. Total concentrations of DDTs, cyclodiens, Aroclors and the ratios of DDT concentrations in fish

Compounds/ Locations	Gediz	Uzunada	Gulbahce	Middle Bay	Aliaga
Σ DDTs (ng g ⁻¹)	1.93	6.05	7.74	1.18	0.93
Σ Cyclodiens ¹ (ng g ⁻¹)	13.43	19.85	20.7	3.84	4.96
Σ Aroclors (ng g ⁻¹)	35.7	67	49.3	35.1	139.6
DDD/DDE	0.81	0.45	0.18	0.20	0.84
(DDE+DDD)/ Σ DDT	0.77	0.88	0.74	0.81	0.73
DDT/ Σ DDTs %	23.3	12.2	26.2	19.5	26.9
DDE/ Σ DDTs %	42.5	60.5	62.5	66.9	39.8
DDD/ Σ DDTs %	34.2	27.3	11.2	13.6	33.3

¹ Σ Cyclodiens: heptachlor + aldrin + dieldrin + endrin

According to this study, health risk assessment was performed for Aroclor1254 and DDTs due to consumed fish. Annual seafood consumption in Turkey is estimated to be about 25 kg per year [12]. Therefore, the daily dietary exposure estimation by an adult person was calculated on basis of an average 68.5 g of fresh fish muscle consumption per day in Izmir, Turkey [13].

Table 4. Estimated daily intakes of DDTs, Aroclor 1254 and OCs in the fish by human (average body wt. 70 kg) in Izmir and Candarli Bays (ng/kg body weight/day)

	Gediz	Uzunada	Gulbahce	Middle Bay	Aliaga	ADI/TDI
Σ DDTs	0.53	1.66	2.12	0.32	0.25	20,000 ^a
Aroclor1254	5.8	10.4	9.0	4.4	12.1	20 ^b
Σ OCs	14.3	26.0	21.6	11.1	40.1	-

^aFAO/WHO (1996b)

^bIPCS (2000)

Estimated Daily Intakes (EDI) of DDTs by the people were far below the acceptable daily intake (ADI) suggested by the FAO/WHO [14] proposing this intake would not pose adverse effect to inhabitants of Izmir at the present. The EDI of Aroclor1254 by the people was below the tolerable daily intake (TDI) for of 20 ng/kg body weight per day, proposed by IPCS [15] suggesting this intake might not pose a health risk in Izmir and Candarli today (Table 4).

4. CONCLUSIONS

Organochlorines were measured in the sediment and fish samples from Izmir and Candarli Bays. *p,p'*-DDE was the predominant DDT congener. Σ Cyclodiens were generally predominant contaminants. Aroclors were found in noticeably higher levels than OCPs in sediments and fish. The highest levels of Aroclors, OCPs were found in sediments of Nemrut which can be attributed to industrial activities. According to SQG, DDTs were lower than the values that may cause adverse biological risk in sediment samples. Aroclor 1254 in sediments only exceeded the TEL value at Nemrut region. The maximum levels of Σ OCPs were found in fish collected from Gulbahce, while Aroclors were measured in Aliaga. According to selected ratios indicated no recent influxes of DDT in the sampling areas. The estimated daily intake of DDTs, Aroclor1254 in fish were below the acceptable daily intake level recommended by FAO/WHO.

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An Anatolian City on History-Future Pendulum; Kutahya-Eskigediz (Turkey) Historical City

Nurhan KOCAN^{1*}, Omer Lutfu CORBACI²

Abstract

Historical cities are placement including livability, identity and original values that have occurred as a result of cultural factors in harmony with nature from past to present. Historical cities expressed in time for visual and semantic features that including meaning in terms of living traditional cultural history and place. Because of these characteristics of such areas must be protected. Using protection is a valid approach in terms of sustainability. Uncovering of the importance of historical cities and ensuring the efficient use of these cities should be created to forefront of the tourism value of these cities, to include in the tour itinerary and/or to attract urban visitors and visitors to the city by highlighting the special factors of these places. In this study Kutahya-Eskigediz historical urban structure were investigated in terms of the quality of the natural and cultural landscapes. Concepts were developed within the protected areas for urban use strategies in the study. These strategies include proposed urban land use decisions, new functions, the maintenance, repair and urban design guidelines within the concept. The suggestions were presented in the form of the landscaping projects in the study. Autocad 2016, Photoshop CS5, Sketchup and Lumion software were used as well as hand drawings and sketches for creation of the landscape project. Recommendations and three-dimensional images have been presented in the form of plans. The projects produced results of the study can be an example for other historical cities of a similar nature.

Keywords: Historical city, historical city protection, landscape planning, landscape design, Kutahya-Eskigediz City.

1. INTRODUCTION

Cultural landscapes constitute parts of our common identity as mirror of the social development, creativity and spiritual richness of human beings. These areas connect the past with the present with their historical, artistic, documentary, functional etc. values so they need to be protected [1].

The physical qualities of the historical urban texture and the interactions of historical elements with each other should be evaluated with a holistic view. Restoration of cultural landscapes with sustainable uses and adaptation they to current living conditions will ensure preservation and continuity for future generations.

Eskigediz historical urban area is an important example for working because it has many examples of immovable cultural heritage, natural landscape and alternative tourism possibilities. In this context, the natural and cultural values of the study area has great importance in terms of the decisions on the preservation and use of historical urban areas for tourism purposes through sustainable usage principles and the presentation of the qualities of the historical urban area.

Traditional residential texture is the material culture document that enables continuity of society with its traditional character; constitute the memory of the place; connect the society's subjects to each other and to the geography where they live. The various dangerous such as changing social structure of the settlement, economic hardships, natural disasters as well as the lack of care in the traditional settlements and migration can negatively affect the development of traditional settlements [2].

^{1*} ¹Bartın University, Faculty of Forestry Department of Landscape Architecture Bartın/Turkey. Email: nurhankocan@myinet.com

² Recep Tayyip Erdoğan University Faculty of Fine Arts Department of Landscape Architecture Rize/Turkey.
Email: omerlutfucorbaci@hotmail.com

1.1. Cultural Heritage and Historical City Protection

Historical cities and original constructions are very important in terms of our cultural heritage. The preservation and revitalization of these areas to meet requirements of contemporary life condition is accepted as conservation idea [2].

The urban places created by each society in the different phases constitute the cultural structure of that society. These qualities are characterized as old for the next stages and they have become historical because they are part of the cultural evolution of mankind.

A concept of conservation based on the understanding of the continuity of history which brought new interpretations by introducing new contents to the concept of contemporary developments is based on the necessity of preserving the historical structure as a whole. Also developing the protection approaches based on the constant change of the physical environment [3].

The best way in urban conservation is active use of these areas and change in the urban environment [4]. Understanding the threats that cultural beings face and carry their values and importance to future can only be achieved by sustainability. The protected traditional urban texture provides social and cultural integration with cultural and touristic attraction. The cultural assets of the area make it a touristic center [4].

The conservation studies that began with restoration of monuments in the past but they have developed in the present to the preservation of historical textures and cities. The conservation and renovation work is included in conservation studies of the horticulture, street and urban building elements which complement the historical buildings. The purpose of preserving and renewing of the historical structure is to ensure historical and cultural continuity, to revitalize the historical landscape in the direction of contemporary living conditions, to maintain its identity, to evaluate historical structures with current functions, to establish urban landscape and traditional settlement model [1].

1.2 Sustainability and Tourism Relations

In line with the differentiation of human needs and the development of technology and demands historical sites have changed and they are undergoing changes. This causes the disappearance of the cultural characteristics of the elements belonging to the locality. Within the changing urban dynamics, the natural and cultural landscaping elements of the city and the settlement texture must be re-evaluated and examined. The investigation of physical place, usage relations, user requirements and expectations will enable the planning and design of these places according to today's conditions [2].

People living in the intense and difficult living conditions of the cities prefer tourism movements towards natural and cultural areas and want to get away from these negative conditions for a while. Natural, cultural and historical areas have attracted people in recent years highly. However, the increasing interest in these areas makes it necessary for the preservation and renewal of qualities of these areas.

Historical environment; it has a special importance and feature because it is a part of the circumstance which is formed in the historical perspective and which will continue its formation [1].

It is necessary to protect and develop the natural and cultural values for the continuity of tourism activities which are important contributions to the economic, social and cultural values of our country. The natural and cultural environment constitutes the basis of tourism. Therefore the protection of the environment is of great importance for a sustainable tourism. The development of tourism based on environmental protection will bring an economic, social, physical and socially improved environment. Tourism can be a vehicle for supporting the preservation of traditional architectural characters in important natural and cultural areas. The environmental quality and value of the area rises, the infrastructure can be improved and the environmental consciousness can be formed in the local area thanks to the tourism [5]. The people participate in alternative tourism to get information about natural, cultural and traditional life, to gain experiences and to spend their vacation in alternative areas [6].

2. MATERIAL-METHOD

The main material of this work is the Eskigediz town of Kutahya Province. Preliminary research about the topic has been used as auxiliary material in the study for literature on the subject. The urban area boundary of the study area was drawn through the Google Earth image and the historical city settlement was shown via the Eskigediz zoning plan. Eskigediz city has been chosen as a study area due to its natural, cultural and historical values for tourism. The continuity of cultural values for tourism future in Eskigediz is very important. In this context in order to enable the development of tourism solutions for protection-utilization balance have been proposed in the study. Evaluation and suggestions were made under the titles of residential gardens, the surroundings of historical buildings, the streets, the preservation of natural resource values, conservation and plant regeneration.

3. FINDINGS

3.3.1. General Characteristics of the Study Area and the Surrounding Area

Eskigediz is a town center connected to Gediz District center in Kutahya Province in inner western Anatolia part of Aegean Region. Eskigediz is 7 km away from the north-east of Gediz district center. Eskigediz is 91 km away from Kutahya city center and 63 km away from Usak. It is surrounded by Hisarcik, Emet, Cavdarhisar in the north, Aslanapa, Altintas in the east, Usak in the south, Manisa in the southwest, Saphane in the west and Simav in the northwest. Mount Murat is in the east and Mount Saphane is in the west [8].



Figure 1. The location of the city in the country and city border

Gediz District was founded by the Phrygians in BC. After the battle of Malazgirt in 1071 Gediz met the Turks for the first time. Between the years (1075-1086) it joined to Turks and in 1233 it joined to the Anatolian Seljuks lands. He joined the Ottoman lands after 1428 and became the center in 1871 [7].

Since its foundation Gediz has faced frequent natural disasters due to its location and ground features. The floods that erupted in 1875, 1901, 1911 and 1945 caused significant damage. The especially the floods of 1875 caused the destruction of the tannery area and so lather craft settled down. The city survived great fires in 1911, 1918 [9].

Eskigediz survived major earthquakes in 1886, 1896, 1944, 1956 and 1970. Gediz has moved with the decision of the Council of Ministers No. 7/1164 on 05.08.1970 because it's tectonic structure which causes the catastrophic events such as landslides and earthquake disaster. The residential area is 7 km distance to Eskigediz on the Simav highway. While Eskigediz was a neighborhood within the boundaries of Gediz Municipality in 1970-1988 it became a center of the province on 07.12.1988 [10].

The population of Gediz district center was determined as 5772 people in the first census of 1927. There are 10651 people in the 1970 census. After the 1970 earthquake there were 1452 people in 1975 census. 7307 people live in the Eskigediz according to the census conducted in 2000 [11].

Eskigediz was built in a valley where Gediz Creek partially collapsed. The topography around the town has a rugged structure. Because settlement area is located in a narrow valley so it cannot be enlarged in the horizontal direction. Horizontal expansion in the houses is only towards to the entry and exit points of the north and south of the valley. The placement on the risky area about earthquake prevented the vertical growth of dwellings [9]. Gediz River which in the south direction of Eskigediz collects the waters from Murat and Saphane Mountains, is important with a water collection area of 17500 km² [11].

Murat Mountain extends in the north-south direction in east of the district. Murat Dagi (2312 m) which is open to mountain tourism is covered with pine forests and ostriches. Murat Dagi has a very rich plant species, is attracting attention with this aspect the tourist especially in the spring and summer seasons with herbal and cold spring waters. Mount Saphane (Ulugedik Summit 2120m) is located to the west of Eskigediz [10].

Eskigediz was built on an undulating plateau with an average elevation of 1100-1200 meters. Mountains rising from the deep valleys opened by the rivers reach 2300 meters. The plains stuck between the mountains stretch along the river valleys in narrow strips [10].

The urban is influenced by the continental climate of inner western Anatolia. The average annual temperature value in the region is determined as 12.9 °C. The summers are usually set. The annual precipitation average is 565 mm. Rainfalls are generally seen in winter and the summer is droughty [11].

The widespread plant species are palm tree (*Quercus aegipolis*). Plants such as plane trees, cranberries, wild plants, roses, blackberries, walnuts, willow, poplar, spruce are spreading in area. (*Pinus nigra*) forests are spreading in there. The plants that adapt to the drought are on the southern slopes which are not very high. There are red pine trees (*Pinus brutia*) in this group. Herbaceous plant species are spread in pasture areas around the vineyards in the region. There are *Cistus laurifolius*, *Astragalus* sp., *Verbascum* sp., *Polypodium vulgare*, *Poterium spinosum*.

Due to its geological structure Gediz was founded on an area where fault lines are widespread. As a consequence of this situation hot waters in the region are much in the area. The Murat Mountain Thermal Spring is 30 km from the east of the Gediz District. The area is the center of tourism located on 1600 m where hot and cold water. The Ilica Hot Springs is 13 km far from the sea and 940 m high from the sea. It is a thermal tourism center established at the height. The thermal springs in 40-85 degrees have an important potential in terms of plateau as well as climate cures. The thermal springs are preferred due to the presence of forests and hot-cold waters around the springs in summer and winter. There are constructions for accommodation. There is no transportation problem on the roads connecting the area to the district and its surroundings [12].

Eskigediz's economic activity is composed of sectors such as trade, social services, construction, industry and agriculture. Due to the rugged nature of the Eskigediz agricultural activities are provided in a small part. Eskigediz is a town center that has not reached the desired development in economic terms. The economic struggle is pushing the townspeople migration [11].

The square kebabs made from the meat of animals thyme-fed in the mountainous region of Eskigediz and Gediz stew has a good reputation in the environment. The Gediz tarhana and Gediz hosmerim sweet are the other important food cultures that reflect cultural values.

3.3.2. The Historical Urban Texture of the Study Area

The character of a cultural landscape is defined both by physical forms such as roads, buildings, walls and vegetation as well as by forms of use that reflect cultural values and traditions [13].

The characteristics of the region are defined by elements such as traditional regional texture, streets, neighborhoods, open spaces, private home gardens, roads and structures that create important region character. Cultural landscape is a geographically can be limited and it gains value over time through the interrelationships between culture and the natural environment and identified by its natural, cultural, visual and semantic qualities [14].

Eskigediz is located in a valley extending in the north-east / south-west direction. The modern buildings in the town are seen in the areas of Sabirgazi and Camikebir in the north and south directions of the area. Park, Kurtulus, Hisar, Ismetpasa and Camikebir streets in Eskigadiz are important for the two-storey wooden carcass houses reflecting the Ottoman architectural style. The town is a rugged place. The streets are formed in a narrow structure [11].

The commercial activities are concentrated in the Kurtulus neighborhood. The modern industrial establishments such as socks factory, tire factory etc. are in the Camikebir district of Eskigediz. The marble factory is located in the Park district, the oil factory in Sabirgazi district. Within the borders of Park and Ismetpasa districts there are workshop type industrial establishments [11].

The city which attracted attention with its historical city texture became a member of the Union of Historic Towns in 2001. Eskigediz was included in the scope of urban, natural and archaeological site with its extraordinary identity. The Asarardi District where ancient Kadoi city remains is preserved as second and third degree archaeological site. 111

buildings were selected as examples of urban sites and architecture. In addition 10 fountains, 11 mosques, 4 bridges, 3 laundry facilities, 1 waterway, 1 aqueduct, 1 water depot and military buildings were protected under the same scope.

The Kursunlu Mosque built in 1540 in Eskigediz and the Ulu Mosque (Gazanfer Aga Mosque) built in 1553 are the oldest buildings in the city. The original states of the constructions were distorted in the earthquake of 1970 [10].



Figure 2. An old view from the city



Figure 3. A view from the city in now

The wooden houses located in the historical texture are the houses that best reflect the Ottoman architecture. The houses are usually two layers and made of stone base walls and upper floors are made by wood. The upper floor consists of sitting units and the lower floors consist of rooms, haystacks and stables. On the second floor there are lounges, rooms, kitchen and bay window. At the back of the house there is a courtyard. You can get out and watch the street from the side windows. The size of the house is the indication of the socio-economic status of the host. The historical buildings in the district are mostly covered with tiles also houses include windows with cages and bay window. The streets in the city have some cobblestone pavement which is traditional stone pavement in some streets while in some streets this feature is broken and the roads are covered with asphalt. The roofs of the houses are square-quadrangular folded roofs in Turkish architecture and roofing material is alaturka tile. The stone, soil and wood materials that are easy to find in the natural surroundings have been selected for construction of the houses.

The gardenless buildings provide direct street or street access to the building. The facade of houses is located in the street direction. The ground floor of the courtyard is covered with stone or compacted soil. The walls are made of stone or mud brick. Because of the small size of the residential gardens there are plants with vegetable horticulture, fruit trees and pine trees that have not been treated with excessive trees and trees.

The streets are of human scale and are curvy and featured to pass through staircases in places. The pavilions of the structures, the stone walls, the courtyards, the entrance gates and the bay windows constitute the vertical limit of the street. Because the roads are very narrow and have an organic structure and there are no pavement and road afforestation. The green places on the historical site are not enough. The small squares in the intersection of hilly and rocky areas, public areas, residential gardens and streets form open green areas.

The narrow roads between city centers and historical districts cause problems for vehicle and pedestrian circulation system because they are open to traffic. There is a parking problem in the city, vehicles parked on the side of the road so cause image pollution and traffic accidents.

The lack of restoration has led to the establishment of low-income families with low socio-economic, cultural and income levels. The new users of some traditional historical houses have damaged the original appearance of the structures and the originality of the building-structure.

4. CONCLUSIONS AND RECOMMENDATIONS

Despite the destruction of disasters such as fire, flood and earthquake in many times in the history of Eskigediz, it attracts attention with its fascinating historical urban texture, natural structure, hot springs and different cultural features. Today, Eskigediz is waiting for tourists as one of the outstanding historical cities of our country with its characteristic feature, its historical architectural texture as stopover place for tourism.

The area has different alternative opportunities for weekend and day trips and congress tourism thanks to its location and close proximity to many cities. The presence of services such as thermal spas makes the area attractive.

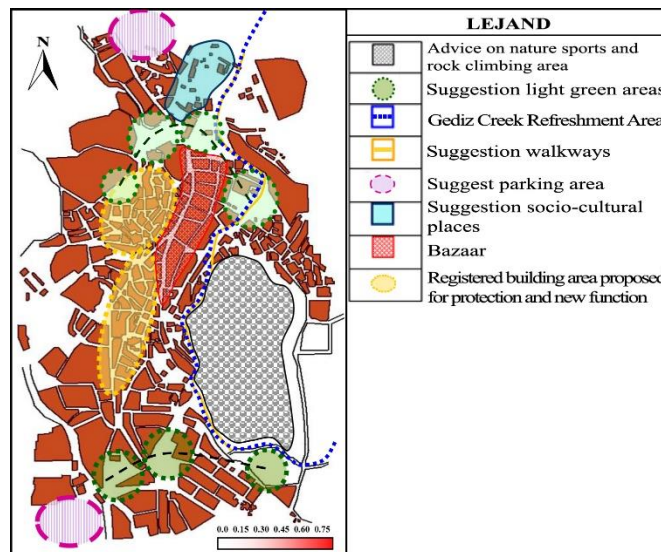


Figure 4. The map of proposal land use

The green spaces around the historical towns and structures should also be considered together in their conservation and development plans. The green spaces, parks, urban afforestation, children's playgrounds are needed to meet the physical and visual needs of the inhabitants and tourists in the region. In this context, gardens of historical houses, openings in the surroundings of structures should be taken into consideration. The materials, accessories and plant material of the active green areas should be in accordance with the original-natural structure and plants of the city. The development of forests and wooded areas around the city is important in terms of appreciation of the city together. The attractive natural visibility of the roadside can be achieved with the green belt system.

The maintenance of existing plants such as drug-pruning should be done and the plants that disturb the urban silhouette should be arranged and redesigned. The pruning of large trees that prevent the perception of housing patterns and overflowing public spaces must be met by the municipality.

The arrangement of some the buildings that have not lost their originality can be used as a museum. It will be an example for preservation. The creation of the creation of areas such as pedestrian areas, local sales products, living and recreation areas, walking paths, culture-information houses, exhibition areas and etc. where cultural activities will stimulate social life will make the historical city tourism center where will be more experienced. The new business opportunities and economic benefits will be provided to the public with tourism. The cafeteria, restaurant, tea garden, sightseeing, recreation, entertainment and needs oriented business are inadequate in the area. The rocky hill where the earthquake monument is located carries the view terrain feature dominated by the settlement. There should be resting places suitable for small and local architecture where visitors can spend more time for relax and they watch the city.

In the historical city, the use of vehicles and parking problems brought about by today's living conditions should be solved and parking lots should be designed in the access road. The routes should be considered in the form of traffic on a narrow road and certain service hours should be set for commercial use.

The suitable routes and paths for hiking and nature walk should be determined and wooden walkways should be provided for all seasons in the city. In the historical areas a standard should be introduced especially all kinds of objects such as canopy, tent etc. that can be seen in photographing.

The prevention should be taken from commercial workplaces to remove complex image because they scatter much of their products to image in the environment. The edge of the creek that passes through the settlement should be cleaned and rehabilitated by considering as a natural area.

The conservation should not only be physical protection but protection as well as socio-cultural structure. The city needs to organize and care for the infrastructure and physical environment when it is considered both for the living and for the sight. The sale of local products which local people can benefit from tourism should be provided.

The co-operation of universities, municipalities and non-governmental organizations with joint decisions will gain speed and the success of application of the protection measures will be provided for the area and the development of tourism. The counseling, guidance staff training and public education centers and tourism bureau should be

established. In conservation and renewal studies protection should be taken to cover the entire city as well as areas such as streets, houses and gardens. These structures play a decisive role on the city identity.

For the integration of the research area into contemporary, economic and social life, it will be a good solution to convert traditional houses into different living spaces and acquire new functions. Eskigediz historical city has the potential of tourism with the potential of ecotourism as a source of cultural values, archaeological and historical places, structures, settlement texture, handicrafts and local culinary features. Providing the traditional Turkish experience and continuity of the characteristic features of the city will define the city as a more interesting place.

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Experimental study using reactive distillation column for biodiesel production

Suleyman KARACAN^{1*}

Abstract

In this experimental studies, a reactive packed distillation column was used for production of fatty acid methyl ester (FAME). The FAME considered as biodiesel was produced from transesterification reaction between sunflower oil and methanol by using packed heterogenous basic CaO catalyst. Steady-state and dynamic studies were investigated in the system. The effect alcohol-oil ratio on the system was investigated. Experiments have shown that the RD process can produce biodiesel at a production of %90 (%m/m) continuously with an alcohol-oil ratio of 6:1.

Keywords: Reactive Distillation, Biodiesel, CaO

1. INTRODUCTION

Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect [1-2]. Base catalysts include homogeneous base catalysts and heterogeneous base catalysts. The commonly used homogeneous catalysts are NaOH, KOH and their alkoxides. Homogeneous alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification [4]. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction. Therefore, it is considerably more costly to separate the catalyst from the produced solution [3-4]. Heterogeneous base catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. Meanwhile, they are much more easily separated from the liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [5]. Many researchers have studied calcium oxide (CaO) as a strong candidate for the heterogeneous catalyst, due to the commercial availability, the economical advantage and the relatively higher activity [6-7]. Heterogeneous catalytic transesterification reactions required higher methanol-to-oil molar ratio to forward the reaction toward product side which leads to increase the production cost of biodiesel. In order to reduce the methanol-to-oil ratio, an ideal system for continuous production of biodiesel is the application of reactive distillation (RD) technique. In the reactive distillation (RD) system, the excess/ unreacted methanol was completely vaporized by the reboiler and the vapors were recirculated in the RD column and utilized in the reactive zone. Hence, the methanol-to-oil ratio is reduced significantly [8]. Transesterification of palm oil with methanol in the presence of potassium hydroxide as homogeneous catalyst in reactive distillation (RD) column was studied by Prasertsit, Mueanmas, and Tongurai 2013. A maximum methyl ester conversion of 92.27% was reported under the optimal conditions of reboiler temperature at 90°C, methanol- to-oil ratio at 4.5:1 and KOH at 1 wt%. Agarwal et al. [9] studied continuous transesterification of karanja oil in the reactive distillation (RD) system and helical tube system using KOH as homogeneous catalyst. Therefore, a heterogeneous catalyst operated RD system is needed to check the feasibility of continuous production of biodiesel.

Niju et al. [10] investigated continuous flow transesterification of waste frying oil (WFO) with methanol for the biodiesel production in a laboratory scale jacketed reactive distillation (RD) unit packed with clam shell based CaO as solid catalyst. The effects of operating parameters on methyl ester conversion were investigated and discussed. In this work, the RD system packed with CaO was studied for the biodiesel production

^{1*} Corresponding author: Ankara University, Engineering Faculty, Department of Chemical Engineering, Tandogan 06100, Ankara, TURKEY, E-mail: karacan@jeng.ankara.edu.tr

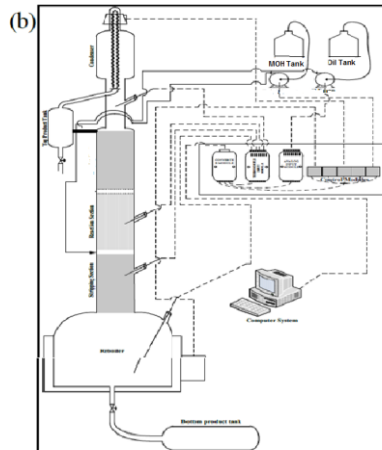
to develop a continuous heterogeneous catalyzed process. The effects of operating parameters on methyl ester conversion were investigated and discussed.

2. MATERIAL AND METHOD

Sunflower oil and methanol were used as a feedstock for the biodiesel production. heterogenous basic CaO catalyst was used for the biodiesel production. Sunflower oil was supplied from an oil production plant. Methanol and CaO were purchased from Sigma–Aldrich. The process involved in this work was a transesterification reaction occurring simultaneously with distillation operation that were carried out in the reactive packed distillation column set up as shown pictorially in Figure 1a and schematically in Figure 1b. The column, excluding the condenser and the reboiler, had a height of 1.5 m and a diameter of 0.05 m. It consisted of a cylindrical condenser with a diameter and a height of 5 and 22.5 cm respectively. The main column section of the plant was divided into two subsections. The upper and lower sections were the reaction and the stripping sections respectively. The stripping section was packed with raschig rings while the reaction section was filled with small lumps ~3-20 mm of CaO solid. The reboiler was spherical in shape with a volume of 3 Liter. The column was fed with sunflower oil and Methanol at the top. All the signal inputs (reflux ratio (R), feed ratio (F) and reboiler duty (Q)) to the column and the measured outputs (top segment temperature (T_{top}), reaction segment temperature (T_{rxn}) and bottom segment temperature (T_{bot})) from the column were sent and recorded respectively on-line with the aid of MATLAB/Simulink computer program and electronic input-output (I/O) modules that were connected to the equipment and the computer system. This block diagram was shown in Figure 2.



(a)



(b)

Figure 1 Reactive packed distillation column: (a) Pictorial view; (b) Sketch view

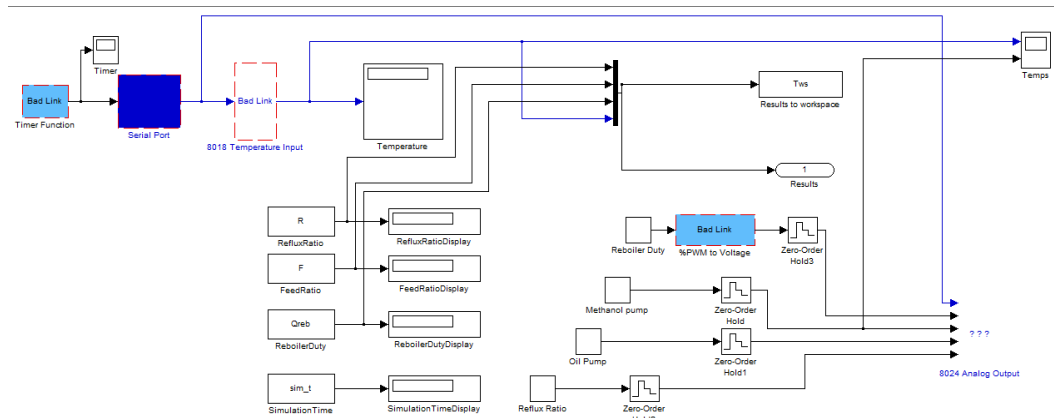


Figure 2 Block diagram in which experimental data are received and recorded

2.1. Transesterification Reaction

Transesterification of vegetable oils with alcohol is the best method for biodiesel production. There are two transesterification methods, which are: (a) with catalyst and (b) without catalyst. The utilization of different types of catalysts improves the rate and yield of biodiesel. The transesterification reaction is reversible and excess alcohol shifts the equilibrium to the product side [11-12]. Fig. 1 shows the general equation of transesterification reaction.

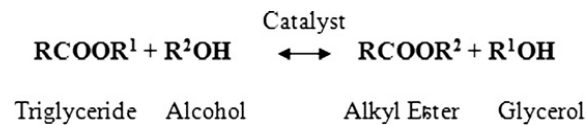


Figure 3 General transesterification reaction equation.

Many different alcohols can be used in this reaction, including, methanol, ethanol, propanol, and butanol. The methanol application is more feasible because of its low-cost and physical as well as chemical advantages, such as being polar and having the shortest alcohol chain [11]. According to Figure 4, R1, R2, and R3 are long chains of hydrocarbons and carbon atoms called fatty acid chains. The reaction is based on one mole of triglyceride reacting with three moles of methanol to produce three moles methyl ester (biodiesel) and one mole glycerol.

Generally the transesterification reaction involves some critical parameters which significantly influence the final conversion and yield. The most important variables are: reaction temperature, free fatty acid content in the oil, water content in the oil, type of catalyst, amount of catalyst, reaction time, molar ratio of alcohol to oil, type or chemical stream of alcohol, use of co-solvent and mixing intensity.

The esterification reaction occurring in the column was an equilibrium type given as:

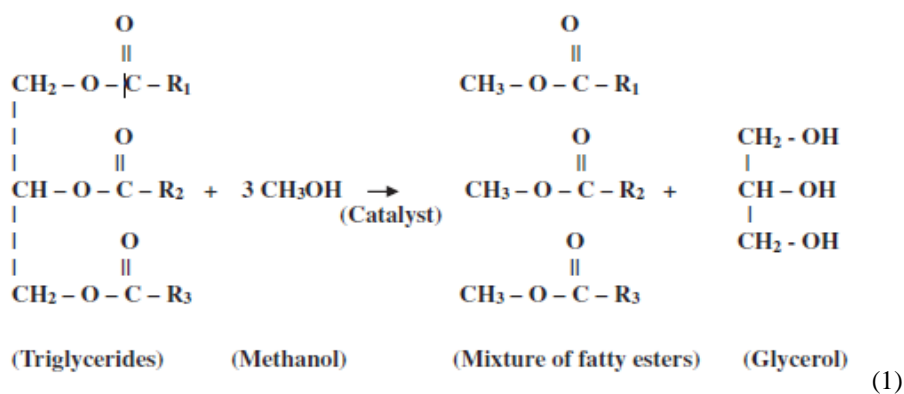


Figure 4. Methanolysis of triglyceride.

3. RESULTS AND DISCUSSION

Steady-state and dynamic studies were carried out in the system. The effect alcohol-oil ratio on the system was investigated. The reactant flow rate is one of the most important parameters in continuous flow RD system. At very low feed flowrates, liquid film formed on the catalyst surface enhanced the mass transfer resistance and lowered the methyl ester conversion. However, an increase in the feed flowrate reduces the mass transfer limitation and results in higher methyl ester conversion. Experimental studies were carried out in a reactive distillation column given in Figure 1. In order to see the effects of the feed flow rate ratio on the system, dynamic experimental studies were carried out by keeping the oil flow rate constant and positively affecting the methanol flow rate. In the steady state condition, the reboiler heat duty, Q value is 490 W, feed flow rates of methanol and oil were 4 ml/min at a 6:1 molar ratio of methanol to oil and reflux ratio was selected as 3. The reboiler temperature, the stripping zone temperature and the reaction zone temperatures were measured in the system. In order to bring the system into a dynamic state, firstly the flow rate of Methanol was increased from 4 ml / min to 5 ml/min for 600 second at a 8:1 molar ratio of methanol to oil. Later, the flow rate of Methanol was increased from 5 ml / min to 6 ml / min for 600 second and then increased from 6 ml / min to 7 ml/min for 760 second at a 10:1 molar ratio of methanol to oil. The experimental data obtained were given in Figures 5-7. As seen in the Figures, the positive effects on methanol flow rate were increased in the temperatures of the reactive distillation column

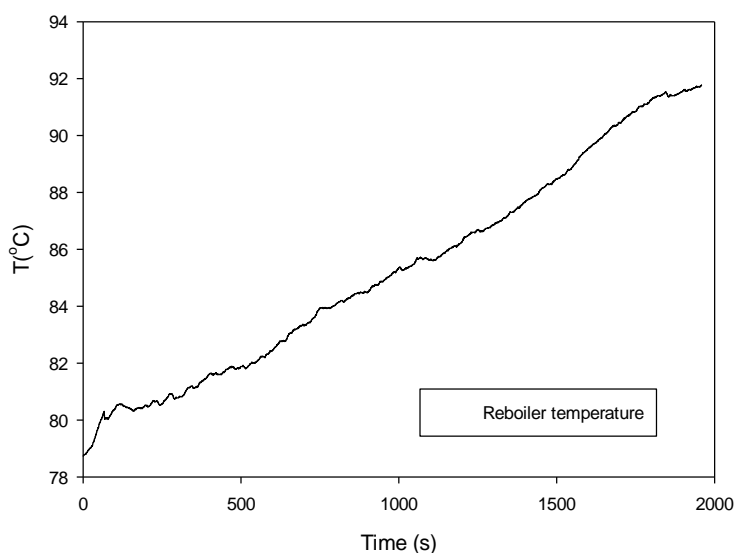


Figure 5 Effect of the flow rate of methanol on the reboiler temperature.

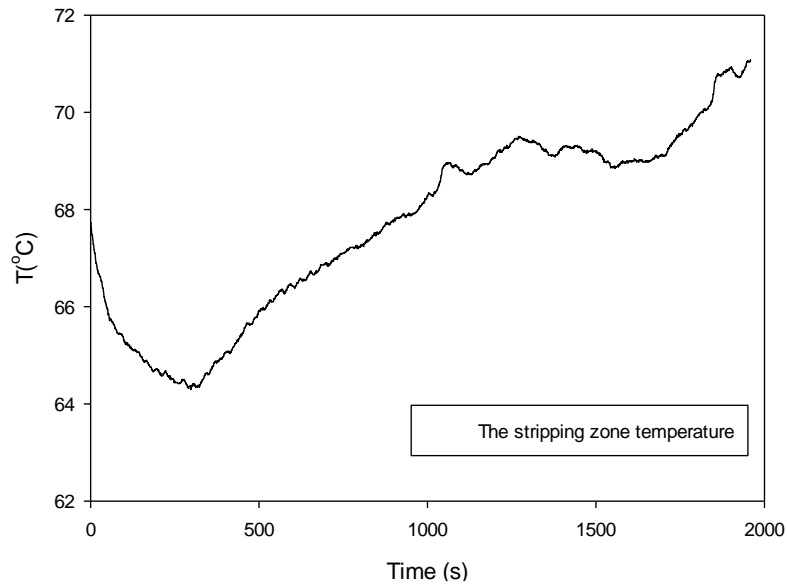


Figure 6 Effect of the flow rate of methanol on the stripping zone temperature

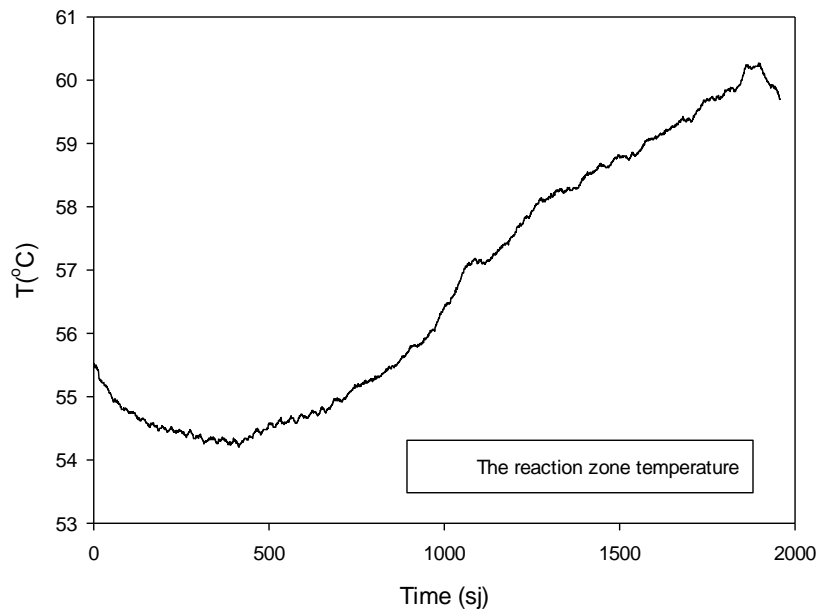


Figure 7 Effect of the flow rate of methanol on the reaction zone temperature

The biodiesel yield could be improved by introducing excess amounts of methanol to shift the equilibrium to the right-hand side. The experimental results, illustrated in Figure 8, indicate the feed flow ratio of methanol to oil has a significant impact on the biodiesel yield. The biodiesel yields grew as the molar ratio increased, and the yield was 78.96 % at a 6:1 molar ratio of methanol to oil when analytical reagent methanol was used.

In comparison, the biodiesel yield increased from 74% to 93% when the molar ratio was increased from 4:1 to 10:1. However, the yields were slightly reduced when the ratio of methanol to oil was higher than 12:1, and the biodiesel yield was only 88% at 14:1. The reason is that the catalyst content decreased with increase of methanol content. Therefore, the optimum molar ratio of methanol to oil was 10:1.

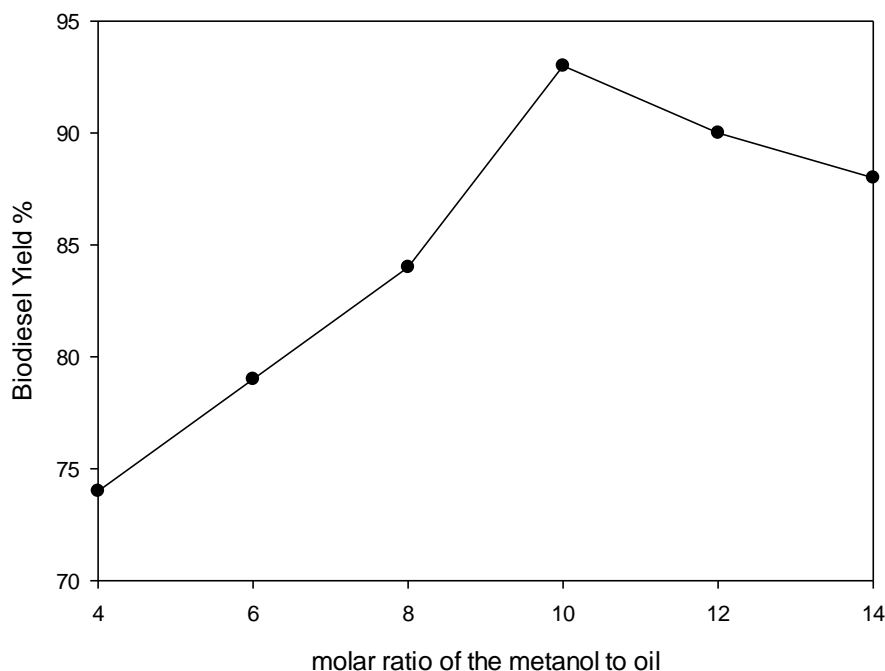


Figure 8 Effect of molar ratio of methanol to oil on biodiesel yield

4. CONCLUSIONS

In the present study, I developed Reactive Distillation system for the continuous production of biodiesel.

by using packed heterogenous basic CaO catalyst was successfully tested as a solid catalyst for transesterification of sunflower oil into biodiesel in the continuous process. A maximum methyl ester conversion of 93% was obtained at a reactant flow rate of 0.4 mL/min, methanol/oil ratio of 10:1 and the reboiler heat duty, 490 W. These results suggest that the RD system packed with CaO is a promising method for the continuous biodiesel production.

ACKNOWLEDGMENT

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Calorific Properties of Flowering Plants

Suryakant CHAKRADHARI^{1*}, Khageshwar Singh Patel²

Abstract

The aroma and coloring chemical compounds inherently present in the flowering plants are thrown in large scale as waste after the harvesting. In view of sustainable waste energy management, the combustion characteristics of 40 flowering plants grown in central India are described. The values of bulk density, moisture content, calorific value and ash residue of the flowering plants (n=40) was ranging from 560 – 1300 kg m⁻³, 1.6 – 4.8%, 4450 – 9500 kcal kg⁻¹ and 3.7 – 17.6% with mean value (p = 0.05) of 953±56 kg m⁻³, 3.3±0.3%, 6657±352 kcal kg⁻¹ and 11.4±1.3%, respectively are presented. The cluster analysis is used for grouping of the energetic plants.

Keywords: Gross calorific value, proximate parameter, flowering plant

1. INTRODUCTION

Flowering plants (angiosperms) are largest genera including > 250000 species, comprise 90% of the Plant Kingdom. They are seed-bearing vascular plants almost every habitat from forests to grasslands. Most flowers grow on receptacles, which are enlarged parts of the plant's stem. They usually have five sets of parts i.e. whorls, corolla, stamens, pistils and seeds. In addition, they survive in the various climatic stresses i.e. drought, cold, salt and low nutrient availability [1]. The calorific value of trees, agricultural and animal wastes was reported [2]-[13]. However, no data for fuel property of flowering plants which having high mass productions were reported in the literatures. In this work, gross calorific value and proximate parameters (i.e. bulk density, moisture content and ash residue) of 40 flowering plants are described for their uses as energetic biomass to meet urgent energy demand in the developing country.

2. MATERIAL AND METHODS

2.1. Study area and sampling

The name and family of plants selected for the proposed work is shown in Table 1. The flowering plants of Raipur city, central India (21° 15' 0" N, 81° 37' 48" E) were selected randomly. The composite sampling of the matured plant parts i.e. stem, leaf and flower was carried out during winter period i.e. February, 2016. The various plant parts (i.e. flower, leaf, stem and root) of the most energetic biomass: Sweet sultan was collected separately. The samples were stored in the cleaned plastic bag with drying in air by sun light for 2 days. They were grinded in the powder form by sieving out particles of size < 0.25 mm. The prepared sample was stored in the cleaned 100-ml glass conical flask and dried at 50 °C for one day in an oven.

2.2. Analysis of proximate parameters and calorific value

The compactness of the biomass affects remarkably the heat value and handling cost. The bulk density (BD) of the biomass was determined by dividing the mass with the volume of the capsule. The moisture content of the samples were analyzed by heating at 105 ± 2 °C for a period of 60 min [14]. The ash content of the materials was determined by heating the sample at 800°C for 5 hr in a platinum crucible [15]-[16]. The ash extract was prepared by equilibrating 5 g of sample with 25 ml of deionized water in ultrasonic bath for 6 hr. The clear extract was decanted out for the pH measurement.

^{1*}Corresponding author: School of Studies in Environmental Science, Pt. Ravishankar Shukla University, Raipur, 492010, CG, India. suryachakradhari99@gmail.com

² School of Studies in Chemistry, Pt. Ravishankar Shukla University Raipur, 492010, CG, India. patelkhageshwarsingh@gmail.com

The gross calorific value (GCV) was determined experimentally using a Digital Microprocessor Based Bomb Calorimeter UTS 1.34, Advance Research Instruments Co., New Delhi as described in the literature. A weighed wood sample was placed in the combustion capsule. The oxygen gas was flowed into the combustion cylinder. The power was then switched on to start the auto temperature adjustment and the stirring motor. The initial temperature was recorded after equilibrium attained i.e. after 5 min. The bomb content was then fired by using the ignition switch. The bucket temperature i.e. final temperature was recorded after stabilization. The difference between the original length and the new length was multiplied by 0.335 to obtain the number of calories liberated by combustion of the fuse. For every sample, gross calorific value in kcal kg⁻¹ was calculated using the following equation [17].

$$GCV = \frac{[W_e \cdot \Delta T] - \{W_1(4.18) + (W_2(0.335))\}}{M}$$

where GCV is the gross calorific value of species, W_e is the weight of sample, W₁ is the weight of cotton thread, W₂ is the weight of fuse wire and ΔT is the rise in temperature, respectively.

2.3. TG-DGA Spectra

The content of volatile compounds, moisture, cellulose, lignin and residue of the biomass was analyzed by using a Mettler Thermogravimetric Analyzer- TG-DGA-2 by heating at rate of 20°C/min. The fixed carbon (FC) fraction was calculated by using following equation [18].

$$FC \% = \frac{W - (VC + AR)}{W} \times 100$$

Where, W, VC and AR represent the initial content of the biomass, volatile organic compounds and ash residue, respectively.

2.4. Cluster analysis

The IBM SPSS Statistics 23 was used for the statistical and cluster analysis in the present work (IBM SPSS 2015) [19].

3. RESULTS AND DISCUSSION

The proximate parameters of the flowering plants are presented in Table 1. The physical and chemical properties of biomass affect the processing efficiency as well as logistical delivery and overall energy production cost. The whole process of thermal utilization of solid biofuels (i.e. fuel supply, combustion system, solid and gaseous emissions) is influenced by their nature, physical characteristics (e.g. particle size, bulk density, moisture content, calorific value) and chemical composition [20].

Table 1. Botanical characteristic, proximate parameters and calorific value of plants

S. No.	Local name	Botanical name	Family	Type	BD, kg m ⁻³	MC, %	GCV, kcal kg ⁻¹	AR, %	pH of AR
1	Sweet sultan	Amberboamoschata	Asteraceae	Herb	1260	1.6	9500	8.4	13.5
2	Daisy	Bellisperennis L	Asteraceae	Herb	950	3	6850	14.8	13.2
3	Pot marigold	Calendula officinalis L	Asteraceae	Herb	1000	3.2	6350	15.2	12.5
4	Corn flower	Centaureacyanus	Asteraceae	Herb	1080	2.2	7930	11.2	12.3
5	Sevanti	Chrysanthemum sp.	Asteraceae	Herb	570	3.8	5630	16.5	13.5
6	Coloured cosmos	Cosmos bipinnatus	Asteraceae	Herb	830	3.4	6810	13.7	13.8
7	Yellow cosmos	Cosmos sulphureus	Asteraceae	Herb	1160	2.1	7940	13	13.5
8	Dahlia	D. variabilis	Asteraceae	Herb	900	2.4	6000	15	12.6
9	Indian blanket	Gaillardia pulchella	Asteraceae	Herb	800	3.8	5160	17.5	12.6
10	Sunflower	Helianthus annus	Asteraceae	Herb	740	4.8	5430	17.5	12.9
11	Beach sunflower	Helianthus debilis	Asteraceae	Herb	660	3.4	5340	7.9	14.4
12	Chandanigen da	Tagetespatula	Asteraceae	Herb	1000	3.4	6980	11.5	14.3
13	Genda	Tagetesrecta	Asteraceae	Herb	890	3.2	5910	8.2	14.3

14	Tithonia	T. rotundifolia	Asteraceae	Herb	750	3.2	5630	17.6	13.7
15	Straw flower	Xerochrysumbracteatum	Asteraceae	Herb	1120	2.2	7830	11	13.3
16	Sadabahar	Catharanthusroseus	Apocynaceae	Herb	1200	2.6	7730	9.4	13.4
17	Mudra	Calotropis gigantean	Apocynaceae	Herb	890	4.1	6960	11	13.2
18	Yellow kaner	Cascabelathevetia	Apocynaceae	Shrub	870	4.2	6100	6.9	14.1
19	Chandani	Tabernaemontanadivaticata	Apocynaceae	Herb	1150	3.8	7470	11.8	13
20	Kaner	Nerium oleander	Apocynaceae	Shrub	1000	2.2	7890	6.9	13.2
21	Piliya	Tecomastans	Bigoniaceae	Shrub	1300	2.4	8320	5.6	13.3
22	Candytuft	Iberisamara L.	Brassicaceae	Herb	950	4.7	6270	8.2	13.9
23	Gudhal	Hibiscus rosasinensis	Malvaceae	Shrub	1120	3.8	7590	4.2	13.6
24	Hollyhock	Althea rosea	Malvaceae	Herb	840	2.6	6380	12.6	13.3
25	Poppy	Papaversomniferum	Papaveraceae	Herb	750	3.1	5740	15.1	14.3
26	Garden phlox	P. drummondii	Polemoniaceae	Herb	860	3.2	5460	14.7	13.3
27	Snap dragon	Antirrhinum majus L.	Plantaginaceae	Herb	850	3.9	4930	15.2	13.7
28	Besharam	Ipomoea carnea	Convolvulaceae	Shrub	1000	3.6	6900	8.2	12.7
29	Flaming katy	Kalanchoeblossfeldiana	Crassulaceae	Herb	800	4.8	5030	17.6	11.4
30	Carnation	Dianthus caryophyllus	Caryophyllaceae	Herb	1030	2.6	7030	12.3	13.9
31	Crown thorns	Euphorbia milli	Euphorbiaceae	Herb	1140	4.1	6780	15.4	12.9
32	Red powder puff	Calliandrahaematocephala	Fabaceae	Herb	1060	2.6	8090	3.7	12.3
33	Sword lily	Gladiolus grandiflorus	Iridaceae	Herb	870	3.6	6220	7.1	12.8
34	Booganbel	Bougainvillea glabra	Nyctaginaceae	Shrub	1280	2.8	8660	8.6	13.3
35	Mogra	Jasminumsambac	Oleaceae	Herb	560	4.8	4450	16.4	13.4
36	Larkspur	Delphinium ajacis L.	Ranunculaceae	Herb	860	4.4	5940	13.2	13.6
37	Rose	Rosa rubiginosa	Rosaceae	Herb	980	4	6150	9	14
38	Madhukamini	Murrayapaniulata	Rutaceae	Shrub	980	2.6	7520	4.4	14.2
39	Petunia	Petunia interifolia	Solanaceae	Herb	950	2.9	6190	14	13.6
40	Raimuniya	Lantana camara	Verbenaceae	Herb	1120	3.8	7170	4	14.2

3.1. Bulk density

The bulk density (BD) is an important parameter of harvested plant for the subsequent processing. It is related to the transport cost and energy production of biomass. The BD value of the plants (n=40) was ranged from 560 – 1300 kg m⁻³ with mean value (p = 0.05) of 953±56 kg m⁻³. The highest BD of plant of Nyctaginaceae family was observed, may be due to presence of higher combustible organics i.e. cellulose and lignin materials as shown in Fig. 1(a).

3.2. Moisture content

The moisture content (MC) in biomass presents as bulk and physically or chemically bound water. Low moisture content results in improved density and durability of the fuel [21]. Most compaction techniques require a small amount of moisture to "soften" the biomass for compaction. The MC value (i.e. physically and chemically bound water) of 40

plants was ranged from 1.6 – 4.8% with mean value ($p=0.05$) of $3.3\pm 0.3\%$. The lowest MC for plants of three families i.e. Caryophyllaceae, Fabaceae and Rutaceae was recorded as shown in Fig. 1(b).

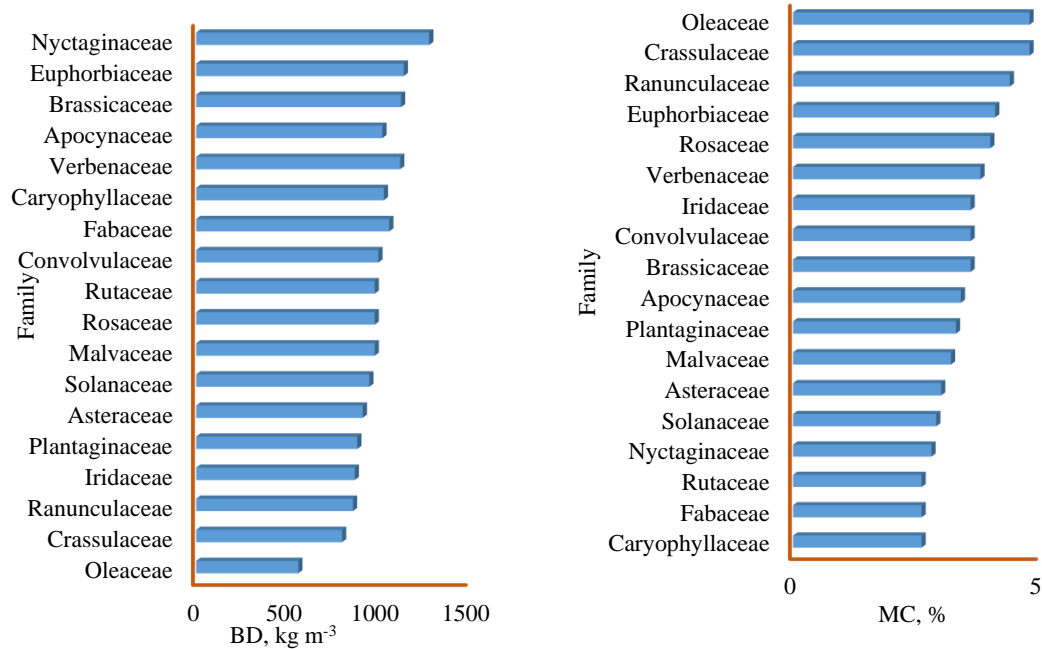


Fig. 1 (a). Bulk density (BD) of plants belonging to 17 family (b). Moisture content (MC) of plants belonging to 17 family

3.3. Calorific value

The most important fuel property of biomass is calorific or heat value [22]. The gross calorific value (GCV) was used to compute the competitiveness of a processed fuel in a given market situation. It represents the absolute value of the specific energy of combustion, in calorie, for unit mass of a biofuel burned in presence of oxygen in a calorimetric bomb under the conditions specified. The GCV of 40 dried plants was ranged from 4450 – 9500 kcal kg⁻¹ with mean value ($p = 0.05$) of 6657 ± 352 kcal kg⁻¹. Remarkably higher GCV for plants of family i.e. Fabaceae and Nyctaginaceae was marked as shown in Fig. 2(a). Among them, the highest GCV for Sweet sultan (Amberboamoschata) was recorded, may be due to presence of higher combustible carbons, Fig. 2(b). The GCV for various plant parts of Sweet sultan is shown in Fig. 3. The energy of different parts of Sweet sultan was found in following decreasing order: flower > leaf > stem < root, may be due to storage of energetic materials through foliage rather than root.

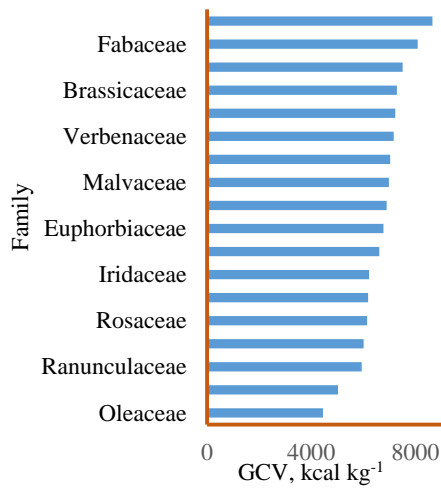


Fig. 2(a). Gross calorific value (GCV) of plants belonging to 17 family



Fig. 2(b). Image of Sweet sultan plant

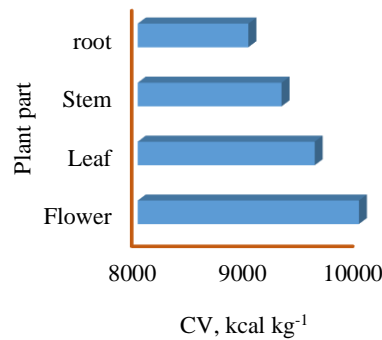


Fig.3. Energy variation of Sweet sultan's plant part

3.4. Ash residue

The fraction obtained from chemical break down of biomass by thermal process is known as ash residue. Inorganic constituents, such as organically bound cations, inorganic salts and minerals make up the ash present in or on the surface of biomass [23]. The ash content of biomass affects both handling and energy conversion cost. The value of ash residue of the plants (n=40) was found to be ranged from 3.7 – 17.6% with mean value (p = 0.05) of 11.4±1.3%. The lowest AR value of plants belonging to family i.e.Fabaceae, Verbenaceae and Rutaceae was recorded as shown in Fig. 4. The AR extract was found to be alkaline in nature, pH value ranged from 11.4 – 14.4 with mean pH value (p = 0.05) of 13.4±0.2. The ashes are usually composed of oxides and salts of Na, K, Mg, Ca, Al, Si, P, S, Cl and Fe [24]. These minerals present with the biomass at high temperature can agglomerate and deposit inside the thermal device leading to slag formation and fouling.

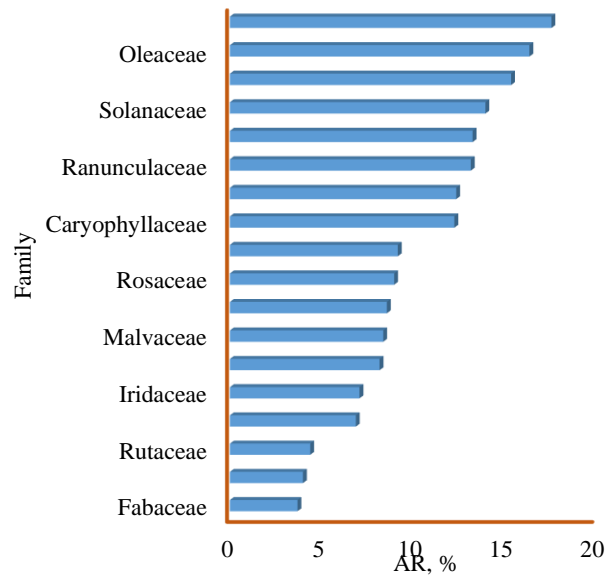


Fig.4. Ash residue (AR) of plants belonging to 17 family

3.5. Correlation of proximate parameters

The correlation analysis of gross caloric value (GCV) with proximate parameters is of tremendous importance for proper selection of biomass for specific purpose due to dependence of heat value on moisture content and chemical composition of biomass. The bulk density (BD) with the GCV had a fare positive correlation of 0.87 as shown in Fig.5 (a). In turn, the MC and AR with the GCV had fare negative correlation of 0.68 and 0.60, respectively as shown in Fig.5 (b-c).

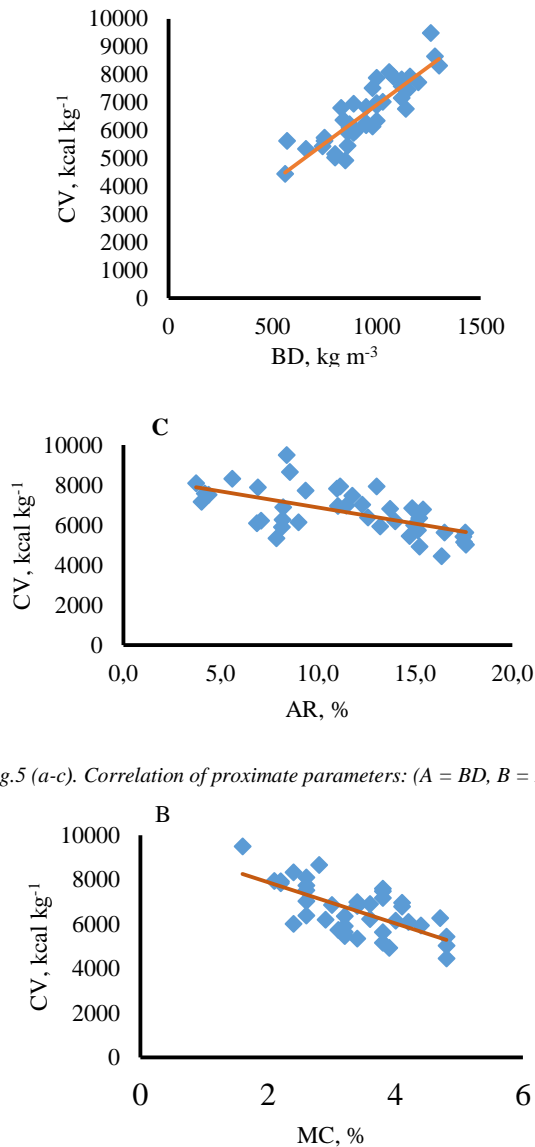


Fig.5 (a-c). Correlation of proximate parameters: (A = BD, B = MC, C = AR) with GCV

3.6. Cluster analysis

The elemental composition (i.e. C, H, N and O) of biomass is varied with respect to genotype of biomass, geographical and climate condition and harvesting methods. Hierarchical cluster analysis was employed to produce a dendrogram, using group-average linkage clustering, Fig. 6(a). The fuel characteristic of 40 plants was classified into two groups when proximate parameters i.e. BD, MC and AR are used as discriminating factors. In the I-group, 28 plants having GCV < 7030 kcal kg⁻¹ was included. In II-group, 12 energetic plants having GCV value >7470 kcal kg⁻¹ was categorized as shown in Fig. 6(b). These twelve energetic plants are herb and shrub of wild nature, commonly found to grow everywhere in India. Among them, four plants are belonged to Asteraceae family.

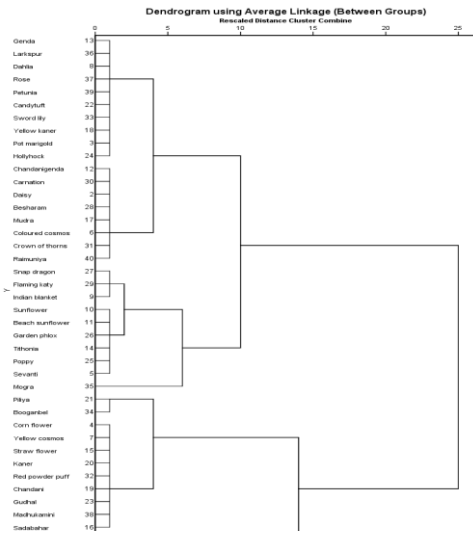


Fig.6 (a) Cluster analysis of energetic flowering plants

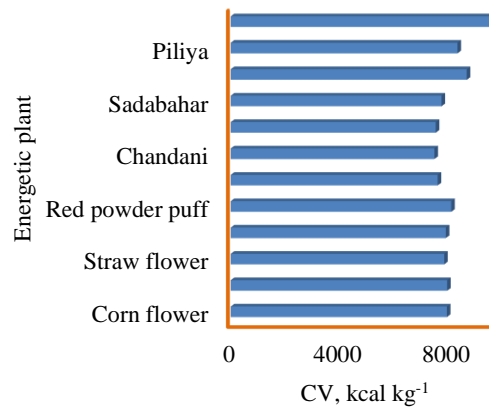


Fig.6 (b). Gross calorific value of energetic plants

3.7. Organics content of biomass

The biomass contains volatile organic compounds, cellulose and lignin materials which evaporate or oxidize at different temperature ranges by leaving fixed carbons. The TG-DGA chromatogram of Sweet sulton (SS) plant is shown in Fig. 7. The pyrolytic decomposition of the SS plant was occurred in six stages over temperature range of 50 – 1000°C. In the first stage, a 7.5% weight loss was seen over temperature range of 50 – 100 °C, may due to evaporation of light volatile compounds including water. In the second stage, a large weight loss of 42.7% along with endothermic reaction was marked over temperature range of 150 – 400 °C, may be due to decomposition of hemicellulose materials. Similarly, 16.2, 10.4, 6.7 and 3.3% weight loss in the third, fourth, fifth and sixth stages were observed over temperature range of 400 – 600, 600 – 750, 750 – 850 and 850 – 950 °C, respectively, may be due to decomposition of cellulose and lignin materials of the SS plant. A residue of 13.1% was found to remain left belonging to fixed carbon and ash residue. The ash residue obtained by the oxidation method was found to be 8.4%. The computed value of fixed carbon was found to be 4.7%. The low fixed carbon content makes biomass tend to prolong cooking time by its low heat release (bake-oven effect) [25]. It also reduced the calorific energy of the briquettes by causing what is called fuel-saving effect. The higher the fixed carbon content the better the charcoal produced because the corresponding calorific energy is usually high [26].

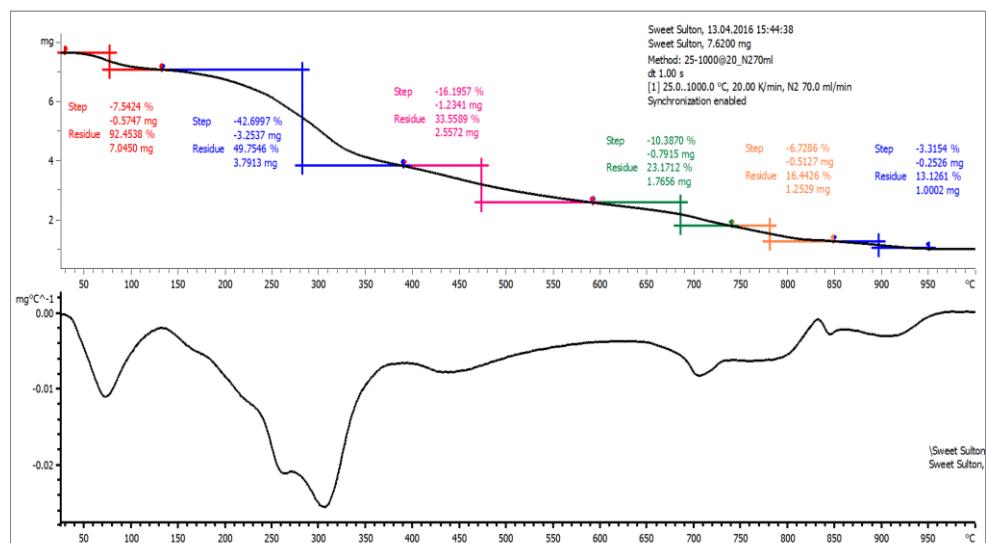


Fig.7. TG-DGA chromatogram of Sweet sulton plant

4. CONCLUSION

The wild plants having higher biomass productivity and climatic stresses adaptability seem to be good energetic biomass. The remarkable high fraction of hemicellulose was observed in the flowering plant. The most of energetic plants belong to economically important family Asteraceae.

ACKNOWLEDGMENTS

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The Effect of Air Pollution on Damages in Historical Buildings, the Case of Gaziantep, Turkey

Tulay KARADAYI YENICE^{1}, Dilsat Deniz OLEKLI²*

Abstract

Conservation of historical buildings and monuments and handing them down to future generations is one of the main issues of architecture. Contrary to popular belief, preserving these constructions for centuries may be difficult under the changing conditions in the world, in spite of the opportunities of the improving technology. Air pollution is one of the greatest protection issues for these structures to be preserved against. The major causes of air pollution may include the use of fossil fuels in transportation and electricity generation, burning of the solid waste, industrial and local use of fuel, and industrial activities. The aim of this research is to determine the impact of air pollution on the deformations at the historical buildings in Gaziantep's historical city center. The traditional monumental and civil architectural works made of stone materials constitute the basic material of the research. In the study, the effects of SO_x and NO_x, and particulate matters, the most important pollutants originating from the weather conditions and causing deformation at the stones, were evaluated and the harms were determined. As a result of this study, it is identified that the most important effect of air pollution on the stone material is the formation of crust. The crusting not only affects the structure of the stone but also it may cause exfoliation and stratification. Abrasion is another effect of air pollution on the stone. However, it has been seen that the importance of this effect is less than the other factors related to air pollution.

Keywords: *Conservation, restoration, air pollution, Gaziantep*

1. INTRODUCTION

Air pollution can be defined as the amount that will harm the health of living things in a general expression atmosphere and the coexistence of one or more of the pollutants in time. The main sources of air pollution are the use of fossil fuels in the production of transportation and electricity, solid waste incineration, industrial and local fuel use and industrial activities. The most important effect of air pollution on stone material is crust formation. This crust affects the structure of the stone as well as exfoliation and separation into plates. Air pollution on the surface of the stone is cleaned together with the products and rain of the layer rising without scaling. Therefore, air pollution-related crust formation and spillage can often be observed in areas protected from rainwater. Another effect of air pollution on the stone is erosion. However, this effect has less precautionary effects than other factors related to air pollution [1].

It is known that the air pollution that occurs due to human activities in the atmosphere structure of the cities and the high level of SO_x (sulfur oxide) and NO_x (nitrogen oxides) contained in the atmosphere forms a crust on the surface by reaching to the surface of the rocks in a gaseous form with wind effect in the absence of rain or snow. In this process, the precipitation rate, porosity and humidity of the surface are important factors as well as the climatic characteristics such as precipitation time, wind speed, relative humidity, and brightness of sunlight [2].

The researches indicate that in the last twenty years the deterioration of historic buildings and monumental stones has accelerated to a great extent in a dirty urban atmosphere. The main atmospheric pollutant that affects building materials is primarily SO₂, which is very reactive and corrosive. The main sources of sulfur gases are coal and crude oil [1]. The limestone, marble and travertine of various large-scale calcareous stones react more strongly with SO₂. The main part of the change observed in the structure of the reaction occurring in the field is the reaction that the sulfur dioxide

^{1*} Corresponding author: Hasan Kalyoncu University, Department of Architecture, 27100, Gaziantep, Turkey. tulay.yenice@hku.edu.tr

² Hasan Kalyoncu University, Department of Architecture, 27100, Gaziantep, Turkey. Dilsat.olekli@hku.edu.tr

gas causes to form on the surface of the stone. The final product of chemical reactions; the calcium carbonate in the stone structure is the more soluble gypsum. The more soluble nature of the gypsum causes the structures to wear out more easily. Particularly, crust formation and breakup occur more rapidly in the rain water or the open areas of the buildings [1,3]. The degree of SO₂ accumulation on the stone and other building materials, or the degree of absorption and degradation, depends on the natural structure of the pollution density, wind speed, surface moisture and building material. However, it is known that daytime sunshine and temperature increase strengthens this effect [4,5].

The purpose of this research is to determine the effect of air pollution in historic buildings in Gaziantep's historical city center. It is believed that the research will contribute to the work to be done on preserving historical buildings and transferring them to future generations.

2. MATERIAL AND METHOD

Gaziantep is Turkey's sixth and Southeastern Anatolia is the largest city. The city, which has a population of about 2 million, has rich historical and cultural texture as well as industrial character. Gaziantep is one of the oldest settlements in Anatolia and is located at the intersection of Mesopotamia and the Mediterranean Region (Figure 1). The city has hosted many important civilizations in history such as the Ottomans, Seljuks, Byzantines, and Rome and maintained its importance in every period of history. Gaziantep has been added to the list in the gastronomy category of UNESCO's Creative Cities Network in 2015.



Figure 1. Gaziantep Historical City Centre and Khan's District

Besides all these, it can be said that the air quality of the city of Gaziantep is very dirty. This pollution is mainly based on three factors: fuels used in heating, industrial production and emissions from traffic. Nearly all of the current air pollution in the city is due to warming. The use of poor quality coals for heating in residential areas is the most important reason for air pollution. Particularly in the winter months, atmospheric pollutant gases and particulate matter are spreading considerably. Gaziantep has been identified as the fifth dirtiest city in Europe according to the World Health Organization's 2017 report.

The subject of this research is the traditional monumental and civil architectural examples made of stone materials located in the historical city of Gaziantep. In this context, traditional buildings affected by air pollution in the historical city center of Gaziantep are examined. In the study, a method was observed which came from two stages. In the first stage, various types of deterioration examples were found on the ceiling due to air pollution. These deteriorations are often seen as breaks, darkening, crusting. The second stage is to examine the factors that cause deterioration on the samples taken. In this frame, the solutions causing the deterioration are estimated by making solutions with various solutions.

3. RESULTS AND DISCUSSION

The basic construction material of the traditional buildings located in the historical city centre of Gaziantep is basalt and limestone, which are limestone based stones. Researchers, such as Harter [6] and Lipfert [7] do not put attention to the effects of air pollution especially on silica-based stones, however they draw attention to the dangerous effects of air pollution on travertine and limestone, which are limestone-based and extensively used in Gaziantep region. It can be observed that the deterioration of these stones due to air pollution is caused by the dissolution of CaCO_3 in their bodies. In particular, the effects of gaseous pollutants such as SO_2 and the effect of acid rain on the stone structure cause dissolution and break-offs in the stone. In various scientific studies, it has been seen that natural stones are separated by a size of up to 4 mm. pieces can break off from the body of natural stones due to air pollution [8]. One of the most important pollutants caused by weather conditions affecting the decay of stones in historical buildings in Gaziantep is SO_2 . It can be said that the level SO_2 is very high in Gaziantep (Table 1).

Table 1: Annual and winter season average sulfur dioxide values in Gaziantep ($\mu\text{g}/\text{m}^3$)

Annual average sulfur dioxide values ($\mu\text{g}/\text{m}^3$)							
2004	2005	2006	2007	2008	2009	2010	2011
51	48	41	25	25	16	19	17
Winter seasons average sulfur dioxide values ($\mu\text{g}/\text{m}^3$)							
2004	2005	2006	2007	2008	2009	2010	2011
58	86	68	46	47	23	32	30

*Data compiled from TURKSTAT Air Quality Statistics [12].

When the annual average SO_2 distribution of the last eight years is examined, it is seen that the average of the six years is above the threshold level set by the World Health Organization (Table 2). It can be said this value reached a high level for all years when examined during the winter season (Chart 1, 2).

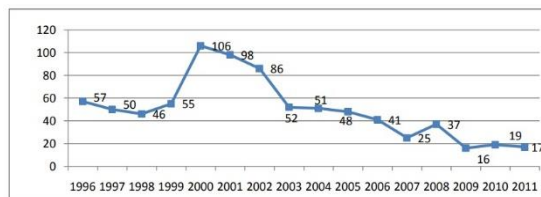


Chart 1. Annual average SO_2 change (1996-2011)

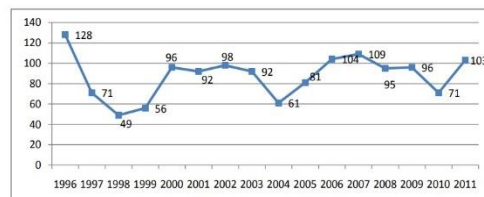


Chart 2. Annual average PM_{10} change (1996-2011)

Table 2: Accepted SO_2 upper values for air quality in the world and in Turkey

	EU Countries	WHO	USA (EPA)	Turkey
24 hours	125	125	365	400
Winter season	20	-	-	250
Annual	-	50	80	150

* Data compiled from Anonymous (2006), Anonymous (2011) [9,10]

In measurements made on 29.11.2011, it is seen that the sulfur dioxide value of Gaziantep is $122 \mu\text{g} / \text{m}^3$. These findings indicate that the value of SO_2 increases especially in the winter months. The deterioration effects on the Gaziantep Historic Buildings due to air pollution can be seen in the form of color change, salt accumulation, crust formation and separation on the facades of the structures (Figure 2).



Figure 2. Examples of darkening - color change on the surface of a building

Liquid or solid materials in the atmosphere are particulate matters in air pollution [1]. It is known that particulate matter (PM₁₀) acts as a catalyst in the oxidation of SO₂ on the surface of a stone and plays an active role in the formation of gypsum minerals, as well as causing the building surface to darken. When air the measurement values of the city of Gaziantep is analyzed according to the PM₁₀ value, it can be said that it is quite high (Table 3). As a matter of fact, it is seen that the PM₁₀ value of Gaziantep is 143 µg / m³ in the measurements made on 29.11.2011.

Table 3: Gaziantep annual and winter season average for Particulate matter PM₁₀ values

Annual average PM ₁₀ values (µg/m ³)							
2003	2004	2005	2006	2007	2008	2009	2010
50	57	46	59	79	60	67	83
Winter season average PM ₁₀ values (µg/m ³)							
2002-2003	2003-2004	2004-2005	2005-2006	2006-2007	2007-2008	2008-2009	2009-2010
69	73	74	77	71	87	49	82

* Data compiled from TURKSTAT Air Quality Statistics [12]

These findings indicate that there is a high level of PM₁₀ in the air structure of the city. When the average annual PM₁₀ values of the city of Gaziantep are examined; according to the EU, World Health Organization and EPA norms (Table 4), this difference increases even more in winter. Deteriorations due to particulate matter in the buildings of the historical region of Gaziantep are seen as darkening on building facades (Figure 3).



Figure 3. Examples of darkening due to air pollution in building stones

Table 4. Accepted PM₁₀ upper values for air quality in the world and in Turkey (µg/m³)

	EU Countries	WHO	USA (EPA)	Turkey
24 hours	50	50	150	100
Annual	20	20	50	60

* Data compiled from Anonymous (2006), Anonymous (2011) [9,10]

Another pollutant that causes deterioration due to air pollution in historical buildings is nitrogen oxides (NO_x). Nitrogen oxides are soil and water based arising from traffic, agricultural activities and exhaust gases [1]. Compared to sulphur dioxide, the rapid cleaning of NO_x from the surface of the stone due to the high solubility of calcium nitrate and other reaction products makes it difficult to detect their effects [2]. However, some research suggests that due to the increase of NO_x sources, they may play a more important role in stone deterioration in the future [11].

It can be said that acid rain is another factor that brings deterioration due to air pollution on the historical Gaziantep constructions. A high level of sulphur and particulate matter causes deterioration. These pollutants, which can be suspended for 2-7 days in the air, bring acid when they react with water and this water comes down to the earth as acid rain. Water drops with a low level of pH value cause erosion on the exterior facades of buildings.

As a result, the surfaces where the rainwater is infiltrated and wetted the roofs, the wet areas formed by the water rising from the walls in regions where collecting the water around the building is insufficient, and the reaction and damage of the particulate matter and gases causing air pollution on the surface of the buildings can be seen in the historical buildings in Gaziantep. It is seen that dry surfaces are cleaner and healthier (Figure 4).



Figure 4. Wet areas on stone surfaces: color change, crusting, salt accumulation

4. CONCLUSIONS

As a result of the research, it has been observed that various distortions occurred in the traditional buildings in Gaziantep city historical urban fabric depending on the air pollution. Especially in the winter months, the deterioration effects on the Gaziantep Historic Buildings can be seen in the form of color change, salt accumulation, crust formation and separation in the fronts of the buildings. Another type of degradation is the formation of gypsum minerals by acting as a catalyst in the oxidation of SO₂ on the surface of the particulate (PM₁₀) matter. These minerals lead to the blackening of the building surface.

It is known that the main cause of air pollution in Gaziantep is caused by poor quality fuel used for heating especially in winter season. It should not be forgotten that the prevention of air pollution will be ensured by local governments with policies that are determined for the whole city in a short and long term. These policies can be based on large and small scale solutions, ranging from urban green space regulations and air circulation corridors to the development of the public transport system to reduce the use of individual vehicles, to the type of fuel used in buildings. The main target is to minimize the sources and elements that cause air pollution and to remove pollution from the urban atmosphere.

The widespread use of natural gas in the historic city center of Gaziantep will reduce the use of poor quality coal used for domestic heating. Therefore, it is thought that it will have a decreasing effect of air pollution caused by the use of fossil fuel for heating purposes. It is also important to reduce the traffic intensity around historic structures as air pollution, such as nitrogen and oxide, caused by intense pollution, accelerates the chemical reactions that sulfur dioxide gas and particles form on the surface of the stone. In this framework, the completion of the pedestrianization projects in the old city center will contribute to the preservation of historical buildings.

There are not enough researches and findings on the effect on the long-term structure of the surface-protective chemical substances, while reducing the deterioration effects of the short-term. For this reason, it is considered that the use of surface preservative chemical substances in reducing the deterioration due to air pollution in the Gaziantep buildings is not an appropriate approach in today's conditions. If air pollution is reduced, deterioration caused by air pollution will not progress. However, a separate investigation should be carried out to determine the protection methods applied to the degraded stones. It may be necessary to remove the salts that have affected the degradation of the stones. How to do such a study or how to clean the contaminated areas without damaging the stone should be determined by working with a material protection laboratory that conducts research on these matters.

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The Investigation of Fuel Properties of E-B Diesel Fuels At Different Blend Ratios

Fatih AYDIN^{1*}

Abstract

In this study, biodiesel production was realized by converting raw oil obtained from safflower seed to Safflower Oil Methyl Ester (Safflower Biodiesel) by means of raw oil extraction with tempering at 90 °C and pressing after Vals process and consequently trans esterification process followed raw oil extraction. Experimental fuels were obtained as in D₁₀₀, E₅B₅D₉₀, E₁₀B₁₀D₈₀, E₁₀B₅D₈₅ and E₅B₁₀D₈₅ forms by mixing biodiesel fuel obtained from safflower with diesel fuel and bioethanol additives at a ratio of 5% and 10% and by mixing in volumetric ratio according to inversely proportion. Fuel properties of diesel fuel and the obtained fuel mixtures were determined with following tests; Kinematic viscosity (40 °C and 100 °C), Density, Water content, PH values, Color determination, Heating value, Flash point, Fogging, Pour and Freezing points, Copper rod corrosion test, CFPP (Cold Filter Plunge Point) and Cetane number tests. As a result of this study, the benefits of using the E-B diesel for the internal combustion engines can be explained as follows:

- *Biodiesel, which has a higher viscosity than the diesel, is reduced in viscosity when it is mixed with Bioethanol-Diesel, thus it is more usable in diesel engines.*
- *The cetane number has been increased by adding to the biodiesel diesel fuel which has a high cetane number.*
- *The cold flow properties of the diesel fuel were improved by bioethanol addition*

Consequently, it has been understood that the E-B Diesel fuel mixtures can be used in diesel engines.

Keywords: E-B Diesel, Safflower biodiesel, Bioethanol.

1. INTRODUCTION

Local resources should be used as much as possible in energy production. Besides, protection of the environment, increasing the productivity, diversity of resources and ensuring continuity are also important. The primary element in energy policies is to switch to reliable, quality, clean and economical energy types so as to meet the energy need in such a way that they support technological and social development [10].

After renewable energy sources have played a key role in the road to a reliable and sustainable energy, the introduction of green technologies within the scope of bio refinery technologies and the production and use of green products have become increasingly important. Bio refineries make it possible to obtain different industrial products such as biochemical, biomaterials and biofuels through various chemical and physical transformation processes [9].

The fuels that countries have obtained using their own herbal or animal sources are briefly called biofuels. Biofuels include all types of liquid and gaseous fuels obtained from vegetable or animal sources. There are alternative fuels such as biogas, bio methanol, bioethanol and biodiesel under the framework of biofuels. However, bioethanol is the most widely used of these [4].

Biodiesel is a mixture of fatty acid methyl esters produced from herbal and animal oil, oil waste and residues and conform to standard of TS EN 14213 and/or TS EN 14214 [5].

Although there are various methods of biodiesel production, the most widely used method today is the trans esterification method. Biodiesel is a nature friendly and renewable bio fuel that is released as a result of the trans

^{1* 1*}Corresponding author: Necmettin Erbakan University, Ereğli Faculty Of Engineering And Natural Sciences, Department of Energy Systems Engineering, 42310 , Ereğli/Konya, Turkey. fatihaydin@konya.edu.tr

esterification reaction of oils or animal oils, which are obtained from oil seeds such as colza (canola), sunflower, soybean and safflower in trans esterification method, with a short chain alcohol (generally methanol or ethanol) by means of a catalyzer [6].

The flash point of biodiesel is higher than diesel fuel. This makes biodiesel a more reliable fuel for use, transport and storage. Biodiesel can be thoroughly mixed with petroleum-derived diesel fuel at any rate, and this feature raises the quality of petroleum-derived diesel fuel. It reduces the emission values of harmful gases generated by combustion, increases the degree of lubrication on the engine [7].

There is biodiesel cycle in Figure 1.

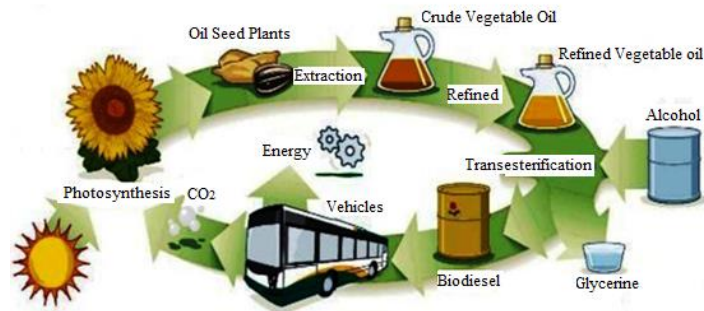


Figure 1. Biodiesel cycle [1]

Bioethanol is a biofuel that can be produced by fermentation of sugary and starchy plants or by acidic hydrolysis of cellulosic sources. The plants such as sugar beet, sugar cane, corn, wheat, potatoes; and also woody plants like stem, straw, bark; agricultural wastes and residues and molasses which are a by-product of sugar production can be used as raw material [2].

Considering that fuels that are easy to self-ignite and reduce ignition delay are preferred in diesel engines, the number of cetane numbers of the fuel becomes important [3].

The solubility of bioethanol in diesel fuel is limited. The phase separation of bioethanol-diesel mixtures and the amount of water in the mixture are important problems. However, the cetane number of bioethanol is extremely low [8].

These adverse effects of bioethanol-diesel fuel mixture are eliminated by the addition of biodiesel.

2. MATERIALS AND METHODS

Safflower seeds in this study were provided from Utek Agriculture Cons. Food Industry Co.ltd located at wheat market in Konya, Ilgin and oil production process was performed by Esen Oil Manufacturer in Ilgin County of Konya. To obtain the oils, the seeds were separately peeled in the peeling machines, then they were heated and annealed through the rolling process, fried at 90°C and later they were squeezed in 200-ton hydraulic press. Biodiesels of these oils were produced at Energy System Laboratory of Energy Systems Engineering Department at Necmettin Erbakan University, Eregli Engineering and Natural Sciences Faculty. During the production, methyl alcohol was used as alcohol, NaOH was used as catalyzer and trans esterification method was preferred. 99.8% pure bioethanol which was produced from molasses by Konya Sugar Industry and Trade Inc. is available in Energy System Laboratory. Diesel fuel was provided from BP Petrol Company in Eregli, Konya.

After biodiesel fuel (B₁₀₀), which was obtained from safflower, was mixed with diesel fuel at the rate of 5% and 10% together with the addition of bioethanol; and mixed volumetrically in inverse proportion, test fuels were obtained at the forms of, D₁₀₀, E₅B₅D₉₀, E₁₀B₁₀D₈₀, E₁₀B₅D₈₅ ve E₅B₁₀D₈₅. Kinematic viscosity, water content, color, heating value, flash point, cloud, pour and freezing point, copper rod corrosion, CFPP(Cold filter plugging point) tests of the mixture fuel were performed at Biodiesel Laboratory of Agricultural Machinery Department, Selcuk University Agricultural Faculty; density, pH amount and cetane number tests were carried out at Energy System Laboratory of Energy Systems Engineering Department at Necmettin Erbakan University, Eregli Engineering and Natural Sciences Faculty and fuel features were determined.

Mixture rates and names of the created fuels are given in Table 1.

Table 1. Names of the fuels and their volumetric constitution percentages

No	Fuels	Diesel	Bioethanol	Biodiesel
1	B ₁₀₀	0	0	100
2	D ₁₀₀	100	0	0
3	E ₅ B ₅ D ₉₀	90	5	5
4	E ₁₀ B ₁₀ D ₈₀	80	10	10
5	E ₁₀ B ₅ D ₈₅	85	10	5
6	E ₅ B ₁₀ D ₈₅	85	5	10

The results of the analysis are seen in Table 2. Standard values in the table belong to TS EN 590 for diesel fuel and to TS EN 14214 for biodiesel.

Table 2. Analyses results of the fuels

Characteristic Properties	Units	Raw								Bio ethanol	Limiting Values	
		Safflower Oil	B ₁₀₀	D ₁₀₀	E ₅ B ₅ D ₉₀	E ₁₀ B ₁₀ D ₈₀	E ₁₀ B ₅ D ₈₅	E ₅ B ₁₀ D ₈₅	Diesel		Biodiesel	
Density (15 ^o C)	g/cm ³	0,919	0,887	0,835	0,834	0,835	0,836	0,832	0,792	0.82-0.84	0.86-0.90	
Kinematic Viscosity (40 ^o C)	mm ² /s	27,442	4,391	3,07	2,524	2,535	2,542	2,543	1,272	2- 4.5	3.5-5	
Kinematic Viscosity (100 ^o C)	mm ² /s	7,389	1,921	1,438	1,381	1,391	1,397	1,398	0,699	—	—	
Flash Point	^o C	170	121	60	—	—	—	—	—	55	101	
Water Content	ppm	20,25	225,42	34,50	78,85	75,45	89,68	83,64	372,8	200	500	
PH	—	3,98	4,12	4,01	4,94	4,89	4,79	5,50	6,24	—	—	
Color	ASTM	2,2	1,8	1,4	1,4	1,4	1,4	1,4	<0,5	—	—	
Calorific Value	kJ/kg	36340	39840	43207	40844	42484	42682	42031	29590	—	—	
Cloud Point	^o C	-1,5	-2,5	-8,4	-8,7	-9,2	-10,1	-9,8	—	—	—	
Pour Point	^o C	-16	-8	-15,1	-15,6	-15,8	-15,9	-15,7	—	—	—	
Freezing Point	^o C	<-20	-10	<-20	<-20	<-20	<-20	<-20	<-20	—	—	
CFPP	^o C	—	-8	-16	-19,4	-21,8	-22	-21	<-50	- 20	-15	
Copper Strip Corrosion	—	1a	1a	1a	1a	1a	1a	1a	1a	No:1	No:1	
Cetane Number	—	61,7	64,8	51,4	56,5	64,5	57,4	62,6	13	51	—	

3. RESULT AND DISCUSSION

3.1. Density values of the fuels

Density values of the fuels are seen in Figure 2. When density test values were investigated, it was seen that density value of B₁₀₀ fuel was higher than other fuels; however, it was within the standards. In mixture fuels, equivalent results to D₁₀₀ fuel were obtained.

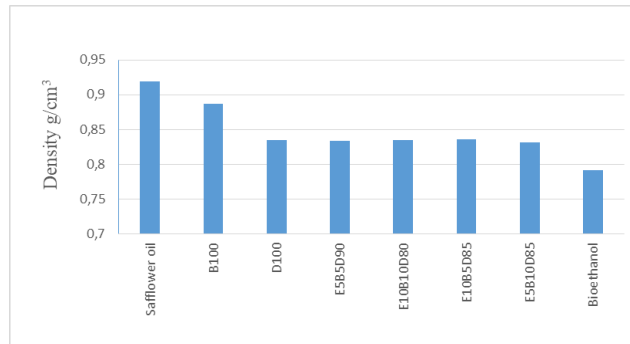


Figure 2. Density values of fuels

3.2. Kinematic viscosity values of the fuels at 40 °C

In Figure 3 kinematic viscosity values of the fuels at 40 °C are seen. When kinematic viscosity values at 40 °C were investigated, it was found out that kinematic viscosity value of B₁₀₀ fuel at 40 °C was higher than other fuels but it was within standards; and in mixture fuels, lower viscosity values were obtained than in D₁₀₀ fuel.

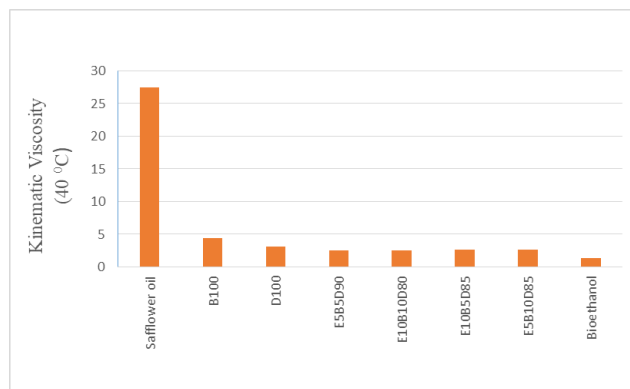


Figure 3. Kinematic viscosity values of the fuels at 40 °C

3.3. Kinematic viscosity values of the fuels at 100 °C

Kinematic viscosity values of the fuels at 100 °C are seen in Figure 4. When kinematic viscosity values at 100 °C were examined, it was found out that kinematic viscosity value of B₁₀₀ fuel at 100 °C was higher than other fuels but it was within standards, and in mixture fuels, lower viscosity values were obtained than D₁₀₀ fuel.

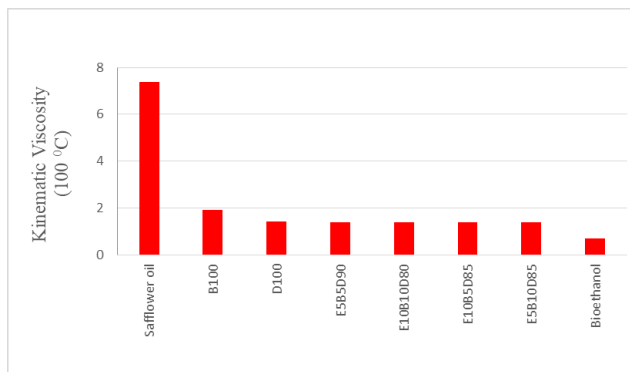


Figure 4. Kinematic viscosity values of the fuels at 100 °C

3.4. Flash point values of the fuels

In Figure 5, flash point values of the fuels are seen. When flash point values were investigated, it was seen that flash point values of B₁₀₀ and D₁₀₀ fuels were conforming to standards. For bioethanol-added fuels, the flash point values were not measured for safety reasons.

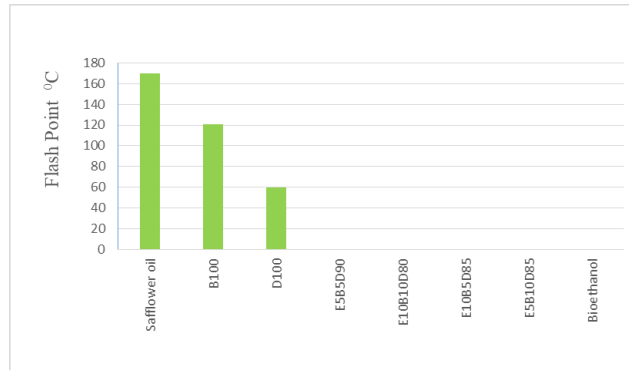


Figure 5. Flash point values of the fuels

3.5. Water content values of the fuels

In Figure 6, water content values of the fuels are seen. When water content values were investigated, it was discovered that water content values of B₁₀₀ and D₁₀₀ fuels were conforming to standards and no problems were encountered in mixture fuels.

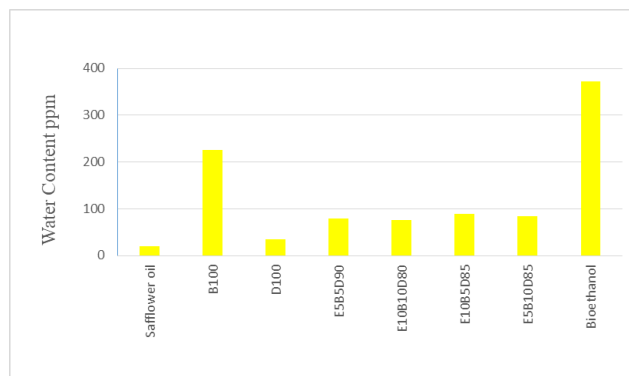


Figure 6. Water content values of the fuels

3.6. pH values of the fuels

pH values of the fuels are seen in Figure 7. When pH test values were investigated, equivalent results were obtained in all fuels.

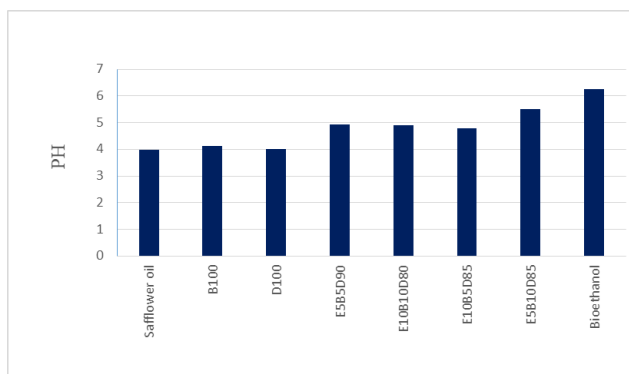


Figure 7. pH values of the fuels

3.7. Color specification values of the fuels

In Figure 8, color specification values of the fuels are seen. When color specification values were examined, equivalent results were obtained in all fuels. The result of color specification measurement of bioethanol does not appear in the graphic because the device gives <0.5 result.

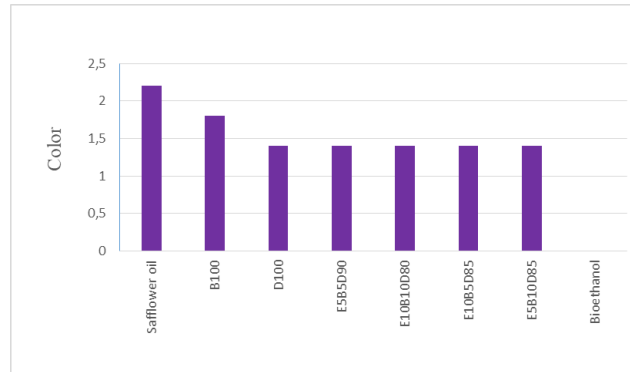


Figure 8. Color specification values of the fuels

3.8. Calorific values of the fuels

In Figure 9, calorific values of the fuels are seen. When calorific test values were investigated, it was seen that mixture fuels gave equivalent results to D₁₀₀ fuel.

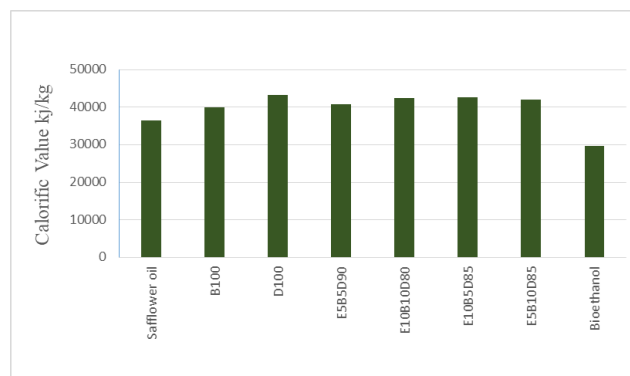


Figure 9. Calories values of the fuels

3.9. Cloud point values of the fuels

In Figure 10, cloud point values of the fuels are seen. When cloud point values were investigated, the values of mixture fuels were better than D₁₀₀ fuel.

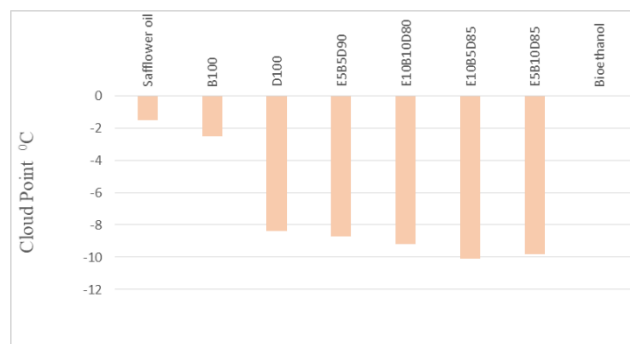


Figure 10. Cloud point values of the fuels

3.10. Pour point values of the fuels

In Figure 11, pour point values of the fuels are seen. When pour point values were examined, it was seen that the values of mixture fuels were better than D₁₀₀ fuel.



Figure 11. Pour point values of the fuels

3.11. Freezing point values of the fuels

When the test values of freezing point were investigated, except for B₁₀₀ fuel, other fuels gave equivalent results. The results could not be given in the graphic because of the fact that the device gave <-20 °C result for freezing point apart from B₁₀₀ fuel.

3.12. Cold filter plugging point of the fuels

In Figure 12, Cold filter plugging point values are seen. When cold filter plugging point values were investigated, the values of mixture fuel values were better than D₁₀₀ fuel.



Figure 12. Cold filter plugging point values of the fuels

3.13. Copper rod corrosion values of the fuels

When copper rod corrosion values of the fuels were examined, 1a value was obtained in all fuels but it was not shown in graphic.

3.14. Cetane number values of the fuels

In Figure 13, cetane number values of the fuels are seen. When cetane number test values were investigated, the values of mixture fuels were better than D₁₀₀ fuel.

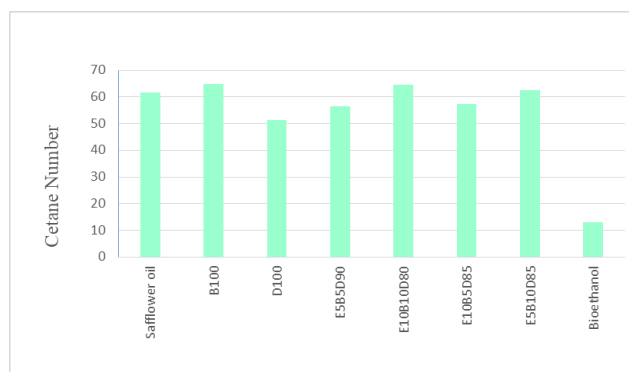


Figure 13. Cetane number values of the fuels

4. CONCLUSIONS

In this study, after biodiesel fuel (B₁₀₀), which was obtained from safflower by means of trans esterification method, was mixed with diesel fuel at the rate of 5% and 10% together with the addition of bioethanol; and mixed volumetrically in inverse proportion, test fuels were obtained at the forms of, D₁₀₀, E₅B₅D₉₀, E₁₀B₁₀D₈₀, E₁₀B₅D₈₅ and E₅B₁₀D₈₅. The tests were performed for kinematic viscosities of the obtained mixture fuels and diesel fuel at 40 °C and 100 °C; for density, water content, pH amount, color specification, heating value, flash points, cloud, pour and freezing points, copper rod corrosion, CFPP and cetane number; and then fuel properties were determined, the obtained data were given in graphics. As a result of this study, the benefits in internal combustion engines by using E-B Diesel can be explained as follows:

- Biodiesel, which had a higher viscosity than the engine, was reduced in viscosity when mixed with the Bioethanol-Diesel and its availability was provided.
- Biodiesel with high cetane number was added in diesel fuel and cetane number was increased.
- Bioethanol was added at a certain rate to the diesel fuel which poses a risk for Pour, Cloud point, CFPP which shows the temperature at which the fuel solidifies or melts and which shows rate of use of fuel in cold weather and the disadvantage of diesel fuel about this matter was eliminated.
- This disadvantage of Bioethanol and Biodiesel, which had lower energy values compared to fossil fuels, was prevented using E-B diesel fuel.
- As a result, it sheds light on the availability of E-B diesel fuel mixture in diesel engines.

ACKNOWLEDGEMENTS

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BIOGRAPHY

Fatih AYDIN was born in Konya in 01.01.1978 and he completed his undergraduate study at Gazi University, Technical Education Faculty, Department of Mechanical Education, Automotive Teaching Program; he did his master degree at Selcuk University, Institute of Science Mechanical Education Department; and he did his doctorate at Selcuk University Institute of Science, Agricultural Machinery Department. He still works as a assistant professor (asst. prof.) at Necmettin Erbakan University, Eregli Engineering and Natural Sciences, Department of Energy Systems Engineering.

Shear Flow of a Microstretch Fluid with Slip

Mehmet Sirin DEMIR^{1*}

Abstract

In this study, the effects of slip boundary conditions on the shear flow of the microstretch fluids are investigated. The field equations of the microstretch fluids are solved under slip boundary conditions which are physically more realistic than no-slip boundary conditions. Exact analytical solutions are obtained for the velocity, microrotation, and microstretch fields for the case of a flow between two parallel plates. It has been shown that the previous solutions corresponding to pure Newtonian fluid and micropolar fluid appear as the special cases of the present analysis. Results are represented graphically for the velocity, microrotation, and microstretch for various values of the slip and micropolar parameters.

Keywords: *Microstretch fluid, Shear flow, Analytical solution, Slip boundary conditions.*

1. INTRODUCTION

Many modern engineering and industrial fluids exhibit certain microscopic effects due to local structures and microdeformation of fluid elements. In these situations the continuum assumption is not valid and the classical Navier–Stokes theory is not adequate for the description of such fluids since the fluid particles considered as material point and cannot support surface tractions and couples. In order to describe these fluids such as polymer melts, blood, suspensions, bubbly fluids, magnetic fluids, biological fluids, and many others Eringen[1,2,3] introduced the theory of microfluids in which the local effects arising from the local structure and intrinsic motions of the fluid elements are taken into account.

The most known subclass of microfluids is micropolar fluids in which the particles are rigid so that the microdeformation is only intrinsic rotational motions. Thus, the micropolar continuum possesses six degrees of freedom; three translational degrees (valid for the classical Newtonian fluid) of freedom and three additional degrees for microrotation. Another subclass is the microstretch fluids in which the fluid particles are considered to stretch (expand or contract) in addition to microrotation. Thus, the microstretch continuum possesses four extra degrees of freedom over the classical fluid dynamics. The most general case is the micromorphic fluids. Micromorphic continuum particles possess nine extra degrees of freedom for microrotation, microshear, and microstretch over the classical fluid dynamics.

Most of the studies on microfluids concern about the micropolar fluid flow problems, but very little work seems to have been done on applications of the theory of microstretch fluids to practical problems. Perhaps this is because of unknown viscosity parameters and the mathematical difficulties. Ariman [4] obtained the exact solution of the Poiseuille flow of a microstretch fluid between two parallel plates. In a subsequent study Ariman [5] analyzed blood flow in small arteries using the microstretch theory. Eringen [6] extended his theory of microstretch fluid to that of thermomicrostretch fluids and applied it to the problem of propagation of acoustic waves in bubbly fluids. In his subsequent study Eringen [7] modeled liquid crystals using the theory of microstretch fluids. Aydemir and Venart [8] solved the problem of unsteady flow of thermo microstretch fluid between two parallel and heated plates. In a following paper Aydemir [9] obtained the solutions for the problem of free convective boundary layer flow of a thermomicrostretch fluid. Electrodynamics of microstretch fluids developed by Eringen [10]. In a following paper Eringen [11] introduced electrodynamics of microstretch liquid polymers. Narasimhan [12] analyzed pulsatile flows of microstretch fluids due to varying pressure gradient in circular tubes. Recently, Moosaie and Atefi [13] analyzed the pipe flow of a concentrated suspension composed of spherical particles dispersed in a liquid by utilizing the theory of microstretch fluids.

It should be noted that the continuum assumption may not be valid in the case of flow problems in micro-nano channels since the characteristic length is too small. Experimental studies show that using no-slip boundary conditions can lead inaccurate results in micro-nano channel flows [14]. For more information about the slip boundary conditions the

^{1*} Corresponding author: Istanbul University, Department of Mechanical Engineering, 34320, Avcılar/Istanbul, Turkey.
demirms@istanbul.edu.tr

reader should consult the review studies by Neto et al. [14] and Shu et al. [15]. Sherief et al. [16,17] discussed the motion of a microstretch fluid by using the slip boundary conditions. In recent years there has been an increased interest in using the slip boundary conditions for micropolar fluids [18-22].

The present paper deals with the steady shear flow of an incompressible microstretch fluid between two infinite parallel plates. The slip boundary conditions applied for velocity and the spin boundary conditions applied for microrotation field. The exact analytical solutions of governing equations has been obtained. The expressions for the shear stress, couple stress, the microstretch force, and the difference between the normal stress and the micropressure have been calculated. The effects of flow parameters on the velocity, microrotation, and microstretch are presented graphically.

2. FIELD EQUATIONS

Following Eringen [3], for an isothermal microstretch fluid the field equations are written as:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (1)$$

$$\frac{Dj}{Dt} - 2jv = 0 \quad (2)$$

$$-\nabla \pi + \lambda_0 \nabla \nabla \cdot \mathbf{v} + (\lambda_v + 2\mu_v + \kappa_v) \nabla \nabla \cdot \mathbf{v} - (\mu_v + \kappa_v) \nabla \times \nabla \times \mathbf{v} + \kappa_v \nabla \times \boldsymbol{\nu} + \rho \left(\mathbf{f} - \frac{D\mathbf{v}}{Dt} \right) = 0 \quad (3)$$

$$(\alpha_v + \beta_v + \gamma_v) \nabla \nabla \cdot \boldsymbol{\nu} - \gamma_v \nabla \times \nabla \times \boldsymbol{\nu} + \kappa_v \nabla \times \mathbf{v} - 2\kappa_v \boldsymbol{\nu} + \rho(l - \sigma) = 0 \quad (4)$$

$$\alpha_0 \nabla^2 v + \pi_0 - \lambda_1 v - \lambda_0 \nabla \cdot \mathbf{v} + \rho(l - \sigma) = 0 \quad (5)$$

where $\mathbf{v} = \mathbf{v}(x,t)$, $\boldsymbol{\nu} = \boldsymbol{\nu}(x,t)$, $v = v(x,t)$, and $j = j(x,t)$ are, respectively, velocity microrotation, microstretch, and the microinertia density that are unknowns to be determined under appropriate boundary and initial conditions. D/Dt material differentiation operator, ρ is the density, π the thermodynamic pressure, π_0 the inertial micropressure, \mathbf{f} the body force density, l the body couple density and l denotes the microstretch body moment density. The spin inertia σ , and the microstretch inertia σ are given by [3]

$$\sigma = \frac{D}{Dt}(j\nu), \quad \sigma = \frac{1}{2} j \left(\frac{Dv}{Dt} + v^2 \right) - j\nu \cdot \boldsymbol{\nu} \quad (6)$$

$\mu_v, \kappa_v, \lambda_v, \lambda_0, \lambda_1$, and α_0 are the viscosity coefficients for the translatory motions, α_v, β_v , and γ_v those for the rotatory motions. The stress tensor, the couple stress, the internal microstretch force density and the difference between micropressure s and $t = t_{kk}$ are respectively given by the following constitutive equations [3];

$$t_{kl} = (-\pi + \lambda_0 v + \lambda_v v_{m,m}) \delta_{kl} + \mu_v (v_{l,k} + v_{k,l}) + \kappa_v (v_{l,k} + \epsilon_{ikm} v_{m,i}) \quad (7)$$

$$m_{kl} = \alpha_v \nu_{m,m} \delta_{kl} + \beta_v \nu_{k,l} + \gamma_v \nu_{l,k} + b_0 \epsilon_{mlk} v_{,m} \quad (8)$$

$$m_k = \alpha_0 v_{,k} + b_0 \epsilon_{klm} \nu_{l,m} \quad (9)$$

$$s - t = -\pi_0 + \lambda_0 v_{m,m} + \lambda_1 v \quad (10)$$

where b_0 is a viscosity coefficient and ϵ_{mlk} is the permutation symbol. Repeated indices denote summation over the range (1, 2, 3) and as index followed by a comma represents partial differentiation with respect to space variable x_m . In general, all material moduli may depend on ρ , j , and temperature. For linear approximation they are considered constants. As a second assumption, the flow is steady and the microstretch fluid is incompressible. In the case of incompressible fluids, π is replaced by an unknown pressure p , and equation of continuity (1) reduces to:

$$\nabla \cdot \mathbf{v} = 0. \quad (11)$$

In linear microstretch theory, $|\mathbf{v}|, |\boldsymbol{\nu}|$, and $|v|$ are considered to be small as compared to other term in Eq. (6) and the spin inertia σ , and the microstretch inertia σ are approximated by [3]

$$\sigma = j \frac{D\nu}{Dt}, \quad \sigma = \frac{1}{2} j \frac{Dv}{Dt}. \quad (12)$$

Also, the flow is microisotropic in the sense that the microinertia tensor $j_{kl} = (1/3)j\delta_{kl}$. For the case of small microinertia j , the inertial micropressure π_0 can be expressed as [3, 12] :

$$\pi_0 = cj \tag{13}$$

where c is a constant. Under these assumptions, and neglecting external body force, body couple and microstretch body moment, the field equations (2)-(5) reduce to:

$$\mathbf{v} \cdot \nabla j - 2j\nu = 0 \tag{14}$$

$$-\nabla p + \lambda_0 \nabla \nu + (\mu_v + \kappa_v) \nabla^2 \mathbf{v} + \kappa_v \nabla \times \boldsymbol{\nu} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = 0 \tag{15}$$

$$(\alpha_v + \beta_v + \gamma_v) \nabla \nabla \cdot \boldsymbol{\nu} - \gamma_v \nabla \times \nabla \times \boldsymbol{\nu} + \kappa_v \nabla \times \mathbf{v} - 2\kappa_v \boldsymbol{\nu} + \rho j (\mathbf{v} \cdot \nabla \boldsymbol{\nu}) = 0 \tag{16}$$

$$\alpha_0 \nabla^2 \nu + cj - \lambda_1 \nu + \frac{1}{2} \rho j (\mathbf{v} \cdot \nabla \nu) = 0 \tag{17}$$

In the subsequent section, we shall obtain the exact solutions of the above equations for steady shear flow of a microstretch fluid.

3. SHEAR FLOW OF A MICROSTRETCH FLUID

Consider the flow of a microstretch fluid between two infinite parallel plates separated by a distance $2h$ as illustrated in Fig. 1. The plates are initially at rest and both plates are suddenly accelerated from rest and moves in their own planes with a constant velocity V to opposite directions. It is assumed that the flow is driven by motions of palates.

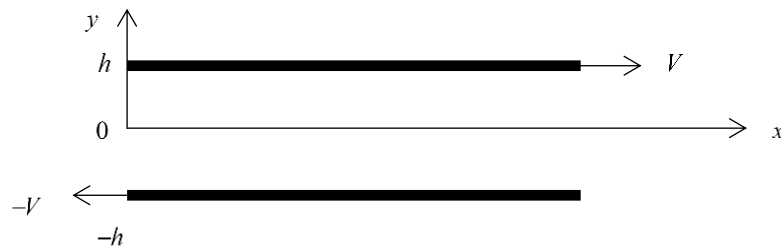


Figure 16. The geometry of the problem.

We seek solutions in which the velocity vector, microrotation vector, microstretch, and microinertia of the fluid are assumed to have the form

$$\mathbf{v} = \{u(y), 0, 0\}, \quad \boldsymbol{\nu} = \{0, 0, \psi(y)\}, \quad \nu = \nu(y), \quad j = j(y) \tag{18}$$

Substitution of Eq. (18) into Eqs. (14)-(17) gives

$$(\kappa_v + \mu_v) \frac{d^2 u}{dy^2} + \kappa_v \frac{d\psi}{dy} = 0 \tag{19}$$

$$\gamma_v \frac{d^2 \psi}{dy^2} - \kappa_v \frac{du}{dy} - 2\kappa_v \psi = 0 \tag{20}$$

$$\alpha_0 \frac{d^2 \nu}{dy^2} - \lambda_1 \nu + \pi_0 = 0 \tag{21}$$

The boundary conditions are as follows:

$$\begin{aligned} u(-h) &= -V + L \frac{du}{dy}(-h), & u(h) &= V - L \frac{du}{dy}(h) \\ \psi(-h) &= -n \frac{d\psi}{dy}(-h), & \psi(h) &= -n \frac{d\psi}{dy}(h) \\ \nu(-h) &= 0, & \nu(h) &= 0 \end{aligned} \tag{22}$$

where, L is a slip parameter and n is spin parameter. $n=0$ indicates that a fluid particle does not rotate at boundaries which called strict adherence condition. $n=1/2$ indicates that a fluid particle rotation is equal to $(1/2)\nabla \times \mathbf{v}$. Introducing dimensionless parameter as;

$$\bar{y} = \frac{y}{h}, \quad \bar{u} = \frac{u}{V}, \quad \bar{\psi} = \frac{\psi}{V/h}, \quad \bar{v} = \frac{v}{\pi_0/\lambda_1} \quad (23)$$

where, bars used to denote a dimensionless quantity. Throughout this paper, henceforth for convenience, unless stated otherwise, we shall drop the bars that appear over the dimensionless quantities.

Substituting Eq. (23) into Eqs. (19)-(22); the dimensionless governing equations and boundary conditions obtained as follows:

$$(1 + \Delta_m) \frac{d^2 u}{dy^2} + \Delta_m \frac{d\psi}{dy} = 0 \quad (24)$$

$$\frac{d^2 \psi}{dy^2} - \lambda_m^2 \frac{du}{dy} - 2\lambda_m^2 \psi = 0 \quad (25)$$

$$\frac{d^2 v}{dy^2} - \lambda_n^2 v + \lambda_n^2 = 0 \quad (26)$$

$$\begin{aligned} u(-1) &= -1 + \beta \frac{du}{dy}(-1), & u(1) &= 1 - \beta \frac{du}{dy}(1) \\ \psi(-1) &= -n \frac{d\psi}{dy}(-1), & \psi(1) &= -n \frac{d\psi}{dy}(1) \\ v(-1) &= 0, & v(1) &= 0 \end{aligned} \quad (27)$$

where, Δ_m and λ_m are micropolar parameters, λ_n is microstretch parameter, β is dimensionless slip parameter and they are defined as follows:

$$\Delta_m = \frac{\kappa_v}{\mu_v}, \quad \lambda_m = \frac{\kappa_v h^2}{\gamma_v}, \quad \lambda_n = \frac{\lambda_1 h^2}{\alpha_0}, \quad \beta = \frac{L}{h} \quad (28)$$

Solving Eqs. (24)-(26) under the boundary conditions (27), velocity, microrotation, and microstretch obtained as follows, respectively.

$$u = \frac{\frac{\Delta_m}{(1 + \Delta_m)} \frac{(N-1)}{\lambda \cosh(\lambda)} \sinh(\lambda y) + 2y}{\left(\frac{\Delta_m(N-1) \tanh(\lambda)}{(1 + \Delta_m)} \frac{1}{\lambda} + \frac{\Delta_m(N-1)}{(1 + \Delta_m)} \beta + 2(1 + \beta) \right)} \quad (29)$$

$$\psi = \frac{\frac{(1-N)}{\cosh(\lambda)} \cosh(\lambda y) - 1}{\left(\frac{\Delta_m(N-1) \tanh(\lambda)}{(1 + \Delta_m)} \frac{1}{\lambda} + \frac{\Delta_m(N-1)}{(1 + \Delta_m)} \beta + 2(1 + \beta) \right)} \quad (30)$$

$$v = 1 - \frac{\cosh(\lambda_n y)}{\cosh(\lambda_n)} \quad (31)$$

where,

$$N = \frac{n(2 + \Delta_m)}{1 + \Delta_m - n\Delta_m}, \quad \lambda = \lambda_m \sqrt{\frac{2 + \Delta_m}{1 + \Delta_m}} \quad (32)$$

For the problem under consideration, it is important to find the shear stress and couple stress. Using the Eqs. (7), (23), and (29), the shear stress τ_{wx} can be written in non-dimensional form as follows:

$$\tau_{wx} = \frac{t_{yx}}{\mu_v V / h} = (1 + \Delta_m) \frac{du}{dy} + \Delta_m \psi = \frac{2 - \Delta_m}{\left(\frac{\Delta_m(N-1) \tanh(\lambda)}{(1 + \Delta_m)} \frac{1}{\lambda} + \frac{\Delta_m(N-1)}{(1 + \Delta_m)} \beta + 2(1 + \beta) \right)} \quad (33)$$

Using the Eqs. (8), (23), and (30), the couple stress m_{wz} can be written in non-dimensional form as follows:

$$m_{wz} = \frac{1}{\gamma_v V / h^2} m_{yz} = \frac{d\psi}{dy} = \frac{\lambda \frac{(1-N)}{\cosh(\lambda)} \sinh(\lambda y)}{\left(\frac{\Delta_m(N-1) \tanh(\lambda)}{(1+\Delta_m)} \frac{1}{\lambda} + \frac{\Delta_m(N-1)}{(1+\Delta_m)} \beta + 2(1+\beta) \right)} \quad (34)$$

Using the Eqs. (9), (23), and (30), the non-vanishing components of the microstretch force vector are given in non-dimensional form:

$$m_{w1} = \frac{1}{b_0 V / h^2} m_x = \frac{d\psi}{dy} = \frac{\lambda \frac{(1-N)}{\cosh(\lambda)} \sinh(\lambda y)}{\left(\frac{\Delta_m(N-1) \tanh(\lambda)}{(1+\Delta_m)} \frac{1}{\lambda} + \frac{\Delta_m(N-1)}{(1+\Delta_m)} \beta + 2(1+\beta) \right)} \quad (35)$$

Lastly, the difference between the normal stress and the micropressure can be expressed by

$$p_w = \frac{s-t}{\pi_0} = -\frac{\cosh(\lambda_n y)}{\cosh(\lambda_n)} \quad (36)$$

4. RESULTS AND DISCUSSION

In this paper steady shear flow of a microstretch fluid is studied theoretically. Exact analytical solutions for the system of coupled partial differential equations governing the velocity field, microrotation, and microstretch are obtained. The effects of the flow parameters have been presented graphically. To the best of authors' knowledge, the numerical values of relevant viscosity coefficients for microstretch fluid are not available in the literature. Therefore, the hypothetical values of flow parameters have been taken.

It should be noted that the velocity distribution corresponding to pure Newtonian fluid appears as the special case of present analysis. If one sets $\Delta_m = \lambda_m = \lambda_n = 0$ in Eqs. (29)-(31), these are obtained as follows;

$$u_N = \frac{y}{1+\beta}, \quad \psi_N(y) = \lim_{\lambda_m \rightarrow 0} [\psi(y)] = 0, \quad v_N = 0 \quad (37)$$

which is the solution of the same problem for a Newtonian fluid. The case $\lambda_n = 0$ corresponds to case of micropolar fluid.

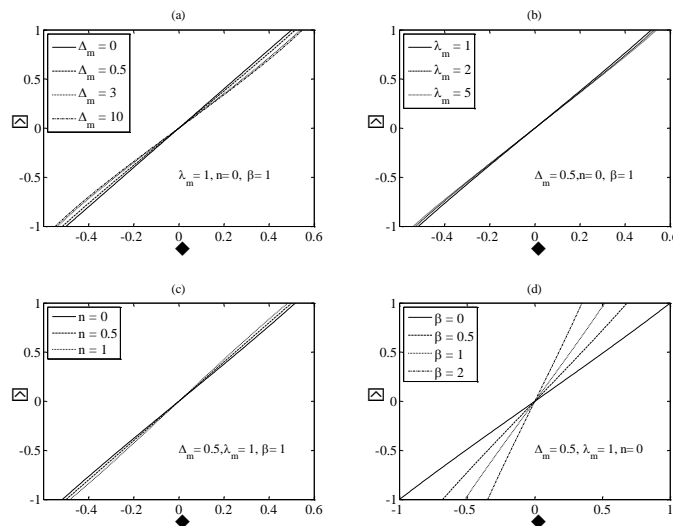


Figure 2. Variation of the velocity profile with flow parameters.

Figure 2 (a) and 2 (b) show that the velocity increases as both micropolar parameters Δ_m and λ_m increase. The line $\Delta_m = 0$ corresponds to the classical case. This investigation of the flow of a microstretch liquid shows that while the behaviour of the microstructure has important effects upon the macroscopic flow.

From the Figure 2 (c), we observe that the velocity decreases as spin parameter increase. The effect of the slip parameter on the velocity is shown in Figure 2 (d).

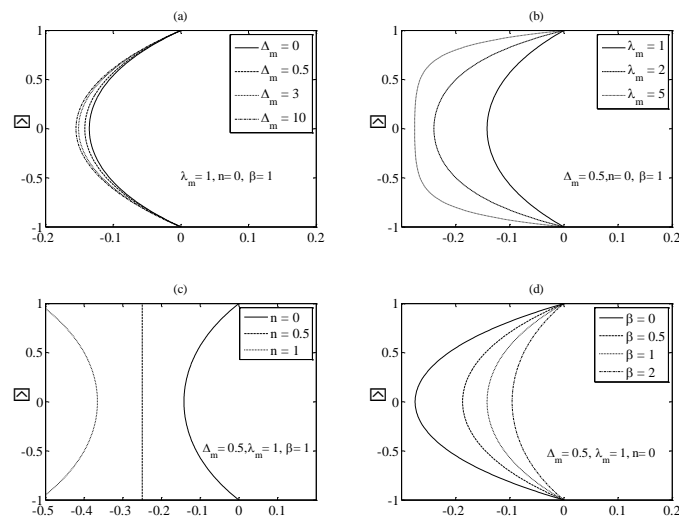


Figure 3. Variation of the microrotation profile with flow parameters.

Figures 3 (a) and 3 (b) illustrate the microrotation profiles for different values of the micropolar parameters. The numerical results show that the effect of increasing values of micropolar parameters result in an increase of the microrotation. Figure 3 (c) shows the variation of microrotation with spin parameter n . The case of $n = 0.5$ indicates that the microrotation is equal to z-component of rotation vector (w) of classical case. $\psi = (1/2)\nabla \times \{u_N, 0, 0\} = \{0, 0, 0.25\}$. Figure 3 (d) shows that the microrotation decreases as slip parameter β increase.

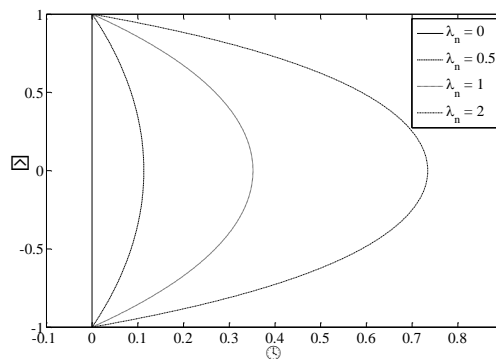


Figure 4. Variation of microstretch.

Finally, Figure 4 shows the variation of microstretch with microstretch parameter λ_n . Increasing values of λ_n result in an increase of the microstretch.

5. CONCLUSIONS

Exact analytical solutions to the shear flow of a microstretch fluid have been obtained. Passage to the classical case has been made. The effects of flow parameters on velocity field, microrotation, and microstretch are presented graphically. The results show that the microscopic behavior of fluid particles contribute the macroscopic behavior of fluid significantly. As a result, the local structure and intrinsic motions of the fluid elements should be taken into account in some cases where the continuum assumption is not valid.

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Determination of Combustion Properties of The Firetex Impregnated Scotch Pine

Cemal OZCAN^{1}, Rasit ESEN¹*

Abstract

*In this study, the effects of impregnation material and impregnation methods on combustion properties of Scotchpine (*Pinussylvestris L.*) have been investigated. The firetex was used for impregnation material. The four different methods were used for impregnation process. Combustion test was performed according to the procedure of ASTM-E 69 standards. The mass reduction, release of gasses (CO, NO, O₂), and temperature differences of samples were determined for each 30 seconds during combustion. According to the test results, Firetex as an impregnation material was found to be the most effective after long-term dipping processing Scotch pine material.*

Keywords: *Scotch Pine, Firetex, Dipping Method, Fire Retardant, Impregnation*

1. INTRODUCTION

Wooden material has a versatile usage area and it is a natural, recyclable and sustainable material. Considering its structure, which allow it to physical, chemical and mechanical modification, it is a very durable construction material. Moreover, this structure provides lots of unique properties to wood such as easy processing, color and pattern difference between species, insulation for noise and heat and makes it a high quality decorative material (e.g. [1], [2]). The combustion of wood relates to the fuel burn rate (or the reaction rate), the combustion product (or the emissions), the required excess air for complete combustion, and the fire temperatures. The processes are extremely complicated, principally, because the wood has a complex physical and chemical composition [3].

Important reactions to fire parameters in the full-scale fire are heat release rate and time of flashover [4]. Flame retardant treated materials may have much better fire performance concerning these parameters than untreated wood products. Combustion of wood involves a complex series of physical transformations and chemical reactions that are further complicated by the heterogeneity of the substrate. Wood, and cellulosic materials in general, do not burn directly; under the influence of sufficiently strong heat sources they decompose to a mixture of volatiles, tarry compositions, and highly reactive carbonaceous char. Gas-phase oxidation of the combustible volatiles and tarry products produces flaming combustion. Solid-phase oxidation of the remaining char produces glowing or smoldering combustion, depending on the rate of oxidation [5]. Wood coatings more often are designed to retard ignition and rate of burn rather than to provide the fire-resistive barrier which is more typical of steel coatings. Typically, coatings protective (or retardant) against cellulosic-type fires are applied in thin film coat up to 1.5 mm (60mils) thick. These coatings are usually not very weatherable; so, for outdoor applications, a protective topcoat is needed [6]. Uysal et al. investigated the effects of finishing materials polyurethane, cellulosic, synthetic, polyester, and acid hardening varnish on combustion properties of Scotch pine. Cellulosic varnish was found to be the most successful varnish according to the CO amounts and mass reduction. According to their results, all of the varnishes used to in their study showed a low resistance against fire and high temperatures [7]. Uysal and Kurt studied the impregnation of the oriental spruce (*Piceaorientalis L.*) with boron compounds, and the test samples were applied to the combustion test. A borax-boric acid % 10 solution was found to be the most successful fire retardant chemical [8]. Kurt and Uysal investigated the effects of fire retardant materials zinc chloride and di-ammonium phosphate were found to be the most successful fire-retardant chemicals in LVL. Since it diminishes combustion, the impregnation of LVL produced from walnut by using PF and PVAc adhesives can be advised to be impregnated by using the pressure-vacuum method [9].

¹ Corresponding author: Karabuk University, Department of Industrial Product Design, 78600, Safranbolu/Karabuk, Turkey.
cemalozcan@karabuk.edu.tr

The aim of this paper is to investigate the combustion properties and emission testing of Scotch pine (*Pinussylvestris* L.), widely used in building construction and wooden materials. The samples were impregnated by using four different impregnatedmethod.

2. MARERIAL AND METHOD

Wood Material

Scotch pine (*Pinus Sylvestris* L.), wood was chosen randomly from timber supplier of Karabuk, Turkey. A special emphasis was put on the choice of the wood material. Accordingly, non-deficient, whole, knotless, normally grown (without reaction wood, decay, insect, or fungal infection) wood materials are selected.

Impregnated Material

Firetex is an effective, natural, non-toxic, ecologic and economic water based fire-retardant and fire-extinguisher. The properties of some physical are given in Table 1.

Table 1. Physical Properties of firetex

Boiling point	98 °C
Freezing point	-3 °C
pH	3,7
TDS	739 ppm
Evaporation (60°C / 24 h)	% 50

Preparation of Test Samples

The oversized test samples were acclimatized until they were stable at 20 ± 2 °C and 65 ± 3 % relative humidity in climate room. Later on they were cut with the dimensions of 9x19x1016 mm according to the procedure of ASTM E – 69[10].Impregnation processes stated at ASTM D 1413-76, TS 344 and TS 345 were applied to the prepared test samples (e.g. [11], [12] and [13]). For this aim, the samples were dipped into the impregnation solution (having packing viscosity) for 2 min, 24 h,7 days and these samples were impregnated by brush. The peculiarities of impregnation were determined before and after impregnation processes. All processes were carried out at 20 ± 2 °C. The samples, oven dried before and after impregnation, can be calculated by the formula

$$R = \frac{GC}{V} \times 10^3 \text{ kg} / \text{m}^3,$$

where R is the retention of impregnation material, $G=T_2-T_1$, T1 is the sample weight before impregnation (g), T2 is the sample weight after impregnation (g), C is the concentration (%) and V is the volume of the samples (cm³). Impregnated test samples were kept at 20 ± 2 °C and at 65 ± 3 % relative humidity until their weights became stable.

Execution Test

The combustion test was carried out according to the principles of the ASTM E –69. But some changes were made in the stand. For this purpose, a digital balance having 0.01 g sensitiveness has been used for determination of mass reduction of materials when they are burnt. Butane gas was used to make an ignition flame. The gas flow is standard as the high of flame is 25 cm, the temperature must be 1000 °C.The distance between the bottoms of the test samples, which were hanged inside of the fire tube and the top of the gas pipe must be adjusted as 2.54 cm. During the test, mass reduction, temperature and released gas (CO, NO, O₂) were determined in every 30 seconds. The test was made under a chimney where the flow of air blown was drawn with natural draft. At the beginning of combustion test flame source was used for 4 minutes then flame source was taken away and it was continued 6 minutes. Totally 10 minutes, the test was lasted.

Statistical Procedure

Descriptive statistics analysis was applied to determine both the amount of retention in the prepared natural and the effects of impregnation material on combustion with or without flame source.

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3. RESULT AND DISCUSSION

The air dry density (0.480 gr/cm³) was obtained scotch pine wood. The proportion of impregnation material is given in Table 2.

Table 2. Proportion of Retention

Test no	Impregnation Method	Retention (%)	
		\bar{X}	HG *
1	Finished with by a brush	3,7	A
2	Short-term dipping (2 min)	6,9	B
3	Middle-term dipping (24 h)	14,4	C
4	Long-term dipping (7 days)	24,8	D

\bar{X} : Average *HG: Groups of Homogeneity

The highest retention proportion was observed (24,8 %) in dipping method of long time, and the lowest (3.7%) in finished with a brush. The averages of mass reduction are given in Table 3.

Table 3. Average of Mass Reduction(%)

Measured of time	Control	Dipping method			with a brush
		2 min	24 hours	7 days	
1	2.23	2.55	1.95	2.24	2.29
2	5.08	6.48	3.95	3.54	3.21
3	9.45	8.38	5.44	5.16	6.62
4	16.18	10.17	7.28	6.60	8.24
5	24.12	13.04	10.29	7.21	11.14
6	31.21	15.59	11.03	8.10	13.94
7	40.68	18.06	12.26	10.13	15.94
8	48.23	21.76	13.58	11.06	17.57
9	55.23	25.60	16.24	13.54	19.09
10	64.57	27.87	18.53	14.80	20.20
11	76.41	29.51	20.52	15.86	21.67
12	81.57	32.18	23.66	16.94	23.59
13	85.79	32.71	25.39	17.49	24.74
14	91.84	34.14	25.83	18.06	25.69
15	94.02	35.79	26.18	19.81	27.05
16	96.33	36.36	26.54	20.53	27.45
17	97.49	37.10	26.90	22.10	27.93
18	98.13	37.56	27.32	22.40	28.37
19	98.53	38.83	28.02	22.83	29.49
20	99.15	39.07	28.61	23.18	30.36

The highest mass reduction was (99.15%) observed in control samples. the lowest value (28.61%) in the impregnated with firetex by middle-term dipping method. The averages of O₂ amounts are given in Table 4.

Table 4. Average of O₂ amounts (%)

Measured of time	Control	Dipping method			With a brush
		2 min	24 hours	7 days	
1	20.75	20.47	20.10	20.11	20.36
2	20.51	20.31	19.73	19.73	19.86
3	20.19	20.15	19.59	19.54	19.61
4	19.95	19.98	19.51	19.35	19.27
5	19.65	19.76	19.43	19.08	19.25
6	19.32	19.58	19.35	18.78	19.28
7	18.95	19.35	19.27	18.66	19.43
8	18.60	19.28	19.25	18.90	19.67
9	18.25	19.03	19.38	19.14	19.85
10	17.95	18.84	19.51	19.53	20.37
11	17.67	18.89	20.11	20.13	20.67
12	17.41	19.13	20.39	20.32	20.84

13	17.32	19.64	20.55	20.48	20.92
14	17.55	20.19	20.60	20.62	20.94
15	18.17	20.56	20.61	20.70	20.97
16	18.76	20.73	20.63	20.85	20.98
17	19.76	20.91	20.63	20.88	20.98
18	20.56	20.94	20.71	20.88	20.98
19	20.86	20.96	20.86	20.89	20.98
20	20.94	20.97	20.99	20.90	20.98

The highest reduction of O₂ concentration (20.99%) was measured in the impregnated with firetex by middle-term dipping method. The lowest change of O₂-concentration (17.32 %) in scotch pine control samples. From the control samples it can be seen that the impregnation chemicals has the effect of fire retardant. Control samples gave the highest CO₂ concentrations. The averages of temperature are given in Table 5.

Table 5. Average of Temperature Values(°C)

Measured of time	Control	Dipping method			with a brush
		2 min	24 hours	7 days	
1	76.9	80.1	73.8	75.6	75.6
2	84.3	93.4	88.1	89.8	91.7
3	105.5	104.3	100.7	99.6	104.3
4	128.4	110.6	111.5	106.8	121.4
5	159.7	117.8	119.6	113.0	134.9
6	183.8	128.6	128.6	119.2	148.3
7	203.0	137.6	136.7	126.7	161.9
8	230.5	145.7	143.9	134.9	175.3
9	283.2	142.0	134.9	132.1	168.1
10	376.5	137.6	123.1	127.7	158.2
11	483.4	129.4	117.8	120.5	147.4
12	511.1	125.9	110.6	113.3	139.3
13	542.4	120.5	105.2	106.0	129.5
14	481.5	115.0	99.8	101.6	121.4
15	414.6	113.2	93.5	97.0	111.5
16	348.9	110.6	89.0	93.5	102.5
17	318.4	104.3	86.3	90.8	96.1
18	282.5	108.8	82.7	89.0	89.0
19	253.3	95.2	78.2	84.5	86.3
20	230.7	91.6	75.5	81.8	80.9

The highest averages temperature (542.4°C) variation was observed in the scotch pine control samples. The lowest (73.8°C) in impregnated with firetex by middle-term dipping method. The averages of variations of CO are given in Table 6.

Table 6. Variation of CO (ppm)

Measured of time	Control	Dipping method			with a brush
		2 min	24 hours	7 days	
1	11.76	61.23	74.06	65.25	54.40
2	27.34	111.89	115.37	117.98	125.06
3	48.74	125.40	141.55	145.91	151.19
4	75.06	137.24	155.32	184.47	175.44
5	117.3	152.07	167.84	242.28	199.24
6	156.6	186.51	169.09	294.66	211.31
7	188.5	195.95	177.82	347.06	194.54
8	247	198.84	176.23	366.81	171.47
9	296.6	203.45	187.22	336.04	140.08
10	355.68	220.96	186.49	315.60	114.64
11	410.92	245.31	166.94	224.71	101.77
12	494.46	203.28	143.82	173.41	86.87
13	500.62	193.42	124.61	110.31	74.29
14	449.85	157.66	122.68	67.86	50.83
15	335.04	123.42	103.64	44.26	38.98

16	269.52	77.61	85.90	28.84	27.54
17	199.04	47.52	73.44	20.33	14.45
18	146.53	29.31	51.45	14.59	9.46
19	101.37	20.49	37.51	8.75	6.46
20	61.85	15.20	17.00	6.02	4.19

The highest increase in CO concentration was (500.62 ppm) observed in the control scotch pine control samples and the lowest in (4.19 ppm) impregnated with firetex by with a brush samples. The averages of variation of NO are given in Table 7.

Table 7. Variation of NO (ppm)

Measured of time	Control	Dipping method			with a brush
		2 min	24 hours	7 days	
1	1.22	19.61	7.28	18.90	5.78
2	2.68	25.37	11.10	29.39	13.95
3	4.12	24.50	13.86	32.34	17.96
4	5.1	21.64	15.16	31.58	20.58
5	7.02	20.34	16.24	31.00	21.93
6	8.78	19.94	16.66	30.24	20.39
7	10.45	18.38	17.22	29.03	15.68
8	11.05	17.14	16.28	25.05	12.88
9	12.34	14.65	15.21	19.21	9.19
10	13.24	9.69	14.65	14.81	6.06
11	15.25	6.64	12.08	9.56	4.80
12	15.62	5.77	9.28	6.27	3.64
13	17.02	4.96	6.44	5.34	3.08
14	13.6	3.67	5.78	4.32	2.70
15	11.45	2.42	4.48	3.79	2.14
16	9.22	2.25	2.61	3.23	1.44
17	5.32	1.72	2.00	2.58	1.26
18	1.81	1.60	1.30	2.02	1.21
19	1.02	1.51	0.65	1.46	1.02
20	0.02	1.46	0.09	0.90	0.32

In this study, the highest increase in NO concentration was observed in the experiment of (32.34 ppm) impregnated with firetex by long-term dipping method samples and the lowest in those of (0.02 ppm) non-impregnated control scotch pine samples.

4. CONCLUSION

According to Table 3, after taking the flame source from the fire tube, the highest mass reduction (99.15 %) was observed in the non-impregnated control samples, the lowest in the impregnated with firetex by middle-term dipping method scotch pine samples (28.61 %) at the second stage of combustion. It has been observed that impregnated with firetex by dipping method scotch pine samples decreases mass reduction values 71.1 % in average.

According to Table 4, the highest O₂ consumption was observed in the impregnated with firetex by middle-term dipping method (20.99 %). The lowest change of O₂-concentration (17.32 %) in scotch pine control samples, impregnated with firetex samples decreases O₂ consumption values 17.4 % in average.

According to Table 5, the highest temperature was observed in the non-impregnated scotch pine control samples (542.4°C). It has been observed that impregnated by middle-term dipping method samples impregnated with firetex samples decreases °C consumption values 85 % in average.

According to Table 6, the highest ratio of CO was observed in control samples (500.6 ppm). According to the averages values, it has been observed that impregnated by with a brush method scotch pine samples impregnated with firetex samples decreases CO ratio values 90 % in average.

According to Table 7, the highest ratio of NO was observed in the impregnated with firetex by long-term dipping method samples (32.34 ppm). According to the averages values, it has been observed that impregnated by long-term dipping method scotch pine samples impregnated with firetex samples increases NO ratio values 97 % in average. Consequently, fire retardant impregnated material was found to be the most successful according to the CO amounts and mass reduction.

It can be proposed that protecting by dipping method or with a brush firetex of historical wooden structure due to fire risk.

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Improvement of Fire-Resistance of Scotch Pine Wood Used On Historical Wooden Constructions

Rasit ESEN^{1}, Cemal OZCAN¹*

Abstract

In this study, the effects of fire retardant finishing materials on combustion properties of 120-years in service historical wooden houses have been investigated. Combustion test was performed according to the procedure of ASTM-E 69 standards. The mass reduction, release of gasses (CO, NO, O₂), and temperature differences of samples were determined for each 30 second during combustion. According to the test results, fire retardant finishing material was found effective to preserve historical wooden structures against fire. Since fire retardant finishing material diminishes combustion, it is possible to advise using fire retardant finishing for varnishing to historical wooden structures.

Keywords: *Scotch Pine, Combustion, Historical Wooden Structures, Fire Retardant*

1. INTRODUCTION

Wood continues to play an important role as a structural material in today's high-tech society. In many countries, wood is widely used as a building material: in some areas as the main construction and decoration material [1].

The combustion of wood relates to the fuel burn rate (or the reaction rate), the combustion product (or the emissions), the required excess air for complete combustion, and the fire temperatures. The processes are extremely complicated, principally, because the wood has a complex physical and chemical composition [2]. Wood material has a number of advantages such as good mechanical properties, but shows a low fire resistance. Wood is a naturally durable material that has been recognized for centuries throughout the world for its versatile and attractive engineering and structural properties (e.g. [3], [4] and [5]).

In our country and the world, the areas which form the best examples of ancient times' human settlements in their original environmental textures reflect the richness of our country. These wooden structures are the products of long-lasting history and culture and economical welfare gained during the strongest periods of Ottoman Empire. These structures still able to perform their duties are unique examples reflecting all the characteristics of traditional Turkish social life and serving their historical and cultural products to the whole world in their original atmosphere [6].

It is well known that there are possibilities to improve significantly the fire performance of wood by chemical treatment and to widen its application options. In general, the amount of flame retardant uptake to the wood is directly proportional to the improvement of reaction to fire characteristics [7]. Important reactions to fire parameters in the full-scale fire are heat release rate and time of flashover [8]. Flame retardant treated materials may have much better fire performance concerning these parameters than untreated wood products. Wood coatings more often are designed to retard ignition and rate of burn rather than to provide the fire-resistive barrier which is more typical of steel coatings. Typically, coatings protective (or retardant) against cellulosic-type fires are applied in thin film coat up to 1.5 mm (60mils) thick. These coatings are usually not very weather able; so, for outdoor applications, a protective topcoat is needed [9].

The aim of this study to investigate combustion properties of fire retardant finishing materials on Scotch pine (*Pinussylvestris* L.) which 120-years in service historical wooden houses.

^{1*} Corresponding author: Karabuk University, Department of Industrial Product Design, 78600, Safranbolu/Karabuk, Turkey.
resen@karabuk.edu.tr

2. MATERIAL AND METHOD

Wood Material

Scotch pine (*Pinus Sylvestris* L.), wood was chosen randomly from timber supplier of Karabuk, Turkey. A special emphasis was put on the choice of the wood material. Accordingly, non-deficient, whole, knotless, normally grown (without reaction wood, decay, insect, or fungal infection) wood materials are selected.

Varnished Material

After a fire starts, any reduction in the propagation of flames can be decisive in saving lives. One of the purposes of fire retardant coatings is to reduce the rate at which the fire spreads and thereby retard it. As regards fire protection, most countries have very strict regulations concerning the performance of fire-resistant and fire-retardant coatings, especially for the treatment of bearing structures, coatings and wooden works. Wood exhibits an important aesthetic importance and fire retardant coatings for wood should combine fire protection with excellent aesthetic results. "Safety performance + Finish performance". When it is mandatory to conform to fire regulations, the architect/designer or authorizer issuer of the fire certificate may calculate the fire load (quantity of flammable material per square meter and relevant calorific power) for each room, assessing the class that each construction element falls into, based on emergency exits, firefighting systems, or internal permanent safety services. The technical specifications of the conventional varnishes are given in Table 1.

Table 1. Some technical properties of the conventional varnishes.

Technical Properties		
	Primer	Finishing coat
Density (g/cm ³)	1.220	1.150
Viscosity (second/DIN CUP 4 mm/20°)	140 sn	
Amount applied (gram/m ²) 100	150 gr/m ²	150 gr/m ²
Drying type	Chemical	Chemical
Drying time (20°)	80 minute	90 minute

Preparation of Test Samples

The oversized test samples were acclimatized until they were stable at 20 ± 2 °C and 65 ± 3 % relative humidity in climate room. Later on, they were cut with the dimensions of 9x19x1016 mm according to the procedure of ASTM E – 69 [10] and finished with fire retardant finishing. 10 samples were manufactured for each test sample 40 test samples were prepared in total.

Execution Test

The combustion test was carried out according to the principles of the ASTM E –69. But some changes were made in the stand. For this purpose, a digital balance having 0.01 g sensitiveness has been used for determination of mass reduction of materials when they are burnt. Butane gas was used to make an ignition flame. The gas flow is standard as the high of flame is 25 cm, the temperature must be 1000 °C.

The distance between the bottoms of the test samples, which were hanged inside of the fire tube and the top of the gas pipe must be adjusted as 2.54 cm. During the test, mass reduction, temperature and released gas (CO, NO, O₂) were determined in every 30 seconds. The test was made under a chimney where the flow of air blown was drawn with natural draft. At the beginning of combustion test flame source was used for 4 minutes then flame source was taken away and it was continued 6 minutes. Totally 10 minutes, the test was lasted.

Statistical Procedure

Multi variance analysis was applied to determine both the amount of retention in the prepared natural and laminated samples and the effects of impregnation material on combustion with or without flame source. Concerning the Duncan test each significant test group was compared with one another and itself.

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3.RESULT AND DISCUSSION

The averages of density are given in Table 2. The air-dry density (0.48 gr/cm³) was obtained in control scotch pine wood. The air-dry density (0.45gr/cm³) was obtained in scotch pine which 120 years of service of Scotch pine wood samples. Solid amounts of varnish types are given in Table 3.

Table 2. Average values of density (gr/cm³).

Control group	120year scotch pine wood
0.480	0.455

Table 3. Solid amounts of varnish types

Varnish Type	Primer	Finishing coat
Solid Amounts	% 76	% 59

The solid amounts of the varnish were measured. The highest solid amount of % 76 was obtained with primer varnish samples. The lowest solid amount of % 59 was obtained with finishing coat samples.

Table 4. Average of Mass Reduction (%)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	3,89	3,15	2,19	2,79
2	6,98	6,23	4,98	4,09
3	10,92	8,58	9,26	5,59
4	16,10	11,22	15,86	8,81
5	26,97	13,93	23,64	13,15
6	36,68	17,31	30,59	16,46
7	45,77	22,40	39,87	18,58
8	50,47	24,89	47,27	22,37
9	59,09	27,76	54,13	23,49
10	65,04	27,97	63,28	23,60
11	75,17	28,71	74,88	24,59
12	81,71	29,13	79,94	25,19
13	85,75	29,60	84,07	25,62
14	89,40	30,59	90,00	25,87
15	95,36	32,14	92,14	26,32
16	96,18	32,67	94,40	26,87
17	96,57	32,79	95,54	28,39
18	97,55	32,89	96,17	29,78
19	97,83	33,13	97,56	30,37
20	98,45	33,25	98,17	30,74

The averages of mass reduction are given in Table 4. The highest mass reduction was (98.45%) observed in unvarnished scotch pine control samples, the lowest value (%30.74) in the 120-year service scotch pine samples with varnished fire retardant finishing. The averages of O₂ amounts are given in Table 5.

Table 5. Average of O₂ amounts(%)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	20,10	20,01	20,71	20,44
2	19,73	19,71	20,47	20,17
3	19,06	19,60	20,15	20,02
4	18,59	19,55	19,91	19,69
5	18,46	19,27	19,61	19,61
6	18,29	19,06	19,28	19,35
7	18,23	19,03	18,91	19,30
8	18,14	19,01	18,56	19,21
9	17,81	19,25	18,21	19,10
10	18,01	19,82	17,91	19,43
11	18,36	20,21	17,63	19,84
12	18,86	20,47	17,38	20,07
13	19,50	20,52	17,29	20,23
14	20,17	20,61	17,51	20,39
15	20,25	20,67	18,13	20,79
16	20,31	20,69	18,72	20,80
17	20,46	20,69	19,72	20,88
18	20,61	20,75	20,52	20,94
19	20,78	20,82	20,89	20,95
20	20,89	20,84	20,96	20,97

The highest reduction of O₂ concentration (% 20,97) was measured in Scotch pine samples varnished with fire retardant finishing, the lowest change of O₂-concentration (% 17,29) in combustion of unvarnished scotch pine control samples.

Table 6. Average of Temperature Values(°C)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	56,19	91,31	68,10	82,46
2	76,76	111,47	85,82	96,71
3	99,87	128,88	107,40	108,93
4	126,03	150,16	130,71	124,20
5	155,65	168,28	162,57	144,56
6	182,12	184,77	187,11	159,83
7	205,03	202,79	206,65	167,97
8	232,92	211,54	234,65	180,19
9	257,55	210,93	288,30	187,31
10	286,97	193,11	383,28	190,37
11	347,65	176,52	492,10	198,51
12	453,42	162,27	520,30	209,71
13	476,22	150,36	552,16	222,94
14	406,59	141,60	490,17	208,69
15	353,76	133,77	422,06	201,56
16	315,27	126,54	355,18	187,31
17	285,65	119,00	324,13	175,10
18	262,44	113,41	287,59	163,90
19	243,91	108,11	257,86	147,61
20	228,44	104,35	234,85	134,38

The averages of temperature are given in Table 6. The highest temperature (552.1°C) variation was observed in the unvarnished and scotch pine control samples, the lowest (56.1°C) in unvarnished 120-year service scotch pine samples. The averages of variations of CO are given in Table 7.

Table 7. Variation of CO (ppm)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	46,05	59,40	9,94	33,80
2	81,12	93,20	23,10	94,64
3	99,79	108,08	41,19	141,12
4	107,40	122,78	63,43	182,52
5	140,19	148,97	99,12	215,48
6	267,70	199,42	132,33	243,36
7	428,58	204,15	159,28	256,88
8	490,69	203,31	208,72	288,15
9	476,58	199,50	250,63	306,74
10	408,73	196,55	300,55	291,53
11	245,47	175,25	347,23	266,18
12	221,47	148,13	417,82	231,53
13	198,41	95,74	423,02	219,70
14	169,93	63,71	380,12	204,49
15	152,86	51,63	283,11	177,45
16	142,89	45,46	227,74	158,86
17	128,10	40,81	168,19	97,18
18	86,27	17,58	123,82	65,07
19	52,47	9,97	85,66	41,41
20	43,69	6,59	52,26	21,97

The highest increase in CO concentration was (490.69ppm) observed in the unvarnished and 120 year service scotch pine samples and the lowest in (6,59ppm) varnished with fire retardant varnish and 120 year service scotch pine samples.

Table 8. Variation of NO (ppm)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	1,56	2,34	1,59	1,04
2	2,73	3,64	3,48	3,64
3	3,64	7,15	5,36	4,68
4	5,59	9,49	6,63	7,80
5	6,37	13,00	9,13	10,92
6	8,71	16,51	11,41	13,78
7	11,31	17,68	13,59	14,82
8	12,48	17,68	14,37	15,60
9	13,52	16,51	16,04	13,78
10	14,56	17,68	17,21	11,44
11	11,05	20,02	19,83	9,36
12	8,71	20,02	20,31	8,06
13	7,41	9,49	22,13	6,50
14	6,76	5,98	17,68	5,46
15	3,77	3,64	14,89	4,68
16	1,69	2,47	11,99	2,73
17	1,17	2,47	6,92	1,43
18	1,04	1,56	2,35	0,91
19	0,52	1,43	1,33	0,65
20	0,52	1,30	0,03	0,39

The averages of variation of NO are given in Table 8. In this study, the highest increase in NO concentration was observed in the experiment of (22.13 ppm) unvarnished scotch pine control samples and the lowest in those of (0.03 ppm) unvarnished service scotch control pine samples.

4. CONCLUSION

According to Table 4, after taking the flame source from the fire tube, the highest mass reduction (98.45 %) was observed in the unvarnished control samples, the lowest in varnished with fire retardant finish and 120 year service scotch pine samples (30.74 %) at the second stage of combustion. It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases mass reduction values 68,77 % in average.

According to Table 5, the highest O₂ consumption was observed in Scotch pine samples varnished with fire retardant finishing (20,97 %). It been has observed that while scotch pine samples finished with fire retardant samples decreases O₂ consumption values 17,54 % in average.

According to Table 6, the highest temperature was observed in the scotch pine control and unvarnished samples (552.10C). It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases temperature values 89,83 % in average.

According to Table 7, the highest ratio of CO was observed in the 120 – year service and unvarnished samples (490.69 ppm). It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases ratio of CO values 98,6 % in average.

According to Table 8, the highest ratio of NO was observed in unvarnished scotch pine control samples (22.13 ppm). Consequently, fire retardant finishing was found to be the most successful according to the CO amounts and mass reduction. It can be proposed that protecting by varnishing fire retardant finishing of historical wooden structure due to fire risk.

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Religion And Environmentalism: A Search For The Religio-Philosophical Basis Of Environmentalism

Ali BAYER^{1*} , M. Ali KIRMAN ¹

Abstract

One of the most important matters in today's world is the environmental problems. People believe is right and wrong environmental degradation such as environmental pollution, deforestation, global warming and source water pollution are arise from human's environmental worldview. Most of the environmental problems although scientists have warned us for decades about the potentially devastating consequences of climate change. The purpose of this study is examining the relationship between religious behavior and environmental worldview. People have customs, thoughts, philosophies, variety of life styles cultures, and beliefs. According to authors the religious world view of the people is their way of approach at environment. These approaches make different postulates about the world and create views that perceive the world differently. People really want to know the high being who holds this cosmos and controls human life. In understanding the role religion has, it can then be determined if religious social structures are a viable option to promote positive environmental behavior. Every religion or ideology has its own environmental purposes and functions. According to Islamic view man is responsible for protecting the environment that was delivered him. As a result if we are to reverse the deterioration of our environment then we have to make some hard choices and change our practices. In other words, ecological change calls for personal change.

Keywords: Religion, change, environmentalism, worldview, philosophy

1. INTRODUCTION

Environmental sociology is a relatively new area of inquiry that emerged largely in response to increased societal recognition of the seriousness of environmental problems. The growth of sociological work on environmental issues has been accompanied by a critique and reassessment of core sociological assumptions and practices.

In the 19th century, there have been fundamental changes such as great migration waves, world wars, famine, reform, renaissance, enlightenment, French Revolution and industrial revolution in the world. These events in social life changed the way people's view of the world, nature and environment. Environment is more than trees, water, land, and air. It is a sense of peace, an understanding of our place in our society. It sustains our satisfaction in life and our interest in caring for the life around us. Recognizing the sustaining forces that make up our environment sometimes requires a time of deep introspection. The world is undergoing accelerating change, with environmental stewardship lagging behind economic and social development. Environmental gains from new technology are being overtaken by increasing population and economic growth. It is still possible, however, to slow down trends towards environmental degradation by shifting economic activity to a more sustainable pattern (Wade-Benzoni, 2007: 166) The emphasis in the study is on consciousness because progress toward solving environmental problems is likely to depend on environmentally beneficial attitudes more so than on environmental behaviors (Pickett et al., 1993). According to Folz et al. (2003), no understanding of the environment is adequate without a grasp of the religious life that permeates the human societies which inhabit the natural environment.

^{1*} Corresponding author: Karamanoğlu Mehmetbey University, 7000, Yunus Emre, Karaman, Turkey:alibayer@kmu.edu.tr

Early period environmental studies focused on personal background factors such as age, income, education, and so on that predispose individuals to environmental concern. Demographics provide only a limited explanation of environmental behavior, however (Granzin and Olson, 1991), and there are members of all demographic categories who are willing to participate in environmental activities. Diamantopoulos et al. (2003) provide a comprehensive review of the literature concerning socio-demographics in profiling green consumers and conclude that: (1) females are more environmentally concerned and participate in more pro-environment behaviors; (2) married people are more likely to participate in pro-environment behaviors; (3) there is a negative correlation between age and pro-environment attitudes; (4) larger families have more positive pro-environment attitudes; and (5) there is a positive correlation between education and all the components of the environmental domain knowledge, attitudes, and behavior (Brennan and Lo, 2002: 13).

2. DEVELOPMENT OF ENVIRONMENTALISM

Each person is born into a social and cultural environment. Humans, like other species, must also have a place to exist, and the environment provides our home—where we live, work, play, travel, and spend our lives. There are three functions of the environment. The environment provides us with the resources that are necessary for life, ranging from air and water to food to materials needed for shelter, transportation, and the vast range of economic goods we produce. Secondly, in the process of consuming resources humans, like all species, produce “waste” products; indeed, humans produce a far greater quantity and variety of waste products than do other species. Finally, the environment is to provide a “living space” or habitat for human populations. Humans, like other species, must also have a place to exist, and the environment provides our home—where we live, work, play, travel, and spend our lives (Dunlap, 2000: 800).

Environmentalism, political and ethical movement that seeks to improve and protect the quality of the natural environment through changes to environmentally harmful human activities; through the adoption of forms of political, economic, and social organization that are thought to be necessary for, or at least conducive to, the benign treatment of the environment by humans; and through a reassessment of humanity’s relationship with nature (Elliott, 2017). Environmentalism works to correct the damage as well as prevent future destruction. Environmentalism began as a movement in the 1960s and 1970s. However, humanity’s relationship and dependence on the earth for survival has existed since the beginning of time. Beginning in the nineteenth century, the Industrial Revolution caused many changes; Western people realized their behavior had a negative impact on the environment. Although nature was the focus of much nineteenth and twentieth century philosophy, contemporary environmental ethics only emerged as an academic discipline in the 1970s. The questioning and rethinking of the relationship of human beings with the natural environment over the last thirty years reflected an already widespread perception in the 1960s that the late twentieth century faced a human population explosion as well as a serious environmental crisis. Lynn White (1967) argued that the main root of Judeo-Christian thinking had encouraged the overexploitation of nature by maintaining the superiority of humans over all other forms of life on earth, and by depicting all of nature as created for the use of humans. White’s thesis was widely discussed in theology, history, and has been subject to some sociological testing as well as being regularly discussed by philosophers. Central to the rationale for his thesis were the works of the Church Fathers and The Bible itself, supporting the anthropocentric perspective that humans are the only things that matter on Earth. Consequently, they may utilize and consume everything else to their advantage without any injustice. For example, *Genesis* 1: 27–8 states: “God created man in his own image, in the image of God created he him; male and female created he them. Likewise, Thomas Aquinas argued that non-human animals are “ordered to man’s use” (Brennan and Lo, 2002: 2).

The confluence of ethical, political and legal debates about the environment, the emergence of philosophies to underpin animal rights activism and the puzzles over whether an environmental ethic would be something new rather than a modification or extension of existing ethical theories were reflected in wider social and political movements. The rise of environmental or “green” parties in Europe in the 1980s was accompanied by almost immediate schisms between groups known as “realists” versus “fundamentalists” The “realists” stood for reform environmentalism, working with business and government to soften the impact of pollution and resource depletion especially on fragile ecosystems or endangered species. The “fundies” argued for radical change, the setting of stringent new priorities, and even the overthrow of capitalism and liberal individualism, which were taken as the major ideological causes of anthropogenic environmental devastation. It is not clear, however, that collectivist or communist countries do any better in terms of their environmental record (Brennan and Lo, 2002: 2).

3. CHANGING THE POINT OF VIEWS: ANTHROPOCENTRISM, BIOCENTRISM, ECO-CENTRISM

Anthropocentrism, philosophical viewpoint arguing that human beings are the central or most significant entities in the world. This is a basic belief embedded in many Western religions and philosophies. Anthropocentrism regards humans as separate from and superior to nature and holds that human life has intrinsic value while other entities (including animals, plants, mineral resources, and so on) are resources that may justifiably be exploited for the benefit of humankind. White (1967) believed religion was influential in determining how people view themselves in relation to their environment. In *The Historical Roots of Our Ecological Crisis*, argues that because the Bible provides guidance for people about how to view the environment, the Bible presents an anthropocentric view of Christianity, which was also a dominant environmental belief in Western society in

the 1960s. White claims that Christianity is “the most anthropocentric religion the world has seen” and this anthropocentric view is the cause of the environmental crisis (White, 1967: 1025).

Aristotle argues that “nature has made all things specifically for the sake of man” and that the value of non-human things in nature is merely instrumental. Generally, anthropocentric positions find it problematic to articulate what is wrong with the cruel treatment of non-human animals, except to the extent that such treatment may lead to bad consequences for human beings. Immanuel Kant (“Duties to Animals and Spirits”, in *Lectures on Ethics*), for instance, suggests that cruelty towards a dog might encourage a person to develop a character which would be desensitized to cruelty towards humans. From this standpoint, cruelty towards non-human animals would be instrumentally, rather than intrinsically, wrong. Likewise, anthropocentrism often recognizes some non-intrinsic wrongness of anthropogenic (i.e. human-caused) environmental devastation. Such destruction might damage the well-being of human beings now and in the future, since our well-being is essentially dependent on a sustainable environment (Brennan and Lo, 2002: 3).

Biocentrism emphasizes the natural integrity of ecosystems at the expense of human use. In contrast with anthropocentric orientation, which places emphasis on human benefits, bio-centric orientation means life-centered and, thus, stresses the value of both humans and nonhuman species. An American biochemist, Lawrence Henderson, coined the term biocentrism in 1913 to delineate that the universe itself was the originator of life. Deep ecologists later adopted this term to refer to the idea that all lives are equally important due to their intrinsic values, regardless of their usefulness to humans (Yu-Jen, 2002: 43).

The philosophical assertion that all things have inherent value is known as ecocentrism. Eco-centrism that emphasizes wildness value also puts a brake on alleged human improvements of nature through anthropogenic production of the properties in virtue of which we value nature. A stability and integrity based eco-centrism would have to judge human activity that enhanced ecosystem stability or integrity as value increasing. A highly humanized ecosystem could be more stable, integrated, and diverse than a natural ecosystem that it replaced. Only an eco-centrism that puts its central focus on wildness value can prevent the unpalatable conclusion that such human manipulation of nature would, if successful, increase intrinsic value (Hettinger and Throop, 1999: 15). Ecocentric philosophies claim that the value or worth of a rock or a tree or water is not judged simply by the ways that humans can use it. Instead, it is valuable because it plays a role in the greater environment. Ecocentrism is directly opposed to anthropocentrism, which claims that humans have more inherent value than other things (King, 1995: 458).

Although both anthropocentric and bio-centric individuals express environmental concerns and have an interest in protecting nature, they have different motives. Anthropocentric individuals care for the environment because they believe that everything in nature can be used to benefit humans. For example, they protect the rainforests because the destruction of rainforests may diminish the possibility of developing new medicines that could save human lives. Conversely, bio-centric individuals protect rainforests because they believe that everything in rainforests has value in itself, regardless of its purpose for human wellbeing. In other words, nature has a spiritual dimension and intrinsic value, both of which are reflected by their experience in nature (Yu-Jen, 2002: 1)

Other environmental ethicists have suggested that it is possible to value the environment without discarding anthropocentrism. Sometimes called prudential or enlightened anthropocentrism, this view holds that humans do have ethical obligations toward the environment, but they can be justified in terms of obligations toward other humans. For instance, environmental pollution can be seen as immoral because it negatively affects the lives of other people, such as those sickened by the air pollution from a factory. Similarly, the wasteful use of natural resources is viewed as immoral because it deprives future generations of those resources. Consequently, this is the view that all the moral duties we have towards the environment are derived from our direct duties to its human inhabitants. The practical purpose of environmental ethics, they maintain, is to provide moral grounds for social policies aimed at protecting the earth’s environment and remedying environmental degradation (Brennan and Lo, 2002: 7).

4. FEMINISM AND THE ENVIRONMENT

By the mid-1970s, feminist writers had raised the issue of whether patriarchal modes of thinking encouraged not only widespread inferiorizing and colonizing of women, but also of people of colour, animals and nature. Sheila Collins (1974), for instance, argued that male-dominated culture or patriarchy is supported by four interlocking pillars: sexism, racism, class exploitation, and ecological destruction. From this point of view, human exploitation of nature may be seen as a manifestation and extension of the oppression of women, in that it is the result of associating nature with the female, which had been already inferiorized and oppressed by the male-dominating culture (Brennan and Lo, 2002: 7). Feminism represents a radical challenge for environmental thinking, politics, and traditional social ethical perspectives. It promises to link environmental questions with wider social problems concerning various kinds of discrimination and exploitation, and fundamental investigations of human psychology. However, whether there are conceptual, causal or merely contingent connections among the different forms of oppression and liberation remains a contested issue. The term “ecofeminism” (first coined by Françoise d’Eaubonne in 1974) or “ecological feminism” was for a time generally applied to any view that combines environmental advocacy with feminist

analysis. However, because of the varieties of, and disagreements among, feminist theories, the label may be too wide to be informative and has generally fallen from use (King, 1995: 462).

5. CRITICAL SCHOOL AND NEO-MARXIST VIEW

While classical Marxists regard nature as a resource to be transformed by human labour and utilized for human purposes, Horkheimer and Adorno saw Marx himself as representative of the problem of "human alienation". At the root of this alienation, they argue, is a narrow positivist conception of rationality-which sees rationality as an instrument for pursuing progress, power and technological control, and takes observation, measurement and the application of purely quantitative methods to be capable of solving all problems. According to the critical theorists, the oppression of "outer nature" (i.e., the natural environment) through science and technology is bought at a very high price: the project of domination requires the suppression of our own "inner nature" (i.e., human nature)-e.g., human creativity, autonomy, and the manifold needs, vulnerabilities and longings at the centre of human life. To remedy such an alienation, the project of Horkheimer and Adorno is to replace the narrow positivistic and instrumentalist model of rationality with a more humanistic one, in which the values of the aesthetic, moral, sensuous and expressive aspects of human life play a central part. Thus, their aim is not to give up our rational faculties or powers of analysis and logic. Rather, the ambition is to arrive at a dialectical synthesis between Romanticism and Enlightenment, to return to anti-deterministic values of freedom, spontaneity and creativity (Brennan and Lo, 2002: 16)

6. RELIGION AND ENVIRONMENT

In general, religion teaches the concept of a God or gods that created the Cosmos and everything in it. They created man in their image and likeness. Man is upon the earth to learn about himself, attain to a certain high level of spiritual development and return home from whence he came – to God and the heaven life, there to stay for all eternity. Most religions in the world emphasizes on human interactions with the environment in various perspectives. Jewish, for instance, celebrate a special new year for plants and crops known as Tu B'Shevat. Similarly, Christians are always exposed to fish, birds and wildlife (as per The Genesis) while Christmas and Easter songs are always related to animals and plants. Sikhs, on the other hand, believe that their God lives on the tree, dreams of animals and wakes amongst humans. Meanwhile, Buddhists celebrate several celebrations by praying for a harmonious environment (A. R. Agwan, 1997). This in a way reflects the close interaction between humans and the environment as the content of most religions in the world. In Islam itself, human interaction with the environment is mentioned multiple times in the Holy Quran, supported by Hadith and further explained in detail by companions and scholars. The verse in the Holy Quran regarding the assignment of humans as the Caliph started with the general interaction between humans and the earth, and supported by many other verses.

In affluent developed nations, the rise in environmental concern at both the government and business levels occurred because environmental risks were perceived by the public and this led to popular demand for corrective and preventive action. Religious environmentalism is a post-materialist environmental philosophy that has emerged from the West and has its roots in the eighteenth century European "Romantic Movement. Religious environmentalists argue that religious traditions teach that the Earth is sacred and that this has traditionally served to exert control over how people interact with the natural world.

7. ISLAM AND ENVIRONMENT

Islamic beliefs, traditions and values provide an effective and comprehensive solution to the current environmental challenges faced by the human race. Islam has a rich tradition of highlighting the importance of environmental protection and conservation of natural resources. According to Islamic law, the basic elements of nature-land, water, fire, forest, and light-belong to all living things, not just human beings. Environment protection is an important aspect of Islam. The main schools of Islamic theology did not pay much attention to a "theology of nature" which would be of significance in the present-day environmental crisis. By contrast, numerous works of Islamic philosophy provide not only an Islamic philosophy of nature, but what in the West would be called a "theology of nature." This is also true of Sufism, which contains the most profound expressions of an Islamic "metaphysics and theology of nature." Certain Sufi texts bring out the most inward meaning of the Qur'anic doctrine concerning the cosmos and human beings' relation to the world of nature. Scientific tradition has much to offer in the process of formulating a contemporary language expressing Islamic views of the relation of human beings and the natural environment. This contemporary Islamic view, in conjunction with various forms of technology developed in Islamic civilization, could help find a way out of the impasse created by the current environmental crisis (Nasr, 2003: 94).

Being stewards of the Earth, it is the responsibility of Muslims to care for the environment in a proactive manner. There is a definite purpose behind the creation of different species, be it plants or animals. Muslims are encouraged to reflect on the relationship between living organisms and their environment and to maintain the ecological balance created by Allah. Protection of the environment is essential to Islamic beliefs and mankind has the responsibility to ensure safe custody of the environment. Human being is one of the entities created by Allah in the whole ecological system. Hence, its existence is always correlated to other environmental entities. This indicates that the perfection of Islam hinges on application of the whole interaction between humans and the environment; physics and metaphysics (Al-Banna, 2016)

Philosophers of Islam, such as Farabi, Ghazālī, Shāṭibī, and Shāh Walīullāh explain that the aim of Shariah is to promote human welfare. This is evident in the Qur'ān, and teachings of the Prophet (s). The scholars explain that the welfare of humans is based on the fulfillment of necessities, needs, and comforts.

Necessities are matters that worldly and religious life depends upon. Their omission leads to unbearable hardship in this life, or punishment in the next. There are five necessities: preservation of religion, life, intellect, lineage, and wealth. These ensure individual and social welfare in this life and the hereafter.

From the (earth) did We create you, and into it shall We return you, and from it shall We bring you out once again. (Taha: 55)

According to the details by previous Muslim scholars, human interaction with the environment can be concluded into a more specific interaction; such as interaction between humans and the God (as worshippers), interaction amongst humans (as human beings in a society) as well as interaction between humans and other entities (as caliphs). This interaction concept is ongoing in every mukallaf and it is carried as amanah. It is not merely an ethic or an alternative task, but an obliged duty of human beings

Plants or flora is substantial entities that always interact and have a big contribution in human's life. In the Holy Quran, flora is given a special attention and there is even a surah named after a plant, At Tin (the fig tree). Furthermore, there are numerous verses that mention about human interaction with flora; e.g An Nahl: 12, Al An'am: 141, Al Anbiya'; 78 and etc. Islam also stresses on several principles related to human interaction with flora; for instance: • Protecting and conserving flora and derivatives in its natural forms; flowers in their colourful hues and leaves in their green tones. This world is beautiful and green and Allah has made you His representatives on it and He sees (all things). (Narrated by Muslim) • Avoid cutting, shearing or causing the plants to die without a reasonable excuse • Make use of the plants appropriately (Al-Banna, 2016).

8. RESOURCE CONSERVATION AND WASTE

The Islamic perspective on environment protection reflects a positive image about Islam and how it embraces every single matter the humans face on earth. The Islamic attitude towards environment and natural resource conservation is not only based on prohibition of over-exploitation but also on sustainable development. The Holy Quran says:

"It is He who has appointed you viceroys in the earth ... that He may try you in what He has given you." (Surah 6:165)

"O children of Adam! ... eat and drink: but waste not by excess, for Allah loves not the wasters." (Surah 7:31)

Islam has always provided the keys to a harmonious life in which humans refuse to take more from nature than they need for their sustenance and enjoyment. Islam has repeatedly warned about the imbalances and inequalities that would arise if one were not to follow its recommendations. According to the Holy Qur'an, environmental conservation is a religious duty as well as social obligation, and not an optional matter. The exploitation of a particular natural resource is directly related to accountability and maintenance of the resource.

Today, with the increasing awareness of the dangers facing our planet and the great interest in green ideas, a reflection on the guidance of the religion in this area proves helpful and relevant.

The modern environmental theory by western scientists did not come up with a holistic solution. In short, the philosophy of Islamic environmental ethics theory as discussed by scholars five rationales (rukun) namely tauhid, khilafah, amanah, wasatiah and tawazun. These five rationales can be further explained into simpler guidelines and should be the pre-requisites to construct the codes of Islamic environmental ethics. Amongst the criteria that should be the fundamentals and emphasized in the Islamic environmental ethics are:

Understanding of the environment, hierarchy, roles and of the attitude of the consumers must be based on the main reference. The personal interests of humans, animals or other ecosystem should not be in the agenda at all. Islamic environmental conservation should frame the importance of wahyu as the primer guidance or in simpler terms, as a God-oriented interaction. The tauhidic concept based on the God as the Creator like this actually ensures total environmental conservation in a more balanced way.

Humans are assigned by Allah as the caliph, with the responsibility (amanah) to manage and administer the environment. The environment acts as the realm for humans to conduct the assigned tasks before being evaluated by Allah. However, humans are not left alone to bear the important duties, instead they are guided by syariat via wahyu. A caliph with strong belief on tauhid will not find difficulties in performing the syariah tasks. Humans who hold strongly and realize their obligation towards Allah when accepting the trust and stewardship (amanah khilafah) will never commit harms on any environmental entities under their stewardship (khilafah). This is mentioned in the Holy Quran:

We did indeed offer the Trust to the Heavens and the Earth and the Mountains; but they refused to undertake it, being afraid thereof, but man undertook it, He was indeed unjust and foolish (Al Ahzab: 72)

Therefore, it is concluded that whatever theories and ideologies applied in the context of environmental science, as long as it is based on the concept of stewardship (khilafah) that carries the responsibilities (amanah) assigned by Allah in implementing the syariah application, it is undoubtedly leading to sustainable environmental management and conservation.

The environment is created with functions to contribute and serve the human beings. This is understandable by many evidences, as one of them explained: And they (the animals) carry your heavy loads to lands that you could not (otherwise) reach except with souls distressed: for your Lord is indeed Most Kind, Most Merciful. (An Nahl: 7)

In today's modern world, commercial values are unreasonably worshipped to the extent that entities in the environmental ecosystem are also valued based on their commercial status. In Islam, social and general welfare should be given a priority more than personal interests or minority entities. Furthermore, in fighting for the rights specified for environmental entities, especially humans as the administrator or manager, the values of responsibility should come before the rights. In the cycle of environmental entity, the interrelated interaction will be harmonious and balanced when each entity performs their roles and responsibilities respectively, hence completing each other. Each entity that cares for and gives priority on other entities will create a mutual respect thus leading to a better interaction amongst them (Fazlun, 2010: 13).

The Islamic theory and philosophy never accentuate on opposites because of the moderation in constructing them by the same main references in harmony of the environmental philosophy. The theory or philosophy in Islam does not incline to opposition due to its moderation in constructing the philosophy and theory that suit the same main reference, contemplating a harmonious environmental philosophy that compiles all views and applications. Theories like anthropocentrism, egocentrism, animal rights, ethnocentrism or any otherwise created by Western extremists are philosophies accepted by Islam moderately, without bias on any and not totally against any.

The environment is readily created balanced and of the best measure specified by Allah. There are numerous verses in the Holy Quran that discuss and explain the balance and measures that Allah has fixed in the creation of the universe. The tawazun concept should steer the actions and decisions in the protection and interaction with the environment. The pairing concept, for instance, should be assimilated so as to hinder the wrongdoings on the environmental entities. The harmonious balance in the ecosystem cycle has been intelligently and perfectly created by Allah. Anything lacking or excessive in the ecosystem cycle may lead to continuous harm and spread to other entities in the cycle.

(Allah) Most Gracious! It is He Who has taught the Qur'an. He has created man: He has taught him speech (and intelligence). The sun and the moon follow courses (exactly) computed; And the stars and the trees - both (alike) bow in worship. And the Firmament has He raised high, and He has set up the Balance (of Justice), (Ar Rahman: 1-7)

The same applies to the balance in other contexts such as in evaluating the hierarchy of environmental entities based on material and non-material values. The values of each entity should be made in a reality context without prejudice on any. Another factor to be considered is the balance of concern on environmental conservation; physically and spiritually and the balance to acquire short term (duniawi) and long term (ukhrawi) returns.

Understanding of the balance in the environment created by Allah should be apprehended and utilized as the core in the application of environmental theory, especially in today's world that sees human greed for their insatiable personal interests that blindfolds them from the real perspective. This consequently leads to opposition, negative competition and fatality in some circumstances. The balanced Islamic concept is in agreement with the moderation concept, hence it should be enhanced based on the fundamentals of tauhid as well as the awareness of trust and stewardship (amanah khilafah)

With the theory application based on the five abovementioned rationales (rukun), environmental philosophies should be inferred more efficiently and effectively in any flexible ways possible. Islam has fixed various guidelines in rules/orders, prohibitions, suggestions and even fundamental principles to be deliberated with research and innovation based on human intellectual for environmental development. As the only perfect (syumul) religion in all aspects, it is undeniable that the evidences in the Holy Quran and Al Hadith are the principal reference that has summarized diverse principles for us to obey. Even the previous Muslim scholars have substantially contributed to the growth, research and the arrangement of guidelines regarding human interactions with the environment as well as in the aspect of environmental management

9. CONCLUSION

Environmentalism has focused the importance of a clean and healthy environment for human existence. Beyond our physical dependency on the environment are the intangible and emotional connections people feel with nature and these connections contribute to overall happiness in life. Environmentalism seeks to protect and preserve the earth for present and future generations; the intangible and emotional connections with nature are at risk. Environmental awareness and protection of natural resource is an integral part of Islamic beliefs. A major objective of Islamic teachings and Prophet traditions is to build and maintain a healthy and clean environment which is devoid of any source of pollution and misuse.

Islam views the attitude of interaction in the environmental ecosystem as a big issue when the trust and stewardship (amanah khilafah) are granted to humans as an important appointment to manage and administer the environment.

As Bryan Norton puts it, the world faces a global challenge to see whether different human groups, with widely varying perspectives, can perhaps “accept responsibility to maintain a non-declining set of opportunities based on possible uses of the environment”.

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Biography: Ass.Prof. Ali Bayer is head of Sociology of Religion at the Faculty of Divinity, University of Karamanoglu Mehmetbey, Karaman/Turkey. His research interest are family, domestic violence, secularization, modernization, religious literacy. He has contributed articles to some journals. He has participated to some national and international conferences.

Biography: Prof.Dr. M. Ali Kirman is head of Sociology of Religion at the Faculty of Divinity, University of Cukurova, Adana/Turkey. His research interests are centered on the modernization, the secularization, the new religious groups in the West and modern Turkey, and related subjects, i.e. religious conversion and family. He is author of five books in Turkish. He has contributed articles to some journals. He has participated to some national and international conferences.

Determination of Noise Levels At Central Balikesir Hospitals

Atilla MUTLU^{1*}

Abstract

In this study, our goal was to determine of noise sources and emission levels from very sensitive environments, such as hospitals, at downtown of Balikesir. In the city centrum, it was also aimed to create noise pollution maps as the first time for those full-scale hospitals in Balikesir by carrying out of this scientific study. According to the study results, it was determined that the noise level in Balikesir State Hospital, where is located to closer to the city center, was higher than the noise level in Ataturk State Hospital. In general, the predicted noise values at Balikesir State Hospital were as high as about 9% (or approximately 7dBa) than the actual measured values. The modeling process was not performed at ASH, because the noise levels in the Ataturk hospital did not exceed the legal limits.

Keywords: Balikesir, CadnaA, Hospitals, Noise

1. INTRODUCTION

It is known fact that noise affects human health. Full-scaled hospitals where locate in the city downtown are assessed within sensitive areas by the environmental noise regulations [1]. Therefore, hospitals are one of the most sensitive spots in terms of noise. During the health service hours, traffic-related noise arises on the on the main streets. Patients and medical staff are adversely affected psychologically, biologically and physiologically due to existing noise levels. This situation affects the quality of the health care services [2], [3], [4]. For this reason, it is necessary to identify sources of noise emissions in which hospitals are exposed and it is also required to prepare noise distribution maps in that sensitive areas [5], [6], [7].

In a previous study, correlations between air pollution and traffic related noise levels were examined. As a result of the study, it was determined that there was a positive interaction between air pollution and noise levels caused by traffic [8]. In another study, the noise level of the traffic was defined as the degree of impact. The net noise level from the source and the number of repetitions that occurred during the traffic activities were consider the main parameters of the noise impact [9]. The another study reports that tires, which are the most important component of the running mechanism of the vehicles, should be produced in relevant qualities in order to reduce potential asphalt noise [10].

In this study, which was made for the first time in Balikesir downtown, it was aimed to determine the noise levels that the hospitals were exposed during the service hours. It was also intended to prepare noise distribution maps for those full-scaled hospitals.

2. MATERIALS AND METHODS

a. Study Area

In this study, noise level measurements were made at Balikesir State Hospital (BSH) and Ataturk State Hospital (ASH) in Balikesir's downtown. Balikesir State Hospital has been serving since 1954 and has a capacity of 200 beds [11]. Ataturk State Hospital, has been serving since 1965 and has a capacity of 521 bed [12]. In the scope of the study, the first stage measurements were made at the main entrance where human and traffic activities are highly intensive (see Figure 1).

^{1*} Corresponding author: Balikesir University, Department of Environmental Engineering, 10145, Cagis/Balikesir, Turkey.
amutlu@balikesir.edu.tr



Figure 17. Balikesir state hospital (a) and Ataturk state hospital (b)

b. Study Plan and Data Collection

Measuring points for noise levels were selected in order to represent daily activities, Rush hours were determined as morning hours (work starts, beginning of school and patient admission) and evening hours (work off, school day). Measurements were made, on Monday and Wednesdays at the BSH with 3 days a week; only on Fridays at ASH, between 07:30 AM - 6:00 PM.

3. RESULTS AND DISCUSSIONS

c. Results of Noise Measurement at Hospitals

The measurement results of the study and the general descriptive statistical parameters of the obtained data are presented in Table.1 and Table.2.

Table 7. Environmental noise levels of Balikesir state hospital

Dates	Minimum	Maximum	Means	Std.Dev.
8 April	54.0	79.8	65.9	4.0
10 April	53.0	81.2	63.8	4.8
15 April	52.1	78.7	62.4	4.6
17 April	49.9	85.9	62.3	4.7
22 April	53.2	82.3	63.2	4.7
24 April	49.9	84.6	63.6	4.4
29 April	42.5	78.4	57.7	5.4
1 May	43.2	78.7	58.2	5.9
6 May	42.5	78.0	58.5	5.5
8 May	53.5	83.1	62.8	4.2
13 May	48.4	88.6	62.2	5.9
15 May	49.6	80.8	61.6	5.0
20 May	50.7	79.5	62.4	4.5
22 May	48.5	83.0	62.3	4.7
27 May	50.9	79.3	61.9	4.7
29 May	51.0	83.5	65.9	5.1
3 June	53.0	82.1	63.0	4.7
5 June	42.9	78.4	59.0	5.5
10 June	48.7	83.5	62.3	4.5
12 June	49.20	80.40	61.2	5.0

As a result of the measurements that performed in BSH, a total of 21 individual measurements were conducted at the BSH's main entrance. The lowest noise level during measurements was recorded as 42.5 dBA, while the highest level was recorded as 88.6 dBA in BSH. According to statistical analysis results, the morning noise levels were higher than evening noise levels in those collected 21 data sets. The results also show that mean noise levels of 8 April and 29 May exceeded the legal limits (65 dBA).

Daily noise levels in ASH were also measured and the measurement results are presented in Table.2.

Table 2. Environmental noise levels of Ataturk state hospital

Dates	Minimum	Maximum	Means	Std.Dev.
5 April	49.5	74.1	55.9	3.0
12 April	49.5	75.3	55.9	2.9
19 April	52.6	72.4	59.3	3.4
26 April	49.9	73.3	59.4	5.4
3 May	51.2	77.0	57.6	2.9
10 May	49.0	74.8	55.4	2.9
17 May	49.7	69.3	55.4	3.4
24 May	50.5	71.4	56.2	3.9
31 May	49.1	73.8	54.8	2.6
7 June	49.9	69.0	55.3	2.8
14 June	49.9	73.4	56.9	3.7

A total of 11 individual measurements were conducted at the ASH's main entrance. The lowest noise level during measurements was recorded as 49 dBA, while the highest level was recorded as 77 dBA in ASH.

d. Modeling and Mapping of Noise Levels

Nowadays, the first step to be taken for the environmental noise problem is to determine the current noise level and create noise level maps [13]. Noise maps are considered as a way of numerically and visually expressing distributions of environmental noise from related sources [14]. In this method, the changes in the potential noise levels from physical factors in the environment are illustrated and also animated on a map. Noise mapping is done by including several preliminary information such as detailed map, road information and population density. Traffic (route) plans, vehicle numbers, vehicle speeds, vehicle types, road features as inputs are transferred to the noise map program in compute [15]. The noise levels, for a specific area, obtained from the noise maps are compared to the official limit values that are found in the legislation [16].

In the second part of the study, noise measurements were conducted at BSH (Balikesir State Hospital), where local traffic activities are more intense, to ensure the validity of the modeling results. In order to determine noise levels that the BSH may be exposed, a total of 15 measurement points are selected around the hospital (See Figure.2).



Figure 2. Measurement points at BSH (Balikesir state hospital)

A software named CadnaA (Computer Aided Noise Abatement, DataKustik, 2016) was used to visually express the change in environmental noise levels in study area [17]. In this program, the number of vehicles (normal and heavy vehicles) passing through the near streets, the coordinates of the hospital, all the transportation lines of the hospital area, the technical specifications (one way / two way, lane width) of the roads are used as input parameters. Also, details of receptors to figure out noise levels of hospital has been exposed are indicated on the map. Estimated and Modeled environmental noise distributions for BSH are presented in Figure 3.

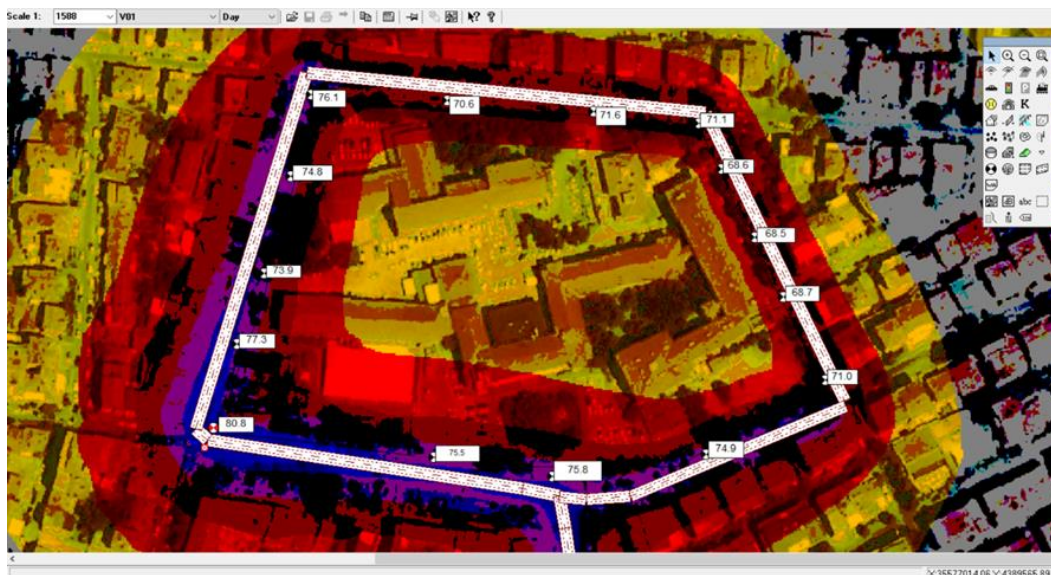


Figure 3. Environmental noise map of BSH (Balikesir state hospital)

After mapping, measurements were made at precisely specified receptor points in the model to investigate the validity of the predicted environmental noise levels. For this process, on-site measurements were held regularly on Mondays, Wednesdays and Fridays as three times a week. The overall results of the measurements are presented in Table 3.

Table 3. Environmental noise levels of Balikesir state hospital

Measurement Points	Minimum	Maximum	Means	Std.Dev.
Point1	47.0	111	<u>68.7</u>	6.4
Point2	49.9	114.9	<u>68.2</u>	6.6
Point3	48.7	98.9	<u>67.4</u>	6.7
Point4	51	84.6	<u>66.7</u>	5.2
Point5	44.3	84.3	<u>68.3</u>	5.7
Point6	49.6	105.1	<u>66.6</u>	5.8
Point7	50.9	88.4	<u>65.2</u>	5.1
Point8	48.2	89.9	<u>65.6</u>	5.2
Point9	51.2	98.2	64.8	6.4
Point10	50.3	89.9	<u>66.2</u>	5.3
Point11	49.1	102.1	<u>64.1</u>	5.7
Point12	52.2	90.6	<u>66.1</u>	5.1
Point13	51.1	94.5	<u>66.4</u>	6.2
Point14	51.8	92.4	<u>68.0</u>	5.3
Point15	48.5	101.2	<u>67.7</u>	5.7

In the last part of the study, the modeled and also the measured environmental noise levels were compared and the results are presented in Figure 4. Generally, it is determined that the modeled values were higher than the measured values by about 9% (in other words about 7dB) in BSH. The modeling process was not performed at ASH, because the noise levels in the Ataturk hospital did not exceed the legal limits.

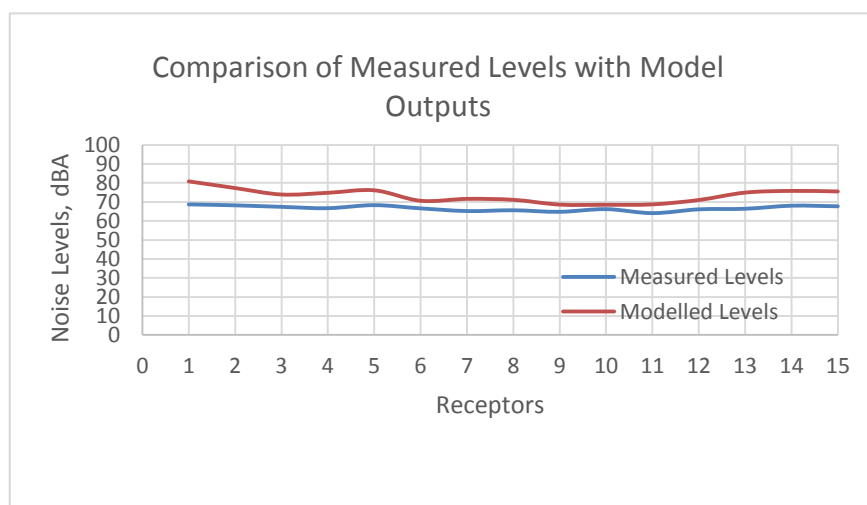


Figure 4. Measured and modeled environmental noise levels of BSH (Balikesir state hospital)

In a similar study in Greece stated that environmental noise levels were measured as 52.6 (\pm 8.2 dBA) and 59 (\pm 2.2 dBA), respectively, in two different hospitals [18]. It might be concluded that the measured noise levels at BSH (Balikesir State Hospital) were about 10% higher than those measured hospitals in Greece. This difference may be occurred that due to the fact that our hospital has more traffic density.

4.CONCLUSIONS

The following results were obtained as a result of the studies that carried out in full-scale hospitals in downtown Balikesir City;

- ✓ The equivalent noise levels in BSH (Balikesir State Hospital) where is located in Downtown Center were found to be statistically higher than ASH (Ataturk State Hospital) where is located in the West side of the Downtown,
- ✓ The equivalent noise levels of BSH were found to be higher in morning time than in other time periods for that hospital,
- ✓ It was determined that the equivalent noise levels in the Ataturk hospital did not exceed the legal limits,
- ✓ When the measurement results are taken into consideration, it was determined that the level of noise in BSH, which is located in the downtown, was higher than the noise level in ASH,
- ✓ As a result of the environmental noise levels obtained from the noise maps, it was understood that the values modeled in BSH, in general, were as high as about 9% (in other words about 7dBA) than the actual measured noise levels.

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BIOGRAPHY

Atilla Mutlu is an Assistant Professor of Environmental Engineering Department at Balikesir University. He received Ph.D. in Biogological and Agricultural Engineering from the Texas A&M University, Texas, USA. He has been active in the area of pollution from agricultural and industrial operations. He has also intended to study in noise pollution from traffic activities in local scales. His international experience includes education and academic areas in United States, South Korea, Turkey. His current research involves study of air pollution monitoring and modeling from industrial sites, greenhouse gases emissions from agricultral sites and also mapping environmental noise in local areas.

Analysis of Air Pollutans Level In Balikesir Using Advanced Level Air Dispersion (AERMOD) And Long-Term Meteorological Data Processor (AERMET) Models

Atilla MUTLU^{1*}

Abstract

It is a known fact that air pollutants have adverse effect to human health and to environment due to rapid development in industrial sites and increasing population density more likely in downtown of cities. In this unsuitable conditions, any protection approaches for controlling air pollutants within their standard limits have more importance than ever before. Nowadays, the major air pollutants are being emitted in downtown sites of cities. In particular, high level air pollution episodes occur in Balikesir during both cold and warm meteorological conditions that may cause severe asthma and allergic symptoms.

The main effect of industrial, commercial-residential sites and mobile sources on the related air pollutant levels will also be evaluated by using both AERMOD (AMS/EPA Regulatory Model) dispersion model and long-term meteorological data processor (AERMET). The output of AERMOD and AERMET models will be expected to understand how to disperse long term pollution levels in the city.

Keywords: AERMOD, AERMET, Air Pollution, Balikesir, PM

1.INTRODUCTION

The World Health Organization (WHO) published a risk assessment report in 2006 and the report emphasizes "fresh air is the most basic necessity for human health and well-being" in the introduction citation. The report has once again demonstrated the importance of clean air for living beings that form human and ecosystem [1]. Globally, the main anthropogenic air polluters are concentrated in urban areas. For instance, traffic, industry and residential heating systems are considered as the main sources of urban air pollution. Meteorology, topographic structure and urban settlements are important factors affecting the dispersion, storage and chemical conversion processes of air pollutants. Clinical studies on humans have been reported to increase respiratory tract diseases of pollutants such as ozone (O₃), sulphur dioxide (SO₂), particulate matter (PM), nitrogen oxides (NO_x), and biogenic antigens such as pollen. [2], [3], [4], [5], [6]. Similar studies have shown that there is a relationship between air pollution level and increased symptoms of respiratory tract, and increased incidence of death [7], [8]. It has been found in other studies that there is a relationship between air pollution levels and adults/children as of increased respiratory tract complaints or hospital and in some cases emergency admissions due to exacerbation of asthma [9], [10], [11].

Particulate matter, especially PM₁₀, emission sources are considered as industrial (especially cement plants), heating, coal and mine, excavation areas, particles from vehicle exhausts, dust from tires and roads [12], [13].

American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD) is an atmospheric dispersion modeling software for air pollutants. AERMOD contains three separate components: AERMOD (AERMIC Dispersion Model), AERMAP (AERMOD Terrain Preprocessor), and AERMET (AERMOD Meteorological Preprocessor) [14]. AERMOD was first presented by USEPA as a new dispersion model that also included ISCST3 (Industrial Source Complex Short-Term model version 3) model in April-2000. The new model has the basic differences and innovations of the old model ISCST3. The differences are as follows; the way that the polluted gas cloud follows is characterized more realistically under different factors, more detailed and comprehensive meteorological data entry, new meteorological data format, more

^{1*} Corresponding author: Balikesir University, Department of Environmental Engineering, 10145, Cagis/Balikesir, Turkey.
amutlu@Balikesir.edu.tr

detailed data entry on surfaces with contaminant distribution, more detailed PBL (Planetary Boundary Level) theory, advanced MLH (Mixing Layer Height) prediction, elaboration of topographic surfaces (detailed elevation parameters and surface characterization features etc.) [15], [16], [17]. Air quality dispersion programs such as AERMOD are employed to predict ground level concentrations of the air pollutants that exists in the atmosphere under different scenarios such as meteorological conditions, topographic properties and time zones [18], [19], [20], [21]. Air quality dispersion models are an alternative method when air pollutants from industry and also livestock are not technically feasible to measure on site or near source [22], [23]. AERMOD is used to determine the dispersion and effects of short and high-level (chronic) contaminant concentrations, and has also shown high performance in long-term (monthly or yearly) epidemiological studies [24].

In this study, the possible dispersion of PM₁₀ emissions from an industrial operation in downtown Balikesir were investigated taking into account the existing meteorological and surface topography characteristics. The aim of this study is to show possible the temporal and spatial variability of the PM₁₀ emissions affecting the air quality in the city center. The use of model such as AERMOD is beneficial in determination of risky areas of the city that may occur due to atmospheric pollution, contributing to the public awareness, it is aimed to present proposals in decision making process to the local authority.

2.MATERIALS AND METHODS

2.1.Study Area

In the study, one of the industrial site that was located nearby the downtown was selected. Industrial site, which are close to downtown, operates in the Organized Industrial Zone, which is located in the south-western region of the city. Location of the industrial site is shown in Figure1. The source is approximately 5 km to the downtown city.

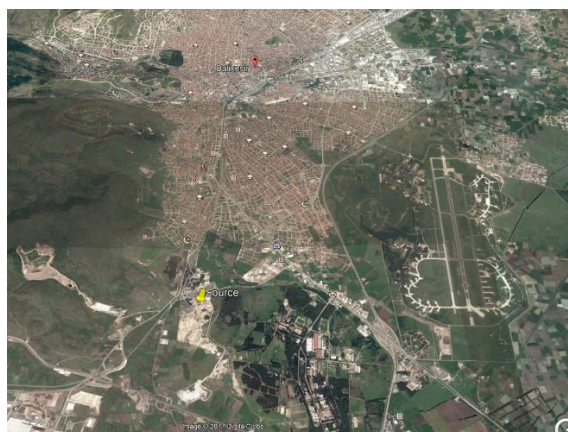


Figure 18. PM₁₀ sources in Balikesir

2.2.Study Planand Data Collection/Analysis

In this modeling study, the PM₁₀ emission data and the physical properties of the stack were taken from the Provincial Environmental Agency within the scope of the "Balikesir Clean Air Action Plan" carried out by Balikesir Governorship. Within the scope of the Clean Air Action Plan, other meteorological data such as hourly wind speed/ direction/ frequency, temperature, precipitation, pressure and cloudiness required for air quality modeling were obtained from Provincial Agency of Meteorology. In the present study, it is important to obtain the representative meteorological and terrain data for the modeling study. The definition of "representative year" must be made for the modeling process. The obtained wind data set for the last five years are used for this purposes. When the wind data of the last five years are examined, the "representative year" was determined as the year of 2016 in terms of wind direction and frequency. For this reason, meteorological values such as hourly wind data, temperature, pressure, precipitation, cloudiness and mixture height of the year of 2016 were used in our study. The latest five-year wind data and the prevailing wind direction are presented in Figure 2.

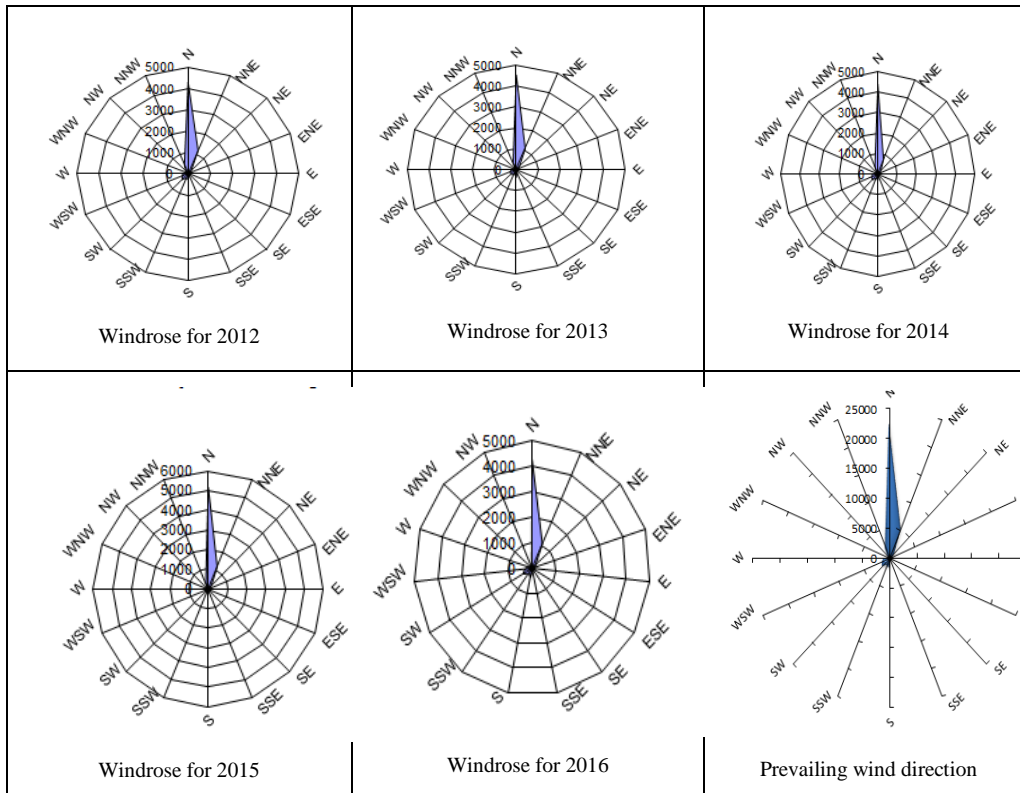


Figure 2. Wind data and prevailing wind direction of the last five years in the study area

All meteorological data of the representative year (2016) were comprehensively arranged and prepared as two separate databases, Surface and Upper meteorological data for the modeling process. Two separate meteorological data bases were then transferred to the AERMET meteorological data processor. The AERMET processor transforms the data into *.sfc and *.pfl files and sends them to the AERMOD processor. The modeling steps are illustrated in Figure 3.

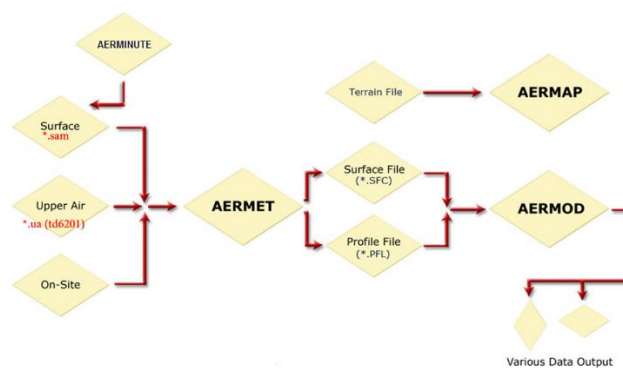


Figure 3. The AERMOD modeling process steps

The AERMOD generates the air quality dispersion maps using the characteristic surface data of the study area and PM₁₀ emissions of the source.

3.RESULTS AND DISCUSSION

3.1.Modeling Results

As a result of the analysis, air quality dispersion maps were created for the maximum average values of three different time periods as in 1 hour, 24 hours and annual. As a result of hourly modeling, it shows the highest mean of PM_{10} downwind concentration value within the whole year.

The daily (24-hour) PM_{10} concentration data are averaged over a day and the highest mean concentration is used for the downwind dispersion value. The maximum daily mean of PM_{10} modeling results from the source are presented in Figure 4.

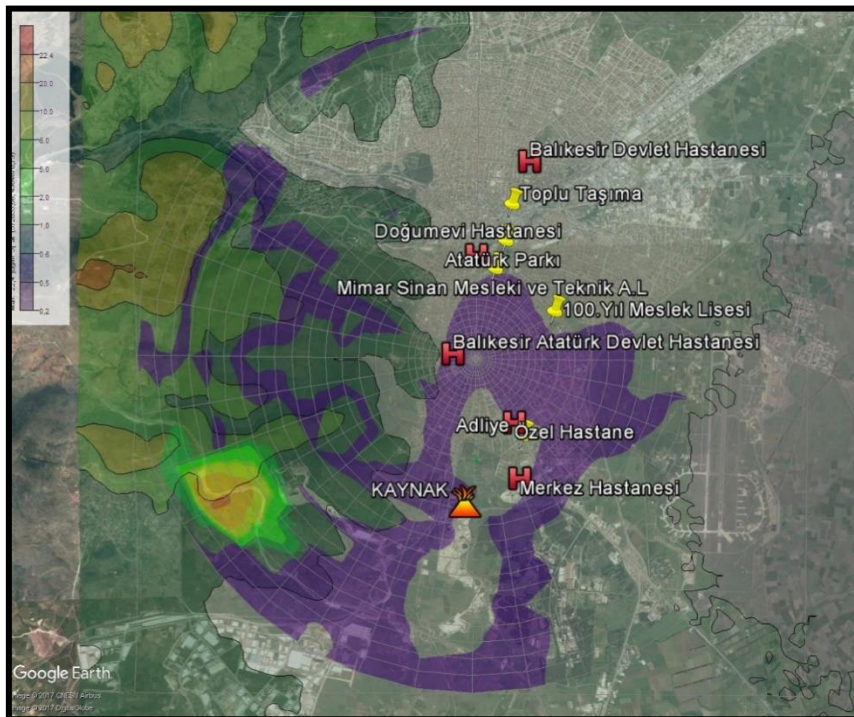


Figure 4. Maximum hourly means of PM_{10} dispersion from the source

The hourly PM_{10} concentrations emitted from the source changes with time as the wind direction changes. According to the modeling result, the maximum hourly mean downwind PM_{10} concentration was estimated to be $66.13 \mu\text{g.m}^{-3}$ at 6 pm on February 29, 2016. It has been determined that the estimated maximum hourly average PM_{10} emission is effective in the southwestern part of the downtown and did not exceed the limit values of the regulation and it was also understood that it did not constitute any risk for the city.

The mean of the daily (24-hour) PM_{10} concentrations are estimated and the highest daily mean concentration is used for the downwind dispersion value. The maximum daily mean PM_{10} modeling results from the source are presented in Figure 5.

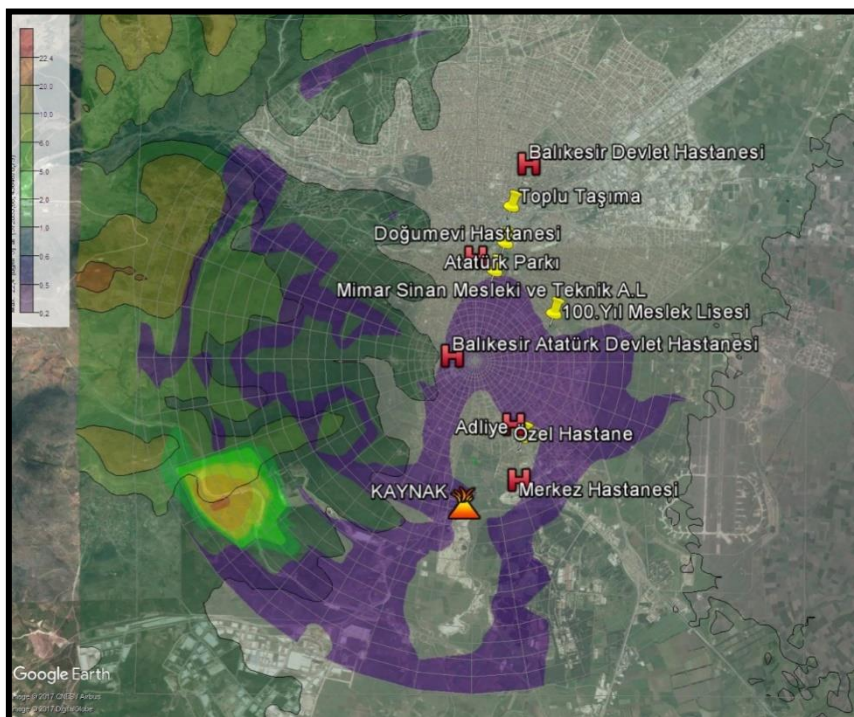


Figure 5. Maximum daily means of PM_{10} dispersion from the source

The daily PM_{10} concentration was influential in the southwest part of the downtown. The estimated PM_{10} downwind concentration from the source was estimated as $22.4 \mu\text{g.m}^{-3}$ at the midnight on February 29, 2016. Considering the modeling result, it was understood that the estimated maximum daily means did not exceed the Short Term Limits (STL-24 hour) specified in the National Air Quality Assessment and Management Regulation ($70 \mu\text{g.m}^{-3}$ for 2017).

The maximum annual mean of PM_{10} concentration was estimated to be approximately $1 \mu\text{g.m}^{-3}$ as a result of modeling. Thus, the estimated maximum annual means did not exceed the Long Term Limits (LTL-Annual) specified in the National Air Quality Assessment and Management Regulation ($48 \mu\text{g.m}^{-3}$ for 2017).

The source used in the modeling is approximately located southwest of the downtown. Considering the source effect, it was understood that the downtown was in the background of the source, and therefore, the PM_{10} emissions emitted from the source were propagated in the south-south west direction, which was opposite direction to the downtown based on the prevailing wind direction.

The effect of the modeled PM_{10} emissions that released from the source were also examined comparatively with measured PM_{10} emissions from the Air Quality Monitoring Station (AQMS) of the Ministry of Environment, located in the downtown of Balıkesir.

The annual mean of measured PM_{10} from the AQMS was determined as $42 \mu\text{g.m}^{-3}$ while the modeled annual mean of PM_{10} concentration at the same location was estimated to be about $1 \mu\text{g.m}^{-3}$. The reason for the difference of the PM_{10} concentration measured by the AQMS at the downtown was thought to be caused by residential heating and transportation-related activities rather than industrial releases.

4.CONCLUSIONS

The following results were achieved in this study, which was made as the first step to contribute to the "Clean Air Action Plan" in Balıkesir City;

Considering the long-term average, the prevailing wind direction for Balıkesir province was determined as north-direction (N) winds.

The source used in the modeling is approximately located southwest of the downtown. Considering the source effect, it was understood that the downtown was in the background of the source, and therefore, the PM_{10} emissions emitted from the source

were propagated in the south-south west direction, which was opposite direction to the downtown based on the prevailing wind direction.

No exceeding release of PM₁₀ concentration from the source has been observed in the downtown. This is considered to be a negative risk for the residents of the city, especially considering the long-term meteorological data including particularly wind speed, wind frequencies, and prevailing wind direction.

The annual mean of measured PM₁₀ from the AQMS was determined as 42 µg.m⁻³ while the modeled annual mean of PM₁₀ concentration at the same location was estimated to be about 1 µg.m⁻³. The reason for the difference of the PM₁₀ concentration measured by the AQMS at the downtown was thought to be caused by residential heating and transportation-related activities rather than industrial releases.

Only one source has been used for this modeling study and the number and types of the source data must be increased in the subsequent studies in future.

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I wish to express my sincere gratitude to the Balikesir University, the Provincial Environmental Agency and Balikesir Governorship for their support in order to complete this study.

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Microemulsion-Based Biofuels from Rice Bran Oil and Ethanol: Production and Fuel Properties

Sakonwan PHOEMBOON¹, Attaphon MANEEDAENG^{1*}

Abstract

Due to environmental concerns and current fossil fuel situations, liquid biofuels have been increasingly explored and vegetable oils are the option of choice. Apart from their renewability and biodegradability, they have high oxygen but have no sulfur and aromatics, which is the main advantage of better fuel quality over the fossil fuel. However, the limitations of their use are the operation problems from low volatility and high viscosity of vegetable oil. The viscosity of vegetable oils can be reduced by a number of ways. However, microemulsion-based biofuel is an effective alternative energy which produced by using natural substances. This study aims to investigate the new microemulsion of rice bran oil and ethanol as main constituents emulsified by Tween 80 and Span 80 together with co-emulsifier of 1-Octanol, at different molar ratios of 1:5, 1:10, 1:20, and 1:30. Ternary phase diagrams of rice bran oil, ethanol, and emulsifier/co-emulsifier revealed that Span 80 exhibits an excellent emulsification as single phase microemulsion region is larger than obtained from Tween 80. This is due to the lower Hydrophilic-Lipophilic Balance (HLB) of Span 80 thus, it can greatly emulsify when a large amount of oil present in the mixture. In addition, 1-Octanol assisted and is capable working with both Tween 80 and Span 80. The increase in amount of 1-Octanol significant increases the single phase microemulsion region. In an aspect of fuel properties, the kinematic viscosity, higher heating value, and emission test of microemulsion-based biofuels were investigated in this work. It can be observed that the high amount of emulsifier, the higher viscosity obtained while higher ethanol amount could decrease the kinematic viscosity. The higher 1-Octanol and rice bran oil content resulted in larger value of higher heating value. The higher heating values increases with increasing molar ratios of emulsifier to co-emulsifier. The emission test revealed that NO_x release is less than of commercial diesel while HC and CO are relatively higher.

Keywords: Biofuel, Microemulsion, Rice bran oil, Surfactant

1. INTRODUCTION

Most of the current energy and fuel are derived from the natural resources. As the energy depletion is concerned, it makes the world aware of new energy alternatives to replace the natural fuels that are gradually run out. The ways to finding renewable energy have been of interest is to develop of biofuels which are energy derived from plants or animals i.e. oil from animal fat, oil from various plants such as oil, palm oil, oil, rice, oil, sunflower etc [1].

In Southeast Asia, palm oil is another source of energy that is of interest in the production of biofuels. However, due to the desire to find alternative energy sources or alternative energy, palm oil is popular in the production of biofuels that made palm oil has been very much needed and more expensive [2]. In 2011 – 2016, research was carried out to find other sources of biofuel, and rice bran oil may be an interesting alternative for Thailand [3] since Thailand is able to produce 31 million tons of paddy per a year. Most of the rice produced is processed and then consumed domestically or exported. But, rice price is expected to grow slowly [4]. With the ability to produce rice if the paddy is extracted into rice bran oil, it will be another way to increase rice value. However, if rice bran oil is used directly in the engine may cause problems with the engine due to its high viscosity, low evaporation, and become a wax when the temperature drops. Hence, it is important to improve the fuel properties of rice bran oil before use. There are four methods to lower the vegetable oil viscosity and improve fuel properties: 1. Mixed vegetable oil with diesel; 2. Pyrolysis; 3. Transesterification reaction and 4. Microemulsion.

Even the most popular method of biofuel production is transesterification reaction, however, the transesterification will produce glycerin as a by-product. The separation of glycerin from biofuels is further required which is a difficult and costly processes. Hence, the production of biofuels by microemulsion has received attention. Because there is no chemical reaction, no more glycerin and this method reduces the cost of biofuel purification. Microemulsion is a mixture of two insoluble liquids that can be homogeneous by the use of emulsifier which is surfactants together with co-surfactant which is a short hydrocarbon chain

alcohol. Surfactant and co-surfactant will cause very small size of colloidal particles (ranged in 10-100 nm). The mixture will become homogeneous and transparent.

In this research, the biofuels from rice oil and ethanol by microemulsion was investigated using different nonionic surfactants (Tween 80 and Span 80) and co-surfactant (1-Octanol). The microemulsion phase behavior was examined from ternary phase diagram. The fuel properties of biofuel was studied through the kinematic viscosity, higher heating value, and emission test.

2. MATERIAL AND METHODS

a. Material

The materials used for biofuel production were: Rice bran oil (commercial food grade) and absolute ethanol 99.8% (ACS reagent grade) from Carlo Alba. Surfactants used are Span 80 (Sorbitane monooleate) from Sigma Aldrich and Tween 80 (Polyoxyethylene (20) sorbitan monooleate) from Acros Organics. Co-surfactant used is 1-Octanol 99.0% from Apex Chemical Co., Ltd.

The research focused to use the individual surfactant with different molar ratios of surfactant (S) to co-surfactant (C) of 1:5, 1:10, 1:20, and 1:30. The solubilization of S/C was found to completely dissolve in each other in all molar ratios.

b. Construction of ternary phase diagram of biofuel

The 5-mL Microemulsion biofuel was prepared with different compositions of three components of S/C, rice bran oil, and ethanol by v/v basis. Biofuel was formulated in 36 different fomulars according to the composition points in ternary phase diagram. Then, All of 36 test tubes were added in the constant-temperature sharking water bath at 40 °C for 72 hr to allow the mixtures reach equilibrium. Monitoring the phase behavior (single or separate phase) in every 12 hr until 72 hr, and then the ternary phase diagrams were obtained.

c. Investigation of fuel properties of biofuel

After the ternary phase diagram was constructed, some microemulsion-based biofuel samples were collected to measure kinematic viscosity and higher heat value as seen in Figure 1 to investigate the effect of S/C ratios, types and amount of surfactant, types of microemulsion (water in oil, w/o and oil in water, o/w).

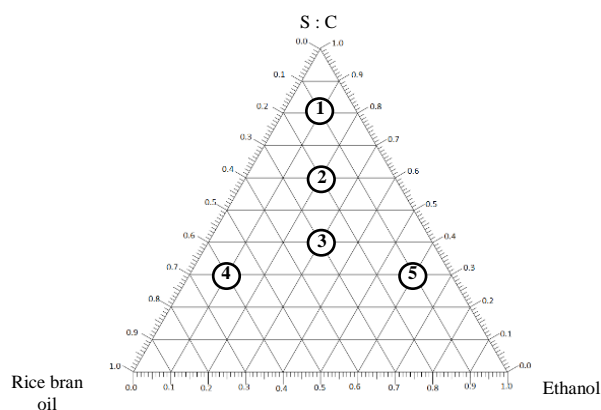


Figure 1. Selected points to sampling for further analysis on Ternary phase

d. Analysis of exhaust gases from a diesel engine

The samples from ternary phase diagram were chose to investigate the exhaust gas from the combustion in a single cylinder diesel engine. The ternary composition at the point number 3 in Figure 1 in Tween 80 and Span 80 with 1-Octanol at molar ratios of 1:10 and 1:30 were used for this analysis. The microemulsion-based biofuel combusted in a single cylinder engine (Fuel analyzer TESTO 350 at ambient temperature of 27 °C) produced the exhaust gases of CO, CO₂ and NO_x together with the exhaust temperature and amount of HC residue.

3. RESULTS AND DISCUSSION

a. Microemulsion phase behavior

Effect of surfactants and co-surfactant

Tween 80

Ternary phase diagrams of microemulsion-based biofuels using Tween 80 with varying S/C molar ratios of 1:5, 1:10, 1:20, and 1:30 were observed in Figure 2. The single phase region (the areas of shaded region) in all four various systems are larger than their separate phase region where two or three phases were observed. The increase amount of 1-Octanol promotes solubilization of rice bran oil and ethanol and thus, single phase microemulsion increases as seen in Figure 2 (a) – (d). In addition, as observed in Figure 2. (a). when S/C molar ratio is 1:5, the ability of Tween 80 itself could not solubilize to homogeneous mixtures when rice bran oil is the main composition with less S/C amount, the separate phase areas in lower left edge in ternary phase diagram is relatively large. This is due to the hydrophilic-lipophilic molecular structure in Tween 80 (HLB = 15.0) which indicates that Tween 80 favors to solubilize in polar phase (ethanol). However, when the molar concentration of 1-Octanol increased, the HLB of Tween 80 decreased and thus, it promoted solubilization of rice bran oil and ethanol, and can be seen in Figure 2. (c) – (d) that the separate phase areas in lower left edge in ternary phase diagram become smaller and smaller. The promotion effects of 1-Octanol on ternary phase diagram of microemulsion-based biofuels are in good agreement with previous researches [5]

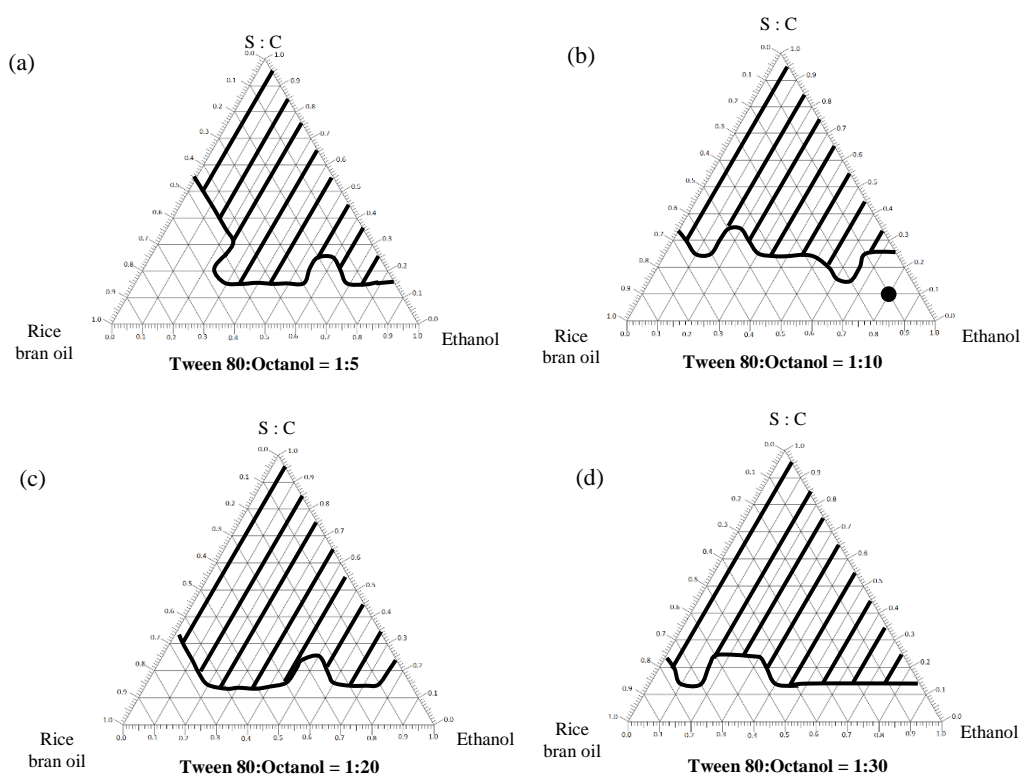


Figure 2. Ternary phase diagrams of microemulsion-based biofuels using Tween 80 with S/C molar ratios of (a) 1:5, (b) 1:10, (c) 1:20, and (d) 1:30

Span 80

Ternary phase diagrams of microemulsion-based biofuels using Span 80 with varying S/C molar ratios of 1:5, 1:10, 1:20, and 1:30 were observed in Figure 3. The single phase region (the areas of shaded region) in all four various systems are larger than their separate phase region as similarly seen in Tween 80 systems in Figure 2. However, the increase amount of 1-Octanol slightly assists to promote solubilization of rice bran oil and ethanol and thus, single phase microemulsion slightly increases as

seen in Figure 3 (a) – (d). This is because of Span 80 capability to solubilize in rich-oil mixture by itself (HLB = 4.3) thus, the increase molar concentration of 1-Octanol is slightly significant. This indicates that Span 80 is more capable to produce microemulsion-based biofuels with slightly amount of 1-Octanol co-assistance.

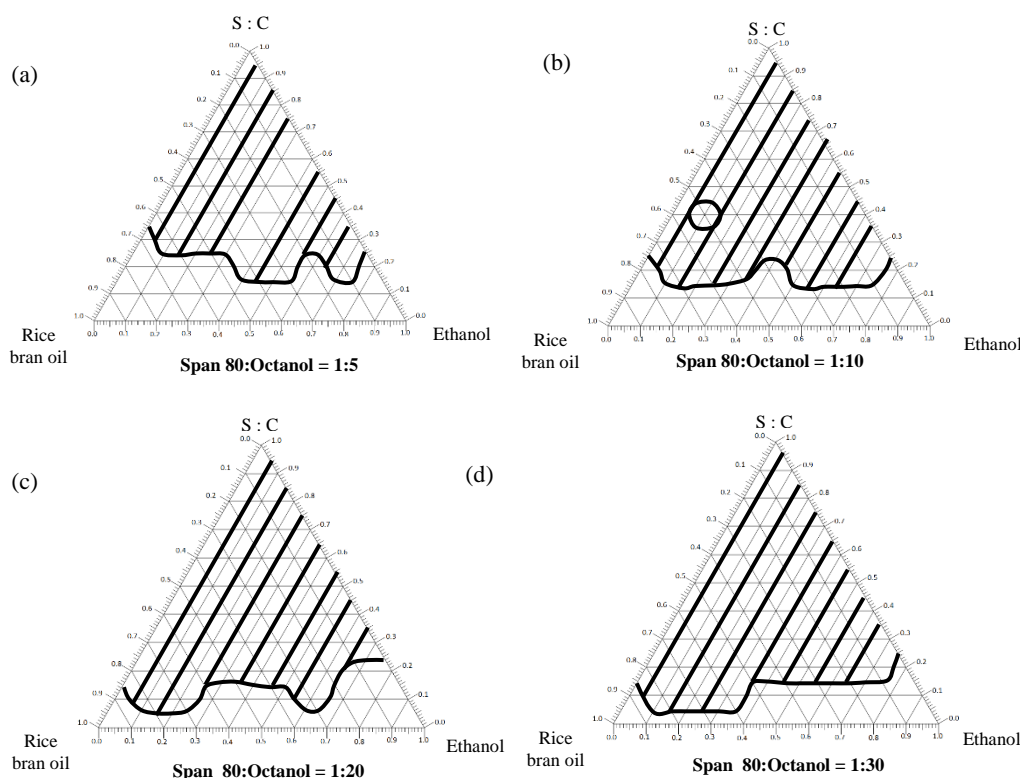


Figure 3. Ternary phase diagrams of microemulsion-based biofuels using Span 80 with S/C molar ratios of (a) 1:5, (b) 1:10, (c) 1:20, and (d) 1:30

b. Kinematic viscosity of microemulsion-based biofuels

Effect of surfactant and co-surfactant on kinematic viscosity

The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 1-3) with varying molar concentration of 1-Octanol and different types of surfactant are shown in Figure 4 (a) Tween 80 and (b) Span 80, respectively. It can be observed that the kinematic viscosity of microemulsion-based biofuels using both Tween 80 and Span 80 decreased as 1-Octanol molar concentration increased. This is because 1-Octanol has a lower viscosity compared to the used surfactant viscosity. Considering the kinematic viscosity in either Figure 2. (a) or (b) as v/v percent of S/C varied, the results showed that the kinematic viscosity increased with percent v/v of S/C increased. When the v/v percent of S/C increased, it means the amount of Tween 80 or Span 80 increased and thus, the influence of surfactant viscosity resulted in higher viscosity values. The standard of commercial biofuel (produced from transesterification method) and commercial diesel are approximately 8.0 and 4.0 cSt, respectively [6]. As can be seen in Figure 4.(b), the kinematic viscosity of biofuels from Span 80 systems are relatively close to the standard of commercial biofuel value while the kinematic viscosity of biofuels from Tween 80 systems could be tuned to be close to the standard value when the molar concentration of 1-Octanol increased.

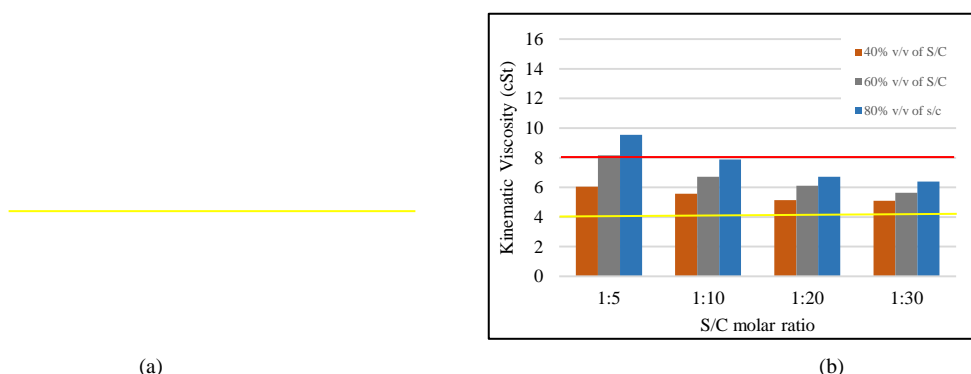


Figure 4. The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 1-3) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80. The red and yellow lines indicate the standard value of commercial biodiesel from transesterification and diesel, respectively

Effect of w/o and o/w on kinematic viscosity

The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 4 (w/o) and 5 (o/w)) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80 is shown in Figure 5. For the prepared biofuels with o/w microemulsion type in both Tween 80 and Span 80 systems, the kinematic viscosity were observed to be similarly and no significant difference because the amount of ethanol is more influent on the viscosity value of the mixtures. The kinematic viscosities of biofuels with w/o microemulsion type were observed to be very higher than the biofuels with o/w microemulsion type because of the existence of rice bran oil as a rich phase which has high viscosity. As can be seen in Figure 5. (a), the kinematic viscosity of microemulsion-based biofuels with w/o microemulsion of S/C molar ratio at 1:5 in Tween 80 system does not show up since this point appears two separate phases from lack of enough 1-Octanol.

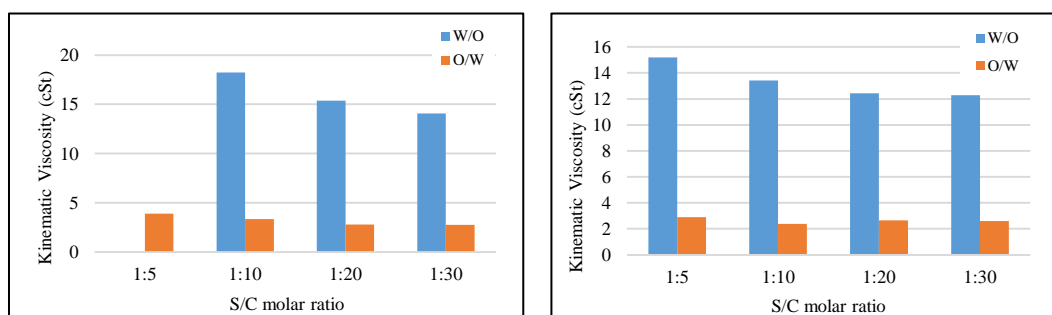


Figure 5. The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 4 (w/o) and 5 (o/w)) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80

c. Higher heating value

Effect of surfactant and co-surfactant

The higher heating value of biofuels for selected systems from Figure 2 (at point no. 1-3) using Tween 80 at different molar concentration of 1-Octanol of 1:5 and 1:10 with varying S/C volume percent are shown in Figure 6. It can be seen that the more amount of 1-Octanol in the biofuels, the larger higher heating value obtained. It is due to 1-Octanol has a large value of higher heating value. In addition, when the amount of Tween 80 increased, it resulted in the larger values of higher heating value of biofuels due to there are so many hydrocarbon molecules in Tween 80 structure to combust in the oxidation reaction. The higher heating value of commercial biofuel (produced from transesterification method) and commercial diesel are approximately 37.24 MJ/kg and 44.80 MJ/kg, respectively [7].

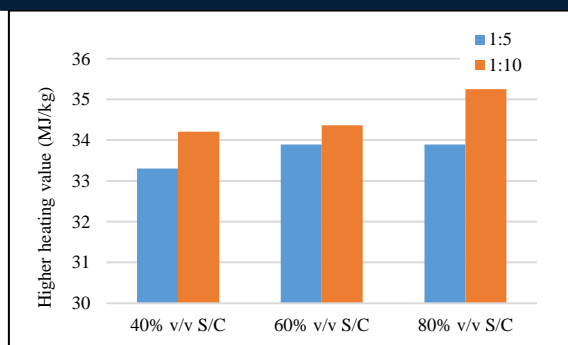


Figure 6. The higher heating value of biofuels for selected systems from Figure 2 (at point no. 1-3) using Tween 80 at different molar concentration of 1-Octanol of 1:5 and 1:10 with varying S/C volume percent

d. Emission test

The experimental results from emission test for exhaust gas temperature, unburn hydrocarbon (HC), carbon dioxide (CO₂), carbon monoxide (CO) and nitrogen oxides (NO_x) are shown in Figure 7-11, respectively. The ternary composition at the point number 3 in Figure 1 in Tween 80 and Span 80 with 1-Octanol at molar ratios of 1:10 and 1:30 were used for this analysis with two different load of 25 and 50 N-m. From Figure 7.(a) and (b) the exhaust temperatures resulted from biofuel combustion in a single cylinder diesel engine for both Tween 80 and Span 80 systems were similarly which indicated that the change in molar ratio of S/C were slightly significant. The main reason for exhaust temperature difference could be due to the load apply. Considering the amount of unburn hydrocarbons of biofuels from Tween 80 and Span 80 systems in Figure 8.(a) and (b), the amount of unburn hydrocarbons from the prepared biofuels remained higher than those of commercial diesel, which is a result from incomplete oxidation reaction due to amount of triglyceride in rice bran oil.

In Figure 8.(a), the molar ratio difference resulted in not so different unburn hydrocarbon remain while the significant difference in unburn hydrocarbon amount were observed in biofuels from Span 80 systems at both different load apply. It indicates that the increase in the molar concentration of 1-Octanol in biofuels when using Span 80 as emulsifier, it shall result in incomplete oxidation reaction in the combustion chamber in diesel engine. This problem could be solved by further addition of oxygen compounds (i.e. ethanol) to the mixtures. Considering Figure 9. (a) and (b), it can be observed that the prepared biofuels from both Tween 80 and Span 80 systems have similar results in CO₂ release comparable to commercial diesel. This can be due to the amount of free fatty acid content (as single chain hydrocarbons) while the HC remained much higher because of triglyceride with in good agreement in the further supporting experimental data of higher amount of CO release in the exhaust gases as seen in Figure 10.(a) and (b).

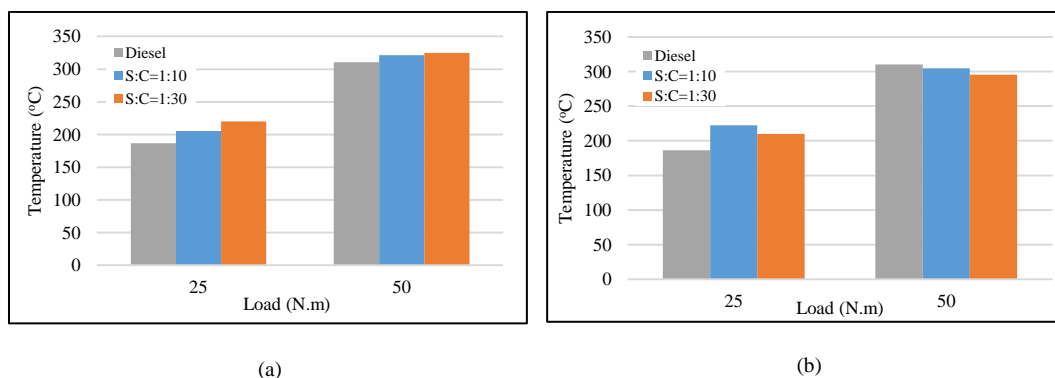


Figure 7. The exhaust gas temperature of prepared biofuels with different load (a) Tween 80 and (b) Span 80

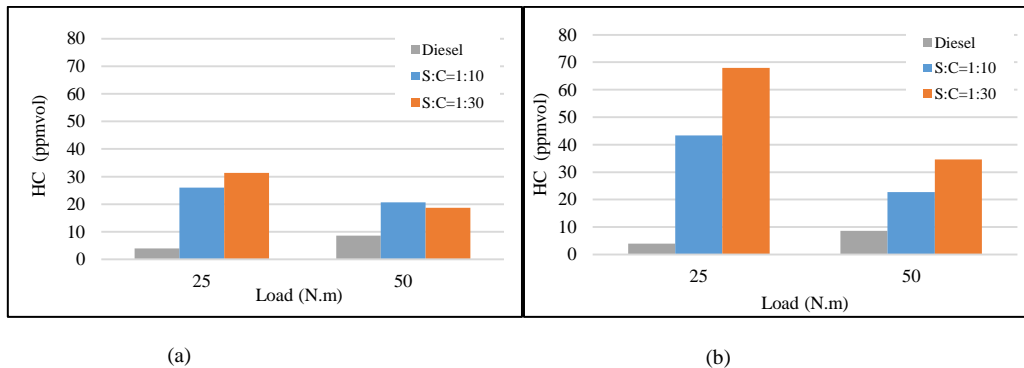


Figure 8. The amount of unburn hydrocarbon of biofuels with different load apply from (a) Tween 80 and (b) Span 80

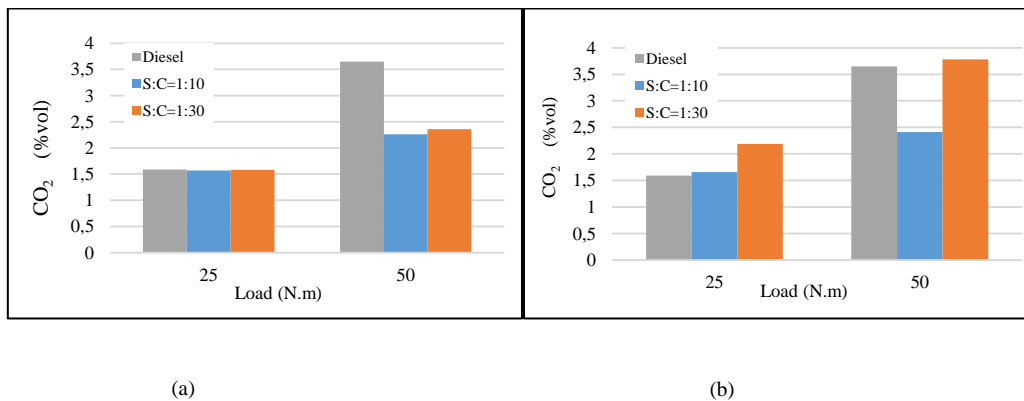


Figure 9. The amount of CO₂ release of biofuels with different load apply from (a) Tween 80 and (b) Span 80

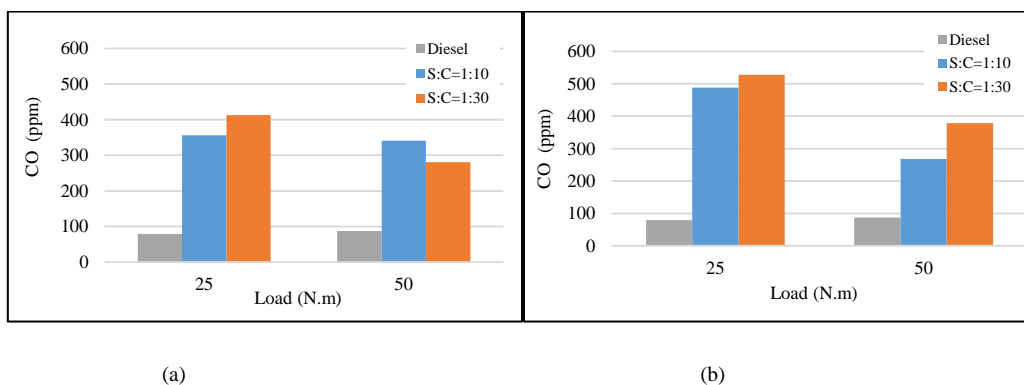


Figure 10. The amount of CO release of biofuels with different load apply from (a) Tween 80 and (b) Span 80

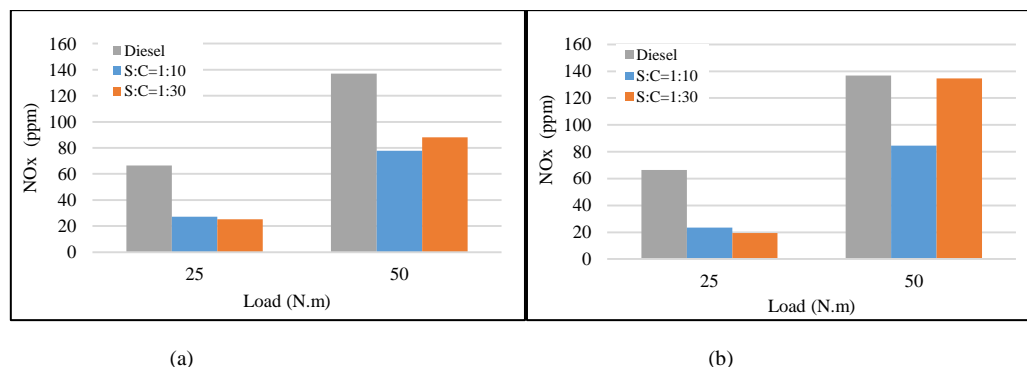


Figure 11. The amount of NOx release of biofuels with different load apply from (a) Tween 80 and (b) Span 80

Due to the co-existence of oxygen compounds (ethanol and 1-Octanol) in the prepared biofuels, the experimental data revealed that the amount of NOx release from the engine was relatively lower than from commercial diesel fuel as can be seen in Figure 11.(a) and (b). In addition, the increase in S/C molar ratio resulted in not very significant in NOx release while the higher load apply resulted in higher NOx release. Overall of the emission analysis results of the prepared biofuels from both Tween 80 and Span 80 systems revealed lower NOx generation together with higher HC, CO₂ and CO amounts from the prepared biofuels. The experimental results are similar to previous researches of biofuels containing vegetable oils [8], [9], [10] and [11].

4. CONCLUSIONS

Tween80 and Span80 have potential to emulsify rice bran oil and ethanol to form the single phase microemulsion of biofuels. The kinematic viscosity decreased with increasing ethanol and it could be higher with increasing Tween 80 or Span 80 amount. The higher 1-Octanol and rice bran oil content resulted in larger value of higher heating value. The higher heating values increased with increasing molar ratios of surfactant to co-surfactant. The emission test revealed that NOx release from biofuels is less than of commercial diesel while HC and CO are relatively higher due to incomplete combustion because of triglyceride in rice bran oil.

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Three Dimensional Simulations of Transport Phenomena in Proton Exchange Membrane Fuel Cell

Djamel OMEIRI^{1*}, Amina LAOUAR¹

Abstract

The aim of this work is to present a three-dimensional isothermal model of a proton exchange membrane fuel cells (PEMFC). This model was developed to improve the fundamental understanding of the transport phenomena in the PEMFC. The effects of various operating parameters on the performance and efficiency of the PEMFC are also examined. This model was implemented in the commercial CFD software Fluent and its PEMFC module. It takes account of the most transport phenomena, including: proton and water transport in the membrane; transport of electrons in the gas diffusion layer (GDL); diffusion of multi-component in the GDL; convective mass and momentum transport in the gas flow channels. The simulations were accomplished for an isothermal system with a single phase. The distributions of the velocity in the gas flow channels; the concentration of species; the current density are presented and analyzed. The model predicts the polarization and power curves of fuel cells for different operating conditions. To examine the effect of various parameters such the air flow rate; the porosity of the GDL and the operating pressure, a parametric study was carried out.

Keywords: Fuel cell performance, Proton exchange membrane fuel cells, Single phase, Three-dimensional model, Transport phenomena.

1 INTRODUCTION

Fuel cells are electrochemical devices that convert the chemical energy of hydrogen and oxygen directly into electricity. Their high efficiency and low emissions have made them a prime candidate for powering the next generation of electric vehicles, and their modular design and the prospects of micro-scaling them have gained the attention of cellular phone and laptop manufacturers. Their scalability makes them prime candidates for a variety of stationary applications including distributed residential power generation. Numerous researchers have focussed on different aspects of the fuel cell. In the early 1990s most models were exclusively one-dimensional in nature ([1]-[3]). In recent years, high-performance computing and advanced numerical algorithms have allowed researchers to model proton exchange membrane fuel cell (PEMFC) systems as well as individual components with greater fidelity than ever before ([5], [7], [9]). In general, PEMFC operations involve simultaneously multi-component, multi-phase, multi-dimensional fluid flow with heat and mass transfer and electrochemical reactions. Hence, a complete mathematical model is necessary to characterize more fully the physical behavior ([8]), to aid our understanding of complex phenomena occurring in a fuel cell system and to provide powerful tools for fuel cell design and optimization. Fuel cell performance is evaluated by the relation between the cell voltage and current density. The voltage loss

^{1*} Corresponding author: Laboratoire de Physico-Chimie des Surfaces et Interfaces, Université du 20 Août 1955-Skikda, Algeria., djomeiri@hotmail.com

¹ Laboratoire de Physico-Chimie des Surfaces et Interfaces, Université du 20 Août 1955-Skikda, Algeria, laouaramina@gmail.com

is mainly caused by the activation loss due to electrochemical reactions, the Ohmic loss due to resistance and fuel crossover and the mass transport loss due to limitation of gas transport inside the cell. In the current study, a three-dimensional isothermal single phase model of a proton exchange membrane fuel cells (PEMFC) is investigated. This model based on the computational fluid dynamics (CFD) approach was implemented in the commercial CFD software Fluent (Ansys fluent user guide, 2011) in which the PEMFC module was loaded.

2. MATHEMATICAL MODEL

The basic structure and operation principle the polymer electrolyte membrane (PEM) fuel cell considered here are illustrated in Fig. 1. This figure shows a disassembling diagram of a PEMFC comprising of two distinct current collectors with flow channels armed on them at both the cathode and anode; an MEA consists a proton exchange membrane sandwiched between two catalyst years. Between the current collectors and the MEA, there are two GDLs on both sides. In this paper, the mathematical model considers all the parts shown in Fig. 1 with geometrical parameters listed in table 1. The computation domain consists of current collectors, flow channels, GDLs, catalyst layers and membrane. The channels are of 125mm length with 1mm (width) x 1mm (height) in the cross-section flow area. The species considered are hydrogen, oxygen, water vapor and nitrogen.

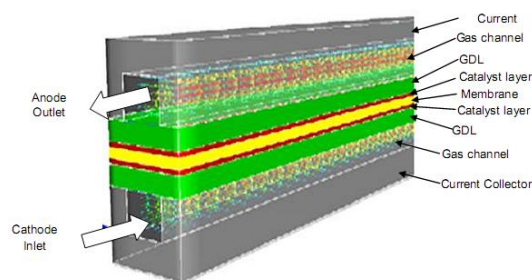


Figure 1. Three dimensional diagram of a PEMFC and its various components

Table 1. Geometrical parameters

Parameter	Value (mm)
Channel length	125
Channel width	1
Channel height	1
GDL thickness	0.21
Catalyst layer thickness	0.021
Membrane thickness	0.036
Current collector height	1.2
Current collector width	2.4

a. Model Assumptions

The assumptions used in developing the model are as follows:

- Ideal gas law was employed for gaseous species.
- The fluid flow in the fuel cell was laminar due to the low flow velocities and the small size of gas flow channels.
- Isothermal operation
- The porous media including membrane, catalyst layers and GDLs were considered to be isotropic.
- The fuel cell cooling was controlled by forced convection heat transfer.

2.2. Governing Equations

The conservation equations of mass, momentum, species concentration, proton and electron, are still formulated exactly in the same forms as in the single-domain framework. They are in the following forms:

Mass

$$\vec{\nabla} \cdot (\varepsilon \rho \vec{u}) = 0 \quad (1)$$

Momentum

$$\vec{\nabla} \cdot (\varepsilon \rho \vec{u} \vec{u}) = -\varepsilon \vec{\nabla} p + \vec{\nabla} \cdot (\varepsilon \mu \vec{\nabla} \vec{u}) + S_\mu \quad (2)$$

Species transport equations (Stefan Maxwell):

$$\vec{\nabla} \cdot (\varepsilon \vec{u} C_k) = \vec{\nabla} \cdot (D_k^{\text{eff}} \vec{\nabla} C_k) + S_k \quad (3)$$

Proton transport

$$\vec{\nabla} \cdot (\kappa^{\text{eff}} \vec{\nabla} \phi_e) + S_e = 0 \quad (4)$$

Electron transport

$$\vec{\nabla} \cdot (\kappa^{\text{eff}} \vec{\nabla} \phi_s) + S_s = 0 \quad (5)$$

Where \vec{u} , C_k , ϕ_e denotes intrinsic velocity vector, molar concentration of k^{th} species and electrolyte phase potential, respectively. In these equations, the source terms are presented in Table 2.

Table 2 Source Terms

	S_u (Momentum)	S_k (Species)	S_ϕ (phase potential)
Gas channels	0		
GDL	$-\frac{\mu}{K} \varepsilon^2 \vec{u}$		
Catalyst layer	$-\frac{\mu}{K} \varepsilon^2 \vec{u}$	$S_{\text{H}_2} = -\frac{j_a}{2F} \frac{\rho}{\varepsilon_m \varepsilon_{\text{mc}}} \text{ anode}$	j
		$S_{\text{O}_2} = \frac{j_c}{4F} \frac{\rho}{\varepsilon_m \varepsilon_{\text{mc}}} \text{ cathode}$	
		$S_{\text{H}_2\text{O}} = -\frac{j_c}{F} \left(\frac{1}{2} + n_d \right) \frac{\rho}{\varepsilon_m \varepsilon_{\text{mc}}} \text{ anode}$	
		$S_{\text{H}_2\text{O}} = -\frac{n_d}{F} j_a \frac{\rho}{\varepsilon_m \varepsilon_{\text{mc}}} \text{ cathode}$	
Membrane	$-\frac{\mu}{K} \varepsilon^2 \vec{u}$		

The other relevant physicochemical parameters are presented in Table 3 and Table 4

Table 3 physical and thermal parameters

Parameter	Value
Reference diffusivity of hydrogen , (m ² /s)	1.1028×10 ⁻⁴
Reference diffusivity of oxygen , (m ² /s)	3.2348×10 ⁻⁵
Reference diffusivity of water vapor , (m ² /s)	7.35×10 ⁻⁵
Reference diffusivity of nitrogen , (m ² /s)	3.2348×10 ⁻⁵
Porosity of the gas diffusion layer anode side (GDL)	0.5
Porosity of the gas diffusion layer cathode side (GDL)	0.5
Porosity of the catalyst layer anode side (CL)	0.5
Porosity of the catalyst layer cathode side (CL)	0.5
Catalyst layer permeability (CL), (m ²)	1×10 ⁻¹²
Gas diffusion layer permeability (GDL), (m ²)	1×10 ⁻¹²
Equivalent molecular weight of the membrane, (kg/kmol)	1100
Protonic conductivity	1
Molar mass M _{H₂,O₂,H₂O(g),N₂} (kg/mol)	0.002, 0.032, 0.018, 0.028
Thermal conductivity, k _{H₂,O₂,H₂O(g),N₂} w/(m.K)	0.1672, 0.0246, 0.0261, 0.0242.
Specific heat cp _{H₂,O₂,H₂O(g),N₂} j/(kg.K)	14283, 919.31, 2014, 1040.67
Dynamic viscosity, μ _{H₂,O₂,H₂O(g),N₂} kg/(m.s)	8.411×10 ⁻⁶ , 1.1919×10 ⁻⁵ , 1.34×10 ⁻⁵ , 1.663×10 ⁻⁵

Table 4 Physicochemical parameters

Parameter	Value
Anodic reference exchange current density, (A/m ³)	1.5×10 ⁺⁹
Cathodic reference exchange current density , (A/m ³)	4.0×10 ⁺⁶
Reference concentration of hydrogen , (mol/m ³)	1000
Reference concentration of oxygen , (mol/m ³)	1000
Anodic transfer coefficient , α _a	0.5
Cathodic transfer coefficient, α _c	1
Cathodic transfer coefficient, β _a	2
Cathodic transfer coefficient, β _c	2

The diffusivities for species concentration equations and ionic conductivity for membrane phase potential equation are modified using Bruggman correlation to account for porous electrodes, which can be expressed as:

$$D_k^{\text{eff}} = \varepsilon_m^{1.5} \cdot D_k \quad (6)$$

$$\kappa_e^{\text{eff}} = \varepsilon_m^{1.5} \cdot \kappa_e \quad (7)$$

2.3 Boundary and Operating Conditions

To close the equations system including conservation equations of continuity, momentum, energy, species, and charge with unknowns: u, v, w, P, c_i and ϕ , the boundary conditions are required. The summary of boundary and operating conditions is listed in Table 5 and Table 6.

Table 5 Boundary conditions

Locations of application	Boundary conditions
Inlet of the anode flow channel	$u = U_{a,\text{in}}; c_{\text{H}_2} = c_{\text{H}_2,\text{in}}, c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O},a,\text{in}}$
Inlet of the cathode flow channel	$u = U_{c,\text{in}}; c_{\text{O}_2} = c_{\text{O}_2,\text{in}}, c_{\text{H}_2\text{O}} = c_{\text{H}_2\text{O},c,\text{in}}$
Outlet of the anode flow channel	$\frac{\partial u_{\text{out},a}}{\partial x} = 0; \frac{\partial c_{\text{H}_2}}{\partial x} = 0; \frac{\partial c_{\text{H}_2\text{O},a}}{\partial x} = 0$
Outlet of the cathode flow channel	$\frac{\partial u_{\text{out},c}}{\partial x} = 0; \frac{\partial c_{\text{O}_2}}{\partial x} = 0; \frac{\partial c_{\text{H}_2\text{O},c}}{\partial x} = 0$
The anode terminal	$\phi_s = 0; \frac{\partial \phi_m}{\partial y} = 0$
The cathode terminal	$\phi_s = V_{\text{cell}}; \frac{\partial \phi_m}{\partial y} = 0$
External boundaries	$\frac{\partial \phi_s}{\partial x} = 0; \frac{\partial \phi_s}{\partial z} = 0; \frac{\partial \phi_m}{\partial x} = 0; \frac{\partial \phi_m}{\partial z} = 0$

Table 6 Operating and boundary conditions

Parameter	Value
Operating pressure [atm]	2
Operating temperature [K]	353
Mass fraction of hydrogen w_{H_2}	0.8
Mass fraction of water vapor (anode side) $w_{\text{H}_2\text{O},a}$	0.2
Mass fraction of oxygen w_{O_2}	0.2
Mass fraction of water vapor (cathode side) $w_{\text{H}_2\text{O},c}$	0.1
Mass fraction of nitrogen w_{N_2}	0.7
Open cell voltage V_{OCV} [Volt]	0.95
Anodic potential V_{anode} [Volt]	0
Cathodic potential $V_{\text{cathode}} = V_{\text{cell}}$ [Volt]	0.75
Hydrogen flow rate q_{H_2} [kg/s]	6×10^{-7}
Air flow rate q_{air} [kg/s]	5×10^{-6}

3.SOLUTION PROCEDURE

The above-coupled set of governing equations and relative equations were implemented and solved in the commercial CFD software Fluent by loading the PEMFC module developed by Ansys Fluent. The computational domains are created in the commercial GAMBIT pre-processor software. The whole domain is defined as a fluid zone, except for the current collector,

which is defined as solid region. The computational grid that was used for the main modeling domain is shown in Fig. 2. There were totally 129600 grid cells in the computation domain used to simulate the physical and electrochemical phenomena in the fuel cell. The solution procedure for pressure–velocity coupling was based on SIMPLE algorithm ([4]). The solution is considered to be converged when the difference between successive iterations is less than 10^{-6} for all variables.

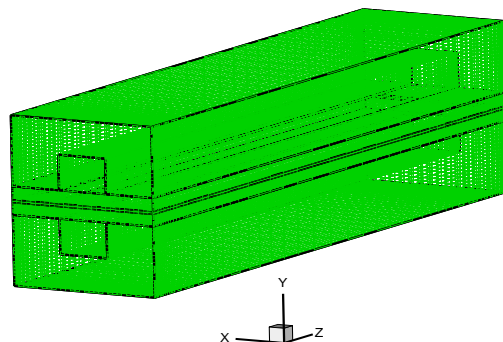


Figure 2 Three dimensional mesh of a PEMFC

4.RESULT AND DISCUSSION

The simulations were accomplished for an isothermal system with a single phase. The distributions of the velocity in the gas channels; the concentration of species and the current density are presented. The model predicts the polarization and power curves of fuel cells for different operating conditions. To examine the effect of various parameters such the air flow rate; the porosity of the GDL and the operating pressure, a parametric study was carried out.

4.1.Code validation

The base case was used to perform a series of simulations from a low operating current density to a high operating current density to validate the model used in this paper. The polarization curve shown in Figure 2 shows strong agreement between predicted results and the experimental data published in the literature by Wang et al.([6]). The predicted curve agrees well with experimental measurement at low current densities but at high current density there is some level of variation between the results. The maximum percentage difference between the numerical and the experimental was below 10%.

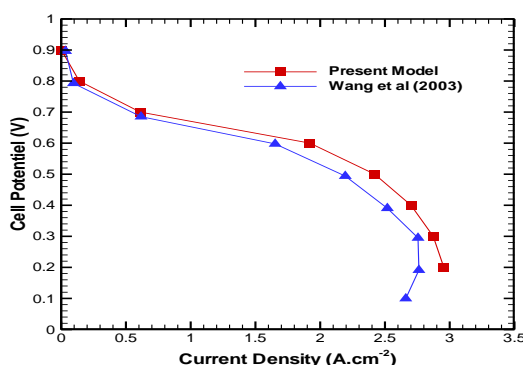


Figure 3. Comparison between present model and experimental polarization curves

4.2 Effect of operating pressure

Fuel cell performance is also largely influenced by operating pressure. In this study, operating pressure was varied from 1 to 2 atm (1,1.5 and 2atm) at a constant operating temperature of 353 K. The polarisation and power density curves for different operating pressure are shown in Figure 4. As operating pressure was increased from 1 to 2 atm, the fuel cell performance also improved. Increasing pressure improves the reactants interaction with the electrolyte hence increasing fuel cell performance. Pressure impact on the fuel cell performance is prominent at higher current density of operation. Generally the polarization curve shift position positively as the pressure increase.

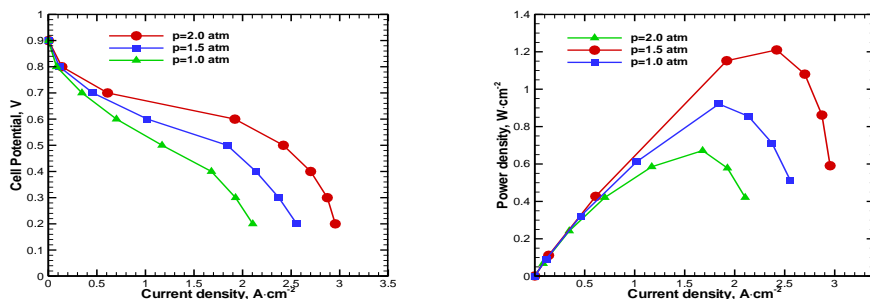


Figure 4 Effect of operating pressure on cell performance.

The effect of operating pressure on mass fraction distribution of hydrogen (anode side) and oxygen (cathode side) in the GDL/catalyst layer interfaces is shown in Fig.5. These figures show that the mass fraction distribution of reactant gas decrease with increasing the operating pressure.

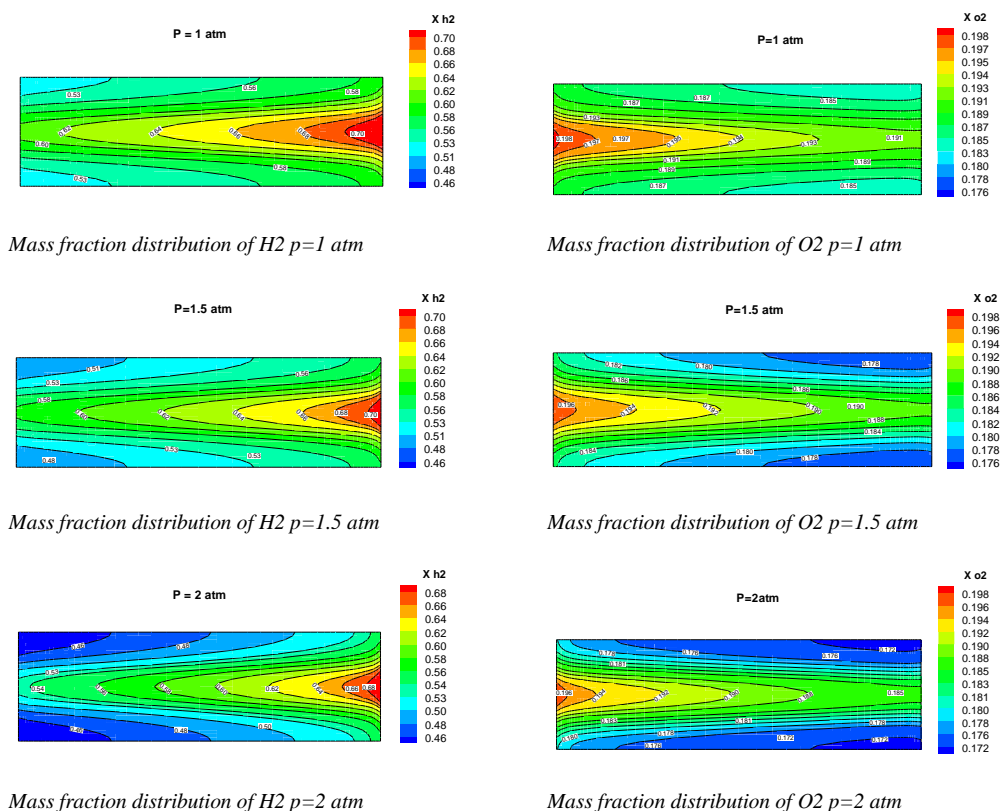


Figure 5 Effect of the operating pressure on mass fraction distribution of H2 (anode side) and O2 (cathode side) in the GDL/catalyst layer interface.

4.3 Effect of cathode gas flow rate

Figure 6 shows the effect of changing the oxygen flow rate on the fuel cell performance. It is observed that when the cathode flow gas is increased, the fuel cell performance is enhanced especially at lower operating fuel cell voltages. The reason is due to the fact that there is an increase in oxygen gas through the gas diffusion layer to the reaction sites, which increases the rate of reaction. At low operating voltages more liquid water is produced due to stronger electrochemical reaction rates, which is expected to reduce fuel cell performance. However, the high oxygen mass flow rates in the porous layer generate high shear forces, which aid the transport of liquid water downstream at the flow channel along the flow direction. The effect is minimal

at high operating voltages as observed on the curves primarily due to low membrane humidification since low amounts of water presence occur at this voltage levels due to slow reaction rates resulting in reduced cell performance.

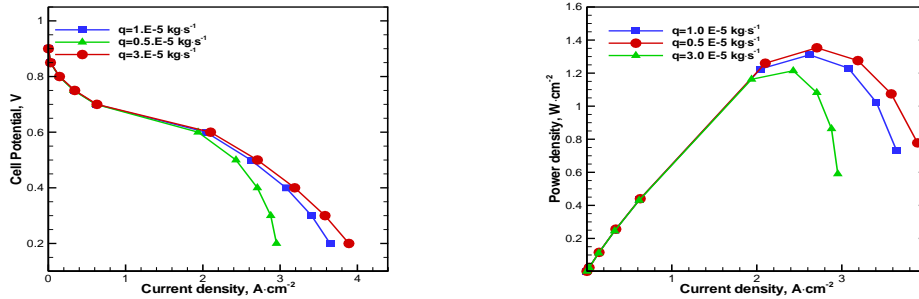


Figure 6 Effect of cathode gas flow rate on cell performance.

4.4 Effect of gas distribution electrode porosity

Porosity of electrodes is another sensitive parameter affecting fuel cell performance. A larger porosity gives room for more space for gas diffusion, which could also lead to high contact resistances in the fuel cell. Hence, for best performance of fuel cell there must be an optimal porosity level for the gas electrodes. Fig. 7 displays the changes in the fuel cell performance with different values of gas electrode porosities at a constant operating temperature of 353 K and pressure of 1 atm. Reduction in porosities of the gas distribution electrodes results in a decrease in fuel cell performance.

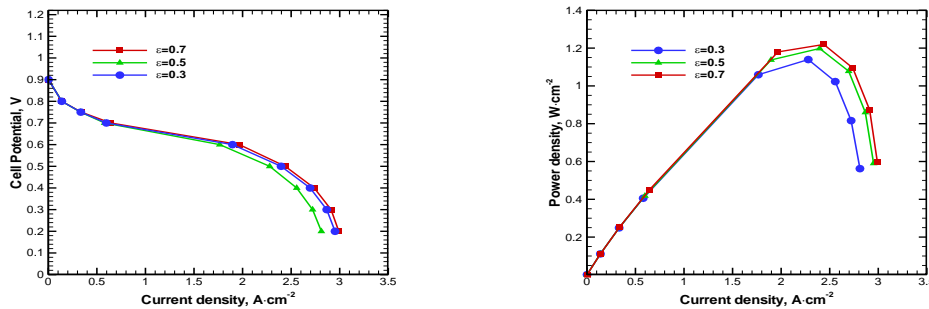


Figure 7 Effect of gas electrode porosity on cell performance.

5 BASE CASE SIMULATION

5.1 Velocity and current density distributions

Velocity distribution and velocity vectors in the flow channels are presented in Fig.8. This figure shows a parabolic profiles in both anode and cathode channels.

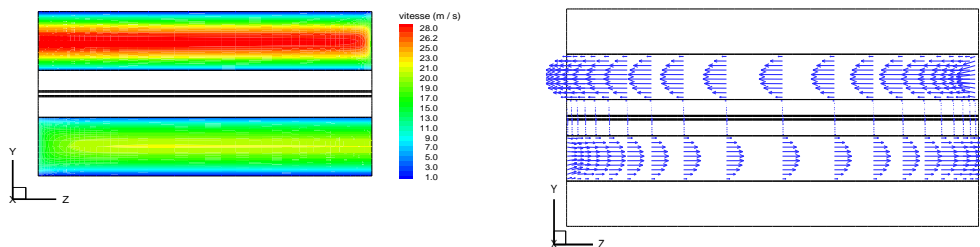


Figure. 8 Velocity distributions and velocity vectors in the flow channels

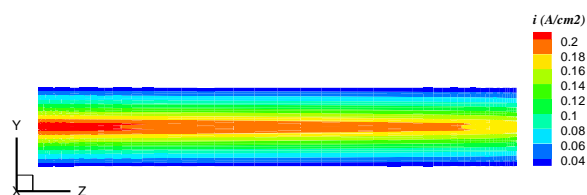


Figure 9. Current density distributions in the MEA

5.2 Reactant gas and water vapor distribution in the fuel cell

Fig. 10 and Fig.11 show the reactant gas distribution inside the gas channels and attached porous gas-diffusion electrodes at a low current density. The depletion of the reactant gases from the inlet (front) towards the outlet as well as the distribution of the reactant gases inside the porous electrodes (wider parts of the “T”) is clearly illustrated.

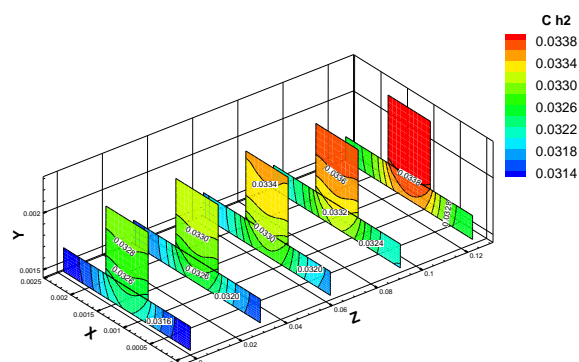


Figure 10 Molar concentration distribution of H₂ in the anode channel and GDL at base case conditions

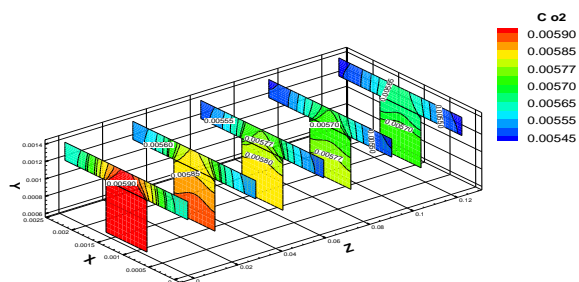


Figure 11 Molar concentration distribution of O₂ in the cathode channel and GDL at base case conditions

Fig.12 shows the distribution of water vapour as assumed in the variable diffusivity models. Contours of water vapour volume fraction are shown at slices along the longitudinal direction. The water vapour volume fraction increases down-stream due to pressure gradient driving the longitudinal convection, and due to the depletion of oxygen from the mixture. The water vapour also diffuses inwards towards the gas channels; this effect is caused by the shoulders and results in the curved lateral contours.

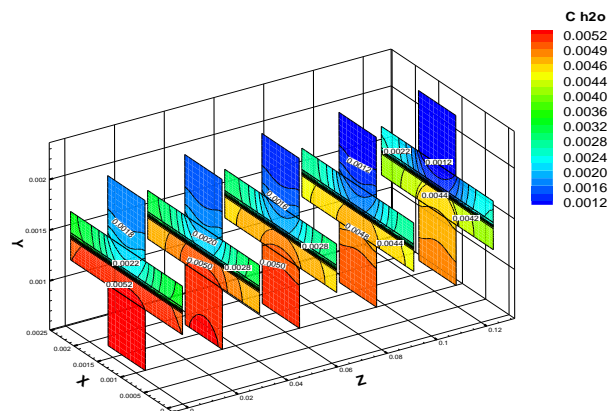


Figure 12 Molar concentration distribution of the water vapour in the gas channels and GDLs at base case conditions

6. CONCLUSION

A three dimensional model has been developed and applied for various operating conditions in order to investigate the effects of flow field on to PEM Fuel Cell performance. The effect is illustrated through the two-dimensional contours of current density and three dimensional plots of species concentrations. The developed model, which incorporated the electrochemical kinetics and multi-dimensional species transport, can be used to understand the complex electrochemistry occurring during the fuel cell operation and simulating the actual operating conditions as a tool for design of PEM Fuel Cells.

NOMENCLATURE

- A Superficial Electrode Area, cm^2
- C Molar Concentration, mol/m^3
- D Species Diffusivity, cm^2/s
- i Current Density, A/m^2
- F Constante de Faraday = 96485, C/mol
- S Source Terms,
- U Inlet Velocity, m/s
- j Transfer Current Density, A/m^3
- \vec{u} Velocity vector, m/s
- p Pressure, Pa
- q Mass flow rate, kg/s

Greek Symbols

- μ Dynamic viscosity, $kg/(m.s)$
- ρ Mass density, kg/m^3
- η Overpotential, V
- ε Porosity
- κ Ionic conductivity, S/m
- ϕ Phase potential, V

Subscripts

- a anode
- c cathode
- e Electrolyte phase
- k species
- m membrane
- s solid phase
- in inlet
- out outlet

Exponents

eff effective
ref Reference value

Notations

GDL Gas diffusion layer
MEA Membrane Electrode Assembly
PEMFC Proton Exchange Membrane Fuel Cell
CL Catalyst Layer

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The Biomass Energy Potential from Agricultural Production in the Black Sea Region of Turkey

Cengiz KARACA^{1}, Gurkan Alp Kagan GURDIL², Hasan Huseyin OZTURK³*

Abstract

The objective of this study is to determine the agricultural residues potential regarding types, quantities, and mapping in The Black Sea Region of Turkey. The Black Sea Region consists of 18 provinces in the north of Turkey. The amounts of residues from the agricultural crops cultivated in Turkey, in tons of dry matter per year, were calculated and estimated using production data of crops with Turkish Statistical Institute for the 2016 seasonal years. The annual gross potential of agricultural residues was determined by using residue to product ratio. The energy potential of residues for each province was calculated by multiplication of the calorific values of agricultural residues with the available residue amount. In this paper, the energy potential of annual crop residues was evaluated with a GIS software. The total amount of unused agricultural crop residues was approximately 1.86 Mt.a⁻¹. It was found that the total calorific value of the agricultural residues was around 33.60 PJ.a⁻¹ for the production period of 2016 in the region. When provinces put in order according to a number of agricultural residues, the top five provinces of the region are Samsun (370.3 kt), Ordu (326.2 kt), Corum (169.5 kt), Giresun (166.6 kt) and Tokat (134.07 kt). The major crops included in the ratio of the total calorific value were hazelnuts (53.54%), maize (13.68%), wheat (12.22%), and paddy (7.69%).

Keywords: Biomass energy, agricultural residues, Black Sea Region, Turkey

1. INTRODUCTION

Energy is central to economic development, and there is a clear correlation between energy consumption and living standards. Energy sources are split into three categories: fossil fuels, renewable sources and nuclear sources [1]. The valid global energy supply depends heavily on fossil sources (crude oil, lignite, hard coal, natural gas). The World's economies are dependent on crude oil. Fossil fuels are limited resources, collected in few regional areas of the world. This creates a permanent and insecure status of dependency on import of energy for the countries of outside this region.

Rural bioenergy is available from biomass, which is a renewable form. Rural bioenergy is still the predominant form of energy used by people in the less developed countries. Currently, much attention has been a major focus on renewable alternatives in the developing countries. Renewable energy can be particularly appropriate for developing countries. Furthermore, bioenergy often accounts for more than 90% of the total rural energy supplies in some developing countries. [2]

Biomass energy includes agricultural residues, domestic waste, fuelwood, animal waste and other fuel derived from biological sources. Estimation is based on the recoverable energy potential from the main agricultural residues, livestock farming waste, forestry and wood processing residues and domestic waste as given in the literature [3].

Biomass has been used by mankind through thousands of years as a primary energy resource, but after the oil crisis of the 1970s, the interest in using this resource in modern energy conversion facilities starts to grow rapidly. Aside from being locally produced and enabling less dependence on oil, biomass is also considered to be CO₂ neutral according to today's terminology. Among different types of biomass, a large amount of agricultural residues is available during the harvest time and as by-products in food industries. Using these residues for energy purposes contributes to avoiding disposal problems. Some

^{1*} Corresponding author: Mustafa Kemal University, Faculty of Agriculture, Department of Biosystems Engineering, Hatay, Turkey.
ckaraca@mku.edu.tr

² Ondokuz Mayıs University, Faculty of Agriculture, Department of Agricultural Machineries and Technologies Engineering, Samsun, Turkey.
ggurdil@omu.edu.tr

³ Cukurova University, Faculty of Agriculture, Department of Agricultural Machineries and Technologies Engineering, Adana, Turkey.
hhozturk@cu.edu.tr

agricultural residues from the harvest are used as fertilizers or as fodder; meanwhile, in many places parts of the residues are still burned in the field. This generates high emission of unburned hydrocarbons and particulate matter causing severe health problems for the local residents [4].

The major problems in using biomass for energy production are the logistics of collection and transportation and the seasonal availability. Due to these factors, there may be wide variability in the biomass supply, which makes the biomass unreliable for energy applications. Therefore, it becomes essential to overcome these barriers for effective utilization of biomass for energy [5].

Agricultural residues involved in the renewable energy resources form a notable potential for the development of bioenergy industry in many countries (nearly 250 Mt.a⁻¹ in Europe). These residues are directly related to the growing and picking of products having nutritional value (straw, stalks, plant leaves, pruning residues, etc.) or processing them industrially (olive stones, hazelnut shells, etc.) in general. When converting these residues, an energy burning method is often used, whereas pyrolysis and gasification methods are only used by researchers in laboratories or a demonstration scale. [6].

Conventional biomass plays a considerable role in energy production in Turkey. Wood is used as a major resource for direct cooking and heating in rural areas, but the use of modern biomass for energy production is a rather recent event. Turkey is an agricultural country; moreover, it has significant forestry potential, especially in the Central Anatolia, Cukurova, and Southern Anatolia regions. Even though the main goal is harvesting cereals and other seeds in agriculture, there is a strong wish to reclaim buried agricultural waste. Agricultural waste is a major source of biomass due to its high potential [7].

In this study we focus on the biomass potential and the energy value, being produced from agricultural residues in Black Sea Region. The potential benefits of the study are significant since the exploitation of agricultural residues and distribution of agricultural residues according to provinces of the region. The major benefits are environmental and relate to the reduction of GHG emissions (since crops are considered CO₂ neutral), conservation of natural resources, and avoidance of fossil fuel consumption. They are complemented by economic benefits (reduction of imported fuel consumption), regional development and investment increase.

2. MATERIALS and METHODS

The Black Sea Region covers approximately 18 percent of the land in Turkey, with a surface area of 141 thousand km². The Black Sea Region, which gets its name and characteristics from the adjacent sea, extends from the border of Georgia in the east to the eastern edge of the Adapazari Plain in the west. All of the provinces of Amasya, Artvin, Bartin, Bayburt, Bolu, Corum, Duzce, Giresun, Gumushane, Karabuk, Kastamonu, Ordu, Rize, Samsun, Sinop, Tokat, Trabzon, and Zonguldak, are in the Black Sea Region [8].

The most important feature of the agriculture in this region is that corn is grown in the coastal parts of this region rather than wheat, which is the main grain type in the other regions. Heavy rainfall makes the scarce lands of the region very fertile, allowing the production of more than half of the world's hazelnut and almost all of the famous Turkish tea. Tea which is grown only in the Eastern Black Sea Region in Turkey, is also among the most important crops in the region. Hazelnuts are the main fruit of the Black Sea Region, especially, in the eastern sections. The Black Sea coastal strip is covered with hazelnut trees. The hazelnut trees, which are sparse in the Rize section, become denser in the Trabzon section and are the densest in Giresun and Ordu Provinces [8].

The amounts of residues from the crops cultivated in Black Sea Region were calculated using production data of crops with Turkish Statistical Institute for the 2016 seasonal years. The annual gross potential of agricultural residues was determined by using residue to product ratio (RPR) (Table1) [1].

The net potential of residues was determined by using the availability of residues. The availability of residues is unused and completely wastes part of residues (Table 1). The available potential of the agricultural residues in each province of the region was calculated based on the Equation 1 [1].

$$(AAR)_i = (AAP)_i \times (RPR)_i \times (A)_i \quad (1)$$

where $(AAR)_i$ is the available amount of agricultural residues of i^{th} crop in ton, $(AAP)_i$ the amount of agricultural product in tons or number of tree or planting area for pruning wastes, $(RPR)_i$ residue-to product ratio of the i^{th} crop and $(A)_i$ the availability of residues.

The residues are material left over the field after agricultural production. Some agricultural residues have already been used for domestic purposes, heating, animal fodder, bedding. Mainly residues from the production of industrial, agricultural products

are left over the field. The species are hazelnut shell and husks, paddy straw and husk, maize stalk, sunflower stalk, cereal straw, pruning, etc.

The energy potential of residues for each province was calculated by multiplication of the heating values of a selection of agricultural residues which was taken heating value per each residue (Table 1) with the available residue amount (Equation 2) [1].

$$(THV)_i = (AAR)_i \times (LHV)_i \quad (2)$$

where $(THV)_i$ the total heating value of agricultural residues of i^{th} crop in GJ, $(AAR)_i$ is the available amount of agricultural residues of i^{th} crop in tons and $(LHV)_i$ lower heating value of air dry residues of i^{th} crop in $MJkg^{-1}$.

The energy content of the selected products for each province was calculated using the above equations. For each province, the calculated values that the total amount and the total energy potential of agricultural crop residues were mapped using the GIS software. The produced maps were provided to see more clearly in the differences of data among the provinces. The mapping can provide the rise of public awareness and policy-makers' reference about these subjects.

Table 1. The ratio of product to residue, availability and heating values of a selection of agricultural residues [1], [3], [9]

Field Crops	Residues	Ratio of Product to Residue (RPR)	Availability (A) (%)	Heating Value (LHV) (MJ.kg ⁻¹)
Wheat	Straw	0.80	15	17.9
Barley	Straw	0.90	15	17.5
Rye	Straw	1.50	15	17.5
Oats	Straw	1.50	15	17.4
Maize	Stalks	1.00	60	18.5
	Cob	0.64	60	18.4
Paddy (rice)	Straw	0.70	60	16.7
	Husks	0.27	80	13.0
Tobacco	Stalks	1100*	60	16.1
Sunflower	Stalks	0.6	60	14.2
Soybeans	Straw	0.75	60	19.4
Fruits Crops				
Hazelnut	Shell	0.30	80	19.3
	Husks	0.30	80	16.0
	Pruning	1500*	80	18.8
Walnut	Pruning	13.00**	50	19.0
Almonds	Pruning	7.40**	80	18.4
Peach	Pruning	8.00**	80	18.0
Kiwi	Pruning	8.00**	80	18.0
Vineyard	Pruning	6,000*	80	18.0

* Per planting area (kg.ha⁻¹)

** Per number of trees (kg.tree⁻¹)

3. RESULTS AND DISCUSSION

The total amount of agricultural residues, including annual crop residues (cereals, maize, paddy (rice), tobacco, sunflower, soybeans), perennial residues (tree pruning) and agro-industrial residues (hazelnut shell and husk, and rice industries), were calculated to be about 1.86 million tons in Black Sea Region (Table2).

Table2. The amount of agricultural product and available residues of Black Sea Region

Field Crops	Amount of Agricultural Product Number of Trees or Planting Area		Residues	Available Residues (AAR) (tons)
	(AAP) (tons) or (ha)			
Wheat	1,895,233		Straw	227,428
Barley	495,581		Straw	64,385
Rye	15,986		Straw	3,597
Oats	22,499		Straw	5,062
Maize	258,704		Stalks	155,222
			Cob	99,342
Paddy (rice)	224,959		Straw	94,483
			Husk	48,591
Tobacco	10,015**		Stalks	6,610
Sunflower	167,592		Stalks	60,333
Soybeans	11,911		Straw	5,360
Fruits Crops				
Hazelnut	332,918		Shell	79,900
			Husks	79,900
Walnut	697,272**		Pruning	836,726
			Pruning	20,481
Almonds	143,394*		Pruning	851
Peach	1,568,448*		Pruning	10,038
Kiwi	731,822*		Pruning	4,684
Vineyard	12,152 **		Pruning	58,328
TOTAL			Residues	1,861,323

* Number of trees

**Planting area (ha)

The residues distribution by the source is field crops (41.4%) and fruit crops (58.6%). Major crops that included in the ratio of the total residue amount are hazelnut (53.54%), maize (13.68%), wheat (12.22%), and paddy (rice) (7.7%).

When all provinces of Black Sea Region are aligned according to the amounts of residue, an alignment is as in Table 3. Also, the distribution map of agricultural residues which mapped using a GIS Software for each province was given Figure1.

Table 3. The alignment of provinces according to amount of agricultural residues

Provinces	Field Crops Residues (tons)	Fruit Crops Residues (tons)	Total Residues (tons)	Share in Total Residues (%)
Aksu	219,203	151,081	370,284	19.89
Antalya	6,873	319,342	326,215	17.53
Artvin	145,615	23,916	169,531	9.11
Burdur	6,794	159,805	166,599	8.95
Çanakkale	92,954	41,120	134,074	7.20
Çorum	32,184	101,748	133,932	7.20
Diyarbakır	126,014	7,356	133,370	7.17
Erzurum	4,739	108,814	113,553	6.10
Gaziantep	17,264	94,152	111,416	5.99
İstanbul	5,773	43,781	49,554	2.66
Konya	36,641	3,727	40,368	2.17
Mardin	21,724	17,177	38,901	2.09
Manisa	21,120	3,144	24,264	1.30
Muş	12,274	11,388	23,662	1.27
Niğde	11,359	0	11,359	0.61
Ordu	4,620	1,585	6,205	0.33
Samsun	5,022	935	5,957	0.32
Sivas	241	1,837	2,078	0.11
TOTAL	770,414	1,090,909	1,861,323	100

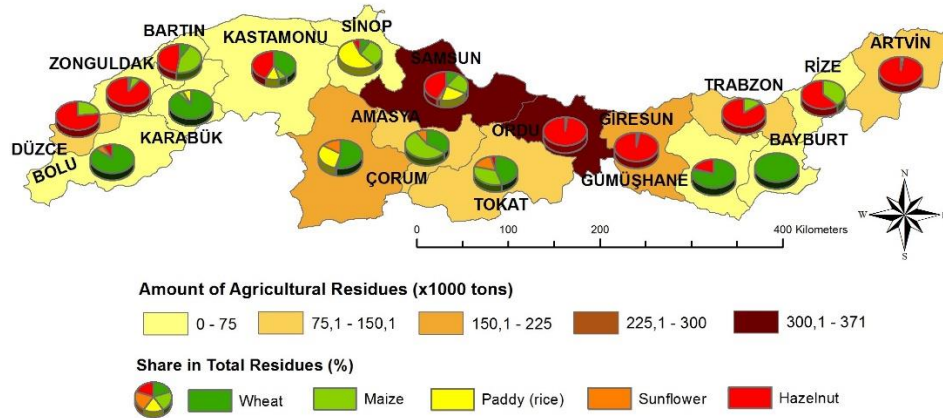


Figure 1. The distribution map of agricultural residues in Black Sea Region

Although, the total production of crop residues in the region is of the order of 1.86 Mt.a^{-1} , but it may be noted that there is a wide variability in the availability of crop residues within the region. The Samsun province produces maximum crop residues (of the order of 370.3 kt) followed by Ordu (326.2 kt), Corum (169.5 kt), and Giresun (166.6 kt). More than half of the total residues are produced in these provinces. It is believed that there will not be a shortage of raw materials for the investment and facilities to be made for obtaining energy from agricultural residues in Samsun and Ordu provinces.

Hazelnut is the product with the highest residues potential in the most of provinces of region (Samsun, Ordu, Giresun, Trabzon, Rize, Artvin, Zonguldak, Duzce, Bartın, and Kastamonu) It is observed that wheat has the highest residues potential in Bolu, Karabük, Corum, Tokat, Gumushane and Bayburt. Besides, it has been determined that paddy in Sinop, corn in Amasya is the product with the highest residues potential.

It was calculated that the total heating value of the agricultural residues was about 33.6 PJ (802.5 ktoe) for the production period of 2016 in Black Sea Region. The heating value of agricultural residues that calculated separately for each product is given in Table 4. The distribution map was given Figure 2.

Table 4. Total heating value of agricultural residues in Black Sea Region

Field Crops	Residues	Total Heating Value (THV) (GJ)
Wheat	Straw	4,070,960
Barley	Straw	1,126,740
Rye	Straw	62,945
Oats	Straw	88,084
Maize	Stalks	2,871,614
	Cob	1,827,899
Paddy (rice)	Straw	1,577,862
	Husks	630,713
Tobacco	Stalks	106,419
Sunflower	Stalks	856,730
Soybeans	Straw	103,983
Fruits Crops		
Hazelnut	Shell	1,542,076
	Husks	1,278,405
	Pruning	15,730,456
Walnut	Pruning	389,135
Almonds	Pruning	15,662
Peach	Pruning	180,685
Kiwi	Pruning	84,306
Vineyard	Pruning	1,049,907
TOTAL		33,594,583

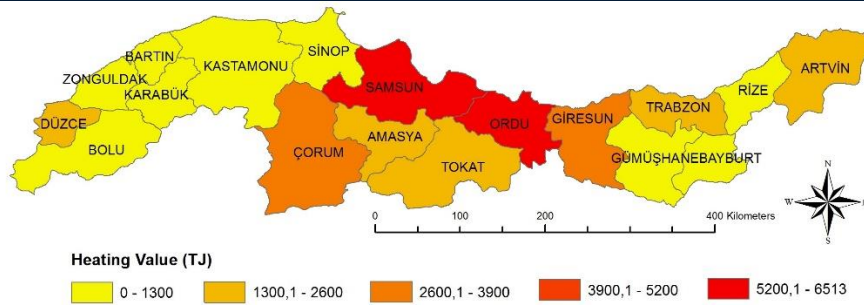


Figure 2. The distribution map of heating value based on agricultural residues in Black Sea Region

These maps (Figure1 and 2) showed that the potential of agricultural residues concentrated in the Samsun and Ordu provinces. In particular, it is observed that the type and distribution of residues in Samsun province, the distribution of agricultural residues according to heating value is ranked as hazelnut (41.2%), maize (20.4%) and paddy (rice) (19.4%) respectively. In Ordu, this ranking consists of hazelnut (97.3%), and maize (1.8%) respectively. Despite these facts, until now, there has not been any investment in these areas related to agricultural residues, which have a great potential for conversion to energy. However, the results of this study show that such a large potential necessarily has to be evaluated by establishing modern facilities.

4. CONCLUSION

This study aimed to determine the distribution of agricultural residues in provinces of Black Sea Region as given on the map. The importance of this paper is increasing more because Turkey is an energy importing country. Black Sea Region has important provinces (Samsun, Ordu, Giresun, Duzce, and Artvin) in Turkey, especially regarding the potential for hazelnut crop residues.

The conversion of biomass into electricity seems to be unavoidable in developing countries due to the growing environmental anxiety and the energy security. Recently, these resources are not utilized to a significant rate owing to a number of challenges. A number of crops such as hazelnut, paddy, maize, cereal crops, sunflowers and vineyard have been identified in this study for energy production. Although, the density of the biomass varies among the provinces of Black Sea Region, but the total biomass potential represents a significant amount of renewable energy resources.

Although Black Sea Region has a large biomass energy potential, this potential cannot be adequately assessed. In this paper, the produced maps were provided to see more clearly in the differences of data among the provinces. The mapping can provide the rise of public awareness, policy-makers' reference and investor's guide about these subjects.

Consequently, agricultural residues are a very attractive choice, since it is economical, sustainable, environmental friendly and a familiar energy source for Black Sea Region.

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Determining and mapping agricultural biomass energy potential in Samsun Province of Turkey

Cengiz KARACA^{1}, Gurkan Alp Kagan GURDIL², Hasan Huseyin OZTURK³*

Abstract

This study is aimed to determine the biomass potential and the energy value, being produced from agricultural residues in Samsun province. Samsun is a province of Turkey in the Black Sea region. Samsun province has 17 districts. The amounts of residues from the agricultural crops cultivated in Samsun province were calculated using production data of crops with Turkish Statistical Institute (TUIK) for the year 2016. The annual gross potential of agricultural residues is determined by using residue to product ratio. The energy potential of each district is calculated by multiplication of the calorific values of agricultural residues with the available residue amount. The total amount of agricultural residues was approximately 366.6 kt.a⁻¹. It was found that the total calorific value of the agricultural residues was around 6.46 PJ.a⁻¹ for the production period of 2016 in the region. When districts put in order according to a number of agricultural residues, the top three districts of Samsun are Bafra (87.43 kt), Carsamba (82.80 kt), and Terme (55 kt). The major crops included in the ratio of the total calorific value were hazelnuts (42.33%), maize (20.60%), paddy (rice) (19.53%) and wheat (10.79%).

Keywords: Biomass energy, agricultural residues, Samsun Province, Turkey

1 INTRODUCTION

Energy sources are split into three categories: fossil fuels, renewable sources and nuclear sources [1]. The valid global energy supply depends heavily on fossil sources (crude oil, lignite, hard coal, natural gas). The World's economies are dependent on crude oil. Fossil fuels are limited resources, collected in few regional areas of the world. This creates a permanent and insecure status of dependency on import of energy for the countries of outside this region. Energy is central of economic development, and there is a clear correlation between energy consumption and living standards.

Currently, much attention has been a major focus on renewable alternatives in the developing countries. Renewable energy can be particularly appropriate for developing countries. But, rural bioenergy is available from biomass. Furthermore, bioenergy often accounts for more than 90% of the total rural energy supplies in some developing countries. [2]

Biomass energy consists of agricultural residues, domestic waste, fuelwood, animal waste and other fuel derived from biological sources. Estimation is based on the recoverable energy potential from the main agricultural residues, livestock farming waste, forestry and wood processing residues and domestic waste as given in the literature [3].

The major problems in using biomass for energy production are the logistics of collection and transportation and the seasonal availability. Due to these factors, there may be wide variability in the biomass supply, which makes the biomass unreliable for energy applications. Therefore, it becomes essential to overcome these barriers for effective utilization of biomass for energy [5]

Aside from being locally produced and enabling less dependence on oil, biomass is also considered to be CO₂ neutral according to today's terminology. Among different types of biomass, a large amount of agricultural residues is available during the harvest time and as by-products in food industries. Using these residues for energy purposes contributes to avoiding disposal problems. Some agricultural residues from the harvest are used as fertilizers or as fodder; meanwhile, in many places parts of the residues are still burned in the field. This generates high emission of unburned hydrocarbons and particulate matter causing severe health

^{1*} Corresponding author: Mustafa Kemal University, Faculty of Agriculture, Department of Biosystems Engineering, Hatay, Turkey. ckaraca@mku.edu.tr

² Ondokuz Mayıs University, Faculty of Agriculture, Department of Agricultural Machineries and Technologies Engineering, Samsun, Turkey. ggurdil@omu.edu.tr

³ Cukurova University, Faculty of Agriculture, Department of Agricultural Machineries and Technologies Engineering, Adana, Turkey. hhozturk@cu.edu.tr

problems for the local residents [4]. When converting these residues, an energy burning method is often used, whereas pyrolysis and gasification methods are only used by researchers in laboratories or in demonstration scale. [6].

Conventional biomass plays a considerable role in energy production in Turkey. Wood is a major resource for direct cooking and heating in rural areas, but the use of modern biomass for energy production is a rather recent event. Turkey is an agricultural country; moreover, it has significant forestry potential, especially in the Central Anatolia, Cukurova, and Southern Anatolia regions. Even though the main goal is harvesting cereals and other seeds in agriculture, there is a strong wish to reclaim buried agricultural waste. Agricultural waste is a major source of biomass due to its high potential [7].

In this study the biomass potential and the energy value, produced from agricultural residues in Samsun province of Turkey were investigated. The potential benefits of the study are significant since the exploitation of agricultural residues and distribution of agricultural residues according to districts of Samsun. The major benefits are environmental and relate to the reduction of Greenhouse Gas emissions, conservation of natural resources, and decreasing the consumption of fossil fuel down.

2. MATERIALS and METHODS

Samsun province in Turkey has located between 41° 17' 25" N latitudes and 36° 20' 1" E longitudes and covering 9,352 km² areas. Samsun Province is a province of Turkey on the Middle Black Sea coast. Samsun province is divided into 17 districts, four of which (Ilkadam, Canik, Atakum and Tekkekoy) are included in the municipality of Samsun city (Center). Other districts include Alacam, Asarcik, Ayvacik, Bafra, Carsamba, Havza, Kavak, Ladik, Ondokuzmayis, Salipazari, Terme, Vezirkopru and Yakakent..

The amounts of residues from the crops cultivated in Samsun were calculated using production data of crops with Turkish Statistical Institute for the 2016 seasonal years. The annual gross potential of agricultural residues was determined by using residue to product ratio (RPR) (Table1) [1]

The net potential of residues was determined by using the availability of residues which signifies the unused part. The available potential of the agricultural residues in each district of the province is calculated based on the Equation 1 [1].

$$(AAR)_i = (AAP)_i \times (RPR)_i \times (A)_i \quad (1)$$

where $(AAR)_i$ is the available amount of agricultural residues of i^{th} crop in ton, $(AAP)_i$ the amount of particular agricultural product in tons or number of tree or planting area for pruning wastes, $(RPR)_i$ residue-to product ratio of the i^{th} crop and $(A)_i$ the availability of residues.

Some agricultural residues are being used for domestic purposes, heating, animal fodder and for litter. Mainly residues from industrial crops like hazelnut shell and husks, paddy straw and husk, maize stalk, sunflower stalk, cereal straw, pruning and etc. are left on the fields.

The energy potential of residues for each district was calculated by multiplication of the heating values of a selection of agricultural residues which was taken heating value per each residue (Table 1) with the available residue amount (Equation 2) [1].

$$(THV)_i = (AAR)_i \times (LHV)_i \quad (2)$$

where $(THV)_i$ the total heating value of agricultural residues of i^{th} crop in GJ, $(AAR)_i$ is the available amount of agricultural residues of i^{th} crop in tons and $(LHV)_i$ lower heating value of air dry residues of i^{th} crop in MJkg⁻¹.

The energy content of the selected products for each district was calculated using the above equations. For each district, the calculated values were mapped using the GIS software. The produced maps definitely helps to see the differences of data among the provinces more clearly. Also, they can rise of public awareness and awareness of policy-makers' about these subjects.

Table 1. The ratio of product to residue, availability and heating values of selected agricultural residues [1], [3], [8]

Field Crops	Residues	Ratio of Product to Residue (RPR)	Availability (A) (%)	Heating Value (LHV) (MJ.kg ⁻¹)
Wheat	Straw	0.80	15	17.9
Barley	Straw	0.90	15	17.5
Maize	Stalks	1.00	60	18.5
	Cob	0.64	60	18.4
Paddy (rice)	Straw	0.70	60	16.7
	Husks	0.27	80	13.0
Sunflower	Stalks	0.6	60	14.2

Soybeans	Straw	0.75	60	19.4
Fruits Crops				
	Shell	0.30	80	19.3
Hazelnut	Husks	0.30	80	16.0
	Pruning	3.00**	80	18.8
Walnut	Pruning	13.00**	50	19.0
Peach	Pruning	8.00**	80	18.0
Kiwi	Pruning	8.00**	80	18.0
Vineyard	Pruning	6,000*	80	18.0

* Per planting area (kg.ha⁻¹)

** Per number of trees (kg.tree⁻¹)

3.RESULTS AND DISCUSSION

The total amount of agricultural residues, including annual crop residues (cereals, maize, paddy (rice), sunflower, soybeans), perennial residues (tree pruning) and agro-industrial residues (hazelnut shell and husk, and rice industries), were calculated to be about 366.6 kt in Samsun (Table2).

58.26% of these residues were field crops and the remaining 41.74% were fruit crops. Major crops that included in the ratio of the total residue amount are hazelnut (40.25%), paddy (rice) (22.28%), maize (19.66%), wheat (10.62%), and sunflower (3.49%).

Table2. The amount of agricultural product and available residues of Samsun Province

Field Crops	Amount of Agricultural Product		Residues	Available Residues (AAR) (tons)
	Number of Trees or Planting Area (AAP) (tons) or (ha)			
Wheat	324,452		Straw	38,934
Barley	20,756		Straw	2,802
Maize	73,244		Stalks	43,946
			Cob	28,126
Paddy (rice)	128,434		Straw	53,942
			Husk	27,742
Sunflower	35,546		Stalks	12,797
Soybeans	11,751		Straw	5,288
Fruits Crops				
Hazelnut	68,032		Shell	16,328
			Husks	16,328
Walnut	47,867,771*		Pruning	114,883
			Pruning	1,815
Peach	425,781*		Pruning	2,725
Kiwi	104,320*		Pruning	668
Vineyard	55 **		Pruning	266
TOTAL			Residues	366,589

* Number of trees

**Planting area (ha)

The amounts of residues in Samsun province are given order in Table 3. Also, the distribution map of agricultural residues which mapped using a GIS Software for each district was given Figure1.

Table 3. The amount of agricultural residues in district of Samsun

Districts	Field Crops Residues (tons)	Fruit Crops Residues (tons)	Total Residues (tons)	Share in Total Residues (%)
Bafra	83,717	3,717	87,433	23.85
Carsamba	30,785	52,011	82,796	22.59
Terme	18,538	36,537	55,075	15.02
Center	11,423	18,015	29,437	8.03
Salipazari	981	24,465	25,446	6.94
Vezirkopru	17,245	478	17,722	4.83
Ayvacik	3,563	11,472	15,035	4.10
Havza	14,244	71	14,315	3.91
Alacam	11,562	413	11,975	3.27
Ondokuz	5,676	4,642	10,318	2.81
Mayis				
Ladik	5,967	153	6,120	1.67

Kavak	5,251	436	5,687	1.55
Asarcik	3,939	472	4,411	1.20
Yakakent	687	130	817	0.22
AL	11,423	18,015	366,589	100

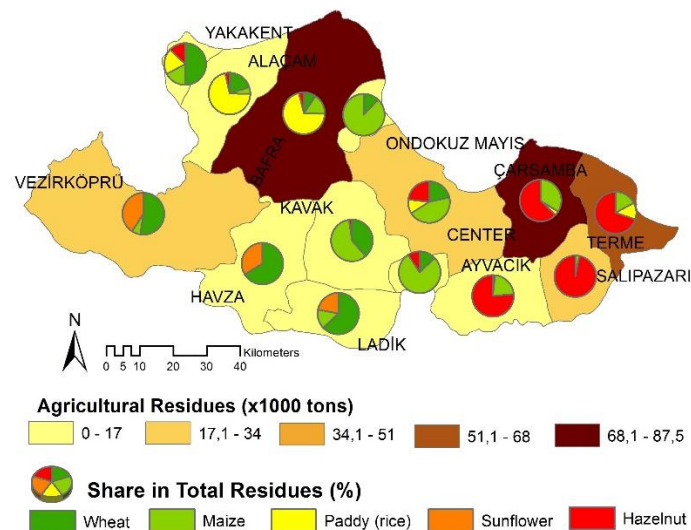


Figure 1. The distribution map of agricultural residues in Samsun Province

Although, the total production of crop residues in the province amounts up to 366.6 kt.a⁻¹, it may be noted that there is a wide variability in the availability of crop residues within the province. The Bafra district produces maximum crop residues (87.43 kt) followed by Carsamba (82.8 kt), and Terme (55 kt), More than 60% of the total residues are produced in these district. It is believed that there will not be a shortage of raw materials for the investment and facilities to be made for obtaining energy from agricultural residues in these three districts.

Hazelnut is the product with the highest residue potential in Salipazari, Ayvacik, Terme and Carsamba districts. It is observed that maize has the highest residues potential in Asarcik, Kavak, Ondokuz Mayıs, and Center. Besides, it has been determined that paddy in Bafra and Alacam, wheat in Ladik, Havza, Vezirkopru and Yakakent is the product with the highest residues potential.

It was calculated that the total heating value of the agricultural residues was about 6.46 PJ (154.25 ktoe) for the production period of 2016 in Samsun province. The heating value of agricultural residues calculated separately for each product is given in Table 4. The distribution map was given Figure 2.

Table 4. Total heating value of agricultural residues in Samsun Province

Field Crops	Residues	Total Heating Value (THV) (GJ)
Wheat	Straw	696,923
Barley	Straw	49,036
Maize	Stalks	813,008
	Cob	517,513
Paddy (rice)	Straw	900,836
	Husks	360,088
Sunflower	Stalks	181,711
Soybeans	Straw	102,586
Fruits Crops		
Hazelnut	Shell	315,124
	Husks	261,243
Walnut	Pruning	2,159,794
	Pruning	34,488
Peach	Pruning	49,050
Kiwi	Pruning	12,018
Vineyard	Pruning	4,787
TOTAL		6,458,205

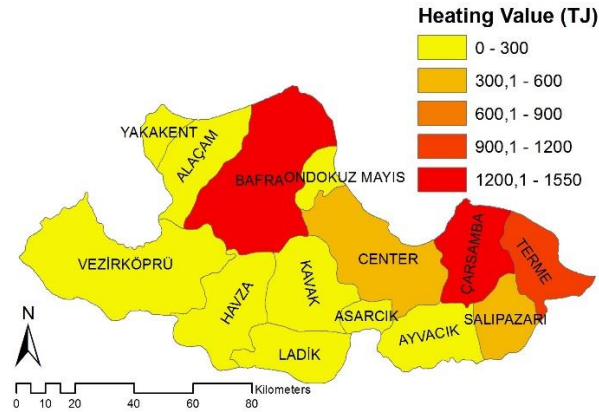


Figure 2. The distribution map of heating value based on agricultural residues in Samsun Province

These maps (Figure 1 and 2) showed that the potential of agricultural residues concentrated in the Bafra and Carsamba districts. In particular, it is observed that the type and distribution of residues in Bafra district, the distribution of agricultural residues according to heating value is ranked as paddy (rice) (65.8%), maize (10.2%) and wheat (4.33%) respectively. In Carsamba, this ranking consists of hazelnut (59.4%), and maize (32.3%) respectively. Despite these facts, until now, there has not been any investment in these areas related to agricultural residues, which have a great potential for conversion to energy. However, the results of this study show that such a large potential necessarily has to be evaluated by establishing modern facilities.

4. CONCLUSION

Turkey is an energy importing country. Therefore, the importance of such kinds of researches is very high. The amount and distribution of agricultural residues in districts of Samsun were given both in tables and on the maps. Samsun has important district (Bafra and Carsamba) in Turkey, especially regarding the potential for hazelnut and paddy crop residues.

A number of crops such as hazelnut, paddy, maize, cereal crops, and sunflowers have been identified in this study for energy production. Total biomass potential in districts of Samsun province represents a significant contribution to renewable energy. But, this potential has to be utilized adequately.

GIS maps show the differences among the districts. In this sense, awareness of public and policy-makers' could be increased on this matter. Consequently, agricultural residues are a very attractive choice, since it is economical, sustainable, environmental friendly and a familiar energy source for Samsun Province.

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The Importance of Waste and Environment Management in Printing Industry

Pelin HAYTA^{1}, Mehmet OKTAV²*

Abstract

All kinds of materials that become useless during production activities, damage the environment and must be exterminated are generally called waste. Waste is also defined as all materials thrown away by its manufacturer or a person or entity who owns it and causes a harmful change at environment.

The most important of the solid, liquid and gaseous wastes produced in the printing industry before, during and after the printing process are waste ink, ink sludge and solvents emerging after machine washing, wastewater of water-based ink, plate and film developer and fixer solutions, waste papers, waste films, faulty prints, cleaning solvents and volatile organic compound (VOC) emissions emerging from IPA use. Some of these wastes fall into the hazardous waste category due to their processing characteristics during the production process. Effective and regular extermination of these wastes is necessary to protect the environment and employee health. This can be provided only by the application of waste management. Some wastes are recycled and reused at printing industry, but in some cases that recycling is impossible, these wastes should be eliminated without harming human health and environment. Especially the materials whose disposal is compulsory should be classified at the source and sent to licensed disposal companies.

As a new sector, waste management industry should develop new and special processes for printing technologies wastes. Owners of printing companies should be informed about waste management. At waste management process, the most appropriate clean production techniques should be used, waste production should be prevented or minimized and wastes should be recycled effectively.

The aim of this study is to provide suggestions and contributions for the possible best ways of preventing the wastes from harming the nature and disposing or recycling of the wastes generated during production in the printing industry.

Keywords: *Waste Management, Printing Wastes, Protecting the Environment*

1. INTRODUCTION

Systems created and sustained by interrelationships between living creatures within a certain area and surrounding inanimate environments are named as "ecosystems".

An ecosystem is consisted of four fundamental components: autotrophs, heterotrophs, saprophytes and habitat. The first three components represent living creatures existing within the inanimate environment created by the latest component. External factors affecting the rings of the habitat chain causes all the system to be harmed. Especially unconscious management of wastes, which is defined as all kinds of materials occurred and thrown away or left as a result of any activity in Environmental Laws, has a great effect on imbalance of ecosystem and rapid exhaustion of natural resources.

As a sector having a close interrelation with environment, printing industry is bound to natural raw materials for paper, ink and printing auxiliary production. As the source of cellulose, trees are highly needed especially in paper manufacturing sector. Trees also have a fundamental role in human life as source of oxygen. During production process, paper manufacturing sites use chemical auxiliaries and pollute the environment by releasing wastewater, chemical gases and various solid wastes besides exhausting oxygen sources rapidly by using trees in production. Usage and waste of paper as an end product requires a reproduction process using raw materials and creating waste. Therefore, paper recycle has an important role in ecosystem

^{1*} Corresponding author: Sinop University, Gerze Vocational High School, Department of Graphic Design, 57600, Gerze/Sinop, Turkey.
pelin@hayta.com.tr

² Marmara University Vocational High School of Applied Sciences, Istanbul, mokratav@marmara.edu.tr

balance in terms of causing a dramatic decline in waste production and tendency of using natural raw materials. When used and wasted without waste management, ink, plastics, bath waters of films and plates and chemicals also become hazardous wastes polluting air and water.

Global Footprint Network, a company studying on human-based consumption tendency on world scale, has stated that the amount of the sources consumed at first 7 months of 2017 is higher than the amount that can be renewed in 12 months. This means humans released carbon, fished, logged and consumed water in an amount beyond the tolerance limit of oceans and forests. [1].

Waste is defined as something lying unproductive, inhabited, or desolate. Generally all waste appears in three forms, namely: solid waste, wastewater (liquid waste), and air emission [2].

Wastes generated in the printing house must be disposed of. The disposal methods can cause a serious threat to the environment and human life [3].

Ink, paper and chemical wastes may be solid, liquid and gaseous in printing industry. Management of these wastes is highly important in terms of minimizing the harms given to human and nature besides raising recycle awareness. By integrating consumed materials in production process, we may help ecosystem to become a renewable source in frame of sustainable life principle and economic growth.

2. EMERGENCE AND RECYCLING OF PRINTING INDUSTRY WASTES

The printing industry uses various printing technologies for printing books, magazine, newspapers, business documents, catalogues, form, etc. These technologies include lithography, rotogravure, flexography, screen, letter-press, and digital technologies including inkjet and electro-photography. The use of these technologies depends on the required quality of the print, number of impressions to be printed, availability of required resources, cost of the equipment, consumables cost per unit, need to use variable content, and other factor [4].

Printing process requires various fundamental printing technologies. Raw materials and chemicals used in production generate or become waste, as water used in some printing systems.

When the waste generated causes financial loss to a company and poses a threat to the environment-air, water, and land, then it becomes a problem to society at large [5].

The waste emerging in production process of printing system should be studied, categorized and treated according to an appropriate waste management procedure.

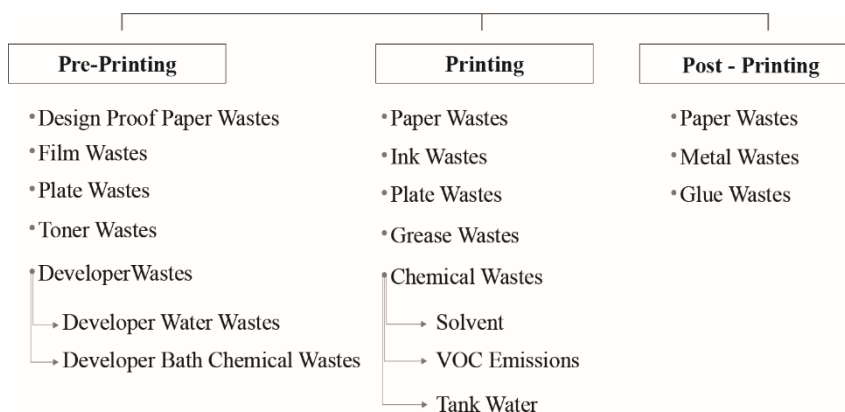


Figure 1: Printing Wastes [6], [7]

2.1. Inks

Ink is the diffusion of colouring agents in an adhesive system and transfers the image on a swage plate material. Inks generally consist of four fundamental materials; pigment, adhesive, solvent and additive agents. Liquid and badigeon inks contain pigment or colorants. Heavy metal content of this colorants pollute environment via waste inks. Titanium dioxide, chromate and molybdenum are some of the heavy metals used in printing inks.

Badigeon inks are used in offset, letterpress and sometimes screen printing systems while liquid inks are used in flexo and gravure printing systems. Solvents in liquid inks used in flexo and gravure printing systems are inflammable. Moreover, toluene in gravure ink is a toxic and inflammable material. Web offset inks also contain high levels of volatile organic compounds (VOC). When the solvents are volatilised and inks are used uncontrolled, these substances pose danger for human health [8].

According to the report of Trucost, a company providing consultancy service about environment and waste, printing plants affect environment by not only waste amount, but also greenhouse gas (disposed to be stored, burnt, reused or recycled) and volatile organic compounds (Volatile Organic Compound – VOC, except metan) they release. [9], [10].

Table 8. Sample formulations of gravure inks

[43]. General	[44]. Printing	[45]. Packaging	[46]. Water-based Printing Inks
[47]. %20 Pigment and Toner	[48]. % 8 Phthalo Blue	[49]. %33 Titanium Dioxide	[50]. % 15 Phthalo Blue
[51]. %28 Resin	[52]. % 15 Chlorinated Rubber	[53]. %22 Nitrocellulose Varnish	[54]. %47 Acrylic Resin
[55]. %47 Solvent	[56]. %10 Phenolic Modified Resin	[57]. %37 Resin Ester Varnish	[58]. %30 Aqua
[59]. %5 Wax, Plasticiser and Additive Agents	[60]. %5 Plasticiser	[61]. %3 Plasticiser	[62]. %2 Alkali
[63].	[64]. %1 PE Wax	[65]. %5 Wax Compounds	[66]. %1 Foam Inhibitor
[67].	[68]. %51 Toluene	[69].	[70]. %2 PE Wax
[71].	[72]. %10 Ethyl Acetate	[73].	[74]. %3 Isopropanol

All solvents in printing inks (except water) are air contaminants. Therefore, waste printing inks should be recycled in frame of a controlled transformation procedure in order to protect human health and environment. The best method of controlled transformation is recycling or burning the solvent. While liquid inks as flexo and gravure ink solvents are generally recycled, web offset inks tend to be burnt.

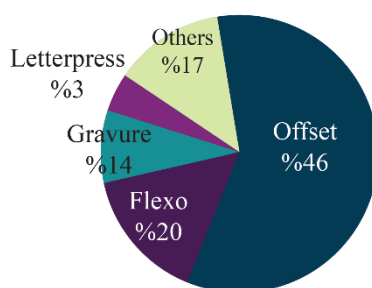


Figure 2: Ink consumption in 2012 according to worldwide printing techniques [11].

Flexo and gravure inks are recycled by a technique requiring organic solvents in printing press dryer exhaust to be imposed in a cabinet frozen by activated carbon and transferred to another cabinet to be cooled. When the exhaust is refrigerated, vapour and solvents are condensed and split into two layers and recycling process is over. Recycled solvents are re-integrated into production process by being sold or reused as a diluting solvent in printing press.

Burning: burning is the best technique to minimise final waste amount besides generating energy as an important recycling product. Moreover, burning is the most expensive recycling method [12].

Burning method aims to neutralise or shrink hygienically or, if economical, use the solid wastes for generating energy [13]. Solvents are burnt and eliminated by three methods; thermal burning, catalytic burning and cooling-condensation.

2.2. Paper / Paperboard in Press Industry

Printed papers are used in a wide range of products as books, magazines, newspapers, cardboard boxes, labels, etc. Paper is defined as printable sheets produced from pulp consisting of virgin fibres obtained from herbal cellulose via mechanic or chemical methods or fibres of used papers [14]. Pulp is the fundamental of all paper types and consists of cellulose, fibres and additive agents. Cellulose is the raw material of paper production process and obtained from trees which are at least 50% cellulose, some plants that are 98% cellulose and recycled papers.

When growth period and production volume of trees and other plants integrated in production process, it can be seen that amount of consumed trees and plants affect the ecosystem.

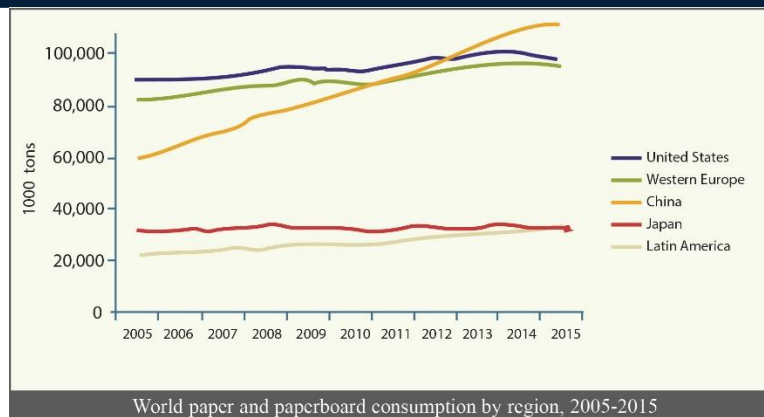


Figure 3: World paper and paperboard consumption by region, 2005 -2015 [15].

Besides a constant growth in production, it is also predicted that volume of paper and paper products will reach at 279 million tonnes in 2018 [16]. This figure shows that production process is in a huge need of raw material. When waste papers are recycled and integrated into production, less amount of raw material will be provided from environment and production costs will be reduced. Moreover, paper recycling enables to save from energy and water resources.

Recycling methods of paper wastes are defined according to paper quality and fibre structure of the papers. Each recycled kinds of paper cannot be integrated in each paper type. For example, as cardboard and corrugated cardboards cannot be used in newspaper production, paper wastes should be categorized after collected. Therefore, there are two types of processing before recycling;

- Special mechanical cleaning process not requiring cleaning the ink. They are integrated in cardboard and corrugated cardboard production processes.
- Mechanical and chemical cleaning process requiring cleaning the ink. Fibres integrated in newspaper, printing paper and carbon paper production process.

The first phase of recycling process is categorisation of papers. Categorisation process is carried out via an infrared sorting machine (this machine is developed by SORT IT European Union Research Project and used in a waste sorting plant in Linz, Austria, where papers coming from all over the Europe are sorted). Halogen lamp in the machine illuminates the wastes to be sorted. The light causes organic substances in papers to vibrate and give some kind of spectral fingerprint according to their compounds. By this means, inky and inkless products can be separated. Sorted papers are then cleaned at pulp production unit by being divided into fibres, grinded, bleached and washed. Then, fibres are transferred into machine approach unit and mixed and diluted. While this process is being carried out, the mixture is sent to pulp mixing unit after required chemicals and fillings are added. Paper machine then produces recycled paper by sieving, pressing, drying and calendaring the pulp coming in a certain thickness and width.

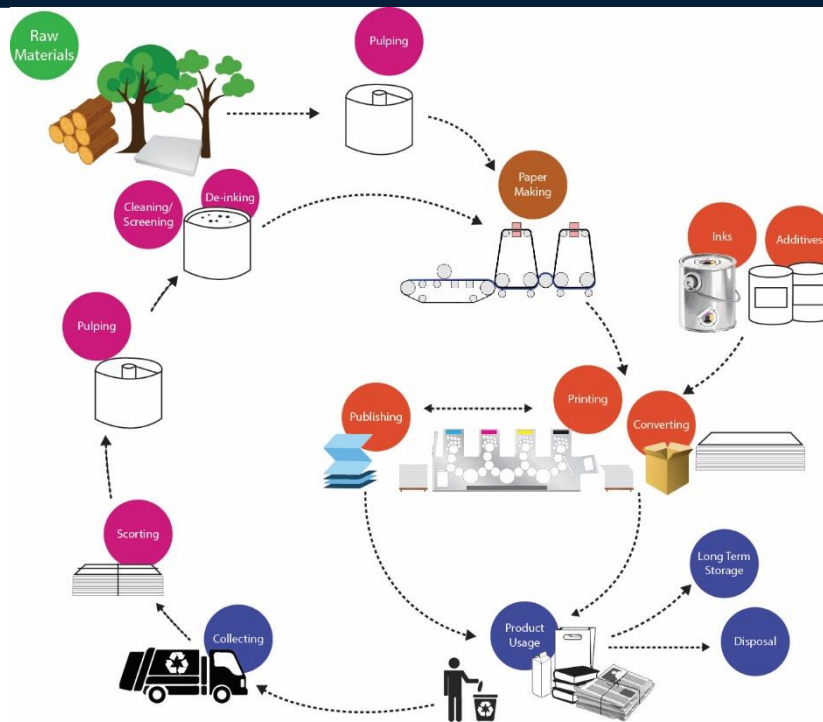


Figure 4: Recycling and Reuse of Waste Paper

Most of the digital and inkjet-printed papers were not be able to be recycled because of the surface coating enabling printing until recently. Organizations as International Association of the Deinking Industry (INGEDE) supporting researches carried out in deinking and collaborating with paper and press machine manufacturers, paper termination industry and additive agents suppliers has been seeking solutions for this problem. Digital Print De-inking Alliance (DPDA) has succeeded in most of the deinking tests on inkjet-papers recently [17]. This developments in paper recycle are shows that special papers produced for printing press can be recycled and integrated in production process in accordance with technological possibilities.

It is seen that recycling waste paper enables to save from water and energy needed for production. Figure 5 shows the advantages of paper recycling according to The State of the Paper Industry, Monitoring the Indicators of Environmental Performance-[15].

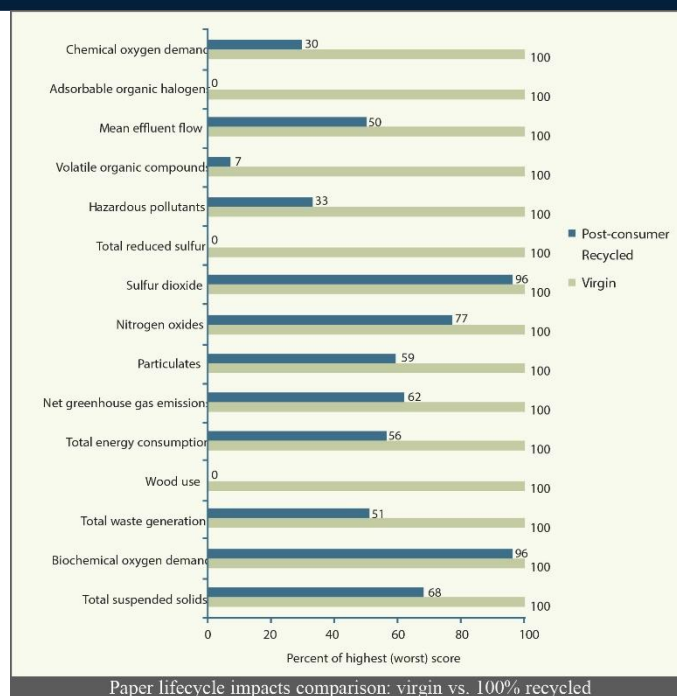


Figure 5: Paper lifecycle impacts comparison: virgin vs. 100% recycled.

2.3. Water and Chemicals

A great amount of wastewater can easily be generated during the printing process, due to the usage of chemicals that are either toxic or difficult to decompose: ink residues (containing zinc, chromium, barium, lead, manganese, benzene, dibutyl/ethyl acetates); waste fountain and cleaning solutions (spent organic solvents, including trichloroethane, methylene chloride, carbon tetrachloride, acetone, methanol); and other solvents and container residues (toluene, xylene, glycol ethers, methyl ethyl ketone, and ethanol). The greatest attention in printing industry deserves a purification and regeneration of wastewater [18].

Each phase of printing process, re-printing, printing and post-printing, generates chemical wastes. While pre-printing process generates plate bath chemicals and bath water wastes, in printing process ink, solvent, roller/plate/blanket cleaners, varnish, UV lacquer and tank water wastes and in post-printing process adhesive and varnish wastes emerge.

When the volume of printing industry is considered, the level of the damage caused by chemical wastes and water wastes can be understood better. Especially toluene, xylene, isophorone and solvents are the most hazardous chemicals. While toluene and xylene are compounds of ink, isophorone is found in some printing inks and adhesives. Solvents are chemicals used for different purposes.

Solvents are mostly used in;

- Flexo printing, gravure printing and screen printing as diluting solvent,
- Roller and blanket cleaning chemicals,
- Plate cleaning chemicals,
- Plate bath chemicals.

Chemical wastes (solvent, ink wastes or tank water wastes) should be burnt by using air filters and recycled by professional chemical waste recycling companies in accordance with related laws. Besides chemical wastes, tank water wastes and bath water wastes are released into environment in various ways and pollute the environment by going into sewage. Manufacturers should be linked to water infrastructure plants via sewage systems to exterminate wastewater. In this way, wastewater can be sorted and exterminated besides preventing contamination of underground waters, seas and potable waters.

2.4. Waste Gases

VOCs are defined as organic substances in 293,15 Kelvin (20°C) and 0,01kPa or higher vapor pressure. [19].VOC is the abbreviation of volatile organic compound. VOCs are chemical having the potential of harming people and human health.

Some international regulations and legislation have been made and some precautions have been taken to decrease VOC emission amount and protect human health. These regulations decrease the limit the amount of solvent used in chemicals used for various purposes as pickling to 20%.

A Volatile Organic Compound (VOC) contains one or more carbon atoms and has a high vapour pressure that allows it to readily evaporate into the atmosphere. Once in the atmosphere, the compound participates in atmospheric photochemical reactions. Ground-level ozone is produced when nitrogen oxides and volatile organic compounds (VOC's) react in the presence of sunlight. This is a major component of urban smog, which, at elevated levels, presents a potential health hazard to people of all ages and possibly damages vegetation and degrades the environment [20].

A number of industrial activities make use of chemical products containing volatile organic compounds (VOCs), which are widely used mainly due to their high volatility. Among the activities that can result in the emission of such compounds in its working environments are the offset printing processes. The main indoor sources for VOCs are solvents and inks in the printing industry due to their low vapour pressure, significant amounts of toluene, xylenes, and other volatile compounds are emitted during the printing process, polluting the workplace environment. In addition, the cleaning procedures can result in exposures that are ten times higher than during other tasks because these cleaning products are petrol-based. The inks used in the offset process are made basically of a mixture of resins, vegetable or mineral oils, pigments, and solvents. The main ingredients of the conventional inks are pigments, binders, carriers and additives [21]. Volatile organic compounds (VOC emissions) consist the 98% or 99% of all toxic gas emissions generated by printing industry. VOC emissions emerge during cleaning of printing solutions, adhesives used in binding and drying phases [22].

3. WASTE MANAGEMENT

Waste management includes environment management activities as diminishing the waste at source, sorting, collecting, temporary storage, interim storage, recycling, exterminate and post-extermination control [23].

Waste management in printing industry varies according to each manufacturer activity and producing process. When pre-printing, printing and post-printing processes are considered, waste management should be applied according to raw material usage and production style. Therefore, ink wastes, paper and paper product wastes, wastewaters and chemical wastes require different waste and environment management methods.

The first aim of waste management is to prevent waste generation as much as possible or recycling the wastes. Accordingly, each manufacturer should define a system in accordance with his/her production style and raw material usage to be able to apply a waste management procedure. Figure 6 shows a general waste management sample in printing industry.



Figure 6: General waste management in printing industry

In waste management process ink wastes, wastewater and waste gases are the types requiring some precautions. These wastes contain hazardous chemicals and therefore should be eliminated after use.

The fundamental precaution is to use vegetable-based inks without heavy metals for printing and to keep the cap of the ink containers tightly closed not to contact with air. Printing process should be carried out in rooms including air tunnel to prevent emergence of waste gases. Moreover, required precautions should be taken to prevent chemicals to contact with human body.

As ink wastes, wastewater, chemical wastes and waste gases are impossible to be recycled, these should be exterminated in accordance with related laws.

Paper and paper wastes are recyclable within waste management system. Process of sorting after production, transferring to recycling plants via paper collecting companies and recycling the papers raises energy save in environment management besides diminishing raw material need to be met from nature.

4. CONCLUSION AND RECOMMENDATIONS

This study examines environment and waste management approach in printing industry. Each production step of printing process generates waste. These wastes may be categorized as solid, liquid and gaseous wastes and some are defined as hazardous wastes. Especially in preventing or recycling of hazardous wastes, printing industry should apply and appropriate waste management procedure.

Printing sector mostly generates paper and cardboard wastes. Paper and cardboards are one of the oldest and most used packaging materials and generate some of the wastes in edge trimming and sizing process, some in printing adjustment process and some in post-printing process. Most of the paper and cardboard wastes can be recycled and integrated as secondary fibres to production process after sorted, washed and deinked. This provides cellulose, the fundamental raw material of paper, to be originated from recycled papers to an extent. Recycling method of paper wastes should be defined according to paper quality and fibre structure.

The second printing material generating most waste is ink. Ink wastes emerge in post-printing phase but they are also hazardous in printing and post-printing phases, because the solvents they contain evaporates and pollutes air (except water-based inks). Therefore, inks should be recycled under control. The safest ways to recycle inks are recycling or burning the solvent they contain. While flexo and gravure inks are generally recycled, web offset inks are burnt. Besides recycling and extermination, modifying production process to prevent wastes is a method of avoiding wastes. This can be realised by use of water or vegetable-based inks in production.

VOC emissions evaporate as gaseous wastes and in hazardous waste class as toxic chemicals in printing industry. Most of the chemicals used in either pre-printing, printing or post-printing phase of each printing technique contains VOC emissions and requires some precautions. These precautions are to use water-based and organic solvents, use CTP while preparing printing press and preferring dry printing.

Waste management process should be carried out in frame of clean production techniques protecting environment and human health and aiming sustainable no waste production. Waste and environment management is also important in terms of maintaining the sustainability of ecosystem besides getting economic advantage by minimizing costs. Preventing the emergence of solid, liquid and gaseous wastes and recycling or extermination of the used products have become a necessity for protecting environment and human health.

When worldwide production volume of printing industry is considered, it can be seen that consumption may be integrated in production by collection, transfer and recycling of all types of wastes. Recycling and reuse of especially paper and cardboard wastes originated from natural raw materials diminish costs, saves energy and supports national economy. Therefore, each manufacturer should define a waste management plan considering its operation style and raw material type it uses. In frame of this plan, manufacturers should pay attention to prefer eco-friendly raw materials, minimizing waste generation in production process and recycling the generated wastes. Usage of non-recyclable and hazardous raw materials should be kept under control.

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Histo-cytological study of *Sternbergia lutea* (L.) Ker-Gawler ex Sprengel in National Park of Llogara, Albania

Matilda SHEHU^{1*}, Zhaneta ZEKAJ (TROJANI)¹

Abstract

In this paper was realised histo-cytological study of *Sternbergia lutea* (L.) Ker-Gawler ex Sprengel in National Park of Llogara. The study was conducted in the framework of PhD thesis on the diversity of flora of Vlore area in Albania. The karyotype of *S. lutea* L. was examined for first time in this habitat.

For histological analysis was performed the Colloidal Technique with nail polish, through which we determined the type of leaf, the distribution of stomata per unit area and the type of stomata. This technique consists in obtaining the stomatal traces in the upper and the lower epidermis of the leaves of *S. lutea*. For chromosome analysis (chromosome number and morphology of chromosomes) was performed the Squash Technique. Preparations were made from root tips pretreated with colchicine and stained with aceto-orcein.

Histological analysis showed that the leaves are of the amphystomatic type, the stomata are of the anomocytic type and the distribution of the stomata per unit area is higher in the lower epidermis. Karyological analysis revealed the chromosome number $2n = 22$. In metaphasic cells was observed 2 large metacentric chromosomes (one of them with satellite), 4 small metacentric chromosomes (one of them with satellite), 9 submetacentric and 7 subtelocentric chromosomes.

Keywords: *Sternbergia lutea*, histological analysis, cytological analysis, squash technique, colloidal technique

1. INTRODUCTION

Sternbergia lutea Ker-Gawl. is a bulbous flowering plant in the family *Amaryllidaceae*, subfamily *Amaryllidoideae*, [1] which is cultivated since ancient times as ornamental plant. It has yellow flowers which appear in autumn before the leaves and grows at altitudes 200-1000 metres above the sea level. *Sternbergia* is a genus containing mostly remarkable autumn flowering taxa within *Amaryllidaceae* [2] which was described by Waldstein & Kitaibel (1803) and the name was dedicated to the memory of the Hungarian botanist Caspar von Sternberg (1761-1838). The distribution range of the genus goes all across the Mediterranean, SE Europe and W Asia. Currently genus *Sternbergia* includes 9 species two out of which occur in Albania: *S. colchiciflora* Waldst. et Kit., and *S. lutea* (L.) Ker Gawler ex Sprengel [3]. In this paper *Sternbergia lutea* Ker-Gawl. has been studied histologically and cytologically. Histological (stomatal analysis) and karyological analysis has been performed for the first time for this specie in Llogara Albania. The main aim of this study has been to contribute with new data in histo-cytology of this specie in the Mediterranean region. There are no data from other authors about stomatal features for this specie.

While from a karyological point of view *S. lutea* is the most frequently studied taxon of the genus. Many different chromosome numbers ($2n = 12, 16, 18, 20, 22, 24, \text{ and } 33$) have been published for it by many authors [4],[5],[6],[7]. [8] have added one more differing number ($2n=3x=30$). Detailed karyotype studies of *S. lutea* (L.) from Italy [9], [10], ex-Yougoslavia [11], Greece [12] all gave basic chromosome number $x=11$. Number $2n = 33$ was reported for cultivated populations.

^{1*} Corresponding author: Department of Biology, Faculty of Technical Sciences, University of Vlora "Ismail Qemali", L. Pavarësia, Rr. Kosova, 9400 Vlorë, Albania.
 Department of Biotechnology, Faculty of Natural Sciences, University of Tirana, Blv. Zogu i I, Tiranë, Albania
matildazeqo@gmail.com, zhaneta.trojani@fshn.edu.al

2. MATERIALS AND METHODS

Plant material was collected in National Park of Llogara Albania and planted in pots for subsequent studies. For histological analysis was performed Colloidal Technique with nail polish [13], which consist of taking stomatal traces in upper and lower epidermis. Was determined stomatal type, stomatal density and stomatal index. Stomatal types were determined based on the classification of stomata on the grounds of nature and number of subsidiary cells [14], [15]. Stomatal Index (SI) was determined using the formula, given by [16],[17]:

$$SI = \frac{S}{E + S} * 100$$

S: Number of stomata per unit area. E: Number of epidermal cells per unit area.

The stomatal density was determined as number of stomata in 1mm² of the microscopic field at 40x magnification under Paralux microscope.

The number of chromosomes and their morphology have been studied in the mitotic division of somatic cells from root-tips. For cytological analysis was performed Squash Technique according to [18]. Karyotype formulas and terminology are according to [19]. Processing of chromosome measurements was carried out with Cromo2 software [20] (as cited at [21]) to build the karyogram and idiogram.

3. RESULTS AND DISCUSSIONS

3.1 Histological traits

Observations are realised in the upper and lower epidermis of the leaves of *Sternbergia lutea* L. Histological analysis showed that the leaves are of the amphistomatic type where stomata are present on both sides of the leaf. At lower epidermis stomatal distribution per unit area is higher than in upper epidermis. Also Stomatal Density and Stomatal Index is higher at lower epidermis (Table1). This result is also obvious in Figure 1.

Table 1. Stomatal measurements in the upper and lower epidermis of the leaves (mean values ± standard deviation)

Cv- coefficient of variation

<i>Sternbergia lutea</i> L.	Stomatal number	Length (µm)	Width (µm)	SI (%)	SD
U.E	14.5 ± 2.4	42.9 ± 4	32.8 ± 3.9	30.9 ± 3.2	77.2 ± 12.9
Cv	16.8	9.4	12	10.4	16.8
L.E	16.9 ± 2.6	49.2 ± 3.1	36.1 ± 3.9	36.7 ± 3.3	90 ± 13.8
Cv	15.4	6.4	11.1	9.1	15.4

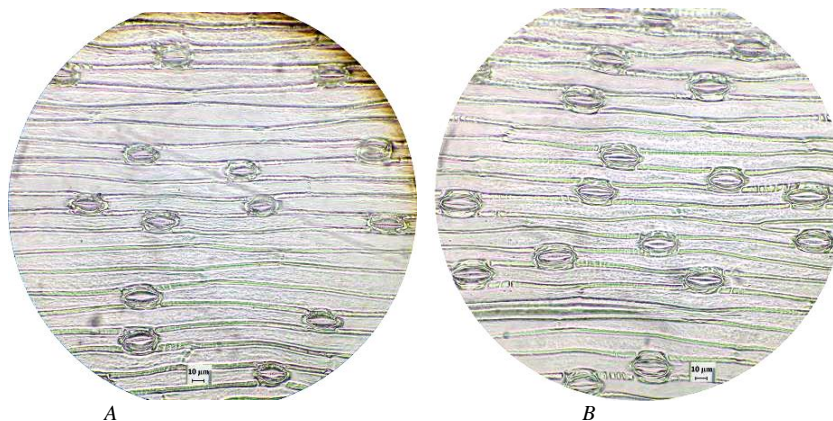


Figure 1. Stomatal distribution in *Sternbergia lutea* (L.) Ker-Gawl. A) upper epidermis, B) lower epidermis (magnification x40 with Paralux microscope)

Epidermal cells are elongated and located parallel to the axis of the leaf and to the axis of stomata (Figure1). This complies with the report of [22] that stomata of monocotyledones are parallel to the axis of the leaf.

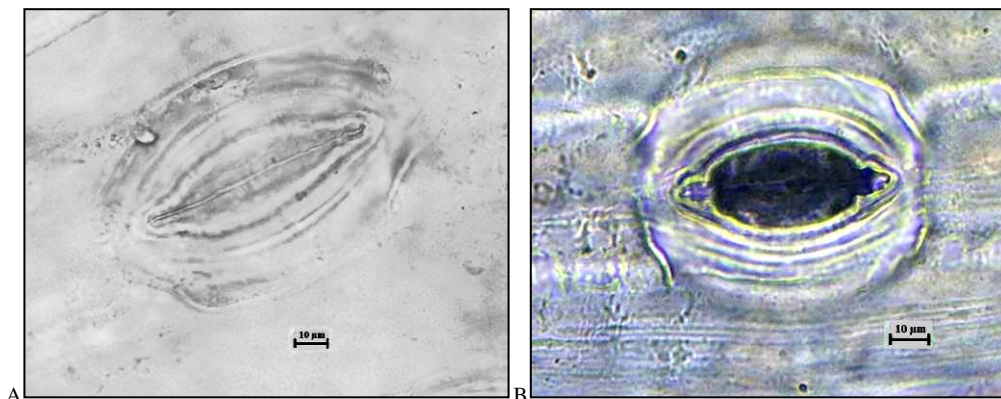


Figure 2. Stomatal type in *Sternbergia lutea* (L.) Ker-Gawl. (x100 magnification with Paralux microscope), A) upper epidermis B) lower epidermis

Regarding the stomatal dimensions were reported stomata with larger size in the lower epidermis than in the upper epidermis (Table 1 and Figure 2). Stomata are of the anomocytic type (with no subsidiary cells) and sunken into the epidermal cells (Figure 3). Our observation complies with the report of [23] which observed that in *Amaryllidaceae* stomata have two guard cells without any subsidiary cells. This type of stomatal complex may have originated under relatively dry condition [23]. *Sternbergia lutea* (L.) Ker-Gawl. grows on dry and shrubby habitats [3]. Maybe this is the cause why in this species are present anomocytic stomata.



Figure 3. Cross section of the leaf of *Sternberia lutea* (L.) showing sunken stomata (at x100 magnification Paralux microscope)

3.2 Cytological traits

Karyological analysis revealed the chromosome number $2n = 22$ (Figure 4); this number also reported for populations of Italy, ex-Yougoslavia, Turkey and Greece, different from other authors which reported chromosome number ($2n = 12, 16, 18, 20, 24,$ and 33).

2 large metacentric chromosomes (one of them with satellite), 4 small metacentric chromosomes (one of them with satellite), 9 submetacentric and 7 subtelocentric chromosomes in metaphasic cells were observed. Satellite at small metacentric chromosome (m) was found to be in bigger sizes than satellite in large metacentric chromosome (M) (Figure 5 and Figure 6).

Karyotype formula according to [19] was determined $2n = 22 = 2x = 1M + 1M^+ + 3m + 1m^o + 9sm + 7st$. All chromosomes are relatively long. The observed chromosomes are mainly submetacentric. The same has been reported in 1970 for *Sternbergia lutea* (L.) Ker-Gawl. in ex-Yougoslavia (in Dojran of Macedonia)[11].

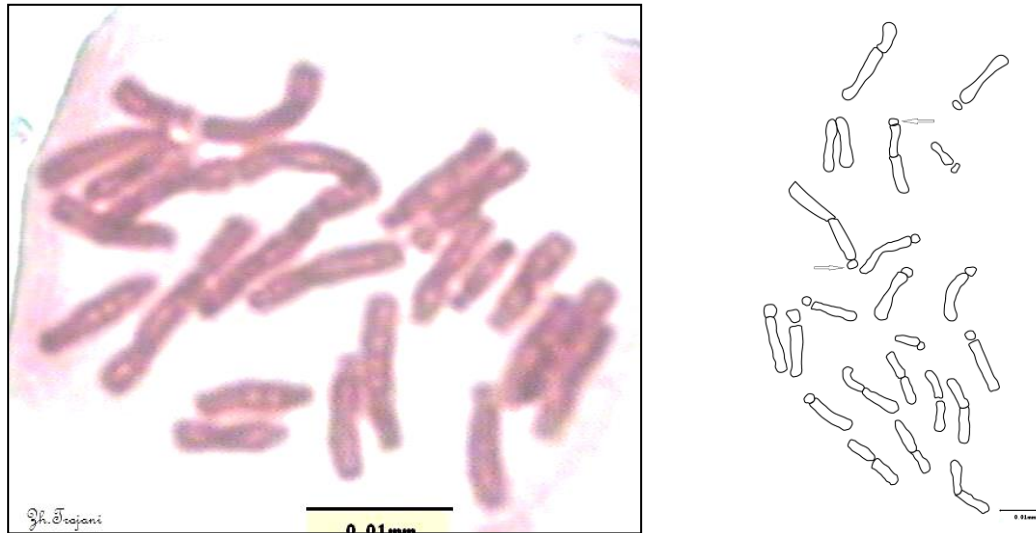


Figure 4. *Sternbergia lutea* (L.) Ker-Gawler ex Sprengel: A) Mitotic metaphase plate, showing $2n = 22$ chromosomes B) sketches of chromosomes (arrows show satellites)



Figure 5. Photokaryogram of *S. lutea* Ker-Gawl.

Different from populations in Italy [24], Greece [11] and Turkey [25], where chromosomes are mainly subtelocentric and telocentric. *Sternbergia lutea* (L.) Ker-Gawl. of Llogara Albania, is closer to the population of ex-Yougoslavia (in Dojran of Macedonia) [11] where chromosomes are mainly submetacentric. Figure 6 shows karyogram and idiogram of *S. lutea* (L.) Ker-Gawl. They represent the typology, sizes of the chromosomes and the number and position of satellites in the haploid and diploid chromosomal set.

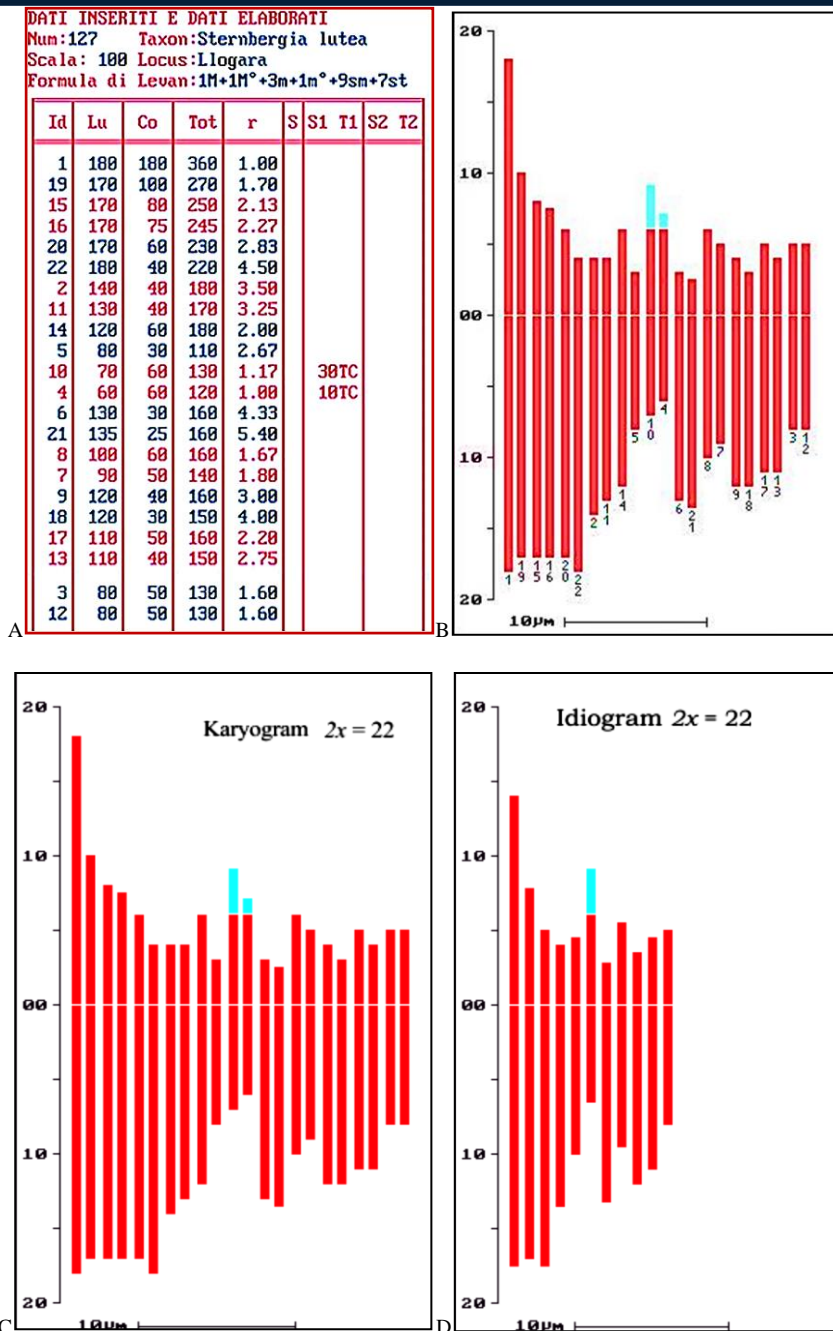


Figure 6. *Sternbergia lutea* (L.) Ker-Gawler ex Sprengel. A. Table with data for chromosomes(long arm, short arm, arm ratio, satellites), B. Numeric karyogram, C. Karyogram, D. Idiogram

4. CONCLUSIONS

In this study histological analysis of *Sternbergia lutea* Ker-Gawl. revealed anomocytic stomata which complies with the report of [22]. Stomatal distribution were higher at lower epidermis. As a result SI and SD were higher at lower epidermis. Our observation reported bigger size stomata at lower epidermis.

Karyological analysis revealed the chromosome number $2n = 22$, the same as reported for populations of Italy, ex-Yugoslavia, Turkey and Greece. Typology of chromosomes resulted different from population of Italy, Turkey and Greece but is closer to the population of Macedonia (Dojran). In this case we have a new cytotype which can be added to the cariology database of this specie in the Mediterranean region.

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Soil Dust Emissions and Their Reduction by Planting Windbreaks

David REHACEK^{1,1}, Tomas KHEL², Anita PETRU³*

Abstract

Recently, long periods of drought are being observed more often during the summer and temperature fluctuation around freezing point in the winter. Such conditions together with unsuitable agricultural management cause increased soil vulnerability to wind erosion. Loss of dust soil particles is a degradation process that causes damage to soil, crops, surface water bodies and it can be connected with numerous health hazards. Windbreaks represent effective protection measure, acting as a natural barrier with enormous ability for wind speed reduction. In this study, measurements of wind speed along windbreaks at 3 experimental plots were carried out. The wind speed was measured by anemometers at height of 1 m above surface. 3 anemometers were set on the windward side and 5 anemometers on the leeward side of the windbreak. The effect of windbreak on wind speed reduction was assessed and put in context using data describing value of optical porosity, height of the windbreak and took into consideration the specification of windward and leeward side. A substantial effect was observed on the leeward side at distance of 12 times the windbreak height. The effect on the windward side was less significant. The size of the protected area correlated with the value of optical porosity which mostly influences wind speed reduction. The porosity is influenced by seasonal changes and by level of foliage density.

Keywords: *Air Circulation, Dust Emissions, Optical Porosity, Soil Conservation, Windbreaks*

1 INTRODUCTION

Soil erosion is a natural and dynamic process caused by detaching and relocation of soil particles. Soil erosion can be caused by different factors and forces, such as water and rain, ice, wind, gravitation or tillage. This paper deals with wind erosion. In general, soil is resistant to certain threshold of wind velocity. In case of increasing wind velocity beyond this threshold, soil particles are detached and relocated by air suspension to a new position. Soil resistance depends on soil, geologic, climatic and anthropogenic factors [1]. The factors which have impact on soil resistance are surface roughness, soil texture, soil aggregation, soil moisture, agricultural activities, vegetation cover, freezing and thawing cycles, the plot size and orientation [2, 3].

Moreover, wind erosion causes soil degradation and simultaneously it poses problems in terms of dust aggradation in natural and inhabited area. Wind erosion brings about other soil degradation processes. Furthermore, dust emissions contained in the air have a harmful impact on human body [4]

Planting windbreaks represents a reliable method how to permanently prevent soil loss [5]. Windbreaks reduce wind velocity and thus the amount of detached particular is decreasing. Appropriate windbreaks arrangement can reduce soil losses up to 80% [6]. Linear character of woody vegetation can be determined as windbreak. Windbreaks have a positive impact on soil erosion and, moreover, on micro climate surrounding the windbreak, i.e. temperature, soil moisture, evapotranspiration, soil temperature etc. [7]. The windbreak structure is determined by the number of tree rows, distance between each woody plant, foliage density and structure of branching, which is established by used woody plants creating the windbreak [8]. Mostly, the windbreak structure is described as a value of optical porosity determined by using photogrammetry methods [9].

^{1*} Corresponding author: Research Institute for Soil and Water Conservation, Department of Soil Science and Soil Protection, Zabovreska 250, 156 27 Prague, Czech Republic rehacek.david@vumop.cz

¹ Czech Technical University in Prague, Faculty of Civil Engineering, Department of Irrigation, Drainage and Landscape Engineering

² Research Institute for Soil and Water Conservation, Department of Soil Science and Soil Protection khel.tomas@vumop.cz

³ Research Institute for Soil and Water Conservation, Department of Soil Science and Soil Protection petru.anita@vumop.cz

The windbreak efficiency in terms of wind velocity reduction differs in many authors, however, the impact of the windbreaks is stated in the range of 20 to 35 time the windbreak height [2, 10, 11, 12, 13, 14].

2 MATERIALS AND METHODS

The measurements of wind velocity along windbreaks were carried out on three permanent research plots (PRP) in the Czech Republic (Figure 19).



Figure 19: Location of permanent research plots

PRP Dobrovíz (50.107493N, 14.229841E) has the windbreak of 3-4 rows of trees, an average height of 18 meters, composed of: *Quercus patraea* (60%), *Acer pseudoplatanus* (20%), *Acer campestre* (10%), *Platanus acerifolia*. The shrub layer consists of *Sambucus nigra* and *Symphoricarposalbus*.

PRP Středokluky (50.119795N, 14.230270E) has the windbreak of 2-3 rows of trees, an average height of 15 metres, composed of: *Quercus patraea* (70%), *Acer pseudoplatanus* (20%), *Platanus acerifolia* (a mixture), Bigleaf Linden - *Tiliapltyphyllos*. The shrub layer consists of: *Symphoricarposalbus*, *Rosa canina*, *Crataegus laevigata*, European elder - *Sambucus nigra*, *Euonymus verrucosa* and *Juglans regia*.

PRP Klapý (50.422654N, 14.032982E) has the windbreak of 4-5 rows of trees, an average height of 22 meters, composed of: *Acer pseudoplatanus* (50%), *Fraxinus excelsior* (25%), *Ulmus laevis* (10%), *Quercus robur*, *Acer platanoides*, *Populus nigra* var. *italica*. The shrub layer consists of: *Sambucus nigra*, *Ligustrum vulgare* L.

The ambulatory measurements of the efficiency of windbreak were taken during favourable meteorological conditions, i.e. at the wind speed higher than 4 m.s⁻¹ and in the vertical direction of the wind to the windbreak. The wind speed was measured by anemometers Vantage Pro 2 by Davis (Figure 20). The extent of measurement is stated by the producer to be from 0.5 to 89 m.s⁻¹ with the accuracy of ± 1 m.s⁻¹ or ± 5%. The anemometers were attached at height of 1 meter above the surface. The range of anemometer sites was from 3H to 9H (in multiple of windbreak height (H)) on the windward side (basically at positions 3H, 6H and 9H) and from 3H to 15H on the leeward side (basically at positions 3H, 6H, 9H, 12H, 15H). The measurements were started in 2014 with 4 anemometers sites available and from 2016 the measurement were carried out by using 8 anemometers sites (Figure 21). During the period of 4 anemometers their position was changing meanwhile a single measurement was taken.



Figure 20: Field measurement of windbreak efficiency

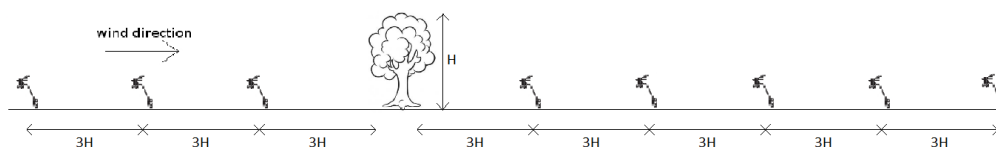


Figure 21: Scheme of wind velocity measurement and anemometry position (H – windbreak height)

The optical porosity was determined on the photogrammetry method. Photographs were taken by digital camera Nikon D5100 (Nikon Corporation, Tokyo, Japan) at the representative part of windbreak in length of 30 meters. For the evaluation of the optical porosity these programs were used: GIMP (version 2.8.2), ArcGIS for Desktop (ArcMap 10.2) and Table Processor Excel 2013. Firstly, the photos were processed in the graphical software GIMP. According to the accessible tools a graphical modification of the photography (highlighting the vegetation cover from the background) in order to create binary picture was carried out. This conversion was very important to determine the cover and the background of the windbreak (black Grid=cover, white Grid=background). Those modified photographs were analyzed in the ArcGIS. Statistical evaluation of the relationship between wind speed and optical porosity was carried out in the MS Excel program (Figure 22).

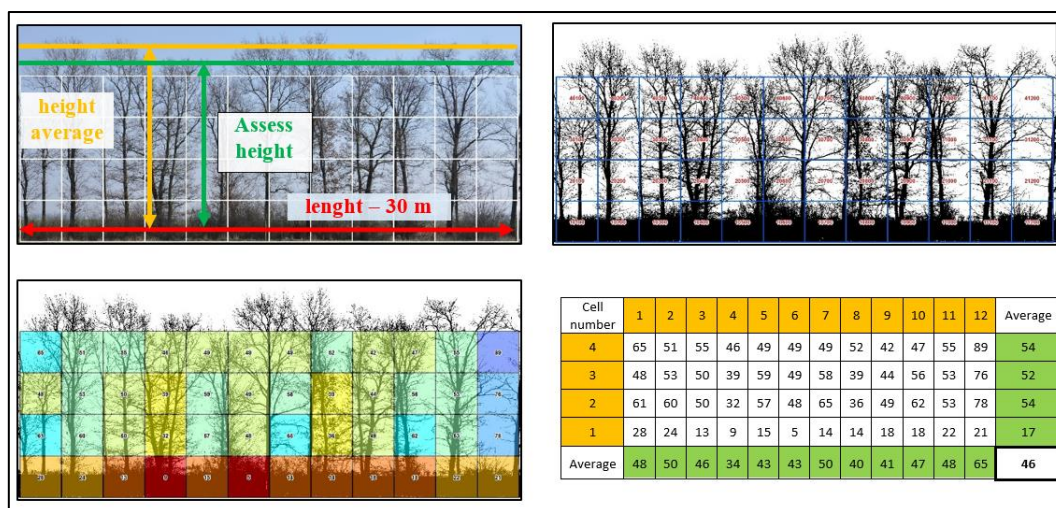


Figure 22: Example of modification of the photography and evaluation of the optical porosity (in %)

Wind velocity was measured between years 2014 and 2017 at the PRP Dobroviz, Klapy and Stredokluky during the different phenological phases of woody plants. The character of windbreak was determined by the value of the optical porosity (OP) in %. The highest distance of windbreak efficiency was set up in 35 times of windbreak height on the leeward side. It is the maximum distance corresponding to other authors.

This paper is a follow-up to an earlier paper of Rehacek et al. [15] and includes new measurement and approaches.

Statistical assessments were carried out by RStudio (version 1.0.153). The data were assessed using polynomial linear regression of the second degree (Fitting Liemar Models).

3 RESULTS AND DISCUSSION

The data were assessed by linear regression model and the results of data are shown in Figure 23. After the linear model was run (wind velocity reduction is dependent on distance from the windbreak and optical porosity of the windbreak), the p-value was much less than 0,05 ($p\text{-value} = 2,2e-16$), therefore, the null hypothesis can be rejected. Hence, the significant relationship between the variables in regression model was found out.

Higher wind velocity reductions is the proof for lower value of OP. Santiago [5] and Cornelis and Gabriels [16] stated the optimal value of OP between 25-35% to reach maximal wind velocity reduction. Based on presented data, even better wind velocity reduction is for lowest value of OP.

The wind velocity reduction was found out up to the last site of measurement at the distance of 18H. The threshold wind velocity reduction of 100% was exceeded at the distance of 17H (OP = 40%) and 12 H (OP = 50%). The value of OP = 60% was shown just on the theoretical level, there was no data from this type of windbreak.

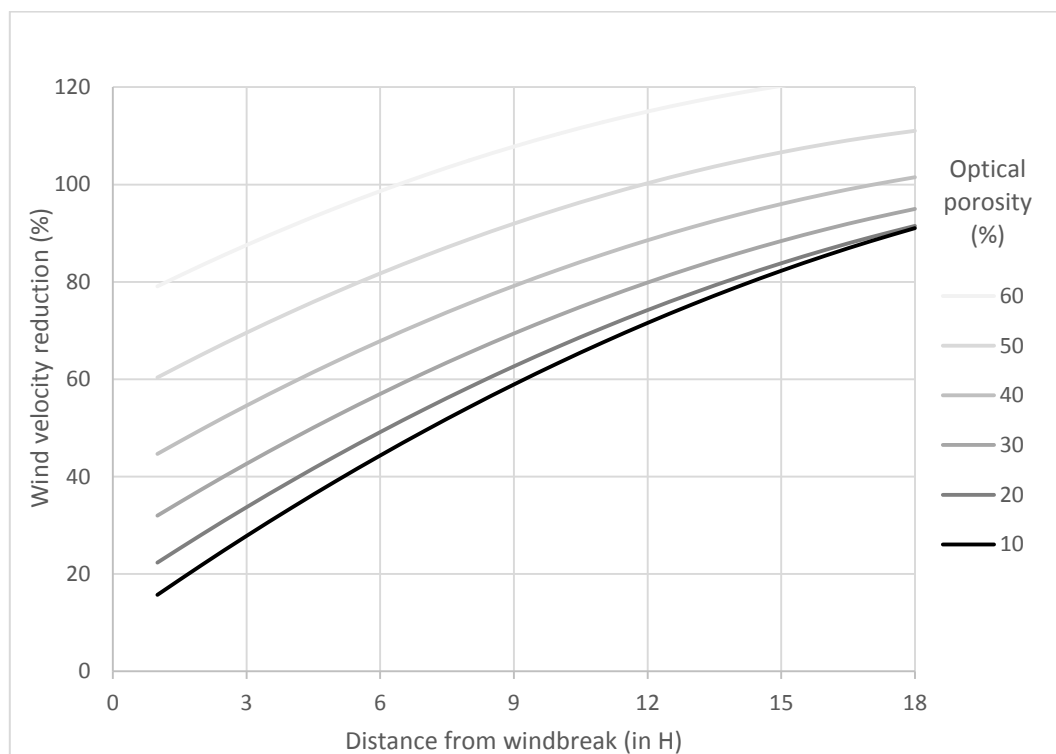


Figure 23: Wind velocity reduction on the leeward side in comparison to the windward side at the distance of 3H (H - windbreak height)

Torita and Satou [17] specified shelter distance of windbreak as a parameter $d70$ which means $U/U_0 < 0,7$ (U_0 - windward speed, U - leeward speed). The shelter area $d70$ in comparison to the presented data is from the distance 3H (OP = 50%) to 12H (OP = 10%). Value OP of 60% has no shelter area in $d70$. Tuyet et al. [18] defined shelter distance $d70$ in range from 8H to 16,5H.

The influence on windbreak velocity reduction on the windward side has not been proven by using statistics methods. It is necessary to carry out further research and field measurement to describe airflow on the windward side.

The windbreak character changes during the year. These changes mainly depend on woody plants and their foliage density. Normally, foliage starts to bud in March and the full foliage phase is in May. Otherwise, foliage starts to fall down at the end of September or in October and it is finished by the end of November. The foliage phases could slightly differ in terms of variable climate. The seasonal changes are expressed by a value of OP. The course of value OP at the PRP are shown in the Figure 24.

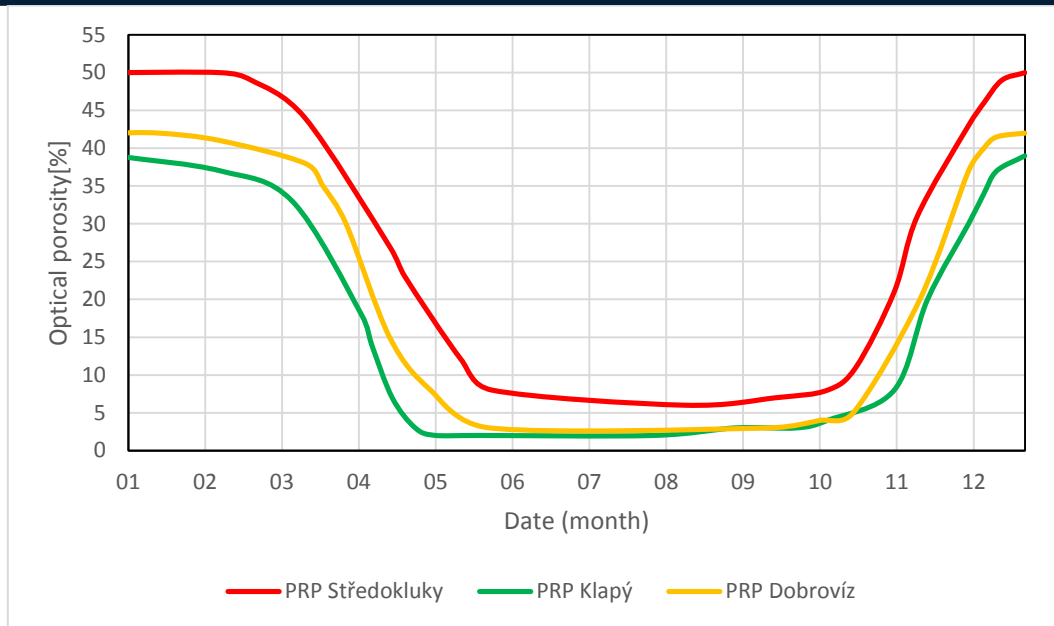


Figure 24: Seasonal change of optical porosity on permanent research plots

Maximum value of OP for PRP is shown in Table 9. Maximum value (in winter period) means the minimum distance of wind speed reduction (protection zone). Hence, the height of windbreak represents an important factor in terms of protection zone.

Table 9: Minimum and maximum value of optical porosity on permanent research plots (in %) and zone of wind velocity reduction (in m)

	PRP Středokluky	PRP Klapý	PRP Dobrovíz
OP min (%)	6	2	3
OP max (%)	50	39	42
Min distance of wind velocity reduction (m)	180	374	306

4 CONCLUSION

The presented data were based on field wind velocity measurement on three permanent research plots in the Czech Republic. The measurements were taken during the time span from 2014 to 2017 at the distances from 3 H to 9 H on the windward side and from 3H to 15 H on the leeward side. The character of windbreak was described by photogrammetry method as a value of optical porosity.

The correlation between windbreak height and optical porosity to wind velocity reduction was found out. The windbreak efficiency was found out up to distance 18H for value OP to 30%. The shelter area parameter d_{70} was carried out from 3H to 12H (for value OP from 50% to 10%).

Further research is necessary in order to describe airflow on the windward side of windbreak. Mainly, research should focus on field measurement and capturing data of wind velocity. However, further measurements on the leeward side are still recommended to reach higher accuracy in airflow modeling.

This research has found out the importance of windbreaks in terms of soil protection against wind erosion. The smallest protected area along the windbreak is during winter time due to high value of optical porosity. It is due to seasonal foliage phases. Appropriate design and arrangement of the windbreaks would improve their efficiency on wind velocity reduction on agricultural land. Hence, there would be smaller amount of soil particles contained in the air (dust emissions).

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Traffic Related Particulate Matter Distribution in Urban and Rural Ambient Air, Adana, Turkey

Esra D. GUNER^{1}, Zeki BOZKURT², Fuat BUDAK¹*

Abstract

Unplanned urbanization and the rapidly increased number of vehicles make a substantial contribution to particle matter beside other sources such as heating, industrial activities. Especially of urban areas, traffic is an important source of particles in ambient air. Particles have received much attention because their ability to be transported over long distances, have a long lifetime in atmosphere. The size of particles is directly related to their potential to causing adverse health effect. The coarse particles ($dp: 2.5$ to $10 \mu\text{m}$) tract effectively filter in the respiratory system, the smaller particles ($dp < 2.5 \mu\text{m}$) are, the more deeply it will penetrate to the respiratory system, more dangerous. Fine and ultrafine particles represent most of the particles in terms of number concentration in the atmosphere, the coarse particles have the less numerous but dominate the mass concentration. For this reason, it is important to evaluate the particulate matter concentration (PC) and particle size together with fraction distributions (PFD). The aim of this research is to determine the PC originating from the traffic by evaluating the ambient air samples of urban and rural sites in Adana province. A portable particulate matter counter was used to measure the concentration and size distribution of particulate matter on a real-time basis. The urban sampling point has high traffic volume and intensity, while the rural sampling point does not contain traffic. The results show that the particulate matter concentration is significantly higher in the urban ambient air compared to the rural ambient air. Urban sampling point has a busy traffic especially in morning and evening hours and the point used by public transportation. It may be contributing traffic emission to high PC measured at the rural sampling point. The concentration of all the fractions of PC showed a traffic related pattern in urban sampling point and all of PFD have a higher level. When comparing the urban sampling point ambient air with the rural sampling point ambient air PC, air quality in rural site is typically decrease. As an important factor that rural site has not traffic flow around the sampling point.

Keywords: *Air quality, Air pollution, Particle concentration; size distribution*

1 INTRODUCTION

Air pollution is highest in major urban sites having the busiest traffic flow, highest population, irregular and rapid urbanization. Deterioration of air quality can be adversely affect people's health risk living so the quality of the air is a significant concerning the environment and public health. Governments carry out strict air pollution control, it still continues to be a significant danger without losing the importance. However exhaust emissions have been achieved the successful reduction, non-exhaust emissions from traffic related are unrelieved. Because of the lack of suitable tracer elements, interactions between a wide range of sources non-exhaust emissions will become more important to evolution traffic related emission.

Atmospheric particles have received special attention because of their potential health effects and their ability to be transported over long distances [1]. In epidemiology studies have highlighted the importance of particle matter on health. The increase in particulate matter exposure even if short time increases in mortality and morbidity [2]. Especially adverse effects on health tightly link to the concentration of particle matter (PC) and particulates size fraction (PFD) [3]. PC and PFD are critical factors in the mechanisms of deposition of particulate matter in various regions of the human respiratory system. Coarse particles (diameter $> 10 \mu\text{m}$) have been tracked the upper part of the respiratory system by the cilia and the mucus in nasal-breathing [4]. They tend to deposit in the nose, trachea (upper throat) or in the bronchi [4] and being removed by way of sneezing and coughing [5]. Especially particles with less than $10 \mu\text{m}$ in diameter are needed to better assess because of more important for the negative health impacts. Particles range to 5 from $10 \mu\text{m}$ in diameter can accumulation bronchioles and the alveoli where

^{1*} Department of Environmental Engineering, Cukurova University, TURKEY. (E-mail: eguner@cu.edu.tr, fbudak@cu.edu.tr)

² Seyhan Municipality, Adana, TURKEY (zbozkurt@seyhan.bel.tr)

gas exchange occurs. Fine particles (diameter $<2.5 \mu\text{m}$) and ultrafine particles (diameter $<0.1 \mu\text{m}$) can easily be inhaled and penetrate deeper into the human lung than coarse particles [6-8]. They can be transported into the blood stream or further into the cell tissue and/or circulation system to cause significant health problems [4]. This effect of urban air pollution on public health can be listed in addition to increased mortality [9, 10], risk of chronic respiratory illness [10, 11], and various types of cancer [11] even if both long-term and short-term or lower concentration levels of PM exposure [12, 13].

In urban areas, road traffic is recognized as an primarily source of both particles and certain metals [14-16]. Understanding emissions from traffic includes identification of the sources, which is also crucial for designing control measures. Road traffic involves numerous potential sources of particles, e.g., combustion products from fuel and oil, wear products from tires, brake linings, bearings, coach and road construction materials, and re-suspension of soil and road dust. As to understanding the relationship between the roadside PM concentration and ambient air PM concentration, is important the measured in urban and rural sites. But it is so difficult to compare because the urban sites and the rural sites are very different and not always well defined.

Currently, however, only the mass concentration in PM10 usually as monitoring parameters in environmental standards. Information about fine and ultrafine particles, the number of concentration is usually not available. In fact, even though there is a little contribution to total particle mass, but it is dominant when considering the number concentration. For this reasons, it is crucial evaluation the relationship between PC and PFD as well the origin and transport of particles in the atmosphere. For this reason, concentration measurements and size distributions of particles larger than $0.3 \mu\text{m}$ were evaluated in urban and rural sites in Adana, Turkey. Thus, it is aimed to determine the contribution of the traffic by comparing rural and urban PC.

2 MATERIALS AND METHODS:

Adana is located in the inland from the Mediterranean, in south-central Anatolia, Turkey. With a population of 2,201 million is a major city in southern Turkey. The city has 607,905 vehicles, of which 303,8 are cars, 94,5 are a van, 125 are motorcycles, and 20,2 are a small truck. Two sites were selected in urban (busy traffic) and rural (non-traffic) to assess traffic impact. The urban site was chosen for its distance to closeness the road and local traffic influence at the sampling locations. The site is close to a significant intersection of several roads and so the geometry of the site is difficult to describe in simple, four-dimensional terms, as the line of buildings. This site experienced the highest traffic flows with a large percent of the traffic consisting of light-duty diesel and fuel vehicles. Also there is traffic lights and parking lots for all directions. The sampler was located on 3.5 m above ground (the pedestrian pavement i.e. the sidewalk). Rural site has quite low traffic comparison with the urban site. This point is the lack of other nearby fine particle emission sources such as traffic, businesses, a residential area generally has large open land site with little activities during the day. The sampler was located within a fenced garden (Arboretum Park) adjacent to the grounds of the Cukurova University, approximately 800 m from roadside. Particle number concentration and size distribution in the size range from 0.3 to $10 \mu\text{m}$ were measured by a particle counter (P611; The Airy Technology). The sampling flow rate of the P611 was adjusted to 2.83 L min^{-1} inlet flow and a 0.1 L min^{-1} CPC flow. This equipment measured particles $0.3 \leq 0.5, 1, 2.5, 5, 10 \mu\text{m}$ distributed across 6 channels. Particles under $0.3 \mu\text{m}$ cannot be detected by the instrument. During the sampling period, the windless day was selected and started at approximately 00:08 pm. Samples collected continuously during the 24-hour (nearly started 0:05- finished 23:50) at the location sites by a particle counter.

3 RESULTS AND DISCUSSION

3.1. Diurnal Variation of Concentrations of Particulate Matter (PC) and Particle Fraction (PF)

The concentration of particles in the urban site showed a time variation, confirming the influence of movable and stationary sources during the 24-hour. Fig.1. presents the concentration of PM distribution in an urban site. The morning (6:00-9:00 am) and afternoon (16:00-20:00 am) peak of PC was the result of direct emissions from traffic-related sources. This hours have rush traffic, congestion and stop and go event in traffic. Furthermore, as shown in the Fig.1., the afternoon peak of PC which was all particle size was nearly 2 times higher than the morning peak concentration. This suggests that the contributions of traffic emissions to PC would be suppressed substantially. The high PC was seen longer hours in the afternoon which may be due to the difference in work and school exit times. Another factor is the accumulation of airborne particles as the PC rises in the afternoon. The PC was visibly decreased considerably between 20:00 am and 06:30 am, as a result from diminished significantly low traffic and a number of vehicle comparison of other hours.

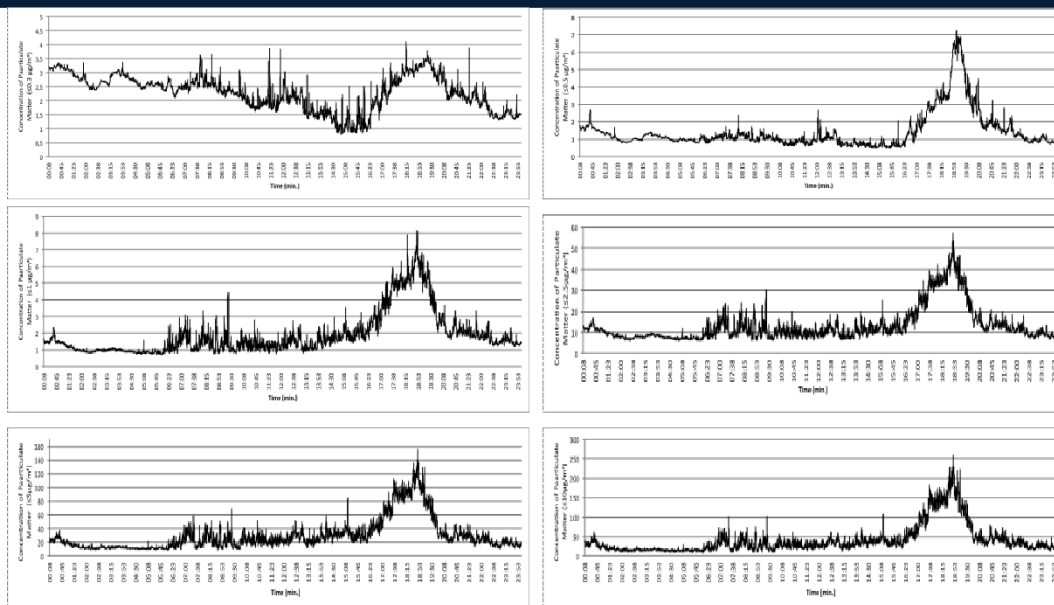


Figure 1. Diurnal Variation of PM concentration in Urban Site (PM_{0.3}, 0.5, 1, 2.5, 5 and 10)

When comparing both sites studied, higher mass concentrations of atmospheric particles were found in the all fraction in the site under traffic influence (urban site). PM_{0.3}, PM_{0.5}, and PM₁ show an average $2 \mu\text{g m}^{-3}$, $0.56 \mu\text{g m}^{-3}$, $0.71 \mu\text{g m}^{-3}$ in an urban site, while in the rural site the fine fraction was $2.3 \mu\text{g m}^{-3}$, $1.43 \mu\text{g m}^{-3}$, $1.89 \mu\text{g m}^{-3}$, respectively. In the rural site, the average concentration of coarse particles (10, 5 and 2.5 μm), respectively, was $6.7 \mu\text{g m}^{-3}$, $14.16 \mu\text{g m}^{-3}$, $16.44 \mu\text{g m}^{-3}$, lower than the average concentration of urban particles ($13.2 \mu\text{g m}^{-3}$, $29.77 \mu\text{g m}^{-3}$, $41.25 \mu\text{g m}^{-3}$). Fig.2. presents the concentration of PM distribution in a rural site. PC also has small peak at early day (00:20 pm-05:00 am) in the rural site then sharply decrease from 05:00 and there is little fluctuation during the rest of the day. This pattern might be attributed to the local situation of the sampler on the main soil dust and wind.

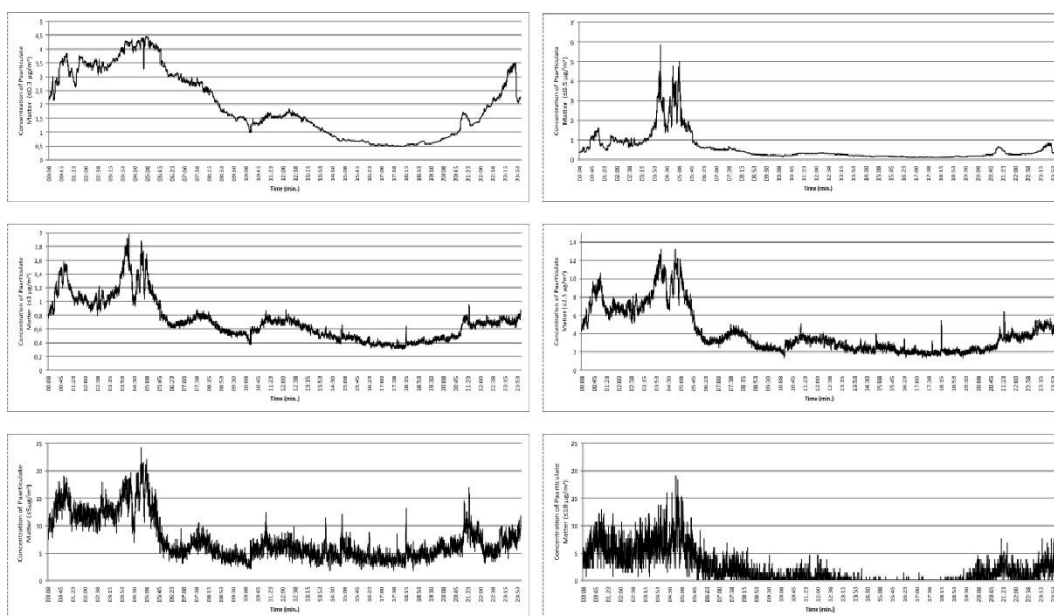


Figure 2. Diurnal Variation of PM concentration in Rural Site (PM_{0.3}, 0.5, 1, 2.5, 5 and 10)

3.2. Comparison of the air quality standards with measured data

The limit values determined by Turkey are not compatible with the limit values defined by the European Union. Comparison of the 2014 Turkish air quality standards with those of the European Union shows that for PM has above the limit values. The aim is to bring the standard for PM10 will be the same from 2019 on (targets are abatement from 70 to 50 $\mu\text{g m}^{-3}$ in daily average and from 48 to 40 $\mu\text{g m}^{-3}$ annual average from 2019 on). Moreover, the regulations in Turkey do not contain any restrictions on the pollutant PM2.5, which cause more health adverse. On the other hand, the average daily concentration value of the pollutant PM10 is permitted to exceed the limit value (50 $\mu\text{g m}^{-3}$) exceeds more than 35 days a year. To increase the air quality, it is necessary to monitor the change within the time of these pollutants and estimate their trend.

Table 1. Comparison of the limit values determined by the EU and limit values determined by Turkey

Limit Values for PM10	EU	Turkey			Permitted excess each year (total number of days)		This Study	
		2017	2018	2019	EU	Turkey	Urban Site	Rural Site
24-hour average	50 $\mu\text{g m}^{-3}$	70 $\mu\text{g m}^{-3}$	60 $\mu\text{g m}^{-3}$	50 $\mu\text{g m}^{-3}$	35 times year ⁻¹	-	$\mu\text{g m}^{-3}$	$\mu\text{g m}^{-3}$
Annual average	40 $\mu\text{g m}^{-3}$	48 $\mu\text{g m}^{-3}$	44 $\mu\text{g m}^{-3}$	40 $\mu\text{g m}^{-3}$		-	-	-
Limit Values for PM2.5							-	-
Annual average	25 $\mu\text{g m}^{-3}$	-	-	-			-	-

At the rural station, PM10 annual averages were significantly below the averages measured at traffic sites. At the rural monitoring station, lowest PM10 24-hour averages were observed.

4 CONCLUSION

PM emissions depend on various sources such as abrasion, wear, and tear of the brake, tires, resuspension of road dust in urban sites. So, motor vehicles are a particularly significant source of aerosols particularly for the particles. It is important to monitor and measure the particulate matter in the real world, especially in areas where urban traffic is intensive. There is also a clear difference regarding particle size distribution between urban and rural sites. As seen in Fig1 and Fig2, the concentration of particle matter in urban site higher variability compared with the rural site. Particle concentrations showed a high variation with time so this might be caused traffic density. Compared with low and heavy traffic hours, PM is significantly reduced during low traffic hours. Traffic-related site is particularly vulnerable to violate the short-term limit. Most of the businesses are near the roadside and generally have activities during the day. Particularly time spent in traffic drivers, pedestrians and people living near busy roads exposure persistent air pollution. In the rural site, PC generally has been measured lower but the increase in PC during an early time in the morning may be due to the wind in the region. Another important point is that the PM10 emission values are above the limit values in the legislation.

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Case Scenario Simulation Concerning Eventual Ship Sourced Oil Spill, Expansion and Response Process in Istanbul Strait

C.ASAN^{1*}

Abstract

Besides its substantial features, sensitivities like around 18 million populations in surroundings, military facilities, ports, oil lay down areas etc. also brings the high risk to use of Istanbul Strait. Based on the statistics of Turkish Ministry of Transportation, Maritime and Communication, although the number of vessel passage in Istanbul Strait is declining, tonnage of hazardous and flammable cargo like oil and chemical transportation is increasing and subsequently the risk of oil pollution, loss of life and property is also rising. Based on the mentioned above; it is crucial to be prepared for the initial and subsequent response to eventual ship sourced oil spill which may cause to block the Strait for an unbearable duration. In this study; preconditioned Istanbul Strait sensitive areas studies has been taken into account and possible oil spill scenario is loaded to PISCES 2 (Potential Incident Simulation Control and Evaluation System) decision support system for the determined specific sea area. Consequences of the simulation like oil expanding process and the effectiveness of the initial response had in hand and evaluated.

Key words—Istanbul Strait, Initial response, Oil spill, PISCES Simulator.

1. INTRODUCTION

The Strait of Istanbul connecting the Black Sea to the Aegean Sea, is one of the major trade artery in the World with an average of 132 transits a day, second to the Straits of Malacca. Istanbul Strait serves as an international seaway and has got economic and strategic importance. Due to physical conditions it requires at least 12 major course alterations as much as 80°, with severely limited vision around these bends. Geographical and oceanographic conditions as well as navigational constraints are the main parametres making the navigation through difficult and risky.

Istanbul Strait faces dense shipping transits. The Strait faced more than 450 marine casualties of different types - i.e collisions, groundings, strandings, fires / explosions and others (such as rudder blockade, vessel's list, or engine breakdown). Safe navigation in Istanbul strait is a matter of vital importance to Turkey as well as to all nations using the Strait. Therefore, the dangers posed by ever increasing shipping traffic to the surrounding inhabited areas and to the environment have compelled Turkey to take immediate action and to reinforce existing regulations of maritime traffic in the Strait.[1]

The Turkish Straits are one of the most important routes of oil transportation in the world. They connect the Black Sea to the Mediterranean and enable transportation of oil from the Black Sea to Europe easily. The Turkish Straits consist of two parts, and the northern half is called the Istanbul Strait. It has lain beside a mega-city, Istanbul, where over 18 million people live. Disasters based on the tanker accidents have happened several times in this strait, and it has directly affected life in the city. Disasters originating from tanker accidents occurred several times in the Istanbul Strait. As the accidents occurred very close to life in the city, it requires a quick a response as possible. [2]

According to statistics of Turkish Ministry of Transport, Maritime Affairs and Communications, although traffic density reduces yearly the amount of transportation increases yearly [3]. Based on the Istanbul Strait accident statistics which has been gained from Turkish Directorate General Of Coastal Safety the highest number of accidents in Istanbul Strait occurred in Ahirkapi and Haydarpasa regions. After possible oil pollution and fire, there might be enviroment disaster in the Strait and it

^{1*} Corresponding author: Piri Reis University, Maritime Faculty, Department of Maritime Transportation and Management Engineering, 34940, Tuzla/Istanbul, Turkey. casan@pirireis.edu.tr

may stir up loss of life and poverty. Due to fact that such oil spills should be simulated with PISCES or similar simulations, measurements should be reviewed and additional precautions should be applied. In this study, probable oil spill and pollution has been simulated and evaluated as a conclusion.

2. MATERIAL and METHODS

This study has been focused on a case study concerning oil spill simulation and initial response based on literature research and simulation of data gained by statistics. Initial case criterias has been setted to Possible Incident Simulation, Control and Evaluation System (PISCES-2) simulation and outputs has been evaluated for the high risk area in Istanbul Strait.

3. RESULTS and DISCUSSION

3.1. Major Inputs of Petroleum to the Marine Environment

Oil spill can be depicted as the arrival of fluid oil hydrocarbon into the sea or waterfronts, because of some human exercises like; leakages because of the impact, agrounding, sinking, and so forth of oil transport vessels, illicit dumping by industries, terrorist exercises and subverts, vessels, oil pipelines and oil stages/wells and so on.

Major inputs of Petroleum to the Marine Environment as described below:

- * 37% comes from Industrial wastes, reach the sea, via storm water drain, creeks, sewage and rivers.
- * 33% from oil vessels during transportation.
- * 2% during explorations and
- * 12% from accidents involving tankers.
- * 7% comes from natural sources like fissures from sea bed.
- * 9% absorbed from atmosphere [4].

The scattering of oil spill by the effect of wind and current on the sea surface is showed below.

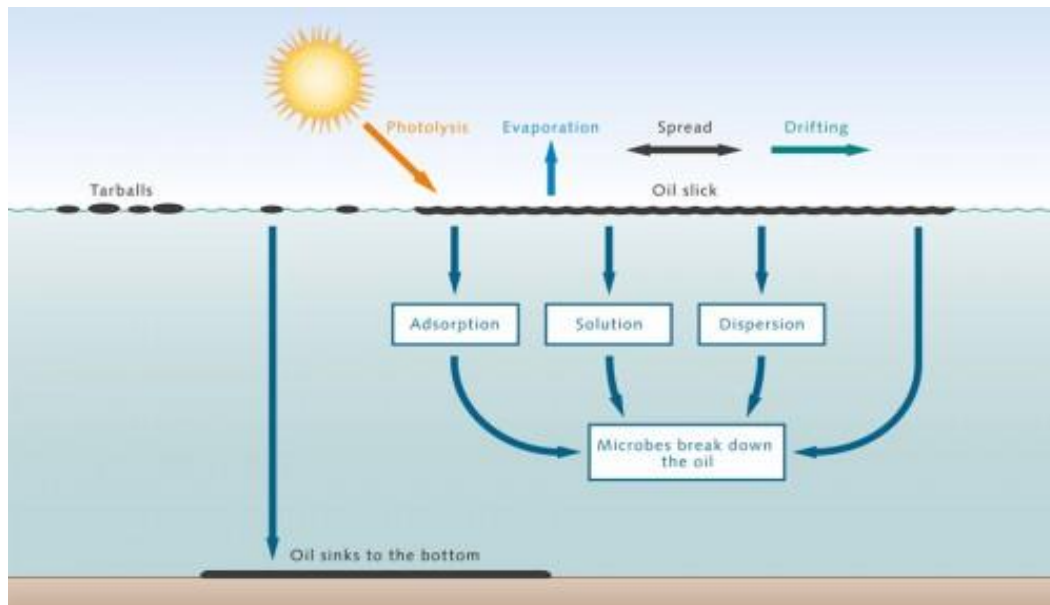
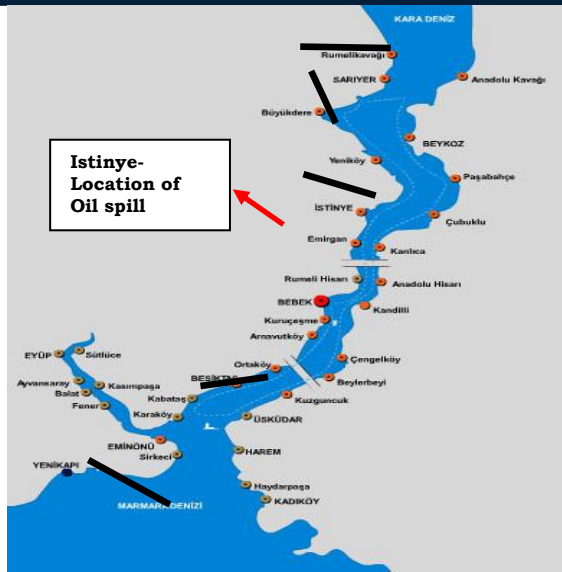


Figure 1. Progress of oil spill on the sea surface. [5]

3.2. Information Of High Risk Areas In Istanbul Strait For Navigation

As it has been mentioned in previous sections, Istanbul Strait has got high sensitivity due to lots of risks. With the high volume of oil being transported through the Istanbul, possible accidents can discharge huge amounts of oil into the marine condition.

Based on output of analyze for collision between 1982 and 2010, the Strait of Istanbul faced the most ship accidents in the Haydarpasa-Eminonu and Ortakoy-Cengelkoy zone with the ratio of 35.2%, and respectively in the Ortakoy-Cengelkoy and Yenikoy-Pasabahce (27.0) [6].



Accident occurrence zones	Freq.	Percentage (%)	Percentage of Total Cumulative (%)
Strait of Ist.	96	12.2	12.2
First Zone	276	35.2	47.4
Second Zone	212	27.0	74.4
Third Zone	121	15.4	89.8
Fourth Zone	80	10.2	100.0
Total	785	100.0	
First Zone	Haydarpaşa-Eminönü and Ortaköy-Çengelköy		
Second Zone	Ortaköy-Çengelköy and Yeniköy-Pasabahçe		
Third Zone	Yeniköy-Pasabahçe and Rumeli Kavagi-Kavak Burnu		
Fourth Zone	Rumeli Kavagi-Kavak Burnu and Anadolu Feneri-Rumeli Feneri		

Figure 2 - Frequency Distribution of Ship Accidents by Zones in Istanbul Strait [6].

Table-1 indicates the accidents which are occurred around Ahirkapi and Haydarpaşa between 2004-2016, which obtained by official appeal from Turkish Directorate General of Coastal Safety. Totally 297 accidents occurred in Istanbul Strait and 182 accidents of total accidents in the strait occurred around Ahirkapi and Haydarpaşa. These values reveal that approximately %60 of accidents in Istanbul Strait occurred around Ahirkapi and Haydarpaşa.

Table 1 - Details of accident around Ahirkapi and Haydarpaşa in Istanbul strait (Source: Turkish Directorate General of Coastal Safety)

Year	Number of Total Accidents	Number of Accidents around Ahirkapi and Haydarpaşa	Ratio of the Accidents Around Ahirkapi / Haydarpaşa
2004	23	13	56%
2005	28	12	42%
2006	27	17	62%
2007	31	23	74%
2008	33	18	54%
2009	33	25	75%
2010	36	23	63%
2011	19	10	52%
2012	14	10	71%
2013	14	7	50%
2014	9	6	66%
2015	9	2	22%
2016	21	16	76%

4. CASE STUDY OIL SPILL PREVENTION AND RESPONSE IN ISTANBUL STRAIT

When statistical data and previous studies have been examined, Haydarpaşa and surroundings have been evaluated as one of the most sensitive area of Istanbul Strait with regards to traffic density, number of accidents and social life areas. In the light of this evaluation it is aimed to create an oil spill scenario occurred around of Haydarpaşa, process it with the help of the PISCES-II Simulator and to present the results.

4.1. Initial Conditions

Table 2 - Initial conditions which are related to case study

First amount of oil spill after the incident	200 tons
Total amount of oil spill	1200 tons
Leaking rate	5 tons/hour
Oil type	Arabian Heavy
Boom type	Open water
Tide (Set-Drift)	S/SE-1,5 kts and 2 kts
Wind	N/NE-15kts
Sea state	1
Wave high	0,5m

4.2. Response Event

In the figure below, the location of the accident, current and wind direction, port of Haydarpasa are indicated.

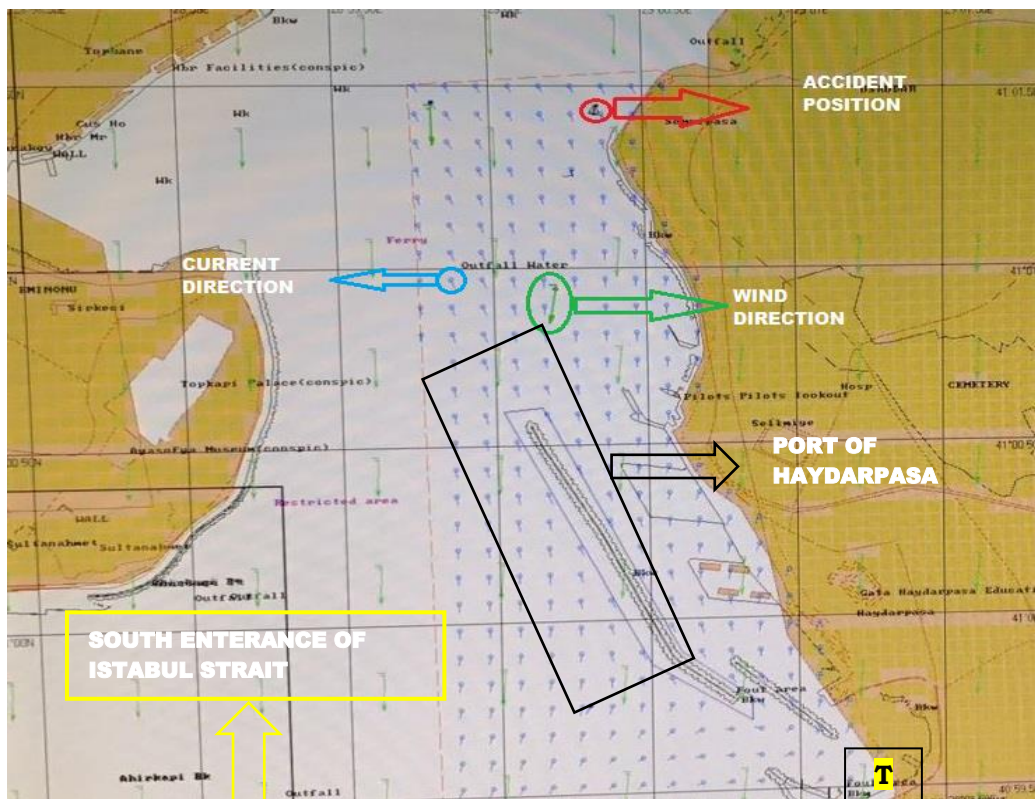


Figure 3 - Initial Conditions (Simulation)

In the figure stated below; it is observed that after the accident, with under the influence of current and wind, the first spill spreads from Haydarpasa Port or breakwater to the South entrance of Istanbul Strait.

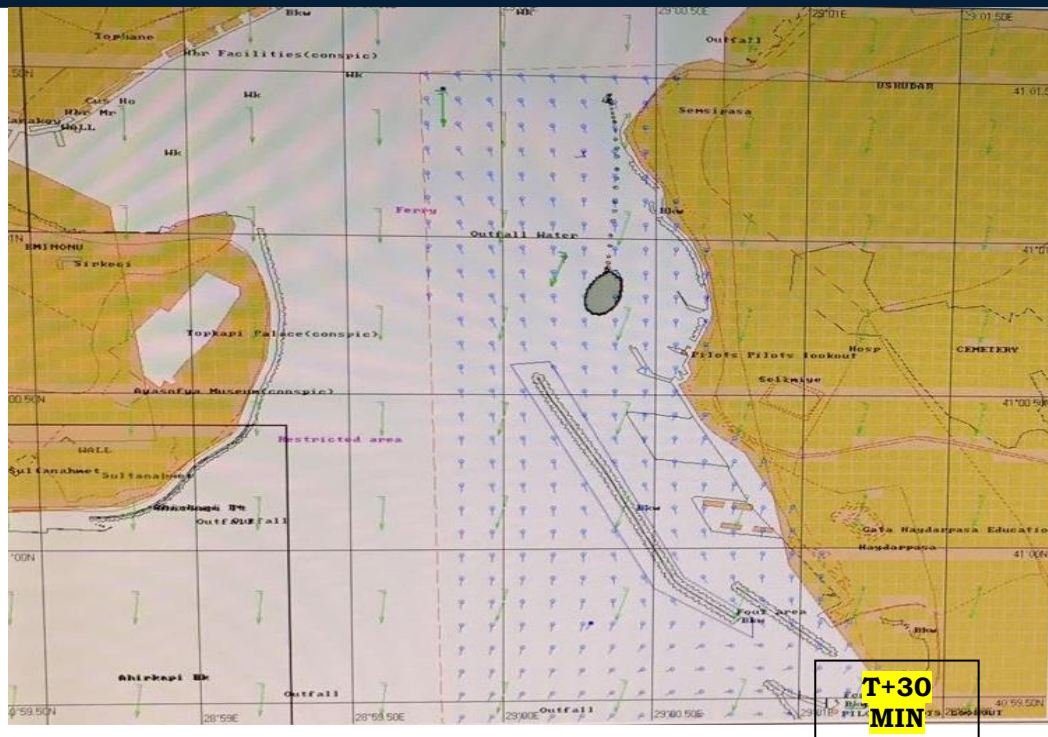


Figure 4 - 200 tons of Oil are spilling from the vessel(Simulation)

Figure 5 shows us spilled oil moves into Port of Haydarpassa. Despite half an hour past, oil spill equipments still are not deployed due to time requirement. Therefore, spilled oil reaches to Hayparpassa easily by supporting wind and current southeasterly.

In the figure stated below shows the oil spill process 45 minutes after the accident.

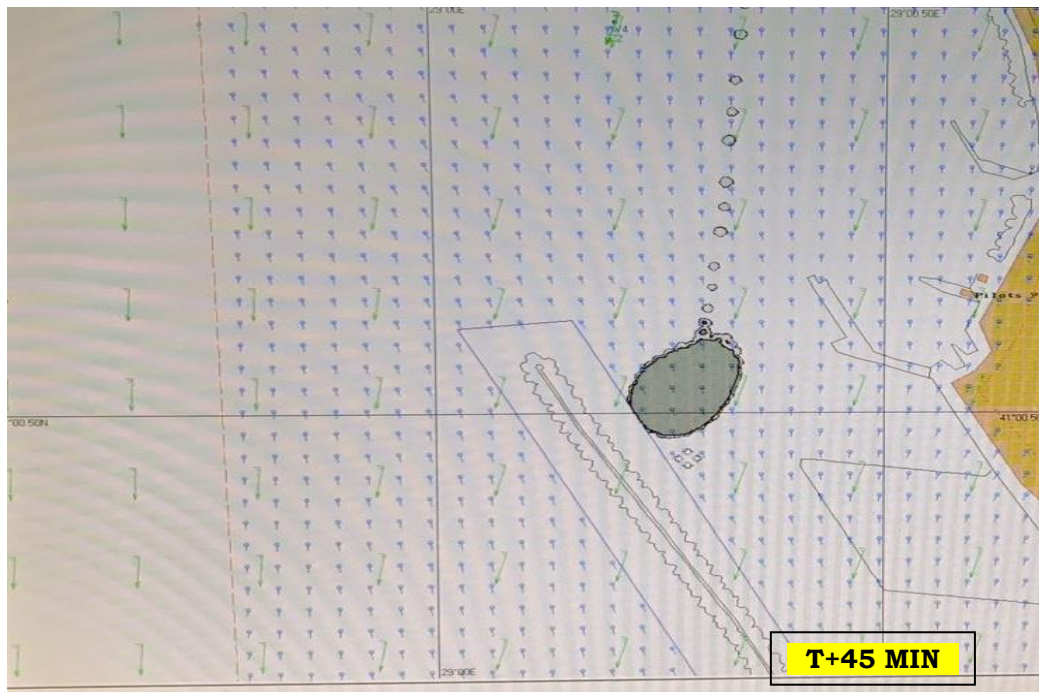


Figure 5 - Oils are spilling under influence of wind and current(Simulation)

As seen in the figure below, Haydarpassa breakwater covers by oil spill 1 hour after the accident. It is more difficult to remove oil spill anymore.

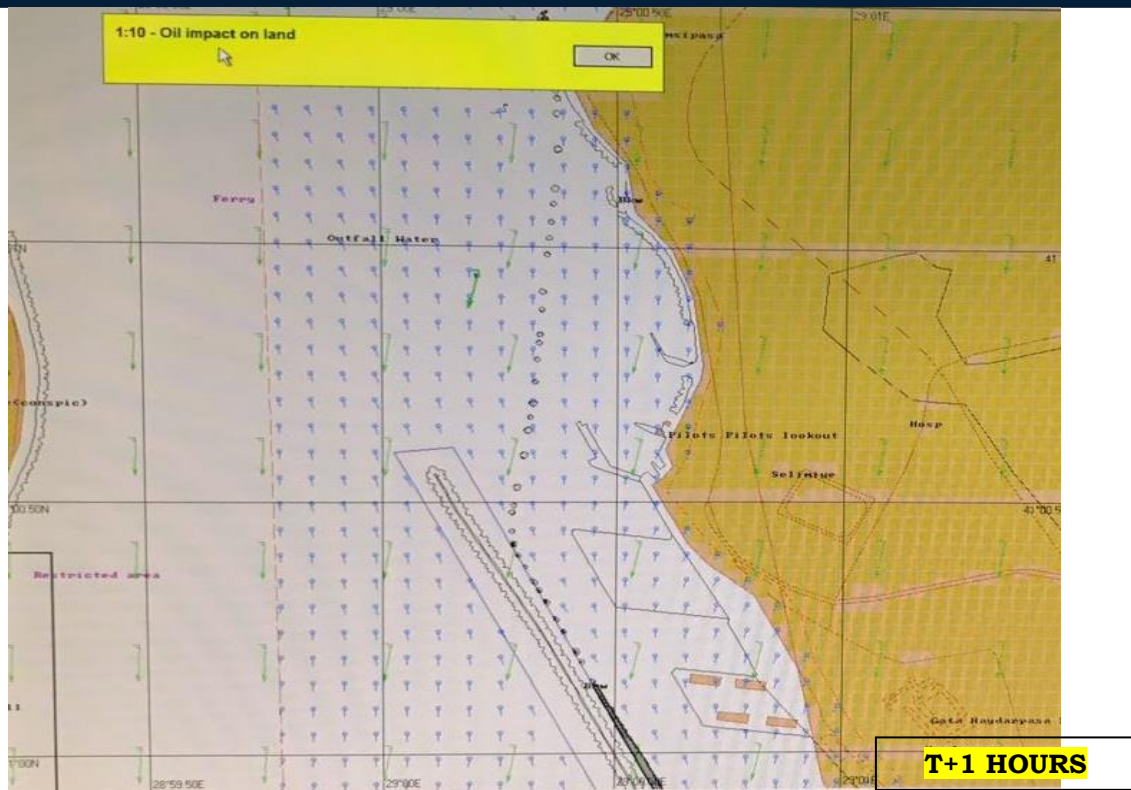


Figure 6 - Oil impact on land. Oil meets with breakwater and it changes it's direction(Simulation)

Due to location of oil spill response assets in Istanbul Strait, Istinye, shown in Figure 1, it is foreseen that after 1.5 hours from the accident, open water oil boom will be able to deployed and the figure stated below shows that it works adequately under the simulation circumstances. Oil boom contains spilled oil in first stage since deployed time. However before deployment of oil boom, high quantity of oil spill moves on South entrance of Istanbul Strait.

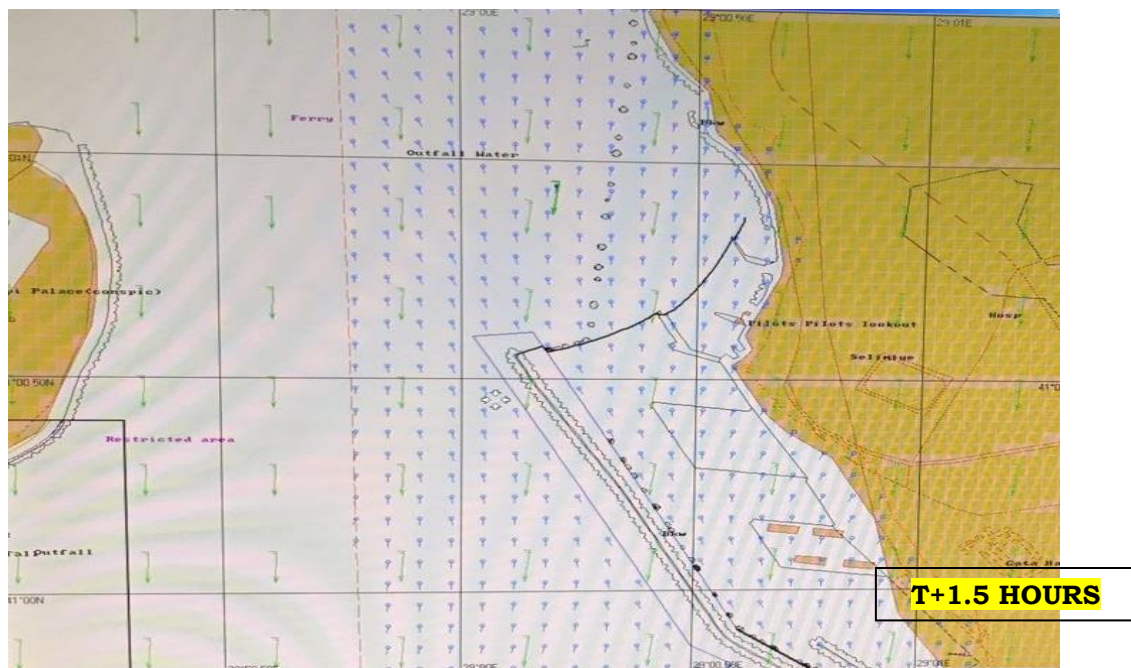


Figure 7 - Open Water booms are deployed after 2 hours of incident(Simulation)

In the figure stated below shows that oil boom could not contain much more oil spill as time passes by wind, current and the amount of oil. Therefore oil boom can't work properly after then.

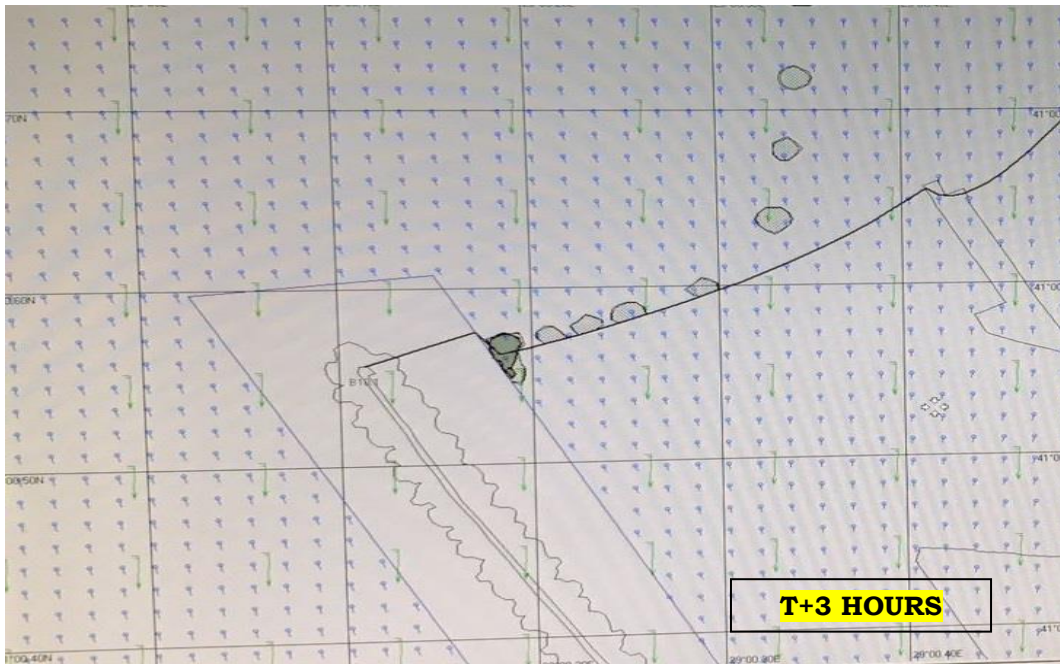


Figure 81 - Open Water booms are not adequate due to amount of contained oil, wind and current effects (Simulation)

Consequently, oil boom disables and oil spill passes through above and below of the boom and scatters towards South.

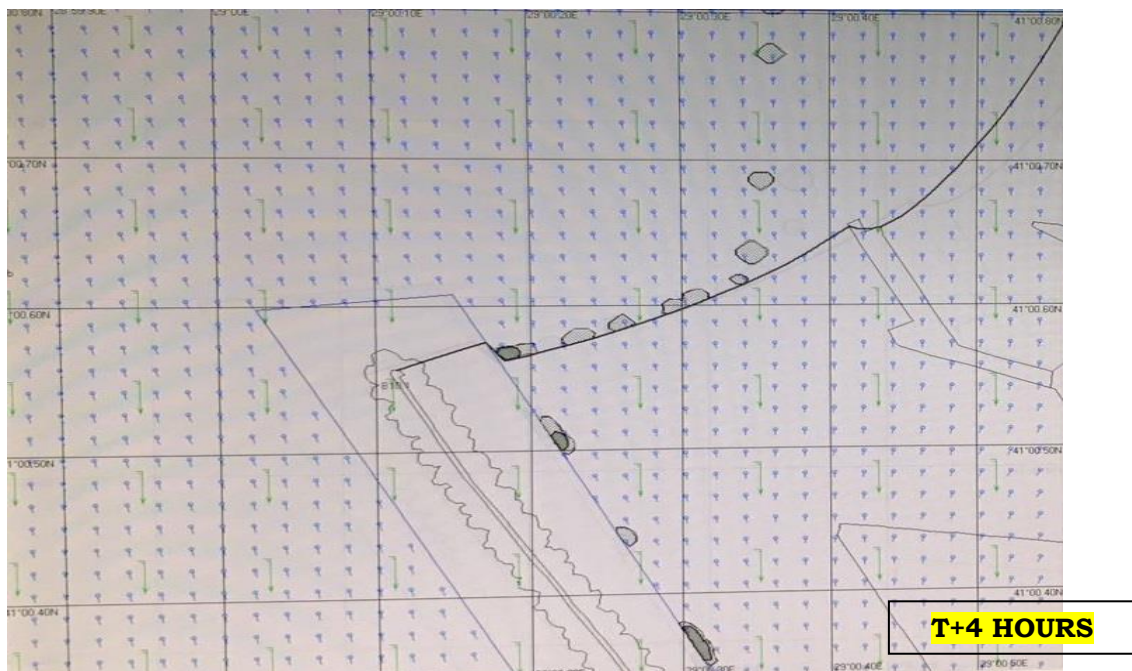


Figure 9 - Oil keeps spilling because of inadequate booms(Simulation)

In the figure stated below, it can be seen the general view of Southern Entrance of Istanbul Strait. Oil spill reaches to Southern Entrance of Istanbul Strait and it is understood that oil boom disables and land is impacted by more oil spill.

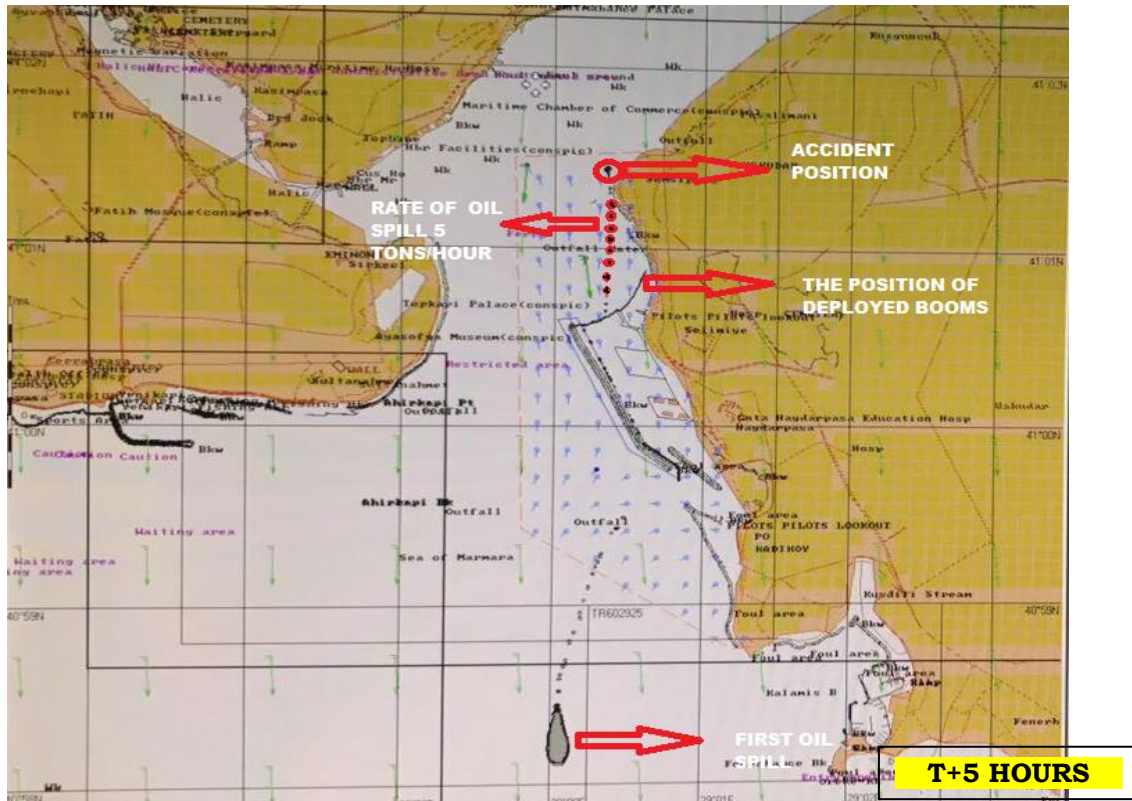


Figure 10 – General view of oil spill after 5 hours of accident (Simulation)

5. CONCLUSION

Istanbul Strait is one of the most important passage ways used by international trade by passing different types of vessels. The waters of the Istanbul Strait are traversed by numerous passenger ships and ferries daily as well as recreational and fishing boats ranging from dinghies to yachts owned by both public and private entities. Moreover Istanbul Strait has narrow passages, sharp turns, traffic density and risky physical conditions. Vessels using Istanbul Strait create possible risks for environment, sealife, sea resource and poverty. Oil tankers are more dangerous than the other types of vessels due to fact that oil or chemical tankers carry flammable and harmful substances cargoes. These types of vessels create risks more than the others due to possibility of oil spill with the conclusion of catastrophic situation.

Based on statistics of Turkish Directorate General of Coastal Safety, despite the traffic density in number of vessels reduces yearly, statistical tonnage of passages increases for Istanbul Strait. By the way, most of the accidents occurred around Ahirkapi and Haydarpassa, which is in detail in the last 12 years %60 of total accidents taking place in Istanbul Strait have occurred around Ahirkapi and Haydarpassa.

Haydarpassa is one of the most significant regions in Istanbul Strait. Since transit vessels and local vessels irrespective of private or state pass around of this area, the possibility of accidental risk is higher than the other places. The ratio of the accidents in Istanbul Strait has expressed relevant to this subject. Hence study has focused on Haydarpassa.

The purpose of this study is to indicate scattering process of spilled oil in Istanbul Strait and effectiveness of initial response reaction with an applied scenario. It has been understood that the oil spill response operation is very difficult where the places have high current condition like in the Istanbul Strait. For instance, it has been observed

that an oil boom established approximately two hours later than the oil spill is insufficient against the 1200 MT oil spill with the effect of the exiting current and wind conditions in Istanbul Strait.

Turkish Ministry of Environment and Urbanization and Ministry of Transport, Maritime Affairs and Communication are responsible for an oil spill response in the first stage. All oil response equipments and means are in Istinye which is placed in the mid of Istanbul Strait. It's highly important that, all equipments and assets have to be deployed in efficient time after the oil spill occurrence. Therefore all organizations and precautions should always be reviewed by realistic drills.

As an obvious it is available to deploy not only single oil boom but also other response equipments and assets for Turkish Directorate General of Coastal Safety and it's possible to simulate in PISCES. This case study is a part of simulation which is focused on the importance of initial reaction which is conducted by single oil boom. Profound study could be done by using different oil spill response equipments as well.

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Evaluation of Environmental Education in the New Science Education Curriculum in Turkey

Gulfem MUSLU KAYGISIZ^{1}, Fatma Melike UCAR¹*

Abstract

In Turkey, environmental education is generally taught in science courses in primary education. The evaluation of new Science Education Curriculum(2017) is so important for improvement of the environmental literacy. Therefore, this study intends to determine the current situation of the environmental subjects in the science education curriculum in terms of the content and objectives. For this purpose, objectives related to environment in each unit were determined, and the units, learning areas and subjects were classified based on grade levels. Besides, the objectives related to environment were analyzed in terms of five different aspects, namely science knowledge, environmental knowledge, sustainability, engineering skills and attitudes, values and perspectives through document analysis. For an effective environmental education, some implications and recommendations were suggested based on the finding.

Keywords: *Environmental Education, Analysis of Science Curriculum, Document Analysis*

1. INTRODUCTION

When considered the environmental problems, it is seen that the major reason of most of them is human behavior [1]. For example, human behavior directly or indirectly leads to global warming, air pollution, water pollution and desertification. Similarly, their solutions are also considered as human behavior [2]. Accordingly, creating an alteration in human behavior toward being more pro-environmental is seen as one of the main elements of environmentalism [3].

Based on the view that the main aim of education is shaping human behavior[4], Reference [5] stressed that education has a crucial role in changing people's behaviors to solve the environmental problems. Because of this important role, increasing international recognition for environmental degradation and sustainable development becomes to be associated with education and schooling in the last 30 years [6]. Nowadays, the concept of environmental education(EE) becomes widespread among curriculum developers, educational policymakers, and researchers. Thus, studies focused on implications of environmental education have increased.

As described in the Tbilisi Declaration, the vital role of EE is as follows: "*Environmental education has an evident role to play if the issues at stake are to be grasped and if all concerned are to be provided with the knowledge, skills and attitudes which can modify the existing situation for the better. The role of education in the face of environmental problems and opportunities is therefore a crucial one. Environmental education should be integrated into the whole system of formal education at all levels to provide the necessary knowledge, understanding, values and skills needed by the general public and many occupational groups, for their participation in devising solutions to environmental questions.*"(p.12)[7]

Accordingly, the quality of environmental education in primary education becomes more important, since cognitive conscience to the environment begins to develop in the age of 9-10, and children can evaluate the interaction between human and nature in this period [8]. In other words, gaining environmental awareness to students starts during primary education years in classroom environment. Therefore, it is vital that environmental education in primary education is well planned.

Reference [4] stated that the deficiency of environmental education programs might derive from several reasons, involving the focus of these programs. According to Reference [9], there is a greater emphasis that is given to the cognitive domain than the affective domain. Besides, knowledge about ecological concepts is perceived as if they are robust environmental knowledge.

^{1*} Corresponding author: Hasan Kalyoncu University, Department of Elementary Education, Gaziantep, Turkey. gulfem.muslu@hku.edu.tr

¹ Hasan Kalyoncu University, Department of Elementary Education, Gaziantep, Turkey. melike.ucar@hku.edu.tr

However, the affective domains as important as the cognitive domain. Reference [10] stated that students do not use only cognitive skills when they learn about environmental problems and make decisions to engage in solutions; they also use affective domains, such as paying more attention to and empathizing with environmental problems. Therefore, the process in which students develop their own values through their interaction with social and natural environments should also be considered and supported by curriculum. Moreover, curriculum should also contribute to students' moral development regarding values, motives, and ethical concerns in order to enable them to cope with environmental problems and to participate in the decision-making processes.

While this is what has to be done, it has been determined through research that the existing situation is in a different form. In these studies, the subjects in the school curriculum from the past to the present are mostly stated as "education about the environment" ([11],[12],[13]). That is, it has been determined that environmental education that is given is aimed at "giving information about the environment" rather than acquiring skills and attitudes[14]. Similarly, several studies determined that the general purposes of environmental education in curriculums are determined as followings; providing awareness of the environment and its problems, giving information, developing positive attitudes, recognizing environmental problems, developing research skills, and contributing to solving these problems([15],[16]). Accordingly, it is clear that there is an understanding that individuals are going to be act more sensitively towards their environment when they are aware of their environment and its problems. Although the emphasis is on being conscious about environment, the literature shows that being conscious is not enough to solve the problems [17]. Likewise, Reference [18] stated that education for sustainable development could be achieved by developing skills, attitudes, values and understanding instead of by passively acquiring knowledge. Therefore, environmental education has a significant role in understanding and interpreting the sustainable development goals since it can make a difference in behavior by providing individual and collective responsibility. For this reason, it was emphasized that "member countries should review their education systems in order to develop a broader understanding of sustainable development" in the final report in Brussels [19]. Additionally, to provide sustainable economic growth, many countries have aimed to raise generations with the 21st century skills indicating a broad set of skills such as critical thinking and problem solving, communication and collaboration, creativity and innovation skills and learning dispositions that is needed to be achiever in 21st century. For this aim, students should be educated to get some skills such as science, technology, math and engineering skills. These skills can be provided with STEM education that is an approach to teaching and learning that integrates the content and skills of science, technology, engineering, and mathematics. Therefore, curriculums should enable to develop such skills for a sustainable life and environmental education should be given with this approach.

Consequently, for an effective EE, there is a need for a curriculum that can contribute to develop students' attitudes, values, understandings, knowledge about environment and sustainability; and skills related to protecting the environment and solving the environmental issues through innovative approaches. This need also exist in Turkey.

In Turkey, EE in primary education is integrated with life sciences lessons and mostly with science lessons. That is, environmental issues are incorporated into scientific subjects in the school curriculum. The last two science education curriculums in Turkey focus on recognizing and understanding the environment, keeping the environment clean, understanding the relationship between the environment and human, and being responsible for the environment [20]. However, The Ministry of National Education [21] has just announced newly developed elementary science curriculum, which begins to be implemented in 2017-2018 fall semester. There are some new objectives related to environment in this curriculum.

Therefore, it is thought that analyzing new science education curriculum and making suggestions can contribute to the improvement of the environmental education. For this reason, the purpose of this study is to reveal the current situation of environmental education in new elementary science curriculum. Therefore, the following questions were examined:

1. What is the current situation of the environmental subjects in the science education curriculum in terms of the content?
2. What is the current situation of the environmental subjects in the science education curriculum in terms of the objectives?

2. MATERIALS AND METHODS

Within the scope of the aim of this research, each unit in elementary science curriculum (3th- 8th grade levels) was examined in terms of the objectives related to EE to determine how well the content is given in terms of the knowledge and skills emphasized in the literature. In other words, this study investigated the extent to which curriculum involves objectives related to developing attitude, value, skill and understanding, besides to objectives related to getting information and understanding the subject. To do this, the objectives related to environment were determined firstly, and these objectives were analyzed in terms of five different aspects, namely science knowledge, environmental knowledge, sustainability, attitudes, values and perspectives, and engineering skills through document analysis.

3. RESULTS AND DISCUSSION

3.1. Results And Discussions Regarding First Research Question

Within the scope of first research question, science curriculum was examined and the units, learning areas and subjects were classified based on grade level. Besides, objectives related to environment in each unit were determined for each grade level.

The number of these objectives and total number of objectives in each unit was determined and thus the percentage was calculated and presented in Table 1.

Table 1. Frequency of objectives related to environment based on grade level, unit and subject in science curriculum

Grade	Unit/ Subject Area	Subject	Frequency of Objectives related to Environment	Frequency of Objectives in Unit	Percent age (%)	
3	3.1. Knowing Our Planet / Earth and the Universe	3.1.1. Shape of the World	5	5	100	
		3.1.2. The Structure of the World				
	3.5. Light and Sounds in Our Environment/Physical Events	3.5.2. Sources of Light	2	8	25	
		3.5.4. Sounds in Our Environment				
3.6. Journey to the World of Living Creatures/ Living Creatures and Life	3.6.1. Knowing the Living Creatures in Our Environment	8	8	100		
	3.6.2. Me and My Environment					
	3.7. Electrical Vehicles / Physical Events	3.7.2. Electrical Sources	1	4	25	
4	4.1. Earth's Crust and the Movements of the Earth / Earth and the Universe	4.1.1. Structure of Earth's Crust	5	5	100	
		4.1.2. Our World's Movements				
	4.5. Lighting and Sound Technologies / Physical Events	4.5.3. Light pollution	6	12	50	
		4.5.5. Sound Pollution				
	4.6. Human and Environment / Living Creatures and Life	4.6.1. Conscious consumers	2	2	100	
5	5.1. Sun, Earth and Moon / Earth and the Universe	5.1.1. Sun's Structure and Properties	9	9	100	
		5.1.2. Moon's Structure and Properties				
		5.1.3. Moon's Movements and Phases				
		5.1.4. Sun, Earth and Moon				
		5.1.5. Destructive Natural Disasters				
	5.2. The World of Creatures/ Living Creatures and Life	5.2.1. Knowing the Living Creatures	2	2	100	
	5.6. Human and Environment / Living Creatures and Life	5.6.1. Bio-diversity	6	6	100	
6	6.1. Solar System and Eclipses / Earth and Universe	6.1.1. Solar System	5	5	100	
		6.1.2. Eclipses of the Sun and Moon				
		6.4.3. Matter and Heat	7	13	53.84	
	Matter and Heat / Matter and Its' Nature	6.4.4. Fuels				
		7.1. Solar System and Beyond / Earth and the Universe	7.1.1. Space Research	1	10	10
7	7.4. Pure Substances and Mixtures / Substance and Its' Nature	7.4.5. Domestic Waste and Recycling	5	16	31.25	
		7.5. Interaction between Light and Substance	2	12	16.66	
		7.6. Reproduction, Growth and Development of Living Creatures, / Living Creatures and Life	3	9	33.33	
		7.6.3. Reproduction, Growth and Development of Plants and Animals				
8	8.1. Seasons and Climate / Earth and the Universe	8.1.1. Occurrence of Seasons	3	3	100	
		8.1.2. Climate and Air Movements				
	8.2. DNA and Genetic Code/ Living Creatures and Life	8.2.3. Mutation and Modification	7	13	53.84	
		8.2.4. Adaptation				
		8.2.5. Biotechnology				
		8.4. Matter and Industry / Matter and Its' Nature	8.4.4. Acids and Bases	3	17	17.64
			8.6. Energy Conversion and Environmental Science / Living Creatures and Life	8.6.1. Food Chain and Energy Flow	15	15
			8.6.2. Energy Conversions			
		8.6.3. Substance Cycles and Environmental Problems				
		8.6.4. Sustainable Development				
	8.7. Electric Charges and Electricity Energy / Physical Events	8.7.3. Transformation of Electric Energy	5	10	50	

When general structure of the Table.1 is examined, it can be seen that the subjects related to environment are not just in the unit, which is specific for environment education; instead, they spread into the whole units. For example, there are four units related to environment in 3th grade. While three of them (Knowing Our Planet, Light and Sounds in Our Environment, Journey to the World of Living Creatures) is directly related to environment, one of them (the unit of electrical vehicles) is not. However, this unit includes information about waste batteries and the harm that they give to the environment. On the other hand, some

units, which seem to be directly related to environment, do not include only environmental subjects or objectives. For instance, the unit of Light and Sounds in Our Environment in 3th grade includes 8 objectives but just two of them are related to environment, although it is expected that all of the objectives in this unit is about environment.

Additionally, the percentages of environmental objectives are not same in each grade level. For example, for 3th grade level, total number of objectives is presented as 25, and total number of environmental objectives is determined as 16. Thus, the percentage is calculated as 64%. This calculation is also conducted for other grade levels and results are as followings: 68.42% for 4th grade; 100% for 5th grade; 66.66% for 6th grade; 21.27% for 7th grade; 56.89% for 8th grade. Accordingly, percentages of environmental objectives are mostly in 5th grade level, while at least environmental objectives are in 7th grade.

3.2. Results And Discussions Regarding Second Research Question

When examined the general structure of the objectives, it was seen that they are mostly related to recognizing environmental problems and developing environmental awareness. Therefore, it can be said that they were similar to previous program in this context. For example, within the general objectives of the new science curriculum, which aims to raise all individuals as a science literate, the following statements regarding environmental education are included:

- *“To give basic knowledge about astronomy, biology, physics, chemistry, earth and environmental sciences and science and engineering applications*
- *To acquire the scientific process skills and scientific research approach in the process of understanding the relationship between human being and environment and discovering nature; and thus solving the problems encountered in these areas.*
- *To recognize the mutual interaction between individual, environment and society; to develop awareness of sustainable development in society, economy and natural resources.*
- *To arouse interest and curiosity about and to develop an attitude towards the events that are happening in the nature.” (p.5).*

In addition to these general objectives, there were also specific objectives related to making research, designing project, development of responsibility in this curriculum. For example,

“F.7.4.5.2. Designing projects for the recycling of domestic solid and liquid wastes.”

“F.8.6.3.5. c. It is mentioned that individuals have duties and responsibilities in the prevention of climate change.”

“F.3.6.2.6. Offering solutions to protect the natural environment by making research.”

In addition to these skills, the engineering skills were also emphasized unlike the previous program. Thus, it can be said that the curriculum aims to adopt STEM approach, which is so current nowadays. The inclusion of the objectives that enable to associate this approach with environmental education can be considered as one of the strengths of the curriculum. However, it should also be noted that the number of such objectives are limited in the curriculum. These objectives should take part in science curriculum to develop students’ 21st century skills.

After presenting the general structure of objectives in the curriculum, environmental objectives are examined in terms of five different aspects, namely science knowledge, environmental knowledge, sustainability, attitudes, values and perspectives, and engineering skills. In this study, these aspects are represented as SK, EK, S, AVP, and STEM, respectively. During the examination, the environmental objectives are classified based on the relevant grade levels, and the number of objectives are calculated. Finally, frequency of these skills and values addressed by the objectives are presented in Table 2.

Table 2. Frequency of environmental objectives in terms of science knowledge, environmental knowledge, sustainability, attitudes, values and perspectives, and engineering skills

Grade	SK	EK	S	AVP	STEM	Total
3	9	4	-	3	-	16
4	4	4	-	6	-	14
5	8	3	-	6	-	17
6	9	-	2	2	-	13
7	2	4	2	4	-	12
8	13	8	5	6	3	35
Total	45	23	9	27	3	

As can be deduced from Table 2, there are 102 environmental objectives in the curriculum. Among them, 107 objectives could be classified as science knowledge, environmental knowledge, sustainability, attitudes, values and perspectives, and engineering skills because some objectives could be used in the scope of more than one category, while some objectives were found not to be put into any category. Accordingly, 16 of them were in 3th grade; 14 of them were in 4th grade; 17 of them were in 5th grade; 13 of them were in 6th grade; 12 of them were in 7th grade; 35 of them were in 8th grade. Therefore, environmental objectives are mostly in 8th grade level, while at least environmental objectives are in 6th and 7th grades. Consequently, it seems that there is no systematic distribution of skills based on grade levels. When these objectives are classified according to the category they address, it was seen that these objectives refer to science knowledge (f=45), environmental knowledge (f=23), sustainability (f=9), attitudes, values and perspectives (f=27), and engineering skills (f=3).

When both grade level and these categories examined together, it was seen that frequency of objectives related to the science knowledge indicating that dealing with science dimension of environment concept in this study is higher than the other aspects in each grade level. In other words, as indicated in the literature and similar to the previous program environment is mostly perceived as a natural environment, that is, the science dimension is highlighted more than the skills related to environment.

In terms of environmental knowledge, it was seen that it is highest for 8th grade and lowest for 6th grade. Actually, there was no objectives that can be considered as environmental knowledge in the 6th grade curriculum. The emphasis was given to the science knowledge in this grade level. At this point, it is important to note that the conceptions of soil, landslide and erosion were not included in the curriculum, contrary to previous program. These conceptions are key elements of both science education and environmental education. Therefore, this situation is one of the limitations of the new curriculum. The inclusion of these concepts is strongly suggested in this study.

Sustainability is considered as one of the key elements of environmental education. Therefore, it is expected that the curriculum should include objectives related to sustainability. However, when were examined the objectives in terms of sustainability, it can be said that the objectives at 3th, 4th, 5th grade level were not associated with sustainability, but some objectives at 6 and 7 grade level were associated with sustainability. Besides, it was seen that there were five objectives directly related to sustainability in the topic of "sustainable development" in 8th grade level.

Additionally, the objectives related to improvement of attitude, value and perspective were distributed almost equally across grade levels. They are just low in 6th grade level. After science knowledge, the highest emphasis is given to the improvement of attitude, value and perspective in the curriculum. As stated in the introduction part, this situation is unexpected because environmental education is generally given with the aim of giving information about the environment rather than acquiring skills and attitudes. Therefore, it can be said that increase in the importance of developing attitude, value and perspective is one of the strength sides of the new curriculum. However, it is also should be noted that the new curriculum also highlights the knowledge firstly, like previous science curriculum, and thus it is recommended that this emphasis on giving knowledge should be reduced.

Finally, the objectives related to developing engineering skills and integrating these skills with science, technology and math was seen at 8th grade level in the curriculum. However, projects, materials, and products should be developed for a sustainable future and this can be possible with improving some skills such as science, technology, math and engineering skills. Therefore, involving these skills into the environmental education has a crucial role. For this reason, increasing objectives related to these skills across all grade levels is recommended.

4. CONCLUSION

For a sustainable life, environmental awareness should be raised and children should be educated for being an environmentally literate. Curriculums are the tools by which students reach this intended point. For this reason, curriculums should be regulated and applied appropriately. However, it is seen that changes in the renewed curriculum are not enough since it still emphasizes the knowledge. In addition to knowledge, students should have positive attitudes, values, and perspectives and support some skills. The number of objectives related to improvement of attitude, value and perspective were higher than the previous curriculum, but it is still lower than the objectives related to giving knowledge to the students. Therefore, emphasis on developing positive attitudes, values, and perspectives should be enhanced in the curriculum [9],[10]. Moreover, although general structure of science curriculum adopts the STEM approach relatively with the inclusion of engineering skills into it, this is not true for environmental education. That is, the great majority of objectives related to environment do not address the engineering skills, whereas, subjects in the environmental education is suitable to improve these skills. Therefore, curriculum should include environmental objectives that can also support these skills and positive attitudes, values, and perspectives. Finally, although environmental education is given for a sustainable life, objectives related to sustainability is so limited in the curriculum. Therefore, it is recommended that the awareness and consciousness of sustainability should begin earlier and should be more.

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Determination of the Optimum Compression Pressure of Miscanthus Reinforced Brake Linings via Taguchi Method

Mahmut UNALDI^{1*}, Recai KUS²

Abstract

One of the parameters that affect braking performance of the vehicles is brake lining and therefore its materials and composition ratios also affect the braking performance. Studies on brake lining compositions without asbestos are still continuing after asbestos was banned in many countries. Production parameters of the brake lining also hold an important place alongside the chemical composition affecting the brake lining performance. Determination of the production parameters and ingredient ratios are usually done according to trial and error method in brake lining production. This method requires production of numerous samples and also leads to difficult data processing due to big amounts of experimental data. Taguchi method was utilized in this study in order to determine the proper compression pressure value for the ingredients that are used for producing brake linings. Experimental results of the samples for density, hardness and wear rates according to the different mixture ratios and compression pressure values were evaluated by means of the Taguchi method which is an experimental design method. Hardness value increased while density and wear rates were decreasing as the miscanthus ratio in the mixture was increased according to the experimental results. Inverse proportion was detected between compression pressure values and wear rate. The optimum compression pressure value was observed as 100 MPa according to Taguchi and ANOVA results for the ingredients and mixture ratios that were used.

Keywords: Brake Lining, Density, Hardness, Miscanthus, Taguchi Method, Wear.

1. INTRODUCTION

Many ingredients (such as antimon trisulphide, copper, lead, tin, potassium titanate, silicon carbide) in brake linings have negative effects on the environment. When the usages of expensive flexten fibers and environmentally hazardous copper and asbestos as reinforcement components are considered, natural fibers become more attractive due to their low cost, low environmental impact and higher mechanical properties [1-3].

Brake linings are one of the most complex composites because their physical and chemical properties depend on many different components. These different properties of the components also affect the production parameters of the brake linings. Recently statistical methods also used for determination of the brake lining production parameters whereas trial and error method has been used till today [4, 5].

The number of the components, their ratios and production parameters for the sample production of brake linings increase the sample number and experiment number to be conducted. Producing samples with numerous components and production parameters and making experiments with them become impractical due to non-economical and time consuming tasks. Reducing these parameters via various means and obtaining experimental data by producing limited number of samples become possible thanks to the statistical methods. The Taguchi method, as one of the most used experimental design method by the scientists in the literature, is a very beneficial tool used for determining optimum combination among different levels of different parameters [6, 7]. The scale for measuring and evaluating the quality in Taguchi Experimental Design method is the ratio of the determined signal (S) to the noise factor (N). While signal value represents the real value that is desired to be measured and provided by the system, noise factor is the ratio of the unwanted factors in the measured value. Calculations are done in this method according to one of the criteria which are Smaller is Better, Larger is Better and Nominal is Best while experimental results are being converted to Signal/Noise (S/N) ratio. The highest S/N ratio is the best result in the conclusion no matter what criteria is

^{1*} Corresponding author: Selcuk University, Cihanbeyli Vocational School, Department of Motor Vehicles and Transportation Technologies, 42850 Cihanbeyli/Konya, Turkey. munaldi@selcuk.edu.tr

² Selcuk University, Faculty of Technology, Department of Mechanical Engineering, Selcuklu/Konya, Turkey: recaikus@gmail.com

selected. Alongside with this, the influence rates of the factors to the experimental results and their confidence levels are determined by means of the performed variance analysis (ANOVA) [8, 9].

In the study reported by Kim, Kim and Jang in 2003, the best production parameters of brake lining samples constituted by 15 different components were determined by using Taguchi method according to surface hardness, porosity, wear and friction characteristics. Hardness and porosity were mentioned to be effective parameters at an important level for compression pressure according to S/N ratios and ANOVA results. 6 minutes compression period, 225 °C temperature and 27 MPa compression pressure were denoted to be the optimum production parameter values proper to the ingredients [10].

Optimum production parameters and friction material formula were determined via Taguchi Optimization technique for the brake lining samples produced using date stone shell as agricultural waste in the work of Ibadode and Dagwa (2008) and 17 MPa compression pressure, 160 °C temperature and 8 min compression time were stated approximately as the results [11].

Zaharudin et al. (2012) analyzed production parameters such as compression pressure, compression duration and temperature with Taguchi method according to physical and tribological properties of the brake lining samples. As conclusion, optimum production parameters were determined as 50 tones, 150 °C and 10 min. for compression pressure, compression temperature and compression period respectively [12].

In the studies for determining mixing periods of the ingredients as the first phase of sample production, 5, 10 and 15 minutes were used in the literature. 10 minutes duration time was stated as sufficient in the studies conducted by Sugoza et al. (2011) and Zaharudin et al. (2012) [12, 13].

Optimum compression pressure value was determined utilizing Taguchi analytical method for brake pad samples produced with miscanthus as reinforcement ingredient in this study. S/N ratios, distribution graphics and ANOVA analysis data were interpreted according to density, hardness and wear rate results of the samples that were produced for different compression pressures in order to determine optimum compression pressure considering mixture ratios of the components.

2. MATERIALS AND METHOD

Miscanthus as reinforcement ingredient, cashew as lubricant, alumina as abrasive, phenolic resin as binding ingredient and calcite as filing ingredient were used for brake lining sample production in this study. The ratios of the ingredients (Table 1) of the produced samples were determined according to the miscanthus which has the lowest density. It was decided to produce samples by putting miscanthus between 10% to 30% mass ratio considering experiences obtained from previous studies. Changes in the miscanthus amounts were counterbalanced by the filling material due to the fact that filling material is an ineffective element. Besides being an energy plant which was cultivated in the context of Ege University Scientific Research Project (BAP No: 2010-ZRF-033) Miscanthus plant is a product that can be used as reinforcement ingredient in composite materials due to its fibrous structure. Characteristic properties and cultivation conditions of the Miscanthus plant were stated by Geren et al. (2011) and its usage as reinforcement ingredient was reported by Acikel et al. (2011) [14, 15]. Phenolic resin was supplied by Cukurova Kimya, Cashew was supplied by Eren Balata and Calcite was supplied by Yapitas Madencilik as the remaining ingredients that were used in the study.

Table 1. Ratios of the components in the brake lining mixtures

Miscanthus	Cashew	Alumina	Phenolic Resin	Calcite
10	10	10	10	60
20	10	10	10	50
30	10	10	10	40

The compression pressure as one of the primer phases of the production process is effected from grain size of the used ingredients. The most utilized method for determining the grain sizes of the materials in powder form is Sieve analysis. Particle distribution results in the sieve analysis are indicated in mass. 500 µm, 250 µm, 125 µm, 63 µm and 45 µm sieves were used respectively according to ASTM B214 [16-18]. Grain sizes of phenolic resin, calcite and alumina are pretty small as they can be seen in Fig. 1. Grain sizes of cashew and miscanthus in the other hand are relatively bigger. Small grains fill the spaces between bigger grains and lead to decreased porosity thanks to small difference between grain sizes of the components [16, 19].

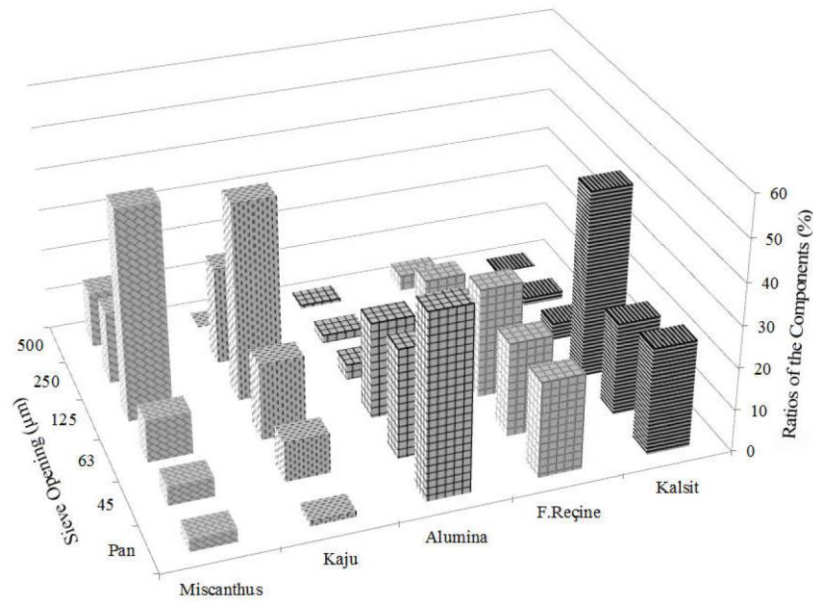


Figure 1. Sieve analysis of brake pad components.

1 mg sensitivity scale was used during preparation of the mixtures and measuring the densities. The duty for mixing the powder materials was done with 600 W power electrical mixer for 10 minute period.

Compression pressure is effected the physical properties of the used components [19]. In the work, brake linings were produced considering the maximum and minimum ratios of the ingredient that has the lowest density in the mixture due to the fact that grain size and mixing ratio of the ingredients affect the optimum compression pressure. Samples were produced by compressing them with double effect press at 50, 100 and 200 MPa for three different mixture ratios according to the Table 1.

Compression was done after the mold was heated up to 150 °C. Mold was kept at 150 °C during the compression and the press was released and applied again three times in 10 minutes period in order to enable gases to flee as it was given in the literature [20]. Surfaces of the samples were grinded with 180, 320 and 400 numbered grinders after the production process.

Wear rates and hardness experiments of the samples were determined according to TSA 555. Wear experiments were carried on using a pin on disk device and a disc manufactured from gray cast iron (190 HB) was used as abradant. Experiments were conducted with 10mm diameter cylindrical sample at 40 N load, 1 m/s speed and for 5000 m distance. Hardness values were measured under 600 N load with 12.7 mm diameter ball in Rockwell test R scale [21].

Density values of the samples depend on the ratios of the components constituting the brake lining and compression pressure. Density values of the samples were determined by means of a precision scale and Archimedes principle according to equation (1) [21, 22].

$$\rho_s = \frac{m_1}{m_1 - m_2} \cdot \rho_w \quad (\text{g/cm}^3) \quad (1)$$

ρ_w : Density of distilled water [$\rho_w=0.9977 \text{ g/cm}^3$ at 22.5°C].

ρ_s : Density of the sample, [g/cm^3].

m_1 : Weight of the sample in air, [g].

m_2 : Weight of the sample in water, [g].

In this study, smaller is the best criteria was selected for the wear rate as the target criteria and larger is the best criteria was selected for density and hardness parameters as the target criteria of the Taguchi Experimental Design in this study. The formulas in order to calculate S/N according to this approach are provided below:

$$\text{Larger is the best } S/N = -10 \cdot \log[\Sigma(1/Y^2)/n] \quad (2)$$

$$\text{Smaller is the best } S/N = -10 \cdot \log(\Sigma Y^2/n) \quad (3)$$

Y= measurement value,

n= trial number.

3. RESULTS AND DISCUSSION

Orthogonal (vertical) L9 array with 3 levels and 2 variables (miscanthus ratio and compression pressure) of the Taguchi was used in order to determine the compression pressure as the first and the most important parameter of the brake lining production process in this study and averaged values and S/N ratios of values from density, hardness and wear rate experiments that were conducted three times are presented in Table 2.

The importance level among production parameters which affect quality characteristics can be determined by means of ANOVA. In Table 3, P values that indicate the pithiness level of each variable on the results, sum of squares (SS), average of squares (AS), percentage distribution (PD) and F values can be seen.

Table 2. S/N ratios according to L9 orthogonal array

Experiment No	Ratio	Pressure	d	H	W	d_S/N	H_S/N	W_S/N
1	10	50	1,83	102,8	3,1E-04	56,41	41,59	-60,29
2	10	100	1,93	105,3	2,5E-04	51,71	40,95	-57,96
3	10	200	1,96	107,1	1,9E-04	57,17	39,96	-56,31
4	20	50	1,68	107,1	2,8E-04	54,74	39,14	-59,94
5	20	100	1,78	109,6	2,2E-04	50,04	38,50	-57,61
6	20	200	1,81	111,4	1,6E-04	55,50	37,51	-55,96
7	30	50	1,64	111,3	2,8E-04	55,27	38,86	-59,15
8	30	100	1,74	113,8	2,2E-04	50,57	38,22	-56,82
9	30	200	1,76	115,6	1,6E-04	56,03	37,22	-55,17

d: Density (g/cm³); H: Hardness (HRR); W: Wear rate

Table 3. ANOVA results

	Density		Hardness		Wear Rate	
	Mixing Ratio	Compression Pressure	Mixing Ratio	Compression Pressure	Mixing Ratio	Compression Pressure
SS	1,44	0,65	0,68	0,18	3,04	32,02
AS	0,72	0,32	0,34	0,09	1,52	16,01
PD	68,90	31,10	79,07	20,93	8,67	91,33
F-value	92,05	41,14	76,82	19,67	5,40	56,94
P	0,000	0,002	0,001	0,009	0,073	0,001

The effect of mixing ratio on wear rate is observed as meaningless ($P > 0.05$) while mixing ratio and compression pressure are seen as meaningful for density and hardness at 1% level ($P < 0.01$) when the analysis results in Table 3 are examined. The importance level among the parameters is interpreted by means of the percentage distribution (PD) calculated from sum of the squares of S/N ratios [23, 24]. It is seen that mixing ratios are very effective on density and hardness values according to variance analysis results given in Table 3. Compression pressure affects the wear rate in an intensive manner while it isn't very effective against density and hardness according to the ANOVA results.

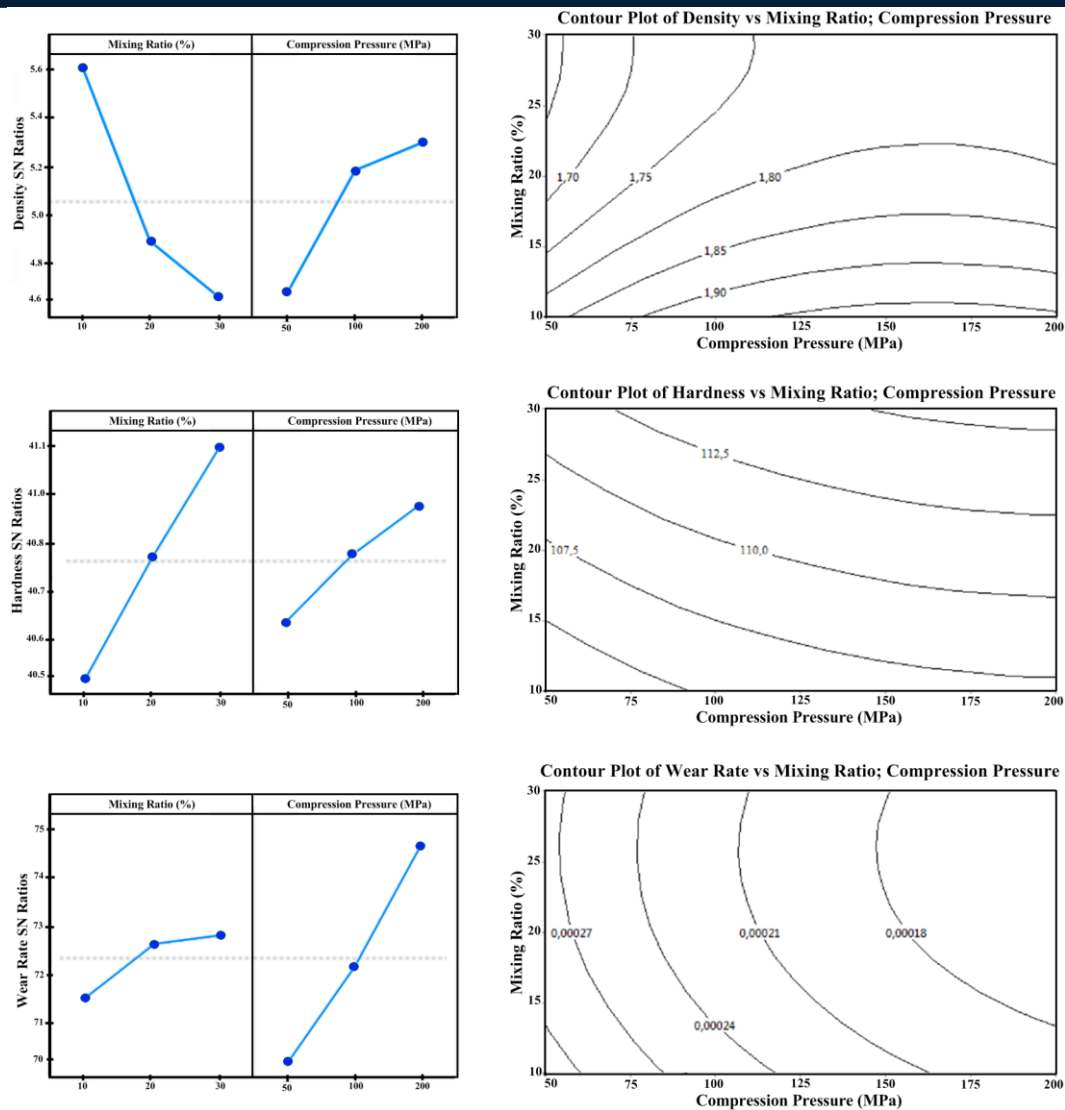


Figure 2. SN ratios and distribution graphics in contours

S/N ratios and distribution graphics (contour plots) of the data derived from the experimental results are provided in Fig. 2. Distribution of average values of density, hardness and wear rate according to mixing ratio and compression pressure are given on the right column of Fig. 2. S/N graphs of density, hardness and wear rate are given on the left column of Fig. 2. It is observed that the density is affected more by mixing ratio while it is also affected by the compression pressure value when the S/N graphics are interpreted. The density is inversely proportional to the miscanthus ratio. In order to produce high density samples, Miscanthus ratio has to be low and compression pressure value has to be high.

Likewise, hardness value is affected by compression pressure and mixture ratio whereas it is affected more by the mixture ratio. For the wear rate, the changes in the compression pressure affect wear rate quite a lot while the effect of the mixture ratio is relatively not much.

In the contour plot graphs, density, hardness and wear rate of samples change lines are seen according to values of compression pressure and mixture ratio. Decrease of wear rate and increase of hardness are seen directly proportional to the increase in mixture ratio and compression pressure when the graphics in the right column of Fig. 2 are examined. Density distribution graphic is the most effective one among these graphics for determining compression pressure. What kind of change the density variation yielded according to the mixture ratios and compression pressures can be clearly seen. Acquisition of the highest density value at 125 MPa for every mixture ratio is realized. 100 to 125 MPa values of the compression pressure being appropriate for the production parameters to be determined are seem to be ideal when density variation graphic is examined considering the hardness and wear rate variation graphics.

4. CONCLUSIONS

Taguchi method was utilized instead of trial and error method considering that there would be time and cost gains by reaching the optimum values in shorter times in this study which was done in order to make experimental results more accurate and meaningful while paying attention to the studies reported in the literature about multi component composites. It was realized that variations in the investigated properties are not only dependent to compression pressure while the effect levels of the ingredient ratios are comprehended whereas the attained data as a result of the conducted study agree with the literature.

Important changes took place in density and hardness values in conjunction with the increase of the ratio in the mixture. Densities of the samples decrease by means of the increasing ratio of the miscanthus in the mixture due to its low density among the other ingredients. But hardness values of the samples are increasing while their density values are decreasing. The change in the mixture ratio didn't affect wear rate too much. Especially wear rate increased a lot by the increase in compression pressure. The increase tendency of the density slows down after 100 MPa compression pressure value. Density doesn't increase further because the porosity between the components reaches the smallest value starting from this compression pressure value. According to the S/N graphics, low ratio of the miscanthus in the mixture that is prepared during the production of the brake lining and high compression pressure to be applied will lead to desired result for making density high. It is understood that the ratio of the miscanthus and value of the compression pressure should be high when S/N graphics of the hardness value and wear rate are considered.

Following statements are provided according to the evaluations at the end of this study:

- It was realized that miscanthus ratio can be taken between 5-25% instead of 10-30% in the next studies.
- It was decided that 100 MPa compression pressure value can be used as production parameter in the studies in which miscanthus, cashew, alumina, phenolic resin and calcite are used for brake pad production due to the fact that making the production at values as low as possible can ease the production.
- Various statistical methods can be utilized in order to optimize production parameters and then these can be compared.
- Determination of the production parameters can be done scientifically by using Taguchi method instead of trial and error method in multi component composite material studies.
- In order to optimize the ratios in the mixture, ratio interval of the ingredients should be determined carefully in the first stage. Following productions should be operated according to predetermined production parameters by optimizing production parameters according to different mixture ratios.

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Estimation of Microbiological Quality of Sea Water on the Coast of Vlore, Albania

Aurora BAKAJ¹, Mirela LIKA (CEKANI)², Aida RAPI³

Abstract

Background: Estimation of microbiological quality of the recreational water is an important environmental health and resource management issue. In order to estimate the microbiology quality various indicator organisms have been used as surrogate markers of risk. The aim of the study: is to determine the hygienic quality of coastal waters in Vlore seacoast. Settings and Design: Is performed, a bacteriological and a chemical study during 2016 in Vlore bay. Seawater samples were taken bimonthly 7 stations evenly distributed on this coast line. Sea water was collected in sterilized and autoclaved bottles. Methods and Material: Total coliform, fecal coliform and fecal streptococci were estimated using MPN method, while environmental parameters were estimated using standard methods. Results: During the investigation period the temperature has been monitored as an environmental factor that has a strong impact on organisms. Our data show that during the year, bacterial indicators had highest concentration during August in most of the sampling stations. This could be due to the high number of people visiting the beaches in the coast line during summer time. High concentration of fecal bacteria was associated with high concentration of nitrite and ammonia. Conclusions: The poorest water quality is especially in the urban discharged points and in the areas close to them. The present study indicates that seawater along the Vlore seacoast is under high anthropogenic impact.

Keywords: *E. coli, environmental parameters, bacterial indicators, chemical indicators, sea water quality.*

1. INTRODUCTION

The different types of pathogenic microorganisms that are transmitted by water to humans include bacteria (including blue-green algal toxins), viruses, and protozoa. The major part of the infectious agents transmitted by recreational water result of faecal pollution (especially human). Sources of faecal pollution include sewage, surface runoff, domestic animals, and wildlife.

Routine examination of recreational water for the presence of intestinal pathogens would be a tedious and difficult, if not impossible, task. It is much easier to demonstrate the presence of some of the nonpathogenic intestinal bacteria such as *Escherichia coli* and *Streptococcus faecalis*. When they are detected in water, it can be assumed that the water has been contaminated with fecal material.

Coliform bacteria (of which *Escherichia coli* is a member) are widely used as indicators of fecal contamination of both fresh and marine waters. Coliform bacteria occur normally in the intestines of humans and other warm-blooded animals and are discharged in great numbers in human and animal waste. In polluted water, coliform bacteria are found in densities roughly proportional to the degree of fecal pollution. Coliform bacteria are hardier than disease-causing, non-spore-forming bacteria; therefore, their absence from water is an indication that the water is bacteriologically safe for human consumption.

However, they are less sensitive than viruses and protozoan cysts to environmental factors (i.e., pH, temperature) and to disinfection. The presence of coliform bacteria, on the other hand, is an indication that disease-causing bacteria also may be present and that the recreational water is unsafe for swimming.

The coliform group includes all aerobic and facultative anaerobic, Gram-negative, non-spore-forming, rod-shaped bacteria which ferment lactose with gas production in prescribed culture media within 48 hours at 35°C. Coliform bacteria include *Escherichia coli*, *Citrobacter*, *Enterobacter*, and *Klebsiella* species.

Bacteriological water quality criteria (fecal pollution bacteria thresholds) have been recommended to ensure bathers' health. These criteria are based on estimates of bacterial indicator counts and gastrointestinal illness rates that are currently believed to provide a high level of protection for bathers' health [1, 2].

Several epidemiological surveys have revealed a number of health impacts associated with recreational water use with known point sources of faecal contamination (such as domestic sewage or storm-drain runoff) has been associated with an increased risk for transmission of infectious diseases (including gastroenteritis, and febrile respiratory, skin, eye and ear illnesses) [3-14]. However, gastrointestinal illness is the most commonly identified problem and also has formed the rationale for water quality criteria world-wide

Almost all the methods used to detect *E. coli*, total coliforms or fecal coliforms are enumeration methods that are based on lactose fermentation [15]. The Most Probable Number (MPN) method is a statistical, multi-step assay consisting of presumptive, confirmed and completed phases. In the assay, serial dilutions of a sample are inoculated into broth media.

Our study is focused on the seacoast line of Vlora, which is one of the priority pollution hotspot. The aim of the study was monitoring the seawater quality, as well as to evaluate the role of seasonal changes of the environmental parameters, on the dynamic of fecal bacteria indicators.

Environmental factors, such as tide, rain, and solar insolation, can also have significant and varying effects on the levels of indicator and pathogenic microbes [16-18]. Evaluation of water quality is performed by measurement of some bio-chemical parameters and concentration of pollution indicators organisms [19]. The bio-chemical parameters analyzed were: temperature, pH, ammonia, phosphate, nitrite and nitrate. Total coliforms, fecal coliforms and fecal streptococci were analyzed as pollution indicator organisms.

2. MATERIAL AND METHODS

2.1. Selection of sampling site

Bacteriological and chemical study was carried out by us from March to September during 2016 on the seacoast of Vlora. The seawater samples were taken bimonthly from 7 stations: (Plazhi i vjetër, Triporti, Kompleksi Marina, Vefa, Plazhi i ri, Kala and Jonufër) evenly distributed on this coast line.

2.2. Recovery methods

Water samples were collected in sterile glass bottles from seawater of Vlora bay over one year period (January, 2016 to January, 2016). The samples were taken from up to 30 cm below the water surface, stored in isothermal containers (about 4°C), and shipped to the laboratory, where they were processed within 4 h of collection.

2.3. Methods for bacteriological analyses

Each water sample was analyzed for total coliforms, fecal coliforms and fecal streptococci. Total coliforms fecal, fecal coliforms and fecal streptococci were estimated using MPN method [20-24], while environmental parameters like temperature, pH, ammonia, phosphate, nitrite and nitrate were estimated using standard methods [23]. In this paper we will present only a part of these parameters.

The number of total coliforms, fecal coliforms in a water sample can be determined by a statistical estimation called the most probable number (MPN) test. This test involves a multiple series of Durham fermentation tubes on lactose broth and is divided into three parts: the presumptive, confirmed and completed tests. While MPN for fecal streptococcus was determined by fermentation test on azid dextrose broth for preliminary test and TTC agar for confirmatory test [23, 24].

3. RESULTS AND DISCUSSION

The objective of our study was monitoring the seawater quality, as well as to evaluate the role of seasonal changes of the environmental parameters, on the dynamic of fecal bacteria indicators. The seacoast of Vlora, is the region under our study. Vlora bay is one of the most visited beaches in Albania and in the same time one of the identified pollution hotspot sites.

Temperature is widely recognized as an important controlling factor in influencing bacterial growth. In climates where water temperatures are warm, bacterial growth may be very rapid. However, the minimum temperature at which microbial activity was observed varied from system to system.

These seasonal fluctuations seem to be related to water temperature. It has been reported [25] that the temperature of water correlates significantly with the die-off of *E. coli*, and is governed by the insolation.

During the investigation period the temperature varied from 11.6°C in March to 23.7°C in summer time (Fig. 1). Temperature changes were a result of climatic conditions and season.

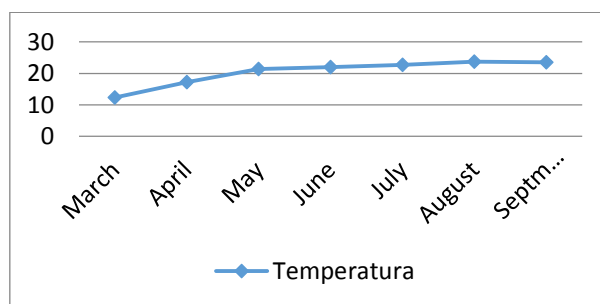


Figure 1. Temperature changes in the seawater of Vlora bay.

Sea water quality criteria proposed by the World Health Organization and other international foundations are usually suggested as microbiological pollution indicators, total coliforms, fecal coliforms, enterococci and fecal streptococci [26-28]. The combination of several indicators is likely to offer a global picture of water quality [28].

In our study we used two parameters for fecal contamination: concentration of total coliform bacteria and the presence of *Streptococcus fecalis*. In Fig. 2 are presented seasonal changes of the total coliform concentrations, measured with MPN method. During 2016 the highest number of total coliform bacteria was registered in August.

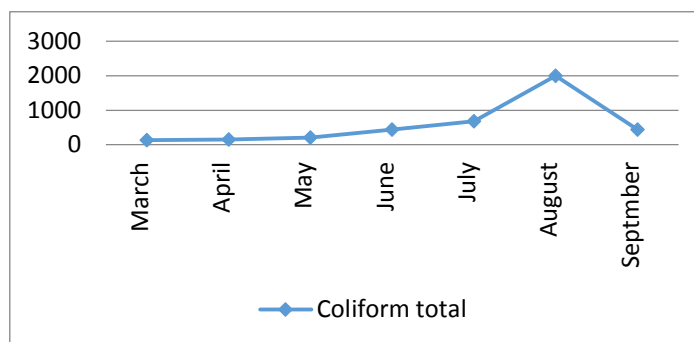


Figure 2. Dynamics of total coliform bacteria during the investigation period

The findings of this study suggest that fecal coliforms represent the most sensitive bacterial indicator when it comes to seasonal fluctuation related to increased human presence during the summer months.

This study suggests that bathing waters may be subject to increased microbiological pollution during months of increased tourist movement, and that this could be attributed

to the excessive human presence despite the increased daylight and solar radiation during the summer months which affect the die-off rate of microorganisms. Fecal coliforms represent the most sensitive indicator of this seasonal pollution.

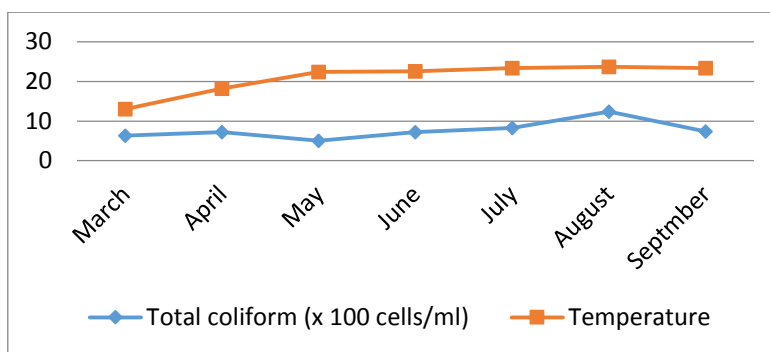


Figure 3. Dynamics of water quality parameters during March – September 2016

Our data show that in general the number of total coliform bacteria during investigation period of 2016, has a peak in August. This month register the highest values of total coliform bacteria in most of the sampling stations. This could be due to the high number of people visiting the beaches in this coast line during summer time.

High concentration of fecal bacteria were associated with high temperature [29]. Comparison of these parameters is very important in determination of water quality (Fig. 3).

Fecal streptococci are unlikely to be the most sensitive indicator of the seasonal fluctuation of sea water pollution according to the results of this study, although their survival in the environment is generally characterized as limited. Fecal streptococci originate from the intestine of warm-blooded animals, so they are an indicator of water contamination by fecal material. Other similar streptococci originating from plants or plant products can also be found in the sea water. So data on fecal streptococci concentration are considered more valid in relation to sea water pollution when combined with fecal coliform data [30].

The presence of fecal streptococci was another parameter for determination of fecal pollution of seawater [31-33].

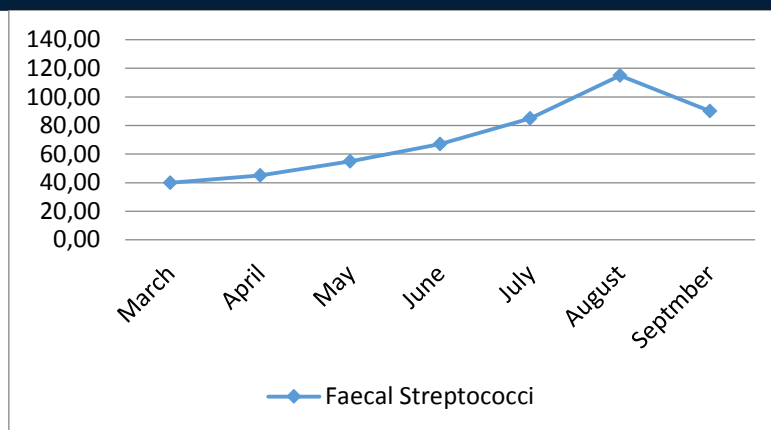


Figure 4. Percentage of sampling stations where faecal streptococci were present

The presence of these bacteria in water could be of human or animal origin. In our study we made a qualitative estimation and not a quantitative one, for these bacteria in seawater (Fig. 4). During 2016 investigation period, we observed an increase in the number of sampling stations where faecal streptococci were present.

4. CONCLUSIONS

The present work represents the study of seawater quality in the selected beach site, which is a popular bathing site. Seawater along the Vlora bay is under high anthropogenic impact.

The results obtained suggested that the quality of the recreational waters, examined in this study, can be strongly influenced by temperature and the increased human presence during the summer months. We observed an improvement in the quality of seawater in Vlora. If this is a tendency, is very important for the people that visit this area during summer time. Nevertheless, there is still much work to do in order the water of some area become safe for bathing.

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COD (Chemical Oxygen Demand) Removal From Wastewater Using Ti/IrO₂/RuO₂ Anode

Baybars Ali FIL¹, Recep BONCUKCUOGLU², Alper Erdem YILMAZ³, Sinan KUL³, Suleyman UZUNER^{1*}

Abstract

In this study, it was investigated that COD (chemical oxygen demand) removal from Pistachio Processing Industry Wastewaters (PPIW) with high organic pollution. As anode material mixed metal oxide coated titanium (Ti/IrO₂/RuO₂) anode and as cathode material cathode stainless steel plate cathode were used. 5 anodes and 5 cathodes were positioned parallel to the fiberglass reactor and required electric current was ensured by a DC power supply. COD removal parameters were selected such as mixing speed and supporting electrolyte species. The effect of mixing speed on the COD removal efficiency has been studied in a wide range of range 0-600 rpm. In studies that examined the effects of the electrolyte support, COD removal efficiencies were investigated no-supporting electrolyte and supporting electrolyte types such as Na₂SO₄, NaNO₃, KCl and NaCl. All experiments were performed in wastewater natural pH (≈5,3), at room temperature and 5 mA/cm² in the presence of current density. From obtained results, mixing speed was not effective a parameter, whereas the type of supporting electrolyte was determined that the COD removal efficiency significantly increases.

Keywords: Supporting electrolyte; Electro-oxidation, Ti/IrO₂/RuO₂ anode, COD Removal, Pistachio Processing Industry Wastewaters (PPIW)

1 INTRODUCTION

Pistachio is a delicious and beautiful meal. The fruits of the peanut tree are bunches and pink color. Pistachio has a wide range of consumption. It is used in dessert and salty foods as it is defeated as a snack. Pistachio grows in areas that are long, hot and dry in summers and relatively cold in winters. In the composition of pistachio, there is an average of 5.6% Water, 19.6% Protein, 53.2% Fat, 19% Carbohydrate and 2.6% Ash [1].

Many methods are used in the treatment of wastewaters with high organic pollution such as pistachio processing industry wastewater (PPIW). some of them can be listed as wet air oxidation [2], biological treatment [3], photo-fenton oxidation [4], ultrasonic irradiation, electrocoagulation [5], ozonation [6], membrane process [7] and electro-oxidation [8, 9].

Electro-oxidation from these methods; is based on the direct or indirect oxidation of organic substances using an insoluble anodic material such as boron-doped diamond [10, 11], graphite [12, 13], coated titanium [14, 15], platinum [16, 17].

In this study, the treatability of Pistachio Processing Industry Wastewaters (PPIW) by electro-oxidation method has been investigated. In the study, Ti/IrO₂/RuO₂ sieve type plates were used as the anode material. The effects of parameters such as mixing speed and supporting electrolyte type on the COD (Chemical Oxygen Demand) removal efficiency were investigated.

2 MATERIAL AND METHOD

The batch experimental design is shown in Fig.1. The monopolar electro-oxidation consists of approximately an 800 mL electrochemical glass-made batch reactor with five Ti/IrO₂/RuO₂ anodes and five stainless steel plate cathodes. The length and width of each electrode is 100 mm and 60 mm, respectively. The total effective electrode surface areas of anode and cathode

^{1*} Balikesir University, Engineering Faculty, Department of Environmental Engineering 10145 Balikesir-Turkey

² Istanbul University, Engineering Faculty, Department of Environmental Engineering 34320 Istanbul-Turkey

³ Ataturk University,, Engineering Faculty, Department of Environmental Engineering 25240 Erzurum-Turkey

*Corresponding author e-mail: suzuner@balikesir.edu.tr

are 2000 cm². The distance between electrodes was selected as 5 mm. The applied voltage was kept constant by means of a power supply (Chroma 6204P-40-120). During the experiments, pH, conductivity and temperature of wastewater samples were measured by a pH-meter (WTW-340i). Every experiment was performed at the room temperature. The initial pH value of the wastewater is about 5.3. NaCl, KCl, Na₂SO₄ and NaNO₃ were used as support electrolyte types.

$$\% \eta = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

$\eta(\%)$: % removal efficiency for COD, C_0 (mg/L): Initial COD concentration, C_t (mg/L): The concentration of the COD remaining in the solution at any time t .

$$J \left(\frac{\text{mA}}{\text{cm}^2} \right) = \frac{I}{A} \quad (2)$$

J (mA/cm²): Current density, I (Ampere): Current intensity, A (cm²): Total wet surface area of anodes and cathodes.

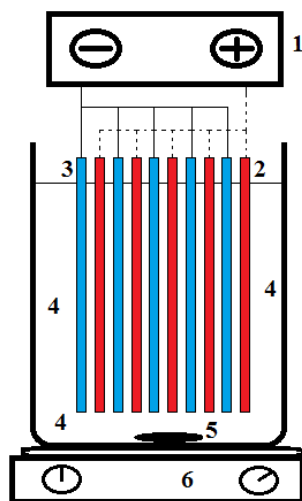


Figure 25. Experimental set up (1. DC Power, 2. Ti/IrO₂/RuO₂ anode, 3. Stainless steel cathode, 4. Wastewater, 5. Magnet, 6. Magnetic stirrer)

3 RESULT AND DISCUSSION

Effect of Mixing Speed

To investigate the effect of mixing speed on COD removal, electro-oxidation process was carried out using various mixing speed varying from 0 to 600 rpm at natural wastewater pH (≈ 5.3) and 5 mA/cm² for 5 h electrolysis time. The effect of mixing speed can be seen from Fig. 2. The increase in mixing speed did not have a significant effect on the efficiency of COD removal. In the experiments in which the effect of the mixing speed was investigated, the lowest removal efficiency was obtained at 0 rpm mixing speed with 39.77% and with the highest removal efficiency at 200 rpm mixing speed with 41.73%. The results show that there is only a 1.96% difference between the highest removal efficiency and the lowest removal efficiency. For this reason, there is no mixing in the subsequent experiments.

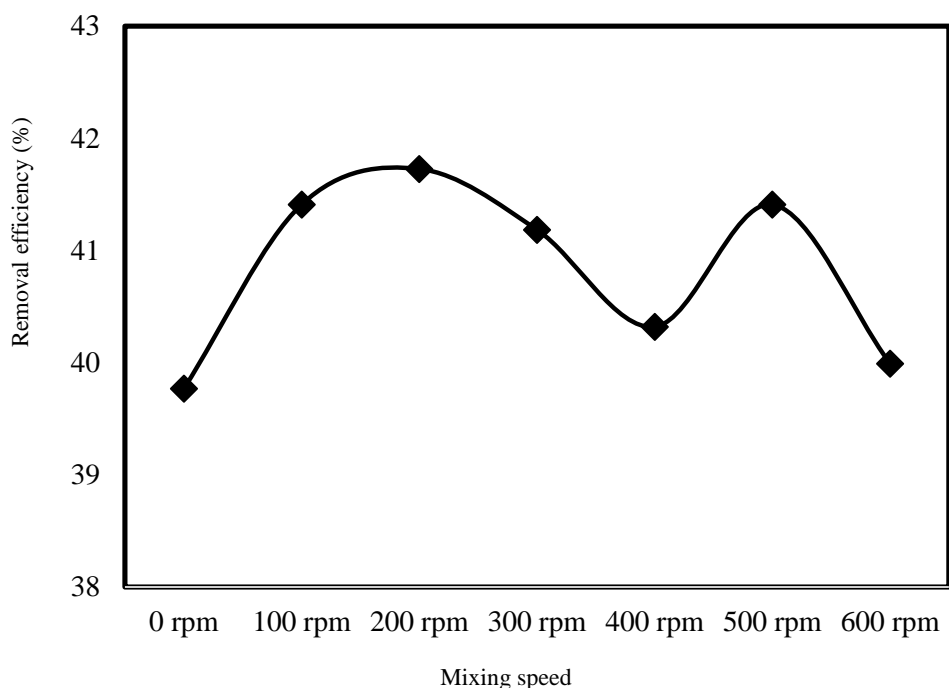


Figure 26. The effect of mixing speed on COD removal efficiency ($J: 5 \text{ mA/cm}^2$, $\text{pH} \approx 5.3$, $T: 25^\circ\text{C}$)

Effect of Supporting Electrolyte Types

Effects of supporting electrolyte type on the COD removal by electro-oxidation was investigated at wastewater natural pH, 5 mA/cm^2 current density, 0.50 M supporting electrolyte concentration for 5h electrolysis time. Supporting electrolyte types were selected different salt types such as Na_2SO_4 , NaNO_3 , NaCl and KCl which have a high solubility in aqueous media. The results were showed in Figure 3. As can be seen from the results, the addition of wastewater support electrolyte significantly affected COD removal. The removal efficiencies were 39.77%, 47.13%, 58.18%, 70.74% and 76.66% for the unsalted, Na_2SO_4 , NaNO_3 , KCl and NaCl , respectively. As can be seen from the results, the highest treatment efficiency were achieved in the type of supporting electrolyte containing chlorine. The chlorine present in the solutions is converted into the oxidant species HOCl and OCl^- by the influence of current density and wastewater pH value. This increases the effect of indirect electro-oxidation. Similar results are available in the literature [18, 19].

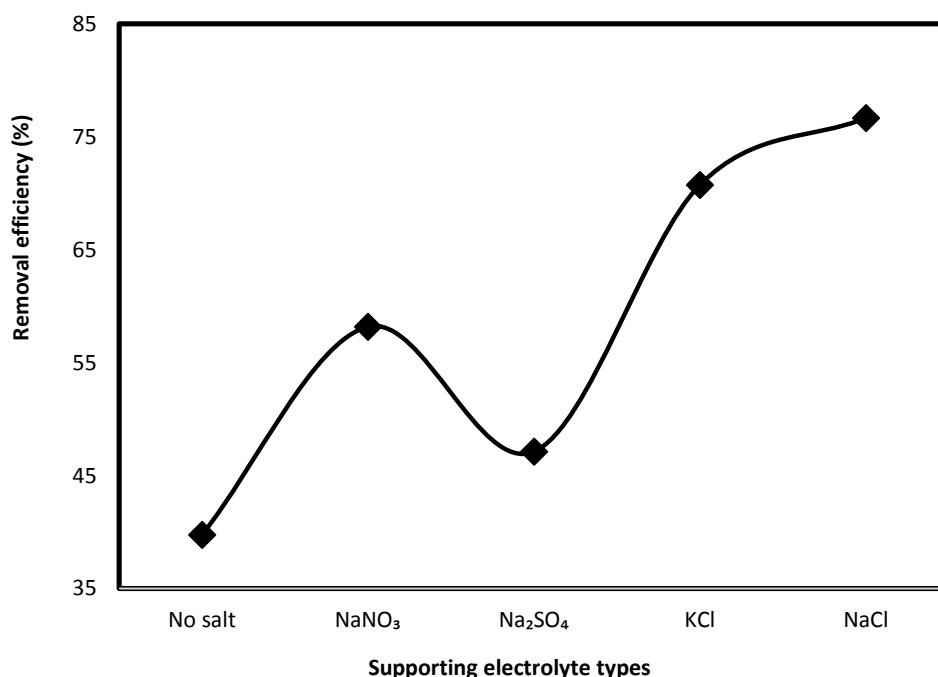


Figure 27. The effect of supporting electrolytic type on COD removal efficiency ($J: 5 \text{ mA/cm}^2$, $\text{pH} \approx 5.3$, $T: 25^\circ\text{C}$)

4 CONCLUSION

In this study, the treatment Pistachio Processing Industry Wastewaters (PPIW) by electro-oxidation method was investigated and the following results were obtained:

1. Studies of the effect of mixing speed have been carried out at speeds ranging from 0 rpm to 600 rpm. However, it has been determined that the mixing speed has no significant effect on the COD removal efficiency.
2. Studies of the effect of supporting electrolyte types were investigated in 0.5 M constructions of Na₂SO₄, NaNO₃, NaCl and KCl salts. Support electrolyte types containing chlorine have been found to significantly increase the efficiency of COD removal.

The results show that electro-oxidation can be used effectively in the treatment of organic wastewaters.

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Study of The Electrochemical Oxidation of Organic Dyes

*Baybars Ali FIL¹, Recep BONCUKCUOGLU², Alper Erdem YILMAZ³,
Burhanettin FARIZOGLU¹, Suleyman UZUNER^{1*}*

Abstract

Dyes used in textile industries lead to many environmental problems. In this study, it was investigated that removal of organic dye by electro-oxidation using graphite rod anode and steel rod cathode. Experimental parameters were selected as effect of supporting electrolyte types and supporting electrolyte concentration in batch studies. Support electrolyte types were selected as NaCl, KCl, Na₂SO₄ and NaNO₃. Experimental results were showed that NaCl and KCl were very effective supporting electrolyte types than NaNO₃ and Na₂SO₄. In subsequent experiments, the effect of supporting electrolyte concentration using NaCl was studied. It was determined that increasing concentrations of NaCl was increased treatment efficiency, importantly

Keywords: *Color removal, Electro-oxidation, Graphite, Supporting Electrolyte, Steel Cathode*

1 INTRODUCTION

When the wastewaters containing the color are applied to the receiving medium without any treatment, both the visual pollution event and the toxic organics which are present in the dye molecules are given to the receiving environment. For this reason, it is important to treat the wastewater from the stained materials up to the permitted limits [1].

Electrocoagulation [2], reverse osmosis [3], adsorption [4], membrane filtration [5], ozonation [6], electro-fenton [7], and chemical precipitation [8] are the most commonly used methods for the dye removal of wastewater. Electro-oxidation is one of the most effective methods recently used for color removal [9].

The basic principle in electro-oxidation is that organic pollutants are broken up in the final production on the surface of the anode and in the solution with the help of insoluble anode [10].

In this study, the treatment of basic yellow dye from synthetic solutions by electro-oxidation using graphite anode and steel cathode has been investigated. As experimental parameters, the effect of supporting electrolyte type and supporting electrolyte concentration on treatment efficiency was investigated.

2 MATERIAL AND METHOD

500 ppm stock solution of Reactive Black 5 (RB) paint was used in the study. The general formula of the RB5 dye is C₂₆H₂₁N₅Na₄O₁₉S₆. The molecular structure of the dye is given in Figure 1 and the molecular weight is 991.789 g/mol. The treatment of synthetic wastewater by electro-oxidation process and the current density are calculated by the following equations;

^{1*} Balikesir University, Engineering Faculty, Department of Environmental Engineering 10145 Balikesir-Turkey

² Istanbul University, Engineering Faculty, Department of Environmental Engineering 34320 Istanbul-Turkey

³ Ataturk University,, Engineering Faculty, Department of Environmental Engineering 25240 Erzurum-Turkey

*Corresponding author e-mail: suzuner@balikesir.edu.tr

$$\% \eta = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

$\eta(\%)$: % removal efficiency, C_0 (mg/L): Initial dye concentration, C_t (mg/L): The concentration of the dye remaining in the solution at any time t .

$$J \left(\frac{\text{mA}}{\text{cm}^2} \right) = \frac{I}{A} \quad (2)$$

J (mA/cm²): Current density, I (Ampere): Current intensity, A (cm²): Total wet surface area of anodes and cathodes.

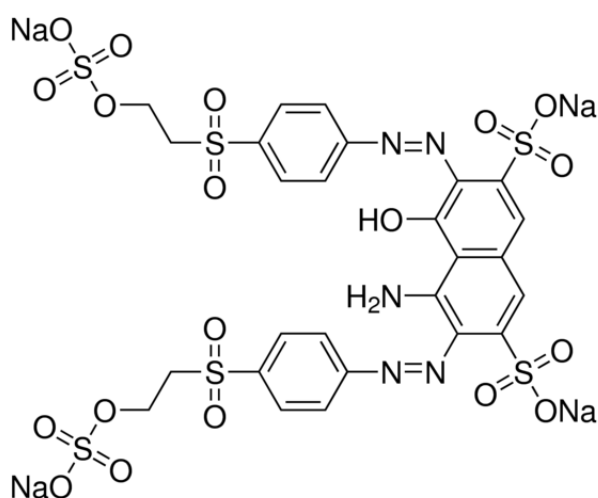


Figure 28. Molecular structure of Reactive Black 5 (RB5)

The initial pH value of the wastewater is about 5.0. Color removal experiments were performed using 750 mL synthetic wastewater samples in a 1 liter coated glass reactor. Four graphite rod anodes were used as the anode material, and four stainless steel rod cathodes were used as the cathode material. Color measurements were made at 597 nm on a Cadas 30-S spectrometer. NaCl, KCl, Na₂SO₄ and NaNO₃ were used as support electrolyte types. The experimental setup in which the experiments are carried out is shown in Fig. 2 [11, 12].

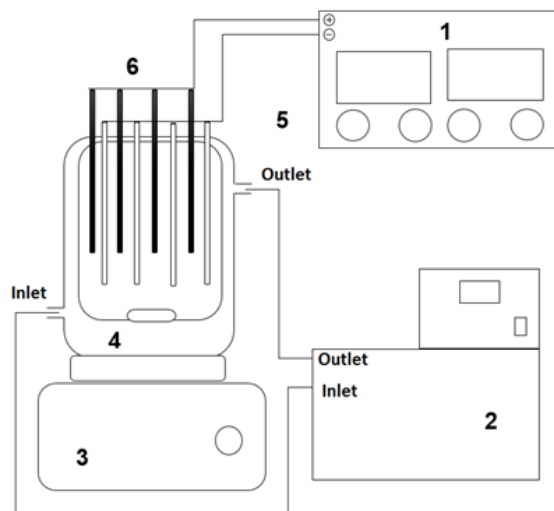


Figure 29. Experimental set up (1. DC Power, 2. Constant temperature water circulator, 3. Magnetic stirrer, 4. Glass reactor, 5. Steel rod cathode, 6. Graphite rod anode)

3 RESULT AND DISCUSSION

Effect of Supporting Electrolyte Types

The effect of the supporting electrolyte concentration was carried out at 5 mM concentrations of NaCl, KCl, Na₂SO₄ and NaNO₃ salts. Other experimental conditions were selected as wastewater pH (≈ 5.0), 2.86 mA/cm² current density, 50 mg/L initial dye concentration, 25° C temperature, 400rpm mixing speed. Experimental data were analyzed during the 30-minute experiment and the results obtained are shown in Fig. 3. % removal efficiencies were obtained for NaCl, KCl, Na₂SO₄ and NaNO₃ as 89.96%, 72.45%, 41.14% and 30.13%, respectively. As can be seen from the results, the highest treatment efficiency were achieved in the type of supporting electrolyte containing chlorine. The chlorine present in the solutions is converted into the oxidant species HOCl and OCl⁻ by the influence of current density and wastewater pH value. This increases the effect of indirect electro-oxidation. Similar results are available in the literature [11, 12].

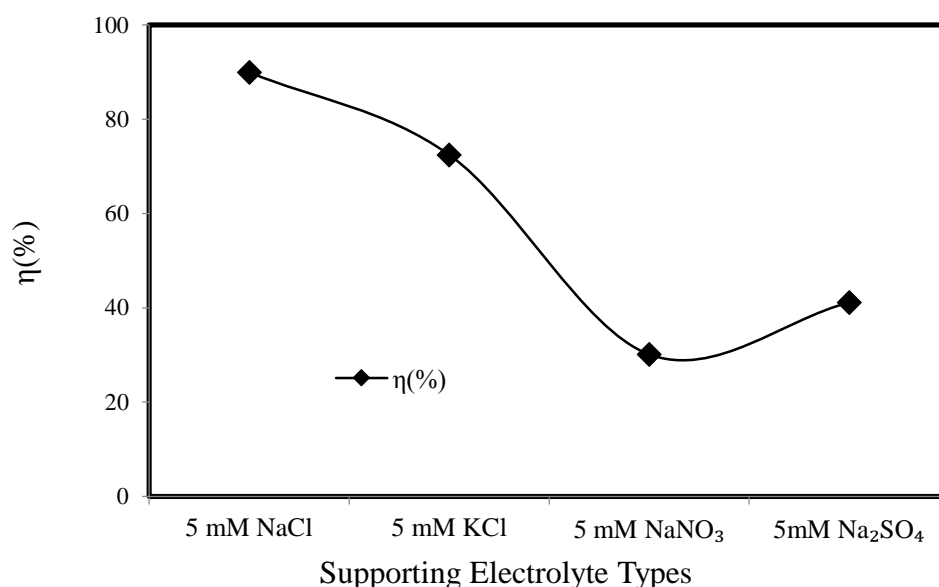


Figure 30. The effect of supporting electrolytic type on dye removal efficiency (C_0 : 50 mg/L, J : 2.86 mA/cm², pH ≈ 5.0 , T : 25°C, SS: 400 rpm)

Effect of Supporting Electrolyte Concentration

The effect of the supporting electrolyte concentration was studied with the NaCl support electrolyte type, from which the highest removal efficiency was obtained. The effect of the supporting electrolyte concentration was determined at a concentration of 2.5, 5.0, 7.5 and 10.0 mM at natural pH (≈ 5.0), at 25° C temperature, at a stirring rate of 400 rpm, at a initial dye concentration of 50 mg/L, 2.86 mA/cm² current density, 30 minutes for the test period. The results obtained are given in Figure 4. Support electrolyte concentration is one of the most important parameters affecting indirect electro-oxidation. As the amount of supporting electrolyte increases, intermediates such as OCl⁻ and HOCl, which are predominant in the oxidative properties of chlorine, are increasing, thereby increasing the efficiency of indirect electro-oxidation [13, 14].

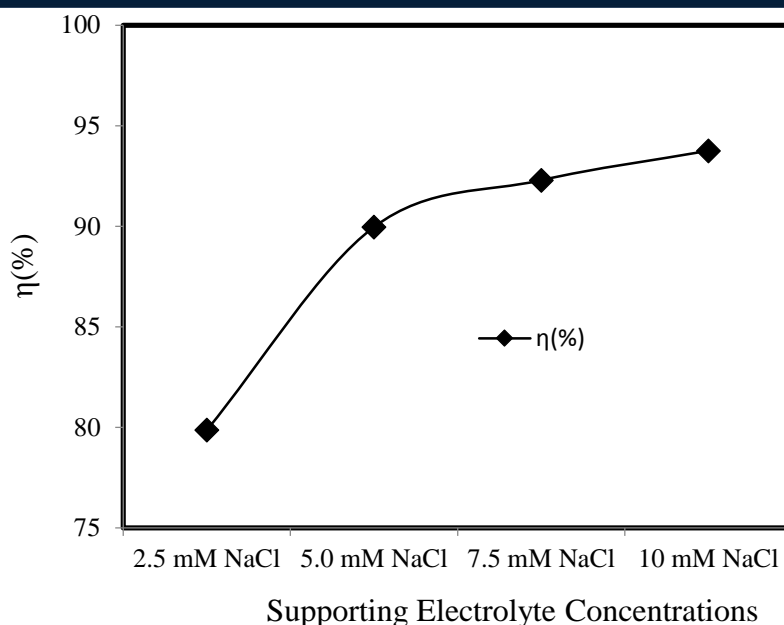


Figure 31. The effect of supporting electrolytic type on dye removal efficiency (C_0 : 50 mg/L, J : 2.86 mA/cm², pH=5.0, T : 25°C, SS: 400 rpm)

4 CONCLUSION

In this study, the treatment of synthetic wastewaters containing Reactive Black 5 (RB5) by electro-oxidation method was investigated and the following results were obtained:

- In studies in which the supporting electrolyte types was examined, it was found that the same concentration of the support electrolyte under constant conditions increased the efficiency of the addition of the support electrolyte and the most effective supporting electrolyte was NaCl with 89.96%.
- In the studies in which the supporting electrolyte concentration was examined, it was concluded that the increasing concentration of added supporting electrolyte increased the purification efficiency and the ideal supporting electrolyte concentration was 5 mM NaCl.

From these results, it can be concluded that electro-oxidation is an effective process in the treatment of wastewaters containing dye and that graphite, which is an economical anode material, can be used effectively.

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Modalities to Reduce the Potential Pollution Risk from Dairy Farms to Avoid Ambient Environment Contamination

Elena POGURSCHI¹, Marin MONICA^{1*}, Dumitru DRAGOTOIU¹, Tomita DRAGOTOIU¹

Abstract

The surveillance, prevention, disproof and disposal of problems arised in livestock farms as a result of uncontrolled and unsafe feeding of animals is an objective in order to maintain the profitability of the production activity. The aim of the paper is to apply a complex but easy-to-integrate technology in the dairy cow production chain that enhances the digestive use of non-protein nitrogen sources (urea) by the addition of a natural mineral product represented by the volcanic tuff. Moreover, it has also been pursued to reduce the nitrogen pollution by retaining the ammonia released in the manure decomposition process using the volcanic tuff in chopped straw used as bedding in the dairy farm. In the experiment, 60 cows from the Holstein Friesian breed were used, which were divided into 4 batches, namely a control batch, for which the volcanic tuff was not used and 3 experimental batches for which both urea and volcanic tuff was used as a food additive in the ratio with the amount of 200, 300 and 400 g of tuff/head/day. Additionally, for the experimental batches the volcanic tuff was used and added to the chopped straw bedding in the amount of 400 g/head/week. It has been found that the volcanic tuff has reduced the release of ammonia in the external environment, improving the climate in the cow housing by reducing unpleasant odors and ammoniacal nitrogen emissions. Also, the use of urea and volcanic tuff has reduced the ammonia content of fresh manure, being observed an improvement in the organic nitrogen content of the manure, which will increase the efficiency and the degree of nitrogen absorption by the plants. In this way biowaste sources are obtained, respectively fertilizers containing nitrogen that will not be toxic to the environment.

Keywords: Volcanic Tuff, Urea, Dairy Farm, Nitrogen, Manure

1. INTRODUCTION

In livestock facilities, ammonia results primarily from the breakdown of urea (present in urine) by the enzyme urease (excreted in feces). Undigested feed protein and wasted feed are additional sources of ammonia in animal production systems. Strategies to reduce ammonia from animal housing focus primarily on preventing ammonia formation and volatilization, or downwind transmission of ammonia after it is volatilized.

The effectiveness of zeolites depends on the type of zeolite used, the purity and physico-chemical properties, and the level of supplementation in rations. In addition, the particle size of the zeolite material, crystal size and degree of aggregation, as well as the porosity of individual particles, determines zeolite action during gastrointestinal tract passage and strongly influences ion exchange, adsorption and catalytic properties.

Supplementation of zeolite ration produces positive effects on productive performance of cows, as well as has a complementary action, namely the prevention of diseases and the improvement of the animal health status [1].

A combination of two practices used to control ammonia emission from livestock housing has been experimented in the present survey: dietary manipulation and mineral amendment of the manure.

The volcanic tuff has been used as alimentary additive included in dairy cows feed but also as added to the litters used on the farm. These processes have been aimed at reducing the pollution with ammoniacal nitrogen both of the air in the shelter, which

^{1*} Corresponding author: University of Agronomic Sciences and Veterinary Medicine of Bucharest, Romania, marin_monica_zoo@yahoo.com

¹ University of Agronomic Sciences and Veterinary Medicine of Bucharest, Romania, dumitrudragotoiu@yahoo.com

will influence the amount of resulting pollutants and the residues resulting in farms in the form of manure mixed with the materials used as bedding.

2. MATERIALS AND METHODS

The biological material used in the experiment was represented by 60 cows belong to Holstein Friesians, homogeneous in terms of body weight, milk production, health status, which were divided into 4 batches, namely a control batch and 3 experimental batches.

All animals received the same ratio, Total Mixed Ratio (TMR), which was composed of corn silage (55.50%), alfalfa hay (10%), maize (7%), triticale (5%), soya meal (8%), beer residues (8%), molasses (1.80%), urea (1%), calcium carbonate (1.20%), dicalcium phosphate (1.00%), salt (0.5%), vitamin-mineral premix (1%).

In the experimental lots the volcanic tuff was introduced in quantity 200 g tuff/head/day for cows belong to experimental batch 1 (E1), 300 g tuff/head/day at the second experimental batch (E2) and 400 g tuff/head/day at the third experimental batch (E3). Also, for the experimental groups the volcanic tuff was used as well as added to the chopped straws bed in the amount of 400 g/head/week (Table 1).

Table 10. Experimental scheme

Batch	Period	n	Treatment	Objectives
Control batch (C)	February 2017 June 2017	15	Total Mixed Ratio (TMR)	-measuring the concentration of ammonia in the air;
Experimental batch E1	February 2017 June 2017	15	TMR + 200 g tuff/head/day 400 g/head/week in bedding	-determination of total nitrogen in the feces and the manure;
Experimental batch E2	February 2017 June 2017	15	TMR + 300 g tuff/head/day 400 g/head/week in bedding	-determination of organic nitrogen from fresh feces.
Experimental batch E3	February 2017 June 2017	15	TMR + 400 g tuff/head/day 400 g/head/week in bedding	

The volcanic tuff used had 2 mm granulation, 63,44% silicon dioxide, 3,45% sodium oxide, 5,18% potassium oxide. The experiment was carried out in two periods, in the winter time, February 2017, and in the summer time, June 2017.

Each period had duration of 21 days, during the ammonia content of the air in the shelters was determined, when the cows were kept in enclosed spaces separated in batches. The measure of the ammonia concentration in the air was done with a sensor which covered the range of 0 to 100 ppm.

At the end of the experimental period samples of fresh manure were collected, as well as removed manure composed of straw, manure and urine.

The determination of total nitrogen from feces and manure was done using the Kjeldahl method, and organic nitrogen from manure using the Barnstein method.

The experimental data have been statistically processed using an application in Microsoft Excel, and the significance of averages differences has been tested with the Student test.

3. RESULTS AND DISCUSSION

The data regarding the ammonia concentration in the shelter air as well as the total nitrogen and organic nitrogen content of the fresh feces and manure are shown in Table 2.

Analyzing the data on the total nitrogen content of the manure from the cows it was found that there were no significant differences between the harvesting periods, values between batches being close, but slightly diminished in experimental groups (3.56-3.87% from DM at the control batch and 3.33-3.84% from DM at the experimental batches).

Table 2. The ammonia concentration in the air and the nitrogen content of manure and manure

Batch	Period	Ammonia concentration in the air (ppm)	Total nitrogen in feces (% in DM)	Total nitrogen in manure (%)	Organic nitrogen in feces (% in DM)
Control batch (C)	February 2017	15	3.87±0.07	0.45±0.001	1.40±0.002
	June 2017	26	3.56±0.19	0.49±0.001	1.24±0.005
Experimental batch E1	February 2017	12	3.54±0.17	0.44±0.002	1.52±0.003
	June 2017	21	3.37±0.24	0.46±0.001	1.49±0.001
Experimental batch E2	February 2017	10	3.56±0.15	0.41±0.001	1.57±0.003
	June 2017	20	3.84±0.09	0.43±0.002	1.64±0.004
Experimental batch E3	February 2017	7	3.51±0.17	0.40±0.001	1.76±0.003
	June 2017	15	3.33±0.08	0.44±0.001	1.88±0.002

The organic nitrogen was also determined from fresh feces, resulting an increase of the proportion at the experimental groups, especially in the third experimental batch (E3), in which an amount of 400 g of tuff / head / day was used in ration, but also as bedding.

Under these conditions, the proportion of organic nitrogen in total nitrogen was 32% in the control group in June, while in the E3 group it was 56% during the same period of the year, the differences being statistically significant.

As a result, we can assert that the use of urea in combination with the volcanic tuff favors the presence of organic nitrogen in the manure, which will facilitate its absorption and use by the plants.

Regarding the ammonia concentration in the air from shelters, there were distinctly significant differences between the values recorded during the winter and the summer time.

In February, they varied between 7 ppm in experimental batch E3 and 15 ppm in the control group, while in June the values were between 15 ppm in the E3 group and 26 ppm in the control batch.

Also, as we have found, the variation of the concentration of ammonia in the air depending on the treatment applied, respectively the application of the volcanic tuff in the bedding combined with its use as an additive favored the retention of nitrogen and the reduction of air losses in the shelter by about 46% in winter and by 57% in the summer.

The obtained experimental data are also confirmed by the researches carried out by specialists in the field who have demonstrated that the application of zeolites to the cow's bedding can reduce ammonia emissions by 55% to 60% compared to an untreated bedding ([2]-[4]).

There are also claims that the use of zeolites, respectively clinoptilolites, in cow ration does not influence the composition or balance of the nitrogen in manure [5].

4. CONCLUSIONS

The use of the volcanic tuff as feed additives in the ration of dairy cows, but also as an addition to the their litter has the effect of reducing ammonia emissions and unpleasant odors in the animal shelter and further into the environment, knowing that livestock farms are a major pollutant for the environment.

The use of zeolites in admixture with urea administered to the cow ration significantly improved the organic nitrogen content of the manure, thus ensuring a universal organic fertilizer that will improve the activity of the macro and microorganisms in the soil and will stimulate the degree of nitrogen absorption by the plants.

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BIOGRAPHY

Name: POGURSCHI Elena. Personal information: 41 years old, animal science engineer, Lecturer PhD at the Faculty of Animal Science – The University of Agronomic Sciences and Veterinary Medicine Bucharest. Professional experience: received a degree in animal husbandry from the University of Agronomic Sciences and Veterinary Medicine (USAMV) Bucharest, Faculty of Animal Science, Romania, 2001. Since 2001 I worked as a lecturer at the Faculty Of Animal Science at the University of Agronomic Sciences and Veterinary Medicine Bucharest. During this time I received the following qualifications: 2001-2003- Master degree - Sustainability in Animal production, USAMV Bucharest; 2007 - PhD degree in fields of animal nutrition, USAMV Bucharest; 2016- Master degree – Nutrition and Food safety, University of Medicine and Pharmacy Carol Davila, Bucharest. Doing researches activities in various projects, and published a number of 67 scientific papers, more of them having as main research subject cattle's feeding and husbandry. The last researches had a big interest in milk quality and identification of antibiotics residues provided by the dairy farms from metropolitan area of Bucharest. Until now, the research career is materialized in success completion of 16 research projects founded by Romanian Government and World Bank.

Froth Flotation of plastics mixtures from WEEE products

Xi JIA^{1*,2}, Youcef BOUZIDI¹, Daniel FROELICH¹

Abstract

The amount of WEEE (Waste of Electric and Electronic) has largely increased these years. Sorting the plastics into their family species is an essential process for plastic recycling. Among different plastic sorting technologies, density sorting and optical sorting are the most widely used methods. However, both of them have their disadvantages, thus, plastics with dark colors or/and similar densities are more difficult to separate. Other limitations of plastic recycling exist as well, since many plastics are added with flame retardants which also set difficulties to recycling process.

In this case of study, we deal with the plastics the most present in WEEE which are acrylonitrile-butadiene-styrene (ABS), polypropylene (PP) and high impact polystyrene (HIPS), with Polyvinyl alcohol (PVA) as surfactant agent, try to separate them by froth flotation. Therefore, the effect of particle size fractions, conditioning time and behavior of surfactant agent including the concentration is analyzed, aim to improve sorting efficiency and find appropriate surfactant.

Keywords: Plastic Recovery; Flotation; Surfactant Agent; WEEE

1. INTRODUCTION

The production of electrical & electronic equipment leads to the growth of waste electric & electronic equipment (WEEE), the e-waste includes computers, consumer electronics, fridges, etc. which have been disposed off by their original users. It contains materials as ferrous/ no-ferrous metals, glass, plastics, etc. and these materials reappear as recycled products or in a form of energy after recycling and valorization.

In 2015, 710 millions of equipment were put on the market in France, representing 1,68 million tons of EEE, with a slight increase compared to that of 2014[1]. According to data from Table.1, with detail information listed, plastic materials take a part of 16.6% in the materials of WEEE (2015). Among these plastic, ABS (acrylonitrile-butadiene-styrene), PS (polystyrene) and PP (polypropylene) are the three types which possess the highest percentage[2]. In a case study of WEEE category represented for instance by IT (computers, phones, printers, etc.), culinary equipment, audio/video and vacuum cleaners, the three most represented is ABS, PP and PS, account for 65% of all plastic species[3]

Recycling of waste plastics can reduce the pollution caused by plastic incineration and landfill, which is of great significance to environmental protection, energy saving and emission reduction. The efficient recycling requires individual polymer types and grades before the regeneration process, to obtain a high purity recycled material. In particular, WEEE consists of about 30% plastics that contain toxic flame retardants such as tetrabromobisphenol-A (TBBA), polybrominated diphenyl ethers (PBDE) or decabromodiphenyl ethane (DBDE). These flame retardants can form toxic halogen dioxin or furan, and HCl or HBr through incineration and landfill activities[4]. According to the DIRECTIVE 2011/65/EU, for the concern of human health and environmental care, the PBDE and polybrominated biphenyls (PBB) as restricted substances, the maximum concentration values tolerated by weight in homogeneous materials is 0.1%[5]. Thus, the plastics containing these toxic chemicals need to be effectively and selectively separated before other distinctive recycling processes are undertaken.

^{1*} Corresponding author: Laboratoire Conception Produit Innovation, Chambéry (LCPI), Institut Arts et Métiers ParisTech, Chambéry, Savoie Technolac, Le Bourget du Lac, France, daniel.froelich@ensam.eu

¹ Centre de Recherches et d'Etudes Interdisciplinaires sur le Développement Durable (CREIDD), ICD, UMR CNRS 6281, Université de Technologie de Troyes, Troyes, France, xi.jia@utt.fr, youcef.bouzidi@utt.fr

Table 1. WEEE composition in France

Components of WEEE	2015	% in total treated WEEE
Ferrous metal	274166	47.7%
Glass	58263	10.1%
Mineral fractions	13644	2.4%
Non-ferrous metal	43074	7.5%
Plastic materials	95226	16.6%
Printed circuit boards	9518	1.7%
Shredding residues	74036	12.9%
Total	574541	100.0%

The general steps of WEEE treatment in France is shown below in the list[1]. When they arrive at a treatment center, WEEE undergoes different processes. These steps vary according to the flows to be treated and the recycling processes implemented by the operators. The generally treatment proceeds in six major steps,

- 1) Separation of different components and extraction of the harmful substances
- 2) Grinding the equipment into pieces with smaller sizes
- 3) Electromagnetic separation of ferrous metals
- 4) Optical sorting to separate the circuit boards which will be conducted in other processes
- 5) Separation of non-ferrous metals
- 6) Separation of plastic wastes by sink-float separation and optical sorting

It's not easy to sort the plastics as plastic materials are composed of several polymer families, most of which are incompatible with others. Table 2 shows the basic information about the existing sorting technologies. Polymers are of different colors and thicknesses[6], however the two most representative industrial sorting technologies do not allow the determination of materials when difference on densities are less than 0.1kg/m³ or they are in dark colors. ABS and HIPS are thermoplastics having styrene phase, which can provide impact strength and rigidity, and easy processing. They have similar densities of 1.05–1.07 and 1.02–1.04 kg/m³, respectively. The density of 20% talc filled PP is also of 1.05kg/m³, similar to ABS and HIPS, and they belong to the intermediate density group[7]. This is an obstacle in their effective separation, especially when these polymers are with dark colors.

Froth flotation is considered as a common method to separate specific plastics from the plastic mixture. The separation of the plastics mixture using froth flotation technic is based on the modification of plastic surfaces in order to differentiate the wettability on the plastics surfaces. With the help of surfactant agents to improve floating efficiency, the hydrophobic plastic surfaces have a higher attachment to air bubbles than the hydrophilic plastic surfaces. Therefore, the more hydrophobic plastics are floated more effectively over the floating medium whereas the more hydrophilic plastics effectively sink down to the bottom of the flotation cell[8].

Table 2. Comparison of basic information of the existing sorting technologies

Sorting technology	Advantage	Disadvantage
Near infra-red	Rapid identification	Useless for dark objects
Mid infra-red	Possible for sorting dark plastics	Identification might be slow and requires relatively appropriate surface.
Fluorescence X	Identification of PVC and additives	Cannot identify other polymer families.

Density separation	A low cost separation method used for any material mixture of different densities	Purity is low for some plastics with similar densities, and slow process.
Froth flotation	Used for any material mixture, applied with a surfactant for changing the wettability	Require a surfactant to modify the plastics. Separation of only one component at a time
Triboelectric separation	Used for plastics of significantly different dielectric constant	Requires a dry and clean plastic surface

2. MATERIALS AND METHODS

Materials

The samples were collected in a local dismantling plant in Savoie. In this plant, the WEEE are at first manually dismantled and then transported to shredders. To ease the evaluation of flotation results, the plastics selected were of different colors. The measured densities of the plastics is respectively, 1.03, 1.04 and $1.08 \pm 0.01 \text{ g/cm}^3$. The sample was shredded using a Wanner Technik 14.13 EZ-SS shredding machine equipped with a sieve of 10 mm. The particles obtained after shredding were classified by particle size. The selected size for flotation experiment on PVA is 3–8 mm. The experimental tests were performed with samples with 10 g of each polymer.

Flotation Experiment methodology

The flotation tests were carried out in a self-designed glass flotation column (Img. 1) with 9 L of volume. This column is mechanically agitated by a rotating impeller located at the bottom of the cell and its motor on above, which allows air bubbles and particles aggregates in a united form, leaving the surface less disturbed by the presence of the impeller. Effect of turbulence is especially important in the flotation of plastics due to the low density of plastics and the weak forces between particles and air bubbles. Polymer particles were stirred with the surfactant agents in the column for 15 mins. Then Compressed air was introduced in the bottom of the cell, and air bubbles were produced due to a porous board in the column, the airflow rate was 1.3 L min^{-1} . The flotation test was conducted for 10 mins. At the end of the flotation test, plastics floated to the interface of water and air were collected, rinsed with tap water, dried in atmosphere, and weighed. The flotation rate of each plastic in the floated product was calculated based on mass balance. The temperature was not artificially changed, which is ambient temperature at 22°C . For the purpose of more approaching industrial application, the water used in the flotation is tap water.



Img.1 Self designed glass flotation column

3. RESULTS AND DISCUSSION

The results of the flotation experiment are expressed in terms of recovery rate in percentage. Through the recovery rate the effect of flotation is can be visually observed, the bigger difference lies in the plastics floating rate, the better separation achieved. The masse of the each plastic floated were weighed after manually sorting from the mixture, the float recovery for each plastic were calculated by equation (1)

$$\text{Recovery percentage} = \frac{m_{fi}}{m_t} \times 100\% \quad (1)$$

where m_{fi} is the mass of the plastic i (ABS, HIPS or talc filled PP) in the floating particles and m_t is the original selected sample mass of plastic i .

3.1 Effect of particle size on recovery rate

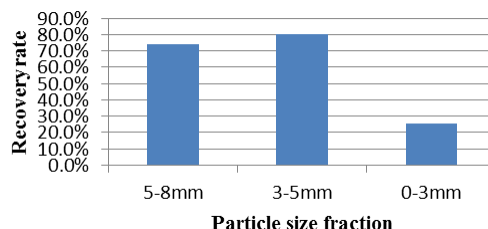


Fig.1 Flotation recovery of talc filled PP as a function of size fraction

The experiment was conducted with 10g talc filled PP of each size fraction and terpeneol concentration at 5mg l^{-1} , the conditioning time was 15min, the flotation time was 10min, and was carried out respectively with 0-3mm, 3-5mm and 5-8mm size fraction. The results are showed in Fig.1. As can be seen from the figure, the recovery rate is related to size fraction of the particles, the recovery rate of 3-5mm is higher than the other two fractions while the smallest size fraction is the least floated. It could be explained by the adhesion action of particles and air bubbles, the hydration shell on the surface of the larger particles is thicker than that of the smaller ones, so that the adhesion of air bubbles on the surface of the larger particles is relatively low [9,10]. The smaller size of the plastic surface can adhere to a sufficient number of bubbles relative to its volume, but when the size is too small, it would make the plastic surface impossible to adhere to a sufficient number of bubbles to float up, and the turbulence circumstance of the system also impacted on it.

3.2 Effect of surfactant agents on recovery rate

Fig. 2 illustrates the recovery rate of 10g ABS, 10g HIPS and 10g talc filled PP, in each test with different concentration of PVA. Plastics are of natural floatability, they could float in tap water when introducing air bubbles, and it is clear that PVA has a evident depressing effect on talc filled PP. Comparing the evolution of recovery rate of the three plastic samples with the effects of PVA concentration, it is indicated that the depressing effect of PVA on talc filled PP is more significant than that of ABS and HIPS. When increasing the concentration of PVA to 100mg l^{-1} , the flotation rate of talc filled PP decreases gradually, but the recovery rate of ABS does not varies as much as talc filled PP, it maintains at around 90%, slightly increased at 50mg l^{-1} then decreased at 100mg l^{-1} . The recovery rate of HIPS decreases when increasing the concentration from 10mg l^{-1} to 25mg l^{-1} , however it shifts at PVA concentration at 25mg l^{-1} that it increases and get closed to the recovery rate at 50mg l^{-1} then decreases again when continue adding the PVA to 100mg l^{-1} .

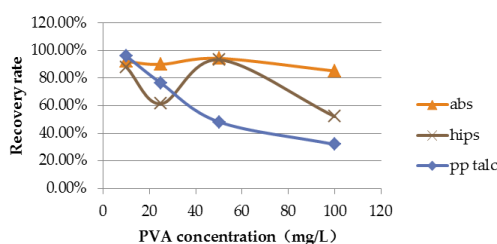


Fig.2 Flotation recovery of ABS, HIPS and talc filled PP as a function of PVA concentration

As the samples are selected from end-of-life products, they might be degraded in different degrees. Most polymers are sensitive to their environment and subjected to aging. According to the phenomena of aging, hydrogen atoms intervene in chemical reaction and create the new bonds[11]. The aging of polymers increased the mobility of the polymer chains, forming bonds as ether carbon (C-O) and hydroxide (-OH), underwent an increase in hydrophilic moieties on their surface[12].

Degradation of a polymer is the change in its physical and mechanical properties, caused by more or less aggressive environmental factors: attack of a chemical product, thermal oxidation, UV radiation, constraint, etc. Together, they will contribute to the damage of polymer, especially on the surface[13], which has a great influence on the flotation recovery rate and thus add the inconvenient for an efficient separation of plastics in WEEE.

3.3 Effect of conditioning time on recovery rate

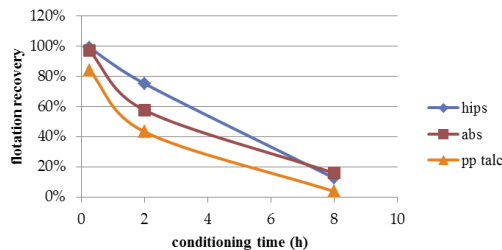


Fig.3 Flotation recovery of ABS, HIPS and talc filled PP as a function of conditioning time

It is found that the conditioning time affects the recovery rates of the plastics. Fig.3 presents the effect of conditioning time on flotation behavior of ABS, HIPS and talc filled PP in the presence of 10 mg l^{-1} PVA. From the figure, it is shown that effect of conditioning time has a suppression impact on the recovery rate of all the three plastics, attributed mainly to the adsorption of PVA solution on its surface[10]. In addition, the plastics could be slightly porous which is caused by crushing, extrusion and granulation processes of materials, especially during the extrusion process, the difference of temperature between inner and outer of plastic particles might generate fine bubbles that come out at the surface and form the pores which to some extent increase the specific surface area.

4. CONCLUSION

In this study, the effect of size fraction, conditioning time and PVA as surfactant agent is analyzed by conducting the flotation experiments and the calculation of recovery rates. From the results, it was found that both particle size fractions and conditioning time have effect on flotation recovery rate. In case that the results are least influenced by these factors, they should be controlled at the same level during each experiment. When the concentration of PVA is 50 mg l^{-1} the recovery rate of talc filled PP differs the most from the mixture of HIPS and ABS, therefore, this concentration could be applied for further separation cases, while the separation of HIPS and ABS requires repetitions of floatation to achieve a successful separation.

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Streetscape Revitalization for Turkish Traditional Urban Texture in Bartın City

Bulent CENGİZ^{1}*

Abstract

Urban textures that are historically, culturally and architecturally rich have significant cultural heritage characteristics with regard to urban identity and sustainability. The city of Bartın located in the Western Black Sea Region of Turkey is one of the rare historical cities with a river passing through it. The traditional Turkish urban texture has been shaped around the peninsula surrounding the Bartın River. Today, the traditional urban texture has been damaged significantly and only a limited area in the city center is under protection as a national Urban Conservation Area. In this study, Uzunyol Street which is part of the traditional urban texture of Bartın has been selected as the study area. Spatial analyses have been made regarding the study area and the characteristics of the street landscape in the traditional urban texture have been determined. A SWOT analysis was carried out for determining the strengths, weaknesses along with the opportunities and threats of Uzunyol Street as part of the city. In this scope, various problems have been determined at the human scale for the organic street texture that is not in accordance with the traditional urban landscape despite the fact that it is still among the important centers of attraction in our day. As a result, strategies have been developed for the revitalization of the characteristics of the traditional streetscape in Bartın within the context of cultural heritage.

Keywords: *Streetscape, Urban Design, Traditional Street, Revitalization, Bartın*

1. INTRODUCTION

The social life of cities depend mainly on streets as public areas [1]. Different parts of the built environment are connected by way of these functional elements and they are also used for the organization of urban transport and drainage systems. The contribution of these factors to urban life is determined by way of street design. The characteristics of urban areas along with the daily lives of inhabitants that make use of these streets such as their choice of the modes of transportation, whether they feel safe or not, public behavior like mingling in the crowd or keeping the curtains open are also shaped accordingly [2].

Streetscape sustainability is one of the most important strategies for sustainable urban design. Since the formation of the visual image of sustainable cities is among the most important factors for city success and touristic attractions, sustainable streetscape is among the defining factors. Unfortunately, the visual image of many cities lacks the correct and sustainable streetscape thereby leading to adverse impacts on the visual as well as their global ranking [3].

Streets taken on a green appearance with all kinds of vegetation that are included as part of streetscape greenery. The objective of this follow-up study is to examine the extent to which the relationship between streetscape greenery and health is affected by stress, social cohesion and physical activity. Thus, the types of greenspace with the most significant impact for providing health benefits as well as exploiting these benefits in a more comprehensible manner may be attained as such [4].

In this article, strategies have been developed for the revitalization of the characteristics of the traditional streetscape in Bartın as a result of the spatial analyses and SWOT analysis carried out for the study area.

2. MATERIAL AND METHOD

The city of Bartın is located at the Western Black Sea region of Turkey 12 km inland from the sea. Its neighboring cities are Zonguldak to the west, Kastamonu to the east, Karabük to the south and the 59 km coastal strip of the Black Sea to the north. The province of Bartın has 92.389 inhabitants, and the population of the city center is 68.881 according to the 2016 data [5].

^{1*} Corresponding author: Bartın University, Forestry Faculty, Department of Landscape Architecture, 74100, Bartın, Turkey.
bcengiz@bartin.edu.tr

Bartın, which is located in the Western Black Sea Region of Turkey became a province in 1991. The Bartın River that was known as Parthenius (God of Waters) in ancient times gave its name to the city in addition to shaping its traditional texture and thus providing an identity to the city. It is one of the rare cities with a river passing through it. The average elevation of the city of Bartın from sea level is 20 m [6].

Historical structures dating back to the 18th century which have been protected until today put forth that the city that developed as a market/bazaar place in the 15th century was shaped during the 19th century. There are registered monumental cultural assets in the city center along with registered civil architecture examples along the Bartın River. It attracts attention with the historical traditional Bartın houses, the urban conservation area and the natural conservation area [6]. Bartın became a member of the Association of Historic Towns in the year 2000 [7].

There are a total of 224 registered buildings in the city of Bartın [8]. Of these, 94 are located in the Urban Conservation and Conservation Impact Transition zone. Bartın houses put forth the civil architecture examples of the Ottoman Period and summarize the recent history. Bartın houses which reflect the Art Nouveau and Baroque arts are generally two-storied and located in a garden surrounded with wooden fences known as “Daraba”. The floors are wood-carved and the ground floors are stone. The entrance area known as “Gulluk” along with the walkways in the gardens are covered with slates. There is a stone well in each garden. Traditional houses have a lot of windows. These are unique guillotine windows with a circular form that lights up only the stairs and alcoves. The moldings known as “Kusluk” located between the windows surround the structure completely. The windows, stairs and ceilings of the houses are decorative elements [9]. The historical environmental integrity of the Urban Conservation Area was disrupted and the area could not be protected sufficiently. In addition to structuring that is not in accordance with the historical texture. The original elements of the street texture to be protected were removed and replaced with concrete cobblestones. Lack of care, conservation failure, getting old, abandonment and transformation to a ruined area are slowly taking place due to the lack of the planning and application works for protection despite the decree for conservation and various issues such as the areas transforming into physical and social ruins take place as the landowners are abandoning the traditional textures [6], [10].

Uzunyol Street that connects the Yukari Carsi district which is very important for the traditional urban identity in the urban conservation area with the Hendekyani Street which is one of the oldest settlements of the city center has been selected as the study area (Figure 1).

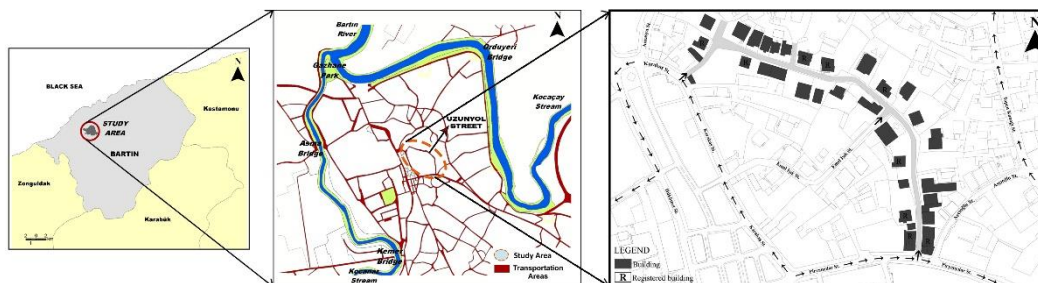


Figure 1. Location of the study area (derived from Cengiz 2007).

Bartın Development and Conservation Plan (1/1000) maps and reports along with the archive of Cultural and Natural Heritage Protection Board, registry decrees and regulations, fieldwork and archive photographs, various national and international books, articles, and the Internet were used in the study. ArcGIS 10.0 and Adobe Photoshop CS5 were used for presenting the acquired data.

Spatial analyses for the study area along with the analyses on natural structure and built environment analyses (fill-gap analysis, structure status analysis, building type analysis, storey heights analysis, ground floor usage analysis, first floor usage analysis, and transportation analysis) have been carried out and the characteristics of the streetscape in the traditional urban texture has been determined. The SWOT analysis carried out put forth the strengths, weaknesses, opportunities and threats of Uzunyol Street in the city as a whole along with the opportunities and threats. As a result, strategies were developed for the revitalization of the characteristics of the traditional streetscape of Bartın with regard to cultural heritage.

3.RESULTS AND DISCUSSION

Natural Structure

Climatic factors affecting pedestrian comfort were examined within the scope of the natural structure analysis. Bartın is under the influence of the Black Sea climate. Annual average temperature is 13,8°C, annual rainfall is 1035.22 mm. There is a northeastern-southwestern wind during the dates of October 15 – March 15. It is suited for disabled individuals since there is almost no slope.

Plants the leaves, flowers and fruits of which are used are among the characteristic attributes of the residential gardens in Uzunyol Street. The primary plant types observed in the front gardens of residences are as follows: *Morus alba*, *Thuja orientalis*, *Cedrus libani*, *Abies bornmulleriana*, *Prunus domestica*, *Prunus cerasus*, *Ficus carica*, *Platanus orientalis*, *Prunus granatum*, *Prunus lauracerasus*, *Nerium oleander*, *Laurus nobilis*, *Rosa sp.*, *Campsis radicans*, *Vitis alba*, *Lonicera sp.*, *Wisteria sinensis*, *Hibiscus syriacus*.

Built Environment Analyses

Uzunyol Street is 310 meters long. The street elevation varies between 15-28 meters. The street has a width of 5 meters on average. Data regarding the identity and characteristic of the street have been obtained via field study. In this scope, a total of structures and their environments have been examined at Uzunyol Street.

Fill-Gap Analysis: The fill-gap ratio along the street texture has positive impact on the sense of space since all structures along the Uzunyol Street have front, rear or side gardens (Figure 2a,6a).

Structure Status Analysis: Of the structures located along the Uzunyol Street, 54% (21 structures) are at moderate state, 31% (12 structures) are in poor state and 15% (6 structures) are in good state (Figure 2b,6b). Of the 9 registered structures along the Uzunyol Street, 67% (6 structures) are in poor state, 22% (2 structures) are in moderate state and 11 % (1 structure) is in good state.

Building Type Analysis: Of the structures located along the Uzunyol Street, 64% (25 structures) are reinforced concrete, 26% (10 structures) are wooden, 10% (4 structures) are masonry construction and are examples of registered civil architecture (Figure 3a,7a).

Storey Height Analysis: Of the structures located along the Uzunyol Street, 54% (21 structures) were 3 storey, 23% (9 structures) were 2 storey, 19% (7 structures) were single storey, 2% (1 structures) were 4 storey and 2% (1 structures) were 5 storey (Figure 3b, 7b).

Ground Floor and First Floor Usage Analysis: When the ground floor use for the structures located on the Uzunyol Street are examined, it can be seen that 72% (28 structures) are residences, 15% (6 structures) are vacant, 13% (5 structures) are used commercially (Figure 4a, 8a), whereas 85% (33 structures) of the floors above ground are residences, 15% (6 structures) are vacant (Figure 4b, 8b). It is also observed that the floors above ground are mostly used as residences.

Transportation Analysis: Traffic on Uzunyol Street is one way. There are sidewalks on both sides of the vehicle lane. Sidewalks are not sufficient for pedestrian comfort. The fact that vehicle lanes are narrow leads to heavy traffic and congestion during the day as well as the vehicles parking on pedestrian walkways thus preventing the passage of pedestrians (Figure 5a, 9a).

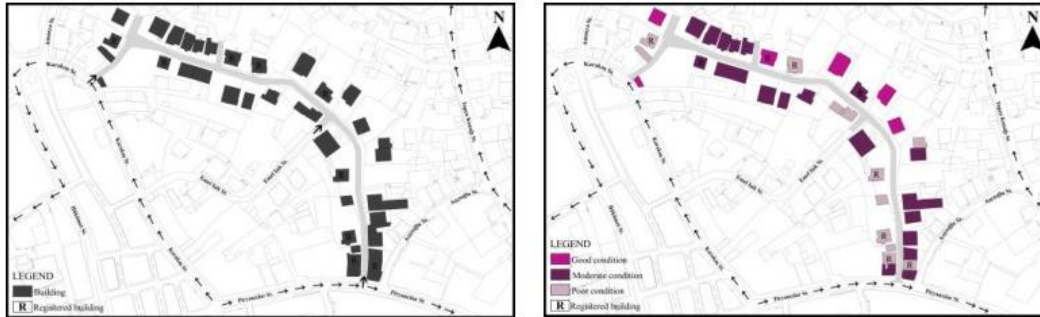


Figure 2. (a) Fill-Gap analysis (b) Structure status analysis

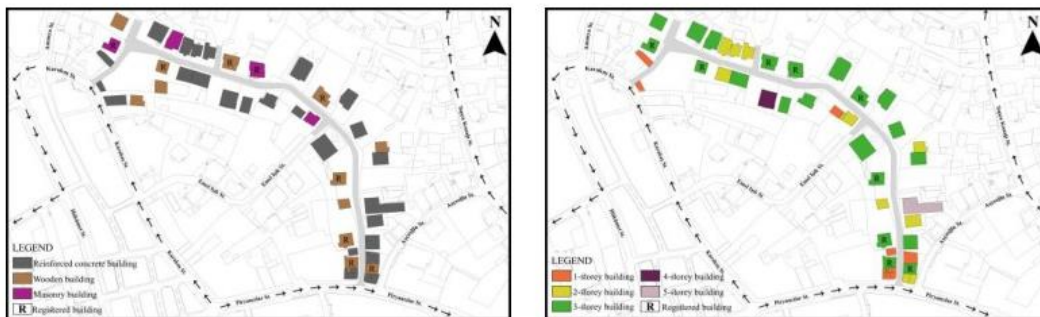


Figure 3. (a) Building type analysis (b) Storey height analysis

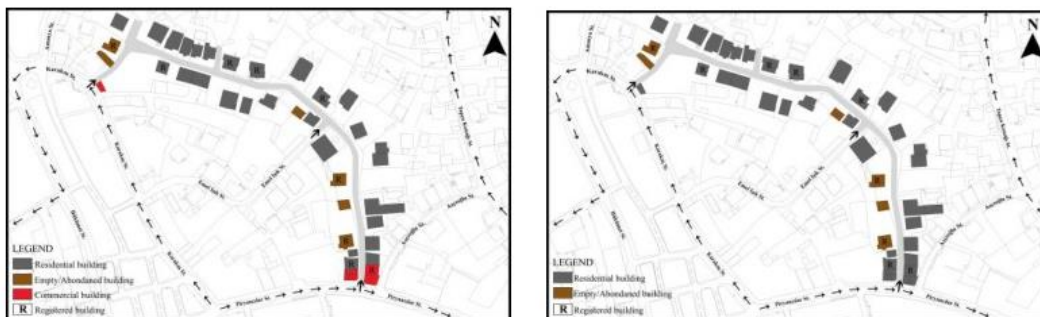


Figure 4. (a) Ground floor usage analysis (b) First floor usage analysis

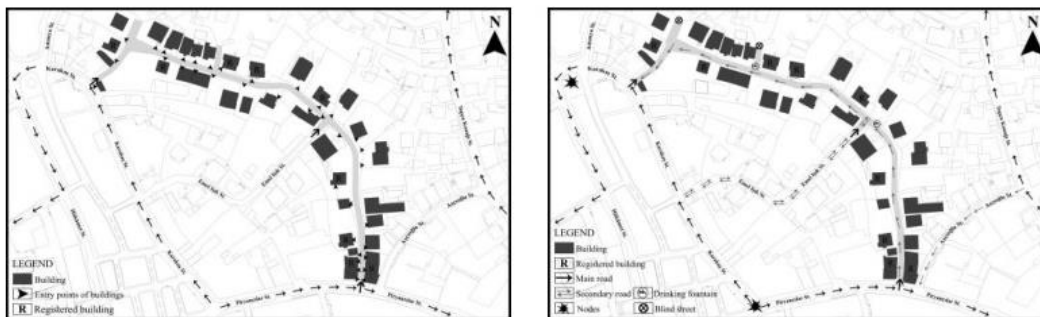


Figure 5. (a) Transportation analysis (b) Entry points of buildings



Figure 6. (a) Fill-Gap analysis (b) Building condition analysis



Figure 7. (a) Building type analysis (b) Storey number analysis



Figure 8 (a) Ground floor usage analysis (b) First floor usage analysis



Figure 9. (a) Transportation analysis (b) Entry points of buildings

SWOT Analyses of Uzunyol Street

Uzunyol Street has been selected as the study area reflecting the traditional Bartın street texture while connecting the Hendekyani Street which is one of the old settlements in the city of Bartın with the Yukari Carsi District which is considered

as the commercial center of the city. SWOT analysis was carried out at the study area with regard to physical, social, economic and method-organization (Table 1).

Table 1. SWOT analysis of Uzunyol Street

	Strengths	Weaknesses	Opportunities	Threats
Physical Structure	<ul style="list-style-type: none"> •Part of the Bartin historical urban texture •Included in the Urban Conservation Area •Including the registered Historical Bartin houses which are under protection •The historical houses have gardens •The traditional urban texture has been partially preserved •Has an organic street texture characteristic •An important artery connecting Hendekyani and the Yukari Carsi (Bazaar) (for pedestrian and vehicle traffic) 	<ul style="list-style-type: none"> •Building facades not in accordance with the street texture in addition to multi-storey buildings •Irregular and unattended front gardens of residences •Insufficient road width •Insufficient sidewalk width for pedestrian crossing •Damages in the traditional texture due to new structuring •Neglected and abandoned historical houses 	<ul style="list-style-type: none"> •Traditional urban texture characteristic •Touristic activity in Bartin •Revitalization of the historical value of registered structures by way of restoration work •Potential for becoming a significant point of attraction when the Bartin urban conservation area is transformed into a tourism area 	<ul style="list-style-type: none"> •Pedestrian and vehicle pressure on the historical environment •Pressure due to the vehicle traffic (traffic load-intensity-noise) •The fact that the gardens of registered buildings are transformed into car parks for commercial purposes
Social Structure	<ul style="list-style-type: none"> •At human scale and having a transition zone characteristic •The fact that fountains which are among the components of the urban texture of Bartin are among the meeting points for the residents of the street •Houses with gardens provide opportunities to individuals to socialize 	<ul style="list-style-type: none"> •Not suited for bicycle use •Street furniture elements used not in accordance with traditional street texture 	<ul style="list-style-type: none"> •Ease of accessibility in Bartin city center •Streetscape greenery provides benefits for urban ecology 	<ul style="list-style-type: none"> •Pressure that might be formed on the cultural identity due to intensive tourism
Economic Structure	<ul style="list-style-type: none"> •Walking distance to the historical bazaar district of Bartin •Commercial use of the ground floors of some buildings 	<ul style="list-style-type: none"> •The fact that Uzunyol Street has a limited capacity with regard to spatial size and use 	<ul style="list-style-type: none"> •Provision of employment to inhabitants 	<ul style="list-style-type: none"> •Changing consumption habits
Management and Organization	<ul style="list-style-type: none"> •The fact that Bartin is a member of the Association of Historic Towns of Turkey 	<ul style="list-style-type: none"> •Insufficient control of applications that do not match the historical pattern building rule which is objected in zoning plan 	<ul style="list-style-type: none"> •Model area characteristic for organization activities within the scope of the sustainability of the traditional urban texture 	<ul style="list-style-type: none"> •Insufficiencies and conflicts in the current laws and regulations

4. CONCLUSION AND SUGGESTIONS

The design, detailing, and choice of materials of the furnishings are important not only for design continuity both also for both durability and ease of maintenance. Appropriate detailing and use of materials in the urban landscape are therefore of primary importance to the success of streetscape. Experienced landscape architects and urban designers should be involved in the design and coordination of this phase of the project development [11].

Cengiz and Kececioğlu Daglı [12]. pointed that maintaining the continuity of pedestrian accessibility in comfort provide social, environmental and economic contributions in the Bartın historical urban identity whole as well as increase the perception of historical and cultural pattern, the creation of safe and comfortable open spaces and pedestrians to be in harmony with the environment, revitalization of the historical urban pattern. Similar results are valid for Uzunyol Street, which is located in Bartın traditional street texture. In this framework, the following streetscape design principles have been determined for the revitalization of the streetscape characteristics for the Uzunyol Street in Bartın with regard to cultural heritage:

Streetscape design principles for Uzunyol Street:

- It should be rearranged as an important transportation corridor that is significant for the pedestrian and vehicle circulation between Hendekyani and Upper Carsi.
- The objective is to effectively organize the pedestrian circulation on Uzunyol Street.
- Preserving and using Uzunyol Street as an exemplary cultural heritage area that reflects the characteristics of the traditional urban texture.
- Providing access to the Bazaar District in the Bartın city center
- Restoration of the historic Bartın houses that are examples of civil architecture with conservation status and re-arranging their gardens
- Rendering the facades of the new buildings, which deteriorate traditional urban texture, compatible with the historic environment.
- Urban equipment elements in accordance with the climate conditions of Bartın should be preferred.
- Traditional residences and their gardens should be arranged as a whole.
- Street fountain and square should be rearranged in accordance with the traditional texture to respond to the needs of the users.
- Making Uzunyol Street a center of attraction
- The structural and plant material in accordance with the traditional texture along the front and side gardens of buildings with facades overlooking the Uzunyol Street should be used.
- Abandoned civil architecture examples should be transformed for touristic purposes.
- The objective is to restore the Bartın houses which are civil architecture examples under conservation along with their gardens.
- Bartın house architecture should be applied to the facades of the buildings that disrupt the traditional texture
- Plant arrangements that are functional and aesthetic as well as in accordance with urban ecology should be preferred for streetscape greening
- Designing and choosing furnishing for a streetscape should be approached in the context of both the comprehensive urban environment of the city and the specific location where the furnishings are to be used. These elements include paving, lighting, seating, planters, trash containers and drinking fountains.

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Proposal for Historical Park Revitalization Project: Sadabad (Istanbul)

Bulent CENGIZ^{1}*

Abstract

Rivers are among the most important building blocks of the urban green area system. They play an effective role in the shaping of cities and their cultures with their ecological, aesthetic, functional and economic values. In this article, Sadabad Recreational Area located at the Kagithane district of Istanbul which has a special historical importance was selected as the study area. Sadabad was one of the most important recreation area during the Tulip Era of the Ottoman Empire with its water based recreational activities and its festival areas. It has changed dramatically from the past to the present and together with the rapidly increasing population, Sadabad Recreational Area has remained as a park in Kagithane. Sadabad Park is an area that should be preserved with its cultural landscape values for the revitalization of its use in the past. In this regard, the landscape design project proposal has been developed for the area. With this study, a qualified recreation area has been designed with the new designs in harmony with the historical identity of Sadabad. The losses in the original texture have been improved and new usage areas have been developed. In the developed revitalization project proposal, the river landscape formed by the Kagithane River was brought to the forefront with regard to its visual, aesthetic and ecological characteristics. Wide meadow areas along with wide green areas for the gathering of crowds in the city have been proposed as important elements of the Kagithane Recreation Area. With this proposed revitalization project, it is aimed to provide green areas that meet the demands of both the city and the citizen that are in accordance with its historical identity while also contributing to urban green area.system.

Keywords: *Historical Park, Revitalization, Landscape Design, Cultural Heritage, Sadabad.*

1. INTRODUCTION

Throughout history, recreation areas have been multi-functional places where activities related with social life take place. Recreation areas have helped the formation of a more colorful urban life while satisfying its users with the contributions they make to urban life, quality life and the life styles of their users.

Recreational areas that were present during the Byzantine Period were preserved and developed during the Tulip Era of the Ottoman Empire thus becoming a living part of public life [1].

Recreational areas which are open areas that serve the cities have provided their services to their users in different ways in the past. These open areas that were beloved by the Sultans have been subject to many changes and designs under different rules. The recreational areas that widened or narrowed under different rules sometimes lost their attractiveness while sometimes acquiring new areas of use [2].

Recreation areas as urban spaces carrying the traces of the past to the present along with the ideas bring these areas into being are significant resources that reflect the life habits and philosophies of the cultures they belong to. It has been difficult in comparison with the architectural structures for the open recreation areas to reach our day and for those present in our day to preserve their authentic characteristics. The reflection of problems between ideologies of different ruling periods have been more severe for landscape cultural heritage elements. Public areas and recreation areas that are important components of the urban memory of the city of Istanbul have changed dramatically from the past to the present and it has not been possible for them to reach our day by preserving their unique characteristics [3], [4]

^{1*} Corresponding author: *Bartın University, Forestry Faculty, Department of Landscape Architecture, 74100, Bartın, Turkey.*
bcengiz@bartin.edu.tr

In the past, Sadabad Recreation Area made up the section that is close to the city of the green band extending from Halic to Kemerburgaz along the Kagithane River. Sadabad Recreation Area is important for establishing a green area for recreation purposes connected with the forested area to the north [4]. Sadabad Park has been open to the public for free since 2007 [2].

Sadabad Park has the characteristics of a historical garden thanks to its characteristics from the past. In addition to recreational activities such as leisure and walking, it has also hosted many traditional competitions as well as wedding and spring festivals in addition to the palaces and shooting areas of the Ottoman Sultans during the Tulip Era when it was used the most. The water use of the Sadabad Park that also reflects traces of the cultural landscape provide a different characteristic to the area. The pool uses of the Kagithane River that stretches along the area enable many activities such as boat trips and swimming. Today, Sadabad Park has remained as the only breathing spot of its vicinity due to the rapid increase in population. This is a good reason for the revitalization of the old uses of the Sadabad Park and it is also an area that should be preserved due to its cultural landscape values.

2. MATERIAL AND METHOD

Kagithane area was home to the most famous recreation area of its time stretching all the way to Halic (Golden Horn) on both sides of the Kagithane River [2] starting from the eastern side of the Terkos Lake (Figure 1). Whereas today, it is used as a residential and industrial area. It has been understood that there was a paper mill here during the conquest of Istanbul and that the production continued until the reign of Bayazid the 2nd (1481-1512); hence the name of the district Kâgithane [1].



Figure 1. Location of the study area.

Spatial information and results for the area were acquired from reports, previous studies, literature surveys, field study and interviews with Kagithane Municipality workers. Slopes, aspect, elevation, hydrology, geomorphological structure analyses generated using the GIS software were used as materials. Various drawing programs (AutoCAD 2010, Photoshop CS5, Lumion 5 ve Sketch up Pro 8) were used for the preparation of the landscape design proposal. Survey Plan, land use decisions, Preliminary Master Plan and 3D modellings were prepared within the scope of the landscape design project.

Throughout the project, the method of Cengiz et.al. [5] was used in this study in following 3 stages:

- i. "Preparation of the Survey Plan",
- ii. "Determination of the Land Use Decisions",

3. FINDINGS

3.1. Survey Plan

The project area is located topographically at the lowest part of the Kagithane District (0-25 m). It starts from Golden Horn, first moves northeast then continues up north towards Cendere Strait and Katirci Valley, this step has extensions on the neighboring valleys and forms the largest area.

The general slope of the Kâgithane District varies between 0 - 30+. There are high slope differences inside the Sadabad Park. The park has a slope of almost zero since it is located on a valley bed.

The Kagithane Valley that starts southwest of Ihsaniye moves southeast parallel to the Alibeykoy Valley. The valley that starts to extend its base combines with another valley coming from the north from a second river branch thus reaching Kemerburgaz, makes a wide arc from the east to the south and enters the borders of Kagithane starting from the TEM expressway.

The mouth of the Kagithane River is located at an elevation of about 130 m on Kocayemis Hill located to the north of the Bosphorus and flows into the Golden Horn southwest of the Bosphorus. The Survey Plan for the study area has been given in Figure 2, whereas the photographs of the related land have been given in Figure 3. Works are ongoing within the scope of the “Golden Horn Development Project” for preventing water pollution in the Kagithane River.

3.2. Determination of Land Use Decisions

Land use decisions related with the preparation of the Preliminary Master Plan designed for the land are as follows:

- Conservation of the historical, natural and cultural characteristics of the project area,
- Conservation and revitalization of the natural characteristics of the Sadabad River which is an important water corridor inside the city,
- Carrying out the planting design application thus revitalizing the ecological cycle by taking into consideration the traces and formation of the recreation area during the Ottoman Period when it was in its prime,
- Effective water use in the revitalization of recreation areas.

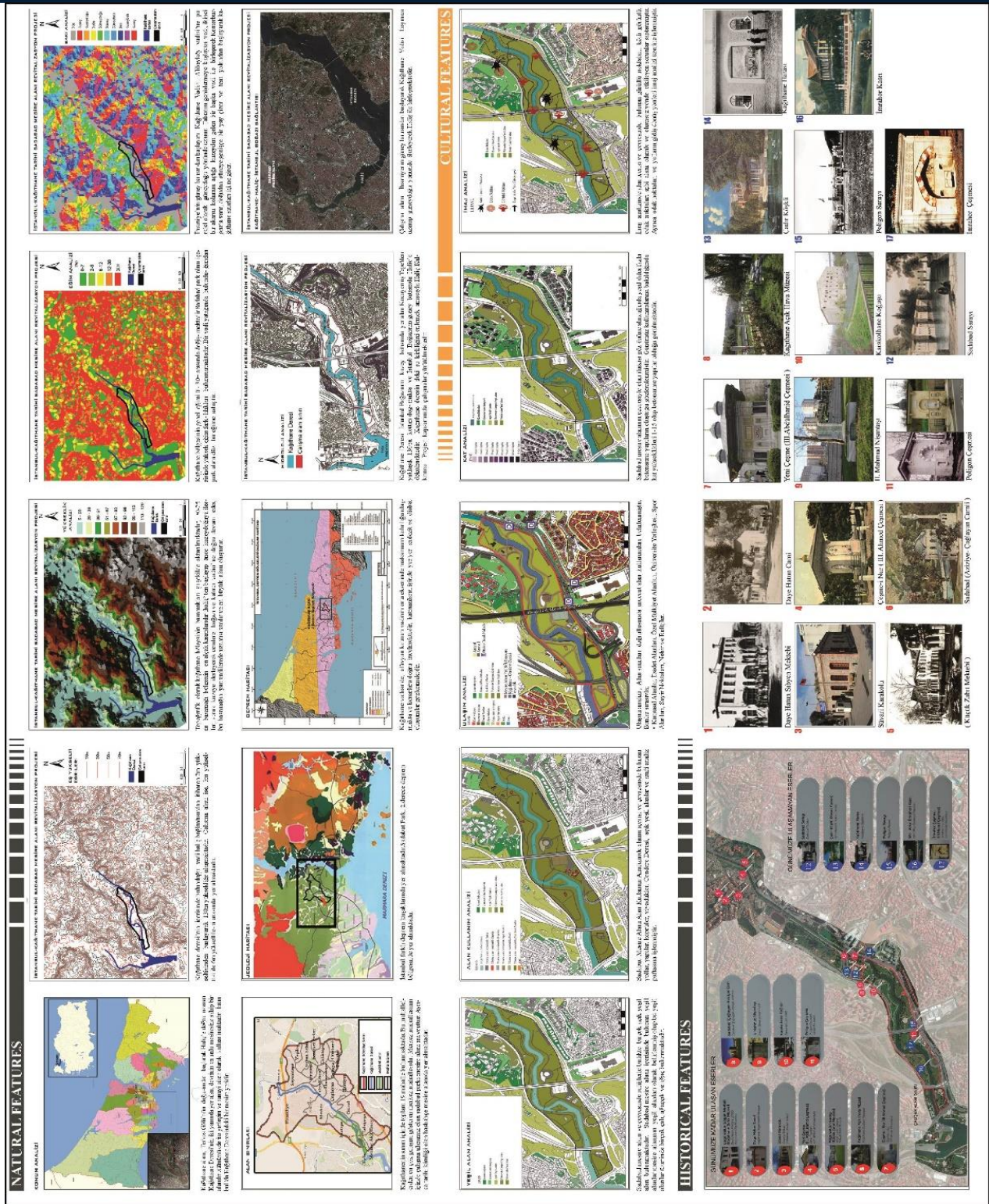


Figure 2. Survey Plan of the Historical Sadabad Park Revitalization Project

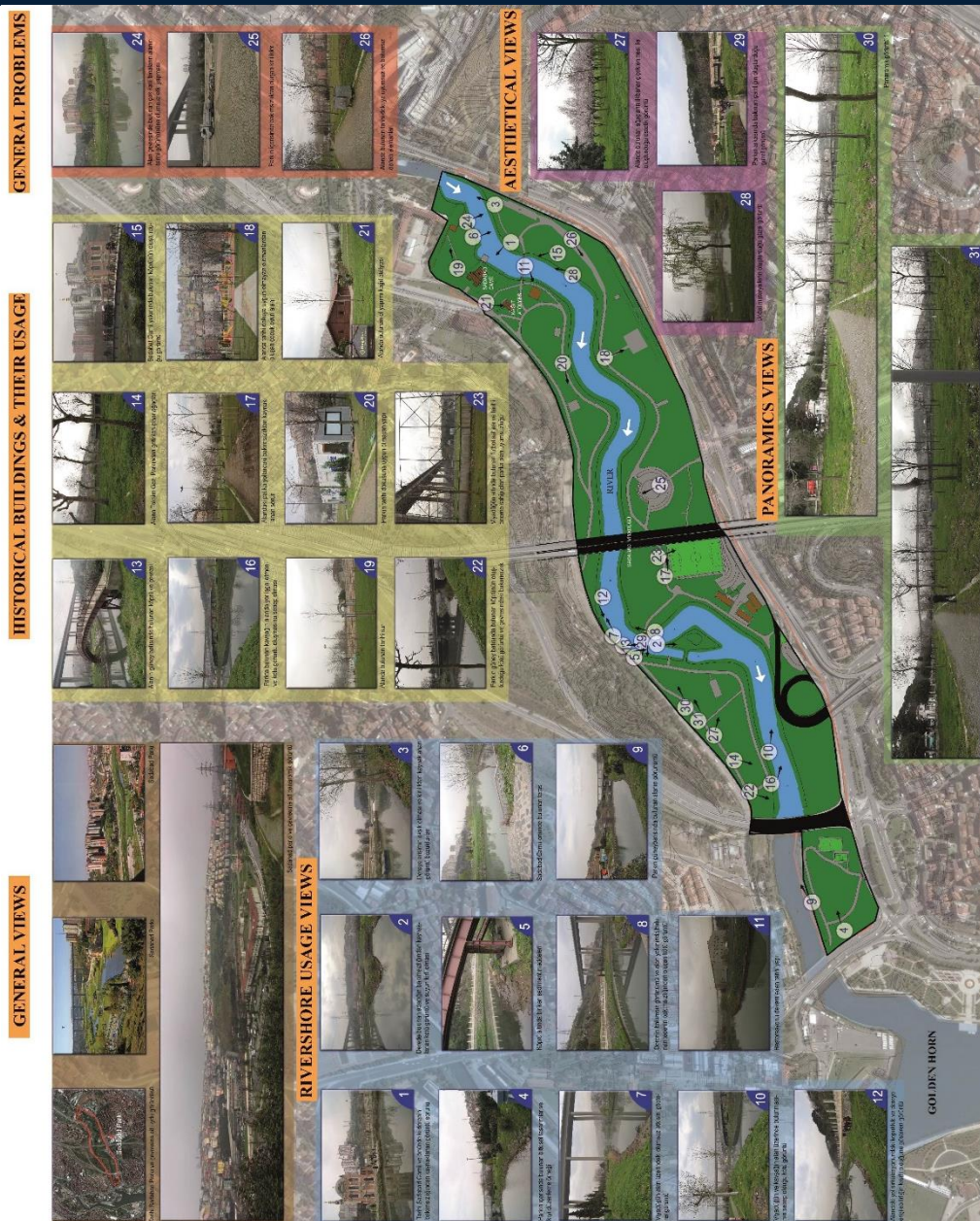


Figure 3. Land Use Photographs of Historical Sadabad Park Revitalization Project

3.3. Preparation of the Preliminary Master Plan and 3D Modellings

The conservation precautions for this area which is a water basin and an important ecological value for the city were increased thus enabling the formation of recreation areas reflecting the historical characteristics of the area with a fine conservation – use balance (Figure 4).

The landscape area that is open to public use was rearranged with modifications such as trees that make up shadowy areas, urban green areas for different purposes and pedestrian bridges, marble docks etc. thereby redesigned the historical uses of the water elements.

Social reinforcements for sports, leisure, culture and entertainment activities were built in accordance with the needs of the recreation area.

Historical Texture Conservation Area:

- Sadabad Mosque, Saltanat Gate and its environs was selected as the historical texture conservation area. The existing mosque, gate and dock in the area was not changed and was improved with landscape design.
- The historical characteristics of the area were taken into consideration and a view terrace was formed by designing a pier with Ottoman motifs on its railings.

Service Area:

- The service area was built by taking the mansions and pavilions at Sadabad for meeting the food-beverage needs of user. Whereas the area around it was enlivened with motifs inspired from the Ottoman garden art.
- Cetvel-i Sim Canal was taken as a model thus enlivening the water and a lively recreation area was thus formed with the pools and fountains.

Picnic Area:

- New recreation areas were formed by making multi-purpose grass areas that are wide in accordance with the recreation understanding as well as the picnic tables under the trees.

Festival Area:

- The main entrance was set as this location, wide hard floors were formed with sparse planting designs for softening up these rough lands.
- The area was connected to the grass amphitheaters and the areas where water shows will take place thus forming activity corridors.

Grass Amphitheaters:

- Grass amphitheaters were designed along the river corridor thus forming new activity areas.

Activity Area:

- Baroque style designs were made in the area inspired by the Ottoman landscape art and the area was enlivened with the use of a fountain marble decorative pool at the center.
- There are leisure areas inside the area where the water games in the pool can be watched.
- Lighting was used to increase the visibility of the pool.

Children Playground Area:

- Play groups were selected according to ages in order to ensure that the playground meets the needs of children from all ages and natural activity areas were formed with the designed artificial grass hill.

Sports Area:

- A sports complex was designed here with a tennis court, a football pitch and a basketball court and viewing areas were built with amphitheaters in between these fields.
- A running track was designed in the area for sports activities.
- This area was slowly taken close to the river corridor, while passing by the alle for eliminating any boredom.

Car Park Area:

- A car park area was designed for solving the parking problems that the individuals who drive to the area may face and the area was enlivened with the planting design.

Tour Route:

- The past use of the Sadabad Recreation Area were taken into consideration and the revitalization of the Ottoman boat tours was planned after which a stop point was placed on the small island on the river.

Refuge Planting Design:

- A planting design was placed in the middle of the circular viaduct passing through the park area.

Wide grass grounds suited to recreational use were designed, the historical texture in the park was enhanced and conserved; active use of the river was targeted with water steps for climbing down thereby connecting the park with the river. The 3D modelling drawn taking the Preliminary Master Project as basis have been presented in Figure 5.

In the direction of these approaches, the Sadabad Recreation Area that contained all characteristics of the concept of recreation during the Ottoman Era in history also reflects the recreation understanding in Istanbul today.

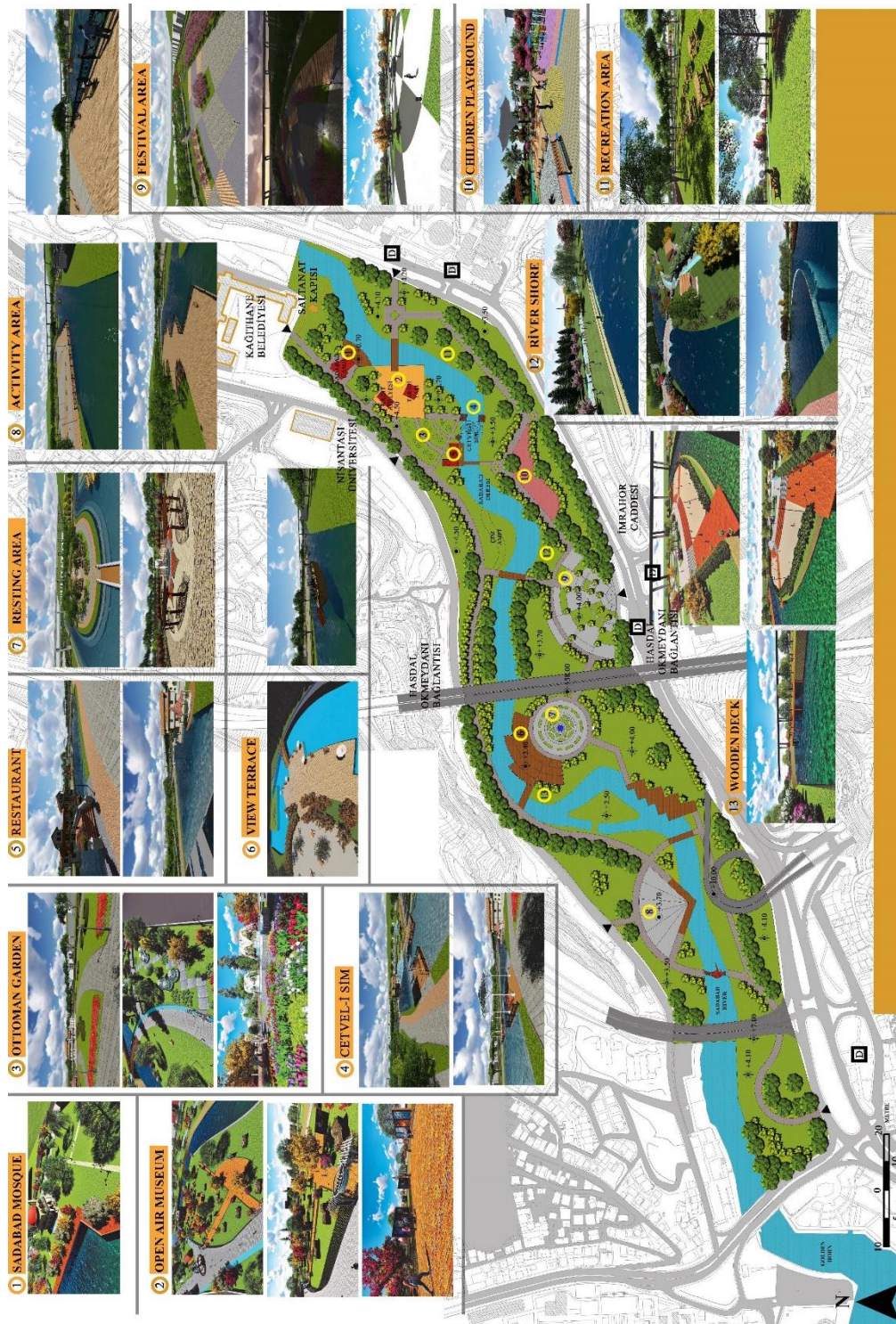


Figure 4. Preliminary Master Plan of the Historical Sadabad Park Revitalization Project



Figure 5. 3D Visuals of Historical Sadabad Park Revitalization Project

4. CONCLUSION AND SUGGESTIONS

It is necessary to conserve the Sadabad Park and to transform it into a qualified recreation area due to its historical cultural landscape characteristics as well as due to the recreation area demand of the region. It has been observed that many cultural heritages have been lost during the urban transformation period in Kagithane Region. Inevitably, these losses will continue unless precautions are taken. A revitalization project was proposed with this study. The Ottoman era usages acquired as a result of the studies carried out and cultural heritage conservation were taken into consideration and contemporary park design approaches were developed. Alternative recreation areas were proposed in the light of the carried out landscape analyses.

Sadabad Park has been designed as a qualified greenspace characteristic area with the contemporary design made in harmony with its historical identity. The losses in the original texture were improved and alternative usages were also formed such as Cetvel-i Sim Canal, Wooden deck, festival area, Ottoman Garden, view terrace etc.

Wide open and green areas suited for the gathering of crowds are also provided as important elements for the Sadabad Park. The water surface of the Kagithane River also provides striking scenes with its reflections. The objective is to present the developing recreation understanding of Istanbul Metropolitan to the city and the citizens while contributing to the urban green area system.

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Developing A New REALLOCATION Model for Land Consolidation Works

Tayfun CAY^{1}, Ela ERTUNC,¹ Huseyin HAKLI,² Harun UGUZ,²*

Abstract

Reallocation studies that is one of the most important stages of land consolidation projects are the most complex part of the process. Block reallocation is a land reallocation and installation problem that there are complex datas and relationships, such as farmers requests, fixed installations, roads and irrigation network, optimal size of parcel, parcel geometry, size of parcel, consolidation of parcel shares, legal entity of village, the condition of pastures and treasure lands, so there isn't a single solution. For block reallocation, the problem has been tried to solve by using distribution model based on block priority, fuzzy logic method, spatial decision support system and by applying different solutions, such as genetic algorithm method.

In this study; genetic algorithms and fuzzy logic method using fuzzy logic in that reasoning about methods of genetic algorithm was applied learning ability matching created a new model for the reallocation phase of the land reallocation phase. In the Konya- Cumra-Uchuyuk district project; As a result of the reallocation, 223 enterprisess were assigned to the 1st preference, 14 enterprisess to the 2nd preference and 3 enterprisess to the 3rd preference. The preferred success rate was 76.61%.

Keywords: *Land consolidation, block reallocation, optimization, hibrid method*

1.INTRODUCTION

Development of agricultural infrastructure is important in the first degree in order to provide more income from unit area and can compete with the world of agriculture in our country. The most important problems to improve the agricultural infrastructure are the size of the existing structural problems, legal arrangements needed in to solve the problems, completion of deficiencies of responsible organizations and procurement of financial resources [1]

In our country, the most important problems of agricultural infrastructure are that lands of the vast majority of agricultural enterprisess are in a scattered and an irregular shape, is in small parcels, and don't benefit from transport and irrigation networks. These conditions cause that family farmers make increasingly production on small and scattered lands, and therefore agricultural development is insufficient. The only remedy of which fragmented and scattered parcels are improvement which the company has is land consolidation

Land consolidation which is application on rural areas of land and plot arrangements is one of important tools providing efficiency increase in agricultural production. In order to increase agricultural production, lands belonging to persons and enterprisess, divided into more piece than one in case of small parcels and formed unfavorable format, are formed and are planed by combining appropriately according to the principles of modern agribusiness [2].

Land consolidation, a tool for increasing land-use efficiency and supporting rural development [3] and an indispensable application for the promotion of sustainable agriculture .[4;5].

It is the most complex and difficult stage block reallocation of land consolidation. The creation of new parcels and the placement of the new parcels, as well as being dependent on technical requirements such as farmers' wishes, fixed facilities, road and irrigation network, optimal parcel size, parcel geometry, parcel size as well as adversary and relatives relationship, social factors need to be taken into account [6].

^{1*} Corresponding author: Selcuk University, Department of Geomatic Engineering, 42130, Selçuklu/Konya, Turkey.

¹ Selcuk University, Department of Geomatic Engineering, elaertunc@selcuk.edu.tr

² Selcuk University, Department of Computer Engineering, hhakli@selcuk.edu.tr

² Selcuk University, Department of Computer Engineering, harun_uguz@selcuk.edu.tr

A total of 4 million hectares of land consolidation work was completed from 1961, when the land consolidation studies were initiated in Turkey, to the present day, which means that land consolidation could be achieved at about 25% of the agricultural land. The most important reason why land consolidation studies are being carried out so slowly is that the intensive labor and time demand is a political and complex process.

A new computer-based distribution based on optimization techniques that can allocate a large number of data (business numbers, business preferences and block numbers) at the same time, evaluating them in an impartial manner so that the parcels can allocate the optimal blocks according to the preferences of the landowners, model has been developed. The most important feature of the model, which is designed in the work, is that the allocation operations are so sensitive that it will not harm the enterprises according to their old conditions. At the same time it is fast enough to reduce the duration of the project. As the working area grows, the time profit to be earned will increase proportionally to the area. In addition to saving labor and time, the reallocation process is carried out by the optimization modules, so that the effect on the decision maker's result will be minimized. In this sense, a more reliable, more objective, more consistent and more legitimate result will be achieved. Thus, objections can be avoided by demonstrating fair and acceptable outcomes in the reallocation of agricultural land, which will increase social well-being by reducing conflicts that may arise from an important issue such as ownership. In addition, different reallocation alternatives will be offered according to the post-deployment business returns with the model planned to be developed, and the need for re-evaluation of the project from the beginning, such as manual distribution, will be abolished and more business satisfaction will be achieved in a much shorter time. Again with the module to be developed in this frame, the block resetting process will be done automatically and no manual intervention will be needed.

2. MATERIALS AND METHODS

The reallocation phase is the most difficult and time consuming part of Land Consolidation [6]. Block reallocation in land consolidation studies is an optimization study. In other words, the best solution is to find the solution. Recently, Hybrid methods have been studied to improve and improve the performance of optimization methods. Block reallocation of an existing project area in the completed project; interviews and fixed facilities are taken into account and genetic algorithm and fuzzy logic method will be developed using a hybrid algorithm was done automatically.

In the study, Fuzzy Logic Method was used to adjust the parameters of the Genetic Algorithm and to adapt the genetic operators (Genetic Algorithm crossover technique and determining the crossover rate).

In the Fuzzy Genetic Algorithm (FGA) method, the crossover techniques and the crossover rate of the basic GA algorithm may vary according to the state of the population. Thus, the FGA is able to behave in accordance with the structure of the problem. In this study, the tournament selection method is used while the FGA method is applied to the land reallocation problem and it is supported by Elitism. The land reallocation problem has a very wide search space, although it varies according to the size of the project. The population needs to be diversified with different crossover techniques to efficiently and efficiently scan this search space. With FGA, not only the level of the crossover technique but also the crossover rate is determined for each iteration with fuzzy logic. The crossover rate is evaluated according to the population of the fuzzy logic rule set according to the situation, and the crossover ratio obtained by clarification is directly used. After the crossover is complete, the iteration is completed by applying the mutation operation in the basic GA method. Until the stopping criterion is reached, the process from the elitism and tournament elections to the mutation process is repeated.

3. RESULTS AND DISCUSSION

The block reallocation phase of land consolidation operations is a process that directly affects the success of the land consolidation. Scientific studies are increasing day by day to ensure that block reallocation, enterprises's demands are met at the highest level and in a shorter period of time. In this work area, the AT-FGA block reallocation algorithm has been developed so that the block reallocation can be performed automatically using Hybrid method. The FGA block reallocation algorithm was tested in Uchuyuk Village (Cumra-Konya) land consolidation project. The following results were obtained for the application area (Table 1).

Table 1: Uchuyuk, FGA automatic reallocation result table view

	Number Of Enterprises	1. Preference	2. Preference	3. Preference	Non Preference	Success Rate (%)
FGA	274	223	14	2	35	76.6025

When we look at Table 1, there are 274 enterprisess in the field of application, and 223 of these enterprisess have settled in preference to 1, 14 enterprisess have settled 2. preference and 2 enterprisess have settled 3.preference. The preference success rate is 76.6025%. 35 enterprisess have settled other than preferences.

When the results of automatic reallocation are examined by using the FGA method proposed for solving the land reallocation problem, the number of parcel and the consolidation ratio are given in Table 2. When we examined Table 2, the number of parcels was found to be more successful in the FGA method than in the traditional method. The average number of parcels according to cadastral status has decreased by 14%.

Table 2. Number Of Parcels in Reallocation Models

The Size of Parcel (Decares)	Cadastral Status	Interview-Based Reallocation Model	Hybrid Reallocation Model
	The Number of Parcel	The Number of Parcel	The Number of Parcel
0-5	32	25	16
5-10	37	20	36
10-20	42	48	61
20-30	38	43	35
30-40	44	28	26
40-50	20	22	14
50-60	16	23	6
60-80	16	14	15
80-100	9	8	13
100-120	6	7	4
120-150	2	5	3
150+	3	0	-
Total	265	243	229
Consolidation Ratio (%)		8	14

When we examined Table 3, there was an increase of 16% in the average parcel post-reallocation size

Table 3. The average sizes of parsels of the reallocation models

The Average Size of Parcel	Area (m ²)	Increase Percentage (%)
Cadastral status	33 044.92	-
Interview-based Reallocation Model	34 409.94	% 4
Hybrid Reallocation Model	36 513.61	% 16

According to Table 4, the number of enterprisess that are single parcels before reallocation is 202 (73.7%). This number is 248 (90.5%) in the interview-based model, and 264 (96.3%) in the Hybrid Method. According to this, according to the number of parcels per enterprisess ; Hybrid method is more successful than traditional method.

Table 4. The number of parcels per enterprises in the reallocation models

The Number Of Parcels	Cadastral Status		Interview-based Reallocation Model		Hybrid Reallocation Model	
	The Number Of Enterprisess	%	The Number Of Enterprisess	%	The Number Of Enterprisess	%
1	202	73.7	248	90.5	264	96.3
2	40	14.6	19	6.9	7	2.5
3	17	6.2	6	2.2	1	0.4
4	8	2.9	1	0.4	1	0.4
5	4	1.5	-	-	1	0.4
6	2	0.7	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	1	0.4	-	-	-	-
TOTAL	274	100	274	100	274	100

4. CONCLUSIONS

According to the results obtained; The AT-FGA block reallocation model, which also takes into account the enterprises preferences, automatically performs block reallocation. The developed model approximates the results obtained from the interview based model used in practice. In addition, the automatic reallocation of blocks in this model will result in considerable time and cost savings for large-scale land consolidation projects planned for the near future. The AT-FGA block reallocation model developed for this reason can be proposed for block reallocation in land planning studies.

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Biography:

Dr. Tayfun Cay is a Prof. Dr. of Geomatic Engineering at the Selçuk University of Konya, Turkey. He has been with Selçuk University since 1989. He completed his PhD study at Selçuk University (1994), in "Project planning and management in land consolidation activities" subject. He has an MSc from Selçuk University, Department of Geomatic Engineering (1989), and a BSc from Selçuk University (1987), in Geomatic Engineering. His research interests; Land consolidation, public works, cadastre law, project planning and management and GIS.

Ela Ertunc was born in Gaziantep-Turkey. She graduated from the Department of Geomatics Engineering of Engineering Faculty of Selçuk University in 2010 and from the Department of Civil Engineering of Engineering Faculty of Selçuk University in 2011 in Konya. She completed her master in 2013 from the Institute of Science and Technology of Selçuk University on Land Management program. She has continued her

doctorate at the Institute of Science and Technology of Selcuk University on Land Management program for 2013 now. She has worked as a Research Assistant in the same University for 5 years now.

Dr. Huseyin Hakli graduated highest ranked student from the Department of Computer Engineering at Selcuk University in 2011. He completed his MS (2013) and Ph.D. (2017) degree at the same department and same university. He has been a research assistant in Department of Computer Engineering since 2011. His interest areas include optimization, nature-inspired algorithms, machinelearning and artificial intelligence.

Dr. Harun Uguz graduated from the Department of ComputerEngineering at Selcuk University in 1999. He received his M.S. degree from thesame department and same university in 2002. His Ph.D. degree was received fromthe Department of Electrical and Electronics Engineering at Selcuk University in 2007. He is a professor at Selcuk University Department of ComputerEngineering. His interest areas include optimization, machine learning, datamining and artificial intelligence systems.

The Usage Of Modified Chitosan For The Removal Of Hexavalent Chromium From Waste Water

Nuran DEVECI AKSOY^{1}, Goknur TURSUN¹*

Abstract

This study presents the results of chromate adsorption upon chitosan modified with thiourea, glutaraldehyde. Firstly modified chitosan was synthesized by using thiourea, glutaraldehyde and chitosan at different molar ratios and adsorption capacities were compared to the original chitosan. The modified chitosan showed higher Cr (VI) retention performance than the original chitosan. While the original chitosan had a percent removal of 32% at an initial concentration of 50 ppm, the percentage of chitosan removal improved to 99.9%. Kinetic and thermodynamic constants are determined at appropriate ambient conditions and adsorption is defined by appropriate adsorption isotherms. Langmuir isotherms were found to be suitable for characterizing the adsorption of chitosan with the modified Cr (VI) ions. Under appropriate experimental conditions, percentages of removal in Cr (VI) removal studies by adsorption using modified chitosan reached 99% and adsorption capacity of 442 mg/g was observed. Characterization of the modified chitosan and original chitosan were characterized by FTIR (Fourier Transform Infrared Spectroscopy), TGA (Thermal Gravimetric Analysis), XRD (X-ray Diffraction) and DSC (Differential Scanning Calorimetry).

Keywords: *Adsorption, Chitosan, Chromium(VI), Wastewater Treatment*

1. INTRODUCTION

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. Heavy metals have a harmful effect on human physiology and other biological systems when they are found above the tolerance levels [1]. The presence of trivalent and hexavalent chromium in the environment is the cause of many well documented toxic effects. The maximum levels permitted in wastewater are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium [2].

Chromium is a transition element which is located to Group VI-B of the periodical table and its toxic effect has been proven. Chromium exists in environment both as trivalent Cr(III) and hexavalent Cr(VI) forms. Hexavalent chromium is toxic and carcinogenic, while trivalent is relatively harmless [3].

High concentrations of Cr (VI) are present in the wastewater of leather, textile, mining and metal industries. These high concentration must be reduced below the permissible limits before Cr(VI) is discharged into the receiving environment [4].

Activated carbon is the world's most widely used adsorbent for heavy metal removal from waste water. Despite its efficient use, active carbon is expensive. Due to the disadvantage, research interest into the production of alternative adsorbents to replace the costly activated carbon. Because of their low cost, natural materials such as chitosan, zeolites, clay and fly ash are classified as low-cost adsorbents [5].

In recent years, studies on the use of chitosan as an adsorbent in heavy metal removal have been investigated. Chitosan is a polymer with polysaccharide structure obtained by alkali deacetylation of chitin. Chitin is the second most common biopolymer after cellulose in nature. It is highly reactive as an adsorbent due to the inclusion of amine and hydroxyl groups in the structure [6].

The degree of deacetylation is one of the most important chemical properties that can affect chitosan performance in many applications. The degree of deacetylation, which determines the content of free amino groups in polysaccharides, can be used to differentiate between chitin and chitosan. FTIR analysis was used to determine the degree of deacetylation of chitosan [7].

^{1*} Prof. Dr. Nuran Deveci Aksoy: Istanbul Technical University, Department of Chemical Engineering, Maslak /Istanbul, Turkey. nuran@itu.edu.tr

¹ Gökür Tursun: Istanbul Technical University, Department of Chemical Engineering, Maslak /Istanbul, Turkey goknurtursun@gmail.com

Various techniques have been employed for the treatment of heavy metals, including chemical precipitation, membran processes, ion-exchange and adsorption. Adsorption technique is economically suitable and technically practicable to remove hexavalent chromium from waste water as it requires less operative controls [8].

Briefly, the aim of this study was to investigate the Cr(VI) adsorption performance of chitosan modified with thiourea, glutaraldehyde.

2. MATERIALS AND METHODS

All the chemicals used were of analytical grade. A stock solution of chromium (VI) (100 mg/L) was prepared by dissolving 3.73 g of $K_2Cr_2O_4$ in 1000 mL distilled water. Desired concentrations were obtained by diluting the stock solution with distilled water. Chitosan was obtained from Sigma and classified to average particle diameter of 0.125–0.250 μm .

Degree of Chitosan Deacetylation

The degree of deacetylation is one of the most important chemical properties that can effect chitosan performance in many applications. The degree of deacetylation, which determines the content of free amino groups in polysaccharides, can be used to differentiate between chitin and chitosan. To determine the deacetylation degree of chitosan, 1 g of chitosan 100 mL of 5% acetic acid solution was added. It was mixed at a speed of 150 rpm at a temperature of 30° for 6 hours to dissolve. At the end of the process a viscous solution was obtained and analyzed by FTIR (Fourier Transform Infrared) spectrometer. It is expected that the structure will be modified with thiourea in addition to the amine groups and the sulphide will have a positive effect on chromium removal [9].

Considering these situations, the strategy of modification has been determined. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity.

Chitosan Modification

Chitosan is soluble in dilute mineral acids except sulfuric acid. For this reason, chemical stability should be increased by chemical treatments such as glutaraldehyde cross-linking for application in a chemical acidic environment. The process creates new bonds between the chains of chitosan, ensuring that the polymer is resistant to dissolution even in strong solutions such as hydrochloric acid solution [10]. In addition, the presence of chitosan amine groups is an important influence on the absorption of a good adsorbent. It is possible to increase the adsorption capacity by increasing the amine groups [9].

Considering these situations, the strategy of modification has been determined. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity. The thiourea and glutaraldehyde were reacted in 20 mL distilled water for 8 hours at 20 °C [9].

Then, 1 g of chitosan was added and reacted for 72 hours. Modified chitosan filtration and washed several times with distilled water. Then, it was dried at 50 °C for 24 hours. Dried chitosan samples are stored in a desiccator [9]. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity. The contents of the modified chitosan samples produced are listed in Table 11.

Table 5.1: Contents of Modified Chitosan Samples

Sample	Chitosan (g)	Glutaraldehyde (mL)	Thiourea (g)
KGT.1	1	1	-
KGT.2	1	2	-
KGT.3	1	4	-
KGT.4	1	8	-
KGT.5	1	1	1
KGT.6	1	2	1
KGT.7	1	4	1
KGT.8	1	8	1
KGT.9	1	1	2
KGT.10	1	2	2
KGT.11	1	4	2
KGT.12	1	8	2
KGT.13	1	1	4
KGT.14	1	2	4
KGT.15	1	4	4
KGT.16	1	8	4

2. Cr(VI) Adsorption Experiments

Stock solution of K_2CrO_4 (1000 ppm) was prepared and diluted as necessary to be used in batch adsorption experiments. The concentration of Cr(VI) was analyzed spectrophotometrically (Shimadzu UV 1240) at 540 nm using 1,5-diphenyl carbazide as the complexing agent [11,12].

The adsorption capacities of original chitosan and modified chitosan samples were determined under the conditions of 50 ppm initial Cr(VI) concentration, pH 2.0 and 1 g L^{-1} adsorbent dose. The removal extent and capacity were calculated from Eq. 1 and Eq. 2, respectively.

$$q_e = \frac{V_i C_i - V_e C_e}{W} \quad (1)$$

$$\text{Adsorption}(\%) = \frac{(A_0 - A)}{A_0} * 100 \quad (2)$$

where C_i and C_e are the initial and equilibrium Cr(VI) concentration of solution (mg L^{-1}), q_e is the equilibrium uptake capacity (mg g^{-1}), V is the volume of solution (L) and W is the mass of adsorbent (g). Where A_0 and A are the initial and final absorbance (nm) of the solution, respectively [13].

The effect of pH was studied within the range pH 1–8.0. Adjustments were made by small additions of 0.1 M HCl or 0.1 M NaOH. Cr(VI) solutions of 50 ppm were contacted with modified chitosan samples (0.4 g L^{-1}) and 250 ppm were contacted with modified chitosan samples (0.6 g L^{-1}) for 24 h.

Time to reach equilibrium was investigated for initial concentrations of 70 and 160 ppm. Samples were driven out at certain time intervals between 1 and 24 h and analyzed for residual Cr(VI) concentration.

The effect of adsorbent dose was investigated within the range of $0.2 - 4 \text{ g L}^{-1}$ using Cr(VI) solutions of 100 ppm and 250 ppm.

Optimal conditions of pH, contact time and adsorbent dose were applied in isotherm studies. Cr(VI) solutions of different concentrations were treated with modified chitosan samples, and collected data were fitted to Langmuir and Freundlich isotherm models.

3. Adsorbent Characterization

Identification of the crystalline species or impurities in original chitosan and the change in crystalline structure after modification with surfactant were provided by X-ray diffraction analysis. Thermalgravimetric analysis of original chitosan and modified chitosan samples was carried out by Perkin Elmer, Diamond TG/DTA in air atmosphere, within the temperature range of 30-1000 °C with a heating rate of 10 °C min^{-1} . The FTIR spectra of samples were recorded with Perkin Elmer Spectrum One Spectrophotometer within $4000-450 \text{ cm}^{-1}$ as an average of four scans.

3. RESULT AND DISCUSSION

Chromium Removal with Chitosan and Modified Chitosan

Comparison of original chitosan and modified chitosan in Cr(VI) removal

Firstly modified chitosan was synthesized by using thiourea, glutaraldehyde and chitosan at different molar ratios and adsorption capacities compared to the original chitosan were compared. The modified chitosan showed higher Cr (VI) retention performance than the original chitosan. While the original chitosan had a percent removal of 32% at an initial concentration of 50 ppm, the percentage of chitosan removal improved to 99.9%. The chrome Cr (VI) holding capacities and removal percentage of the original chitosan and modified chitosan are shown in Table 2.

Table 2: The Cr (VI) holding capacities and removal percentage of the original chitosan and modified chitosan

Sample Name	Amount of Retention (mg/g)	Removal Percentages (%)
KGT.1	46.62	89.24
KGT.2	45.36	90.73
KGT.3	48.45	96.91
KGT.4	49.94	99.88
KGT.5	47.22	94.44
KGT.6	47.47	94.93
KGT.7	48.45	96.91
KGT.8	47.59	95.18
KGT.9	44.37	88.75
KGT.10	48.45	96.91
KGT.11	47.09	94.19
KGT.12	48.95	97.90
KGT.13	47.34	94.69
KGT.14	46.97	93.95
KGT.15	49.97	99.95
KGT.16	49.32	98.64
Original Chitosan	16.43	32.85

The modified chitosan No. KGT.15 was synthesized to be used as an adsorbent when the appropriate conditions for Cr (VI) removal were determined using the results.

Effect of pH on Cr(VI) removal

pH is one of the important parameters affecting the adsorption capacity due to its influence on the surface properties of adsorbent and metal ionization. The results of experiments conveyed at different pH levels are shown in Fig.1.

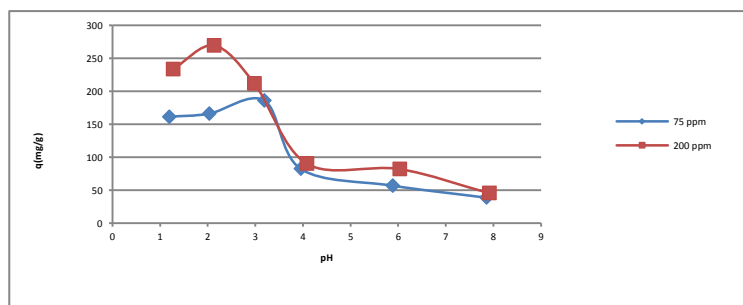


Figure 1. Determination of the appropriate pH range for adsorption of Cr (VI) ions on modified chitosan; $t = 24$ hours, $T = 293$ K.

Effect of contact time on Cr(VI) removal

The effect of contact time was examined in the range of 1h to 24 h for 70 and 160 ppm initial Cr(VI) concentrations, and the results are shown in Figure 2.

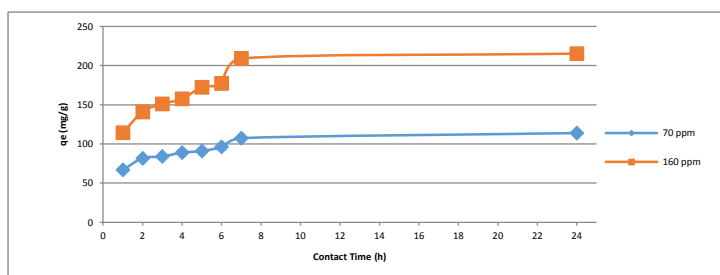


Figure 2. Determination of the equilibrium time of adsorption of Cr (VI) ions on modified chitosan; $t = 24$ hours, $m = 0.03$ g $T = 293$ K.

Figure 2 shows that the duration of the equilibrium is independent in the initial concentration. It was observed that the amount of retention increased at negligible level after the first seven hours. For this reason, it can be said that the seven hour contact period of Cr (VI) ions is sufficient for adsorption with modified chitosan.

Effect of adsorbent dose on Cr(VI) removal

Determination of the appropriate adsorbent dose is important for the efficiency and cost of the adsorption process. In the experiments, the effects on adsorption were investigated by changing the adsorbed dose at two different initial concentrations. The effect of the adsorbent dose on the amount of retention and percentages of removal is shown in Table 3 and Table 4.

Table 3. The effect of the adsorbent dose on the amount of retention and percentages of removal at initial concentration 100 ppm

Adsorbent Dose (g/50 mL)	Amount of Retention (mg/g)	Removal Percentages (%)
0.03	126.4	75.83
0.04	114.3	91.41
0.05	98.0	97.96
0.07	69.8	97.59
0.10	49.8	99.44
0.15	33.3	99.81
0.20	25.0	99.94

Table 4. The effect of the adsorbent dose on the amount of retention and percentages of removal at initial concentration 250 ppm.

Adsorbent Dose (g/50 mL)	Amount of Retention (mg/g)	Removal Percentages (%)
0.03	227.2	54.52
0.04	203.9	65.25
0.05	172.1	68.86
0.07	145.0	81.23
0.10	112.7	90.13
0.15	79.9	95.82
0.20	62.4	99.93

The difference between the percentages of removal increases with each step from 0.01 g to 0.07 g to the adsorbent dose. It is seen that the difference between the percentages of elimination in adsorbent dose increases after 0.07 g is negligible. It has been decided that the appropriate adsorbent dose should be between 0.07 g / 50 mL and 0.1 g / 50 mL.

4. Adsorption Isotherm Studies

As a result of the studies, the optimum environment conditions for hexavalent chromium removal from waste water with modified chitosan were determined as solution pH 1-3, adsorbent dose 1.4 (g / L) and contact time 7 hours. After selection of optimal operating conditions, isotherm studies were conducted to characterize the adsorption of Cr(VI) upon modified chitosan. It was studied with different initial concentrations at constant temperature to obtain isotherm graphs. Relationship between the adsorbate concentration of the equilibrium solution and the amount of adsorbent material per unit adsorbent should be established. It should be determined again by changing the temperature to determine the effect of the change with temperature. For this purpose, five different initial concentrations and three different temperatures were used. The relationship between the amount of retention and the concentration of solution in equilibrium is shown in Figure 3.

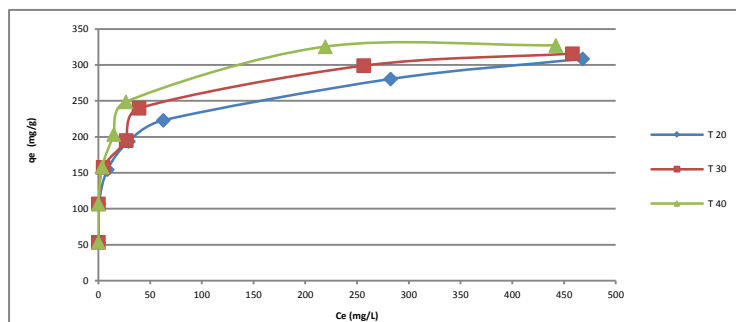


Figure 4: Determination of adsorption capacities at different temperatures; Initial concentration (C_0) = 75, 150, 225, 300, 375, 675, 900 ppm.

To determine whether the obtained data correspond to Langmuir isotherms, a graph of C_e / q_e values versus C_e values was drawn. This is shown in Figure 5.

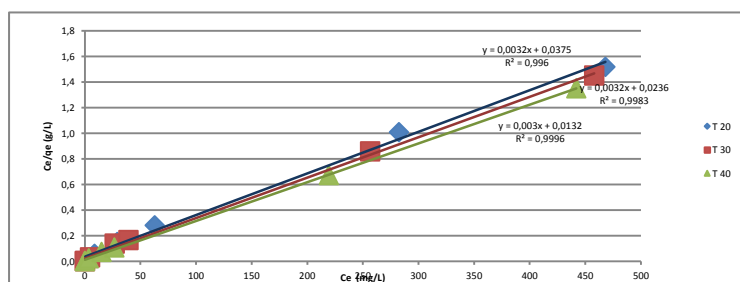


Figure 5. Langmuir constants for different temperatures in the adsorption of Cr (VI) ions with modified chitosan.

The correlation constant in the three different temperatures being greater than 0.96 indicates that the Langmuir isotherm is suitable for characterizing the adsorption of the Cr (VI) ions with the modified chitosan. Data were fitted to linearized forms of isotherm models and results are given in Table 5.

Table 5. Lagmuir Constant

Sıcaklık (K)	Sabitler				
	K_L (L/g)	a_L (L/mg)	q_m (mg/g)	R^2	Dagilma Sabiti R_L
293	26.66	0.085	308.4	0.996	0.012
303	42.37	0.135	315.7	0.998	0.008
313	75.75	0.227	327.2	0.999	0.004

5. Characterization of Chitosan and Modified Chitosan

X-ray diffraction analysis

X-ray diffraction of the original chitosan and modified chitosan is shown in Figures 6 and 7.

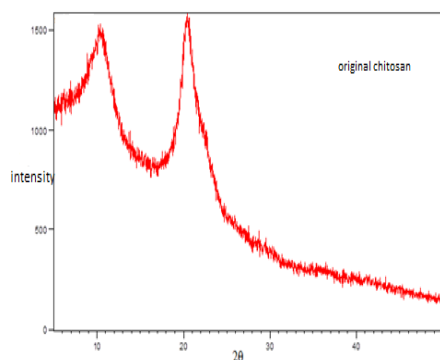


Figure 6. Original chitosan XRD pattern

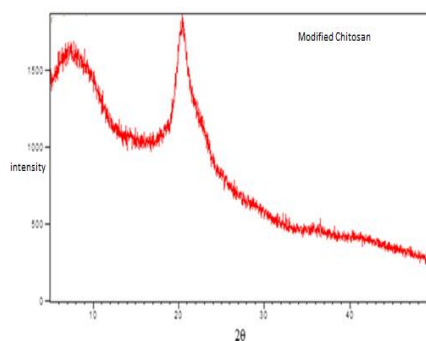


Figure 7. Modified chitosan XRD pattern

XRD analysis was also made for the proof of modification. The modification of chitosan with glutaraldehyde and thiourea showed a peak flattening at 11 ° with the resultant original chitosan, indicating a significant decrease in crystallinity as a result of chitosan cross-linking with glutaraldehyde. The crystallinity of the chitosan polymer may play a limiting role in metal retention capacity. The crystallinity parameter of chitosan is an important parameter of accessibility to the inner region for both water and metal ions. Many studies have shown that reducing the crystallinity results in an improvement in metal ion retention properties [14,15].

Thermal gravimetric analysis of adsorbents

Figure 8 shows the mass change graph due to the temperature obtained at 25 - 1000 °C temperature by Thermal Gravimetric Analysis (TGA) method of chitosan and modified chitosan. In order to examine the thermal behavior of chitosan and modified chitosan in detail, differential thermogravimetric (DTG) curves of the materials are given in Figure 9.

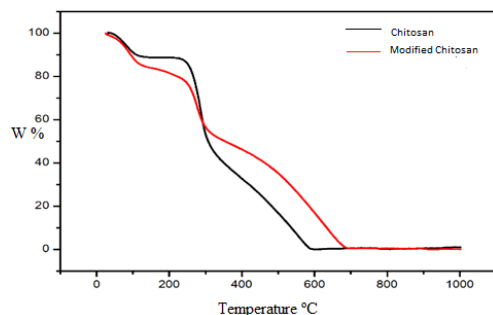


Figure 8. Chitosan and Modified Chitosan TGA Curve

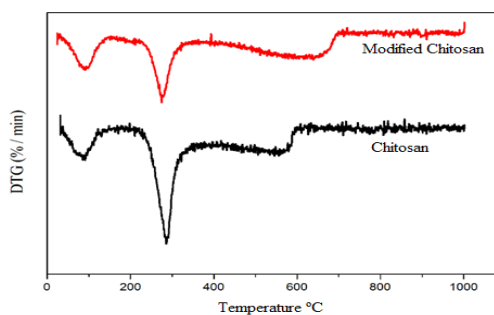


Figure 9. Chitosan and Modified Chitosan DTG Curve

Both samples showed mass loss at 100 °C, while at the same time DTG curves both peaks at 100 °C on both samples. When studies done in the literature are examined, the initial weight loss at about 100 °C is due to the evaporation of water. The other weight loss at 200-500 °C is due to the deterioration of the structure of the chitosan molecule [16]. Thermal gravimetric analysis gives information on the composition of chitosan and modified chitosan. On the other hand, information about the connections between the chitosan and the modified chitosan was needed. For this reason, analysis with XRD and FTIR and study with TGA was supported.

FTIR analysis of adsorbents

The chemical structures of the chitosan and modified chitosan and the changes in the functional groups of the compounds were investigated by FT-IR spectroscopy and the peak intensities were interpreted in accordance with the literature. The FTIR spectra of the original chitosan and modified chitosan are given in Figure 9.

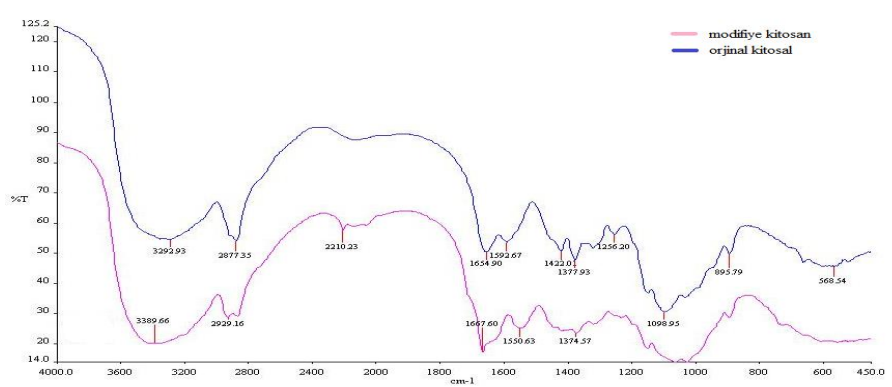


Figure 10. Original chitosan and modified chitosan FTIR spectrum.

The disappearance of the NH₂ band in the cross-linked chitosan as a consequence of the cross-linking mechanism with glutaraldehyde at 560 cm⁻¹ in the original chitosan is evidence of the cross-linking of chitosan [16].

4. CONCLUSIONS

In this work, chitosan was first modified with glutaraldehyde and thiourea. The modified chitosan showed better performance in chrome removal compared to the original chitosan. The effects of different experimental conditions on the adsorption process were investigated by studying different solution pH, temperature, initial concentration, contact time and adsorbent dose. As a result of the studies, the optimum environment conditions for hexavalent chromium removal from waste water with modified chitosan were determined as solution pH 1-3, adsorbed dose 1.4 (g / L) and contact time 7 hours. Langmuir isotherm has been identified as the most suitable isotherm. Chitosan and modified chitosan are characterized by XRD, FTIR and thermal gravimetric analysis.

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Exploring Solutions to Overcome the Barriers of Household Waste Separation Behaviour

Metehan Feridun SORKUN^{1}, Mine YILMAZER², Meltem ONAY²*

Abstract

This paper aims to identify the barriers of the household waste separation behaviour, and searches for their main causes in order to eliminate them. Solid waste management has importance for economies because the amount of waste generated has been increasing continuously; therefore, recovering value from these waste provides low-cost inputs (e.g. plastics, glass, paper, metals etc.) to the firms' production. It also helps firms accomplish source reduction, and sustainable development. However, two reverse logistics costs – waste separation and collection – are critical reverse logistics activities, because the escalation of their costs due to poor solid waste management might obscure the economic advantages abovementioned. Hence, this study examines the behaviours, thoughts, and beliefs of members of households in Seferihisar, a district in the Izmir region, to identify the respective barriers for waste separation behaviour. The results indicate that people's behaviours, thoughts, and beliefs towards waste separation processes vary with respect to demographic variables such as gender, income, and education level. This study discusses the theoretical and managerial implications of the results as well.

Keywords: *Reverse Logistics; Solid Waste Management; Circular Economy; Closed-Loop Supply Chain; Sustainable Production*

1. INTRODUCTION

The amount of waste collected by Turkish municipalities in 2014 exceeded 28 million tons [1]. This statistic indicates many economic opportunities. The collected waste can be composted to produce energy and used to power the production of firms at low costs [2]. However, the latter function also brings operational challenges in terms of reverse logistics activities, such as separating, collecting, and sorting waste [3]. The poor implementation of these reverse logistics activities can incur high costs that obscure the economic advantages abovementioned. This situation calls for technologies that can automate waste collection and separation activities in a cost-effective manner.

To the best knowledge of authors, there is no such technology yet, at least in developing countries such as Turkey, for collecting and separating waste cost-effectively. For this reason, especially for waste separation activity, in order to decrease costs, promoting the involvement of households in solid waste management seems as a good strategy, as this removes an important portion of cost burden from municipalities. However, since this is a voluntary act, it is essential to eliminate all barriers that prevent people from separating their waste. Only if people find waste separation easy, meaningful, and useful, it will be possible to encourage waste separation behavior. This requires first, to identify all barriers of waste separation behavior, and then to examine the causes of these barriers for their elimination with proper solutions.

With the aim of identifying the barriers that prevent people from separating waste, this paper reports on survey conducted in Seferihisar, a district in the Izmir region. During data collection process, 128 respondents with different demographic traits (e.g. gender, age, job, income, and education) responded to survey questions. The data analysis on these responses reveal the major thoughts, beliefs, and difficulties that have an effect of on waste separation behaviors. Then, this paper outlines a roadmap to overcome the barriers that discourage people to separate waste.

^{1*} Corresponding author: Izmir University of Economics, Department of Business Administration, 35330, Balçova/Izmir, Turkey. metehan.sorkun@ieu.edu.tr

² Manisa Celal Bayar University, School of Applied Sciences, 45140, Muradiye/Manisa, Turkey. mine.yilmazer@gmail.com

² Manisa Celal Bayar University, School of Applied Sciences, 45140, Muradiye/Manisa, Turkey. meltemonay@gmail.com

In addition to the theoretical contribution of the findings, this study also provides important insights for municipalities to increase the rate of participation in waste management programs by separating waste. The results enable policymakers to observe the current attitude of people towards waste management activities. The findings further allow exploration into the causes of resistance to waste separation. While some causes can be eliminated by removing difficulties, others seem to require extensive effort, such as increasing households' education level, employment rate, and income.

2. MATERIALS AND METHODS

This study used a survey for data collection. The sample targeted the households in Seferihisar, the district of Izmir, Turkey. Non-probability convenience sampling, in which members of the target population do not have equal opportunity to be sampled, was used for data collection [4]. To ensure comprehension, the survey was prepared in Turkish, the native language of respondents. The first part of survey consists of various demographic questions. Table 1 shows the demographic characteristics of the sample below:

Table 12. Demographic Characteristics of Sample

Demographic Variables	N=128
	%
Gender	
Male	43.3
Female	56.7
Marital Status	
Married	52
Single	48
Age	
16-25	29.7
26-35	22.7
36-45	19.5
46-55	9.4
56-65	14.1
66+	4.7
Income	
Min. Wage - 3000 TL	40.2
3001 - 5000 TL	26.8
5001 - 7000 TL	18.1
7001 - 9000 TL	11
9001 TL +	3.9
Household Size	
1 person	8.6
2 persons	18
3 persons	27.3
4 persons	36.7
5 persons	7.8
6 persons	1.6
Education	
Primary & Elementary	18
High School	32.8
Bachelor	42.2
Master/PhD	7
Job Status	
Employed	49.2
Retired	14.1
Housewife	14.1
Student	19.5
Unemployed	3.1

The second part of the survey was designed as a Likert scale of five points, with the end points "strongly agree" and "strongly disagree". These scale items, used to identify the barriers to waste separation behavior, were developed based on the scales of other studies on waste separation behavior ([5],[6],[7],[8],[9],[10]). At the end of survey, five multiple-choice questions measured the respondents' knowledge on the waste separation process. In other words, these questions measure how effectively respondents are able to separate their waste. Table 1 illustrates the survey items in the second and third parts of survey.

Table 2. Survey Items for the Barriers of Waste Separation Behavior

Item No.	Survey Items Design
S1	For me, household recycling is a difficult task.
S2	Recycling is too complicated.
S3	I do not have enough time to sort the materials for recycling.
S4	I do not have enough space to store the materials for recycling.
S5	Recycling bins are far from my house.
S6	Recycling programmes are a waste of money.
S7	The recyclables that I store attract pests.
S8	I am willing to pay extra tax if it is used to increase the municipality's recycling activities.
S9	I believe the municipality's recycling activities positively affect the economy.
S10	I am familiar with the recycling facilities in my area.
S11	I am familiar with the materials accepted for recycling in the recycling facilities in my area.
S12	My family reacts positively when I recycle household materials.
S13	My friends react positively when I recycle household materials.
S14	I leave my used cooking oil at collection points.
S15	I usually separate and dispose of all recyclable materials.
S16	I am not in the habit of recycling.
S17	I feel good about myself when I recycle.
S18	I know how to recycle my household waste.
S19	I know where to take my household waste for recycling.
S20	I believe that my recycling activities will help reduce pollution.
S21	I believe that my recycling activities will help meet energy needs.
S22	I believe that my recycling activities will contribute to the economy.
S23	Household waste do not harm environment.
S24	Recycling helps meet energy needs.
S25	Recycling contributes to the economy.
S26	People who do not sort their household waste should be fined.
S27	The municipality should reward me when I recycle my household waste (e.g. with a shopping discount, cinema ticket).
S28	The municipality should carry out curbside collections for my household waste.
S29	Sorting materials for recycling should be the responsibility of the municipality.

The final sample size of this study is 128. The statistical analysis was conducted on responses to determine the major barriers that discourage people from separating waste. These barriers were also examined with respect to various demographic variables using non parametric independent samples mean tests (Mann-Whitney U test for two samples and Kruskal Wallis test more than two samples). The software package SPSS was used for all these analyses.

3. RESULTS AND DISCUSSION

Table 3 illustrates the descriptive statistics. According to the results, the most significant difficulty that respondents face while separating their waste is the distance between their houses and recycling bins. In addition, the responses reveal that time and space are other significant constraints for the separation of household waste. Last, the hygiene problem that might occur due to the waste separation process is stated as another major barrier.

The positive aspects of the findings are that respondents do not find waste separation difficult, complicated, or unnecessary. Besides, the results indicate that most of respondents are aware of nearby recycling facilities, and know which materials are collected for recycling. Similarly, people have high level of knowledge on how to separate their waste and where they should bring their waste for recycling.

The findings show that the positive externalities are available for waste separation behavior. Positive reactions from friends and family encourage respondents to separate their household waste. The approval of friends and family members may be interpreted as the antecedent of another finding, that respondents feel positive when they recycle. The respondents believe that their recycling activities (i.e. separating their waste) are not negligible, but positively affect environment and economy.

Another positive finding is that respondents support the municipality recycling activities and find these efforts worthy. Respondents believe that the waste programs of municipalities have positive effects on environment and economy; however, they are unwilling to pay extra taxes to the municipality to increase recycling activities. On the other hand, the results show that municipality is expected to locate recycling bins close to residential areas. Besides, respondents expect to be rewarded when they separate their waste because they believe that not all people make the same effort.

Table 3. Descriptive Statistics of Survey Items

Item No.	N	Median	Mean	Standard Deviation
S1	126	2.00	2.2381	1.47202
S2	126	2.00	2.3333	1.49666
S3	126	3.00	2.8095	1.53734
S4	125	3.00	2.9840	1.53971
S5	125	4.00	3.2080	1.65245
S6	126	1.00	1.6825	1.12179
S7	123	3.00	2.9187	1.56076
S8	125	2.00	2.4240	1.41001
S9	126	4.00	3.7698	1.29097
S10	126	4.00	3.2619	1.62076
S11	124	4.00	3.7097	1.44703
S12	125	4.00	3.9120	1.25091
S13	125	4.00	3.7760	1.34323
S14	122	3.00	2.8934	1.59445
S15	126	3.00	3.1587	1.47736
S16	128	3.00	2.7734	1.49126
S17	127	4.00	3.6850	1.30749
S18	127	4.00	3.6063	1.43182
S19	127	4.00	3.1732	1.48588
S20	125	5.00	4.0240	1.38228
S21	128	4.00	3.8828	1.40091
S22	128	4.00	3.8828	1.39527
S23	127	1.00	2.0394	1.35928
S24	125	4.00	4.1200	1.09692
S25	128	4.00	4.0781	1.18128
S26	127	3.00	2.7795	1.44152
S27	126	4.00	3.5079	1.47375
S28	127	5.00	3.9764	1.28152
S29	126	3.00	2.6587	1.41513

Table 4 below shows the significant ($p < .05$) independent samples mean tests on survey items in Table 3 with respect to various demographic variables, which are gender, marital status, age, education, income, and employment. While Mann-Whitney U test was applied on demographic variables composed of two groups, e.g. gender and marital status, Kruskal-Wallis test was applied on demographic variables composed of more than two categories (e.g. age, income, education, and job status).

The findings reveal that male respondents find waste separation more difficult and complex, and are more concerned on potential hygiene problems due to the waste separation process. Female respondents have also higher level of knowledge on the materials collected for recycling. Similarly, female respondents report a stronger positive reaction from peers when they recycle, and female respondents have stronger belief that their waste separation behavior contributes to economy.

The second demographic variable examined is marital status. Results show the married respondents find waste separation more difficult. This may be because married respondents are more likely to live in a larger household sizes, which could escalate the amount of waste. Other finding is that unmarried respondents more strongly support the idea that those who do not separate their waste should be fined.

According to results, age plays role especially in the awareness of respondents about locations where the waste separated is collected. Respondents between 56-65 years-old have more accurate information on collection points than younger respondents. However, the respondents over 65 years old have much less information on the collection points of municipality where they are assumed to bring their waste after having been separated.

Table 4. Non Parameter Independent Samples Mean Tests

Demographic Variable	Survey Item	Test	Sig.
Gender	For me, household recycling is a difficult task.	Mann-Whitney U	.045
Gender	Recycling is too complicated.	Mann-Whitney U	.008
Gender	The recyclables that I store attract pests.	Mann-Whitney U	.028
Gender	I am familiar with the materials accepted for recycling in the recycling facilities in my area.	Mann-Whitney U	.014
Gender	My friends react positively when I recycle household materials.	Mann-Whitney U	.009
Gender	Recycling contributes to economy.	Mann-Whitney U	.019
Marital Status	For me, household recycling is a difficult task.	Mann-Whitney U	.050
Marital Status	The people who do not sort their household waste should be fined.	Mann-Whitney U	.023
Age	I am familiar with the recycling facilities in my area.	Kruskal-Wallis	.036
Age	I know where to take my household waste for recycling.	Kruskal-Wallis	.026
Education	For me, household recycling is a difficult task.	Kruskal-Wallis	.030
Education	Recycling is too complicated.	Kruskal-Wallis	.015
Education	I do not have enough time to sort the materials for recycling.	Kruskal-Wallis	.000
Education	I do not have enough space to store the materials for recycling.	Kruskal-Wallis	.000
Education	Recycling bins are far from my house.	Kruskal-Wallis	.014
Education	I am familiar with the recycling facilities in my area.	Kruskal-Wallis	.003
Education	I leave my used fried oil to collection points.	Kruskal-Wallis	.003
Education	I am not in the habit of recycling.	Kruskal-Wallis	.000
Education	I know where to take my household waste for recycling.	Kruskal-Wallis	.025
Income	I do not have enough time to sort the materials for recycling.	Kruskal-Wallis	.007
Income	I do not have enough space to store the materials for recycling.	Kruskal-Wallis	.007
Income	Recycling bins are far from my house.	Kruskal-Wallis	.006
Income	I believe the municipality's recycling positively activities affect the economy.	Kruskal-Wallis	.022
Income	I am familiar with the recycling facilities in my area.	Kruskal-Wallis	.001
Income	I leave my used cooking oil to collection points.	Kruskal-Wallis	.036
Income	I usually separate and dispose of all recyclable materials.	Kruskal-Wallis	.015
Income	I am not in the habit of recycling.	Kruskal-Wallis	.005
Income	I know how to recycle my household waste.	Kruskal-Wallis	.014
Income	I know where to take my household waste for recycling.	Kruskal-Wallis	.023
Income	I believe that my recycling activities will help reduce pollution.	Kruskal-Wallis	.031
Income	I believe that my recycling activities will help meet energy needs.	Kruskal-Wallis	.019
Income	I believe that my recycling activities will contribute to economy.	Kruskal-Wallis	.024
Income	Recycling helps meet energy needs.	Kruskal-Wallis	.003
Job Status	I usually separate and dispose of all recyclable materials.	Kruskal-Wallis	.006
Job Status	People who do not sort their household waste should be fined.	Kruskal-Wallis	.025

The findings illustrate that education level positively affects the ability of respondents to overcome the difficulties related to the waste separation process. The respondents with higher education degree perceive the waste separation as a relatively easier task, and can find practical solutions to difficulties such as time and space constraints. Likewise, this better-educated group of respondents do not consider that the location of containers (bins), for collection of separated is far from their houses. This result indicates the effect of education level on the knowledge of people on recycling facilities in region. Furthermore, education level positively influences the actual waste separation behaviour of people.

The income level is another demographic variable that affects various aspects of waste separation behaviour, knowledge, and beliefs. As the income level decreases, the space and time constraints become more problematic. In addition, the lower-income respondents believe as strongly as the higher-income respondents that recycling activities have positive effects on the environment and economy. Moreover, the responses show that the lower-income respondents have a greater level of knowledge regarding the waste separation and waste collection points.

The last demographic variable examined is the job status of respondents. Job status was found to have significant effect on both the actual waste separation behaviour and also the opinions on sanctions for people who do not separate their waste. Regarding the first issue, retired respondents and students are more likely to separate waste than working people and housewives. This result might be associated with the amount of free time. Another issue on which there is significant difference with respect to job status is the opinion on how to deal with people who do not separate their waste. Here, while retired people and housewives seem to be more tolerant, the unemployed are the most insistent that people who do not separate their waste should be fined.

4. CONCLUSION

With fairly negligible efforts, collaborative action can enable people to manage complex processes and to achieve significant tasks [11]. The implementation of reverse logistics activities in municipalities' waste management programs is a good example for this case. The success of municipality's waste programs considerably depends on people's willingness to support these programs. The ability to recover value from household waste has positive effects on the economy and environment. However, the cost-effectiveness of reverse logistics activities plays a crucial role at this point. Especially, waste separation and collection are two reverse logistics activities that if ignored or resisted, might reduce the positive impact of waste management programs. Therefore, overcoming resistance and involving households in these two activities, by encouraging them to separate their waste, and bring them to the appropriate municipality recycling bins can make a major contribution to economy.

It is difficult to motivate people without short-term rewards. Therefore, the critical issue while encouraging people to separate their waste for no financial reward, but for long-term economic growth requires satisfying a set of conditions. First, there is a need to eliminate all physical barriers that make waste separation more difficult. Second, people should be made aware of long-term economic benefits obtained through their waste separation behaviour.

In the pursuit of these goals, this study has made the first step by attempting to identify the barriers of waste separation behaviour. The barriers considered in this paper are not limited to physical ones. By collecting data on people's beliefs and thoughts on the waste management programs, this study has also identified the mental barriers. Correspondingly, the results illustrate the existence of mental barriers besides physical ones. Furthermore, these barriers are assessed in this study with respect to various demographic variables, such as gender, marital status, education level, job status, and income level. The findings show each demographic variable has an effect on specific physical and mental barriers.

The results of this study provide some valuable managerial implications for the public managers of municipality. In the short-term period, they should aim to eliminate physical barriers, such as locating recycling bins closer to houses. Moreover, they can find customized solutions based on the analysis on demographic variables. For example, the results show that male respondents find waste separation more complex and difficult than female respondents, probably, women spending more time in kitchens where waste is usually stored. The municipality's promotion activities for providing information on the waste separation process may focus on the interest areas of males to show them how simple waste separation is. The solution of other barriers related to prejudices and negative thoughts on the utility of waste programs require extensive effort, such as increasing the education levels. Building on the findings of this study, future research can find practical solutions to overcome the barriers of waste separation behaviour. In addition, future studies may attempt to establish a model and/or design a system in which the waste separated by households can directly contribute the productivity of firms.

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BIOGRAPHY:

Metehan Feridun Sorkun is an Assistant Professor of Operations Management at Izmir University of Economics. He completed the PhD program in management, in 2016, jointly organized by Ca' Foscari University of Venice, the University of Padua, and the University of Verona. Dr. Sorkun earned his bachelor degrees in Logistics Management and International Trade & Finance from Izmir University of Economics in 2010. His recent research interests are reverse logistics, solid waste management, technology management, supply chain design, and new product development. He has taught operations research, logistics, and supply chain courses at graduate and undergraduate levels. He has been an ad hoc reviewer for journals such as International Journal of Operations and Production Management, and Asia Pacific Journal of Logistics and Marketing.

A Comparison of SBR and CSTR Activated Sludge Reactors in COD and Nitrogen Removal

Abdullah KIZILET¹, Amar ĆEMANOVIĆ², Mehmet Akif VERAL³, Ozer CINAR^{4}*

Abstract

Since the emergence of the biological wastewater treatment, the activated sludge process has been the most common process in use throughout the world. While a great amount of variations on the process were developed in the past century, this paper focuses on the comparison of the Sequencing Batch Reactor (SBR) and the Continuous Stirring Tank Reactor (CSTR) systems for the removal of COD and nitrogen. The former operates in batch mode in a single tank, although it can be coupled to additional tanks for continuous operation. The CSTR system operates by default in continuous mode and in steady state, and allows for easier setup of nutrient removal processes. While both have been proven efficient in COD and nitrogen removal, the available literature suggests that the SBR system may be the process of choice when low cost and small footprint are to be achieved, whereas CSTR systems may be preferred for high flow rates and for high levels of toxicity in the influent. At last, the decision which method to apply in a specific situation depends on a great number of factors and has to be assessed individually for each application.

Keywords: Domestic Wastewater, Biological Treatment, COD Removal, Nitrogen Removal, CSTR, SBR

1. INTRODUCTION

The activated sludge process is the most prominent process for biological wastewater treatment from various sources. It has been discovered in 1914 by Ardern and Locket [1] and it took only three years for the first full-scale treatment plants to come into operation. The process has been developed into many different variations that differ greatly with regards to the type of influent wastewater and the overall system design. The name refers to the microbial consortia that are suspended in the treatment tank (called aeration tank if the process is aerobic) and that utilize the organic matter in the influent wastewater as carbon and electron source, thereby oxidizing it to simpler products.

The activated sludge itself is composed of various microorganisms – bacteria, rotifers, crustacea, protozoa, nematodes, sometimes even viruses [2]. The microbes that are doing most of the work on the decomposition, and are dominant by mass, are heterotrophic bacteria [3]. Nevertheless, there exists significant competition for resources among the various species of microorganisms. Hence, the microbial composition and physical properties of the sludge is subject to change due to changes in influent wastewater characteristics and environmental conditions (such as temperature, pH, nutrient availability, DO concentration etc.) [2].

¹Department of Bioengineering and Sciences, Kahramanmaraş Sutcu Imam University, 46100, Kahramanmaraş, Turkey

²Department of Environmental Engineering, Istanbul Technical University, 34469 Maslak/Istanbul, Turkey

³Department of Bioengineering, Yildiz Technical University, 34220, Esenler/Istanbul, Turkey

⁴ **Corresponding author:** Department of Environmental Engineering, Yildiz Technical University, 34220, Esenler/Istanbul, Turkey. ocinar@yildiz.edu.tr

The SBR is a fill-and-draw system (also known as batch system) for wastewater treatment using activated sludge. During the 20th century this technology has gained popularity mainly due to its operating advantages and flexibility as well as the development of microprocessor-based programmable logic controllers (PLCs). The new technology meant that the process could be automated and precisely controlled, which eliminated the previous disadvantages.

The Continuously Stirred Tank Reactor (CSTR; same as chemostat) is considered one of the simplest systems for wastewater treatment. It has been devised as an upgrade to the initially used batch systems due to the need to handle a continuous flow of wastewater.

COD removal encompasses the oxidation of organic matter in the wastewater to simpler products, preferably CO₂ as the end-product. Nitrogen removal occurs in two main steps – nitrification and denitrification, and for them to happen there need to be alternating aerobic and anoxic conditions. Namely, aerobic conditions favor the conversion of ammonia into nitrate via nitrite (nitrification), while anoxic conditions imply that nitrate is used as an electron acceptor to become reduced to nitrite and finally to nitrogen gas (denitrification). Nitrification is performed by autotrophic aerobic bacteria – ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). They include genera such as *Nitrosomonas*, *Nitrobacter*, *Nitrococcus* etc. Denitrification is conducted by heterotrophic facultative anaerobes, such as species of *Bacillus*, *Pseudomonas* etc. Factors such as pH, temperature, and DO concentration are the main factors affecting the biological nitrogen removal.

This paper offers an overview of the basic differences between the two systems, as well as specific applicative comparisons from the literature.

2. SBR VS. CSTR SYSTEM

2.1. Characteristics of the SBR

The SBR system operates in five major phases: fill, react, settle, draw and idle (Figure 1).

Fill. Wastewater to be treated is introduced into the reactor. This period lasts around 25% of the full cycle time and ends when the tank is either full or when a maximum time for filling is reached. Filling can be conducted under different conditions depending on the aim of the process.

While in the reaction phase both the mixers and aeration units (for aerobic processes) are on, the filling phase can occur in three modes: static fill, mixed fill and aerated fill. Static fill means that the wastewater is added to the reactor without any mixing or aeration. This favors floc-forming microbes over filamentous organisms, which is desirable given that the subsequent step is settling [4].

Mixed fill implies that the influent wastewater is mixed with the activated sludge, which induces the biological reactions. After the residual oxygen has been used up, denitrification is starting to occur in the newly-established anoxic conditions. If provided enough time, the conditions in the tank may turn into anaerobic, thereby initiating further specific reactions [4]. In aerated fill mode, on the other hand, the influent is aerated while filling is still underway. This mode kick-starts the biological reactions that will happen during the react phase.

In case there is a continuous influent, there should either be a storage tank in place or an additional SBR tank in order to handle the incoming wastewater.

Reaction. During the reaction period, the suspended biomass consumes the substrate under controlled environmental conditions. It can last around 50% of the full cycle time.

This mode can be accomplished in aerated react or mixed react mode. In aerated react mode, the aerobic biodegradation reactions can be completed together with nitrification. In mixed react mode, it is possible to achieve anoxic conditions that enable denitrification. If needed, anaerobic conditions may as well be attained (e.g. for phosphorus removal) [4].

Settle. Mixing and aeration are stopped to allow the sludge to settle and hence obtain a clarified effluent. The excess of sludge can be wasted in this phase. Since sludge does not build up very fast, however, only occasional sludge wasting is required.

Draw. The clarified and treated wastewater is drawn from the reactor, after which the system is ready to start a new cycle. This may take 5-30% of the full cycle time. Drawing may be achieved using a fixed pipe or an adjustable or floating weir. Whichever method is used, it is important to design the system in such a manner so as to prevent escape of sludge or other floating matter from the tank.

Idle. In this phase the reactor is left idle after discharging and before refilling. Its length depends on the effluent removal and influent flow rate as well as the operating strategy. It can also be eliminated from the process.

Aeration in an SBR can be performed using one of the following: fine or coarse bubble diffusers, jet aeration devices or floating aerator/mixers [5].

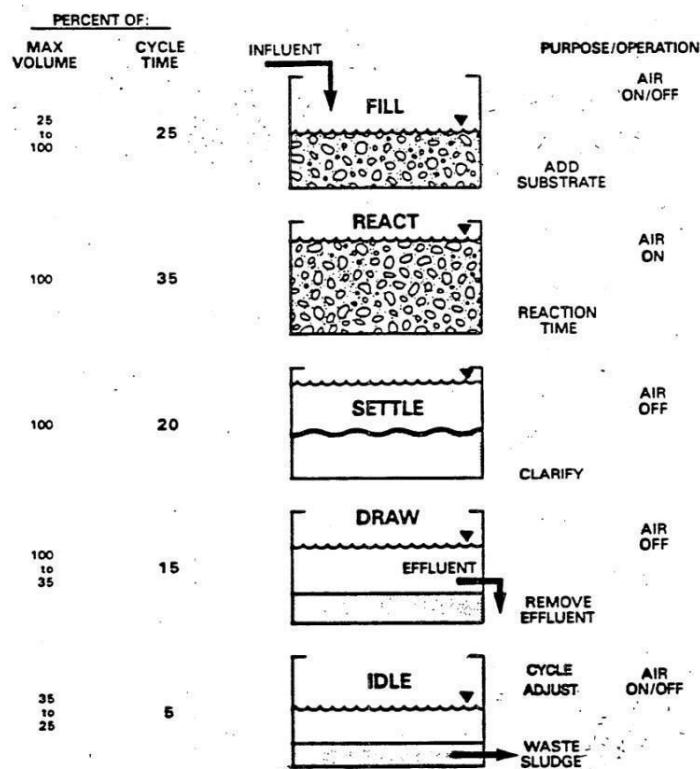


Figure 1: Typical SBR operation for one cycle [5]

2.1.1. Advantages and disadvantages of SBR systems

As the whole process occurs in one tank, this system is simple and cost effective and has a minimal footprint. It has a high degree of process flexibility in terms of sequence and cycle time. Additionally, the system aeration may be adjusted to provide anaerobic/anoxic zones or time periods in order to achieve nutrient removal.

A further advantage of SBR systems is that there is low waste activated sludge (WAS) production, and since sludge is reused in the same tank, there is no need for return activated sludge pumps or primary sludge pumps as in conventional activated sludge (CAS) systems.

The fact that there is no flow in the reactor provides near ideal quiescent settling conditions. Being a batch system, it is also more resistant to fluctuating influent loading and doesn't require additional equalization tanks as in CAS systems [6],[7]. It is also possible to add activated carbon to the system to further enhance the treatment efficiency.

Furthermore, each batch can be tested for effluent standards compliance before discharge.

When it comes to disadvantages, SBR systems require sophisticated equipment (e.g. timing units, controls, automated switches and valves) and high levels of maintenance [4]. Furthermore, there is time loss since the treatment does not occur for the whole operation cycle (fill, settle and draw require a considerable amount of time).

During the draw phase, some sludge may escape from the tank together with the treated wastewater. Equalization and high capacity outfalls are mostly required after the draw phase due to the high sudden flow rate. Additionally, due to the long SRT's, denitrification can take place during the settle phase and the resulting nitrogen gas formation may interfere with the settling of the sludge [5].

2.2. Characteristics of the CSTR

CSTR can be defined as an agitated tank bioreactor with suspended growth and a continuous flow (Figure 2). It operates in a steady state, and most full-scale systems are considered to operate as ideal CSTR systems. That means that within the main reactor tank, the content is perfectly mixed and hence uniform in concentration of substrate and biomass at all points. Accordingly, the effluent is identical in composition as the contents of the bioreactor. The effluent enters a clarifier/settling tank where the treated wastewater is separated from the biomass, a part of which is recirculated into the bioreactor and the rest

wasted as excess sludge. Once it has attained steady-state conditions, treatment efficiency does not depend directly on the influent substrate concentration.

CSTR reactors can be set up to work in series, thereby approaching the PFR system in effect. PFR, or plug flow reactor, is a system whereby complete mixing is achieved only radially as the influent passes through the elongated reactor tank, without longitudinal mixing. This system enhances the treatment efficiency as compared to the CSTR, which is why CSTR in series was devised as a kind of hybrid system.

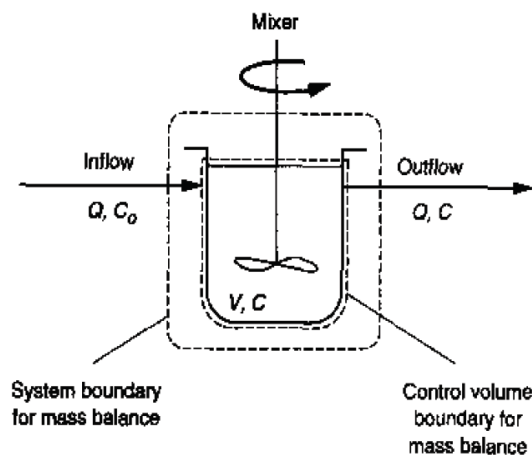


Figure 2: CSTR reactor scheme [8]

2.2.1. Advantages and disadvantages of CSTR systems

CSTR has the advantages that it operates in a continuous, steady state, and is relatively well controllable.

Due to its perfectly-mixed nature, the CSTR system immediately dilutes the incoming contaminants. This may be a negative factor for the biodegradation rates (depending on the specific system), but it could also be favorable when those contaminants are toxic or have a very high or very low pH and could therefore cause harm to the biomass in its influent concentration [9].

As for disadvantages, continuous pumping in the CSTR means that abrasion causes wear down of the equipment, so operation and maintenance costs may go up. Furthermore, its design requires a large area for setup due to the need for pre-treatment facilities as well as settling tanks/clarifiers and waste sludge recycling and disposal facilities.

2.3. Comparison of SBR and CSTR

The unit processes of the SBR and CSTR systems do not differ. The main difference is that SBR performs all steps of the biological treatment in the same tank, one batch at a time, while the CSTR has a continuous operation mode with several different tanks employed. This is considered an advantage of the SBR system over the CSTR, since having all processes occur in one tank means that there is a smaller footprint (i.e. space saving). SBR can also be set up to treat a continuous inflow of wastewater by using additional storage or SBR tanks, as mentioned before.

A second advantage of the SBR system is the ability to tightly control the treatment process, as flow does not have to be taken into consideration during the react phase.

Another important difference between the two system is that CSTR systems can and should reach a steady state (a state where the biomass and substrate concentrations are stable), whereas in SBR systems this cannot happen.

Both systems may work with granular sludge, which is a special form of sludge that forms gradually by interaction of different microbial species with varying roles in treatment. Compared to conventional activated flocs, granular sludge has a regular and dense physical structure which enables for fast and efficient settling [10]. Granules enable multiple reactions to occur within a small volume thanks to an oxygen and wastewater gradient that is established through the EPS matrix of the granule. Specific conditions promote the formation of such granules, such as operating mode of SBR as well as organic loading rate, substrate composition, feeding strategy, DO, settling time etc. [11].

The efficiency of treatment in both types of reactors can be enhanced by applying suitable pretreatment, including physical methods as well as chemical (such as coagulation and flocculation, chlorination etc.)

The authors in [12] compared a CSTR and an ASBR (anaerobic SBR) reactor performance for fermentative hydrogen gas production. Namely, under varying substrate concentrations, they have shown that although the ASBR had a greater biomass concentration and carbohydrate degradation efficiency, the CSTR reactor produced hydrogen more effectively at all substrate concentrations tested.

Reference [13] analyzed the effect of a specific feeding strategy on the long-term selective inhibition of nitrate-oxidizing bacteria (NOB) in CSTR and SBR reactors. They found that by fluctuating concentrations of free ammonia and nitrous acid in the reactors under conditions of unlimited sludge age, NOB activity could be permanently restricted in the SBR reactor. On the other hand, the bacteria in the CSTR reactor showed potential for adaptation and were able to restore activity even under such inhibitory conditions. This testifies to the ability of CSTRs to resist inhibitors when it comes to reactions involved in the nitrogen removal process.

The study presented in [14] used a set of mathematical simulations to demonstrate that enrichment of microbial cultures for the synthesis of polyhydroxyalkanoates (PHAs) under a designated feast-famine ratio can be performed both in an SBR and a two-stage CSTR system, but that the selective pressure for PHA-producing organisms is significantly higher in the former.

Authors in [15] tested the potential for treatment and toxicity reduction in a CSTR and a SBR system treating synthetic wastewater simulating coke oven plant effluents (containing significant levels of phenol and cyanides). The study showed that the SBR system can achieve both better pollutant removal as well as toxicity reduction as compared with the CSTR system.

Reference [16] evaluated the performances of an SBR reactor under conditions of biological nitrogen fixation versus CSTR reactors functioning under either nitrogen fixing or nitrogen supplemented conditions for the treatment of nitrogen deficient thermomechanical pulping wastewater. The results displayed that the SBR system had slightly lower removal levels of organic material, but had much better removal of suspended solids as well as improved sludge settleability and dewaterability.

The research in [17] compared the efficiency of a CSTR versus a soil slurry SBR (SS-SBR) reactor for the treatment of a soil contaminated with polycyclic aromatic hydrocarbons (PAHs). The experiment showed that in the SS-SBR reactor, significant production of biosurfactants took place compared to no production at all in the CSTR. This resulted in an important amount of emulsification of PAH in the SS-SBR system and hence improved PAH removal – 93% as compared to 66% in the CSTR system. Similarly, the study in [9] tested the same type of reactors for the treatment of diesel fuel-contaminated soil. The SS-SBR system showed a 96% removal of diesel fuel compared to 75% in the CSTR system. Furthermore, the authors proved that conversion of the SS-SBR into a CSTR system lead to loss of biosurfactant production and hence decreased diesel fuel degradation. In the same manner, conversion of the CSTR into an SS-SBR system produced the opposite effect.

Authors in [18] compared the performance of 14 full-scale sewage treatment plants divided into four aerobic technologies: aerated lagoon (AL), CAS, extended aeration (EA) and SBR. They reported that in terms of effluent quality, all systems had organic matter and TKN removal efficiency up to 90%, and TSS and TP up to 90% and 50%, respectively, with no significant difference among the technologies evaluated. However, when it comes to waste sludge production and energy consumption, the SBR systems had around 40% lower values compared to the other systems, which renders it the preferable configuration overall.

3. CONCLUSION

Although the unit processes are the same both in SBR and CSTR systems, there are some significant differences in their setup and mode of operation. SBR is a batch system where all steps occur in a single tank, whereas CSTR operates in a continuous treatment mode under steady-state conditions, and requires more than one tank for all processes to take place. Both systems are very effective in COD and nitrogen removal, although the latter is more easily set up in the CSTR due to the possibility for using multiple tanks.

While it is difficult to derive general conclusions, the findings from the available literature can be used as a guide in the process of choosing the right treatment methodology and plant design for a specific application. From the available research, it can be devised that SBR systems may be preferred for cost and area saving (when low footprint is desired), as well as for treatment of hydrocarbon-polluted soils. On the other hand, CSTR may be preferred for high flow rates, and when higher toxicity is present in the influent due to the dilution potential of the system.

Ultimately, since each project is unique, the decision which system to apply has to be taken after careful evaluation of all factors involved in the specific process, including the wastewater characteristics, effluent regulations, desired footprint, available budget etc.

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Effect of Resin Content in the Core Layer on the Properties of Three Layered Medium Density Fiberboard (MDF)

Nadir AYRILMIS^{1*}, Turgay AKBULUT¹

Abstract

MDF panels are commonly used in the furniture industry. The main objective of this project was to increase production capacity without decreasing its performance. The surface layers of the MDF consisted of fine fibers while the core layers consisted of the coarse fibers. It is aimed to decrease the amount of wood and resin used in production of MDF by using coarse fibers in the core layer. The amount of the resin in the core layer was gradually decreased from 10.5 to 6.5% by weight. As for tree species, the softwood fibers (pine wood fibers) were used in the face layers while the hardwood fibers (beech wood fibers) were used in the core layer. The physical and mechanical properties of the MDF panels were determined according to EN standards. The results showed that the physical and mechanical properties of the MDF panels were negatively affected by the decreased resin content. There was no significant difference in the properties of MDF panels as the resin content decreased from 10.5 to 9.5 wt%.

Keywords: Fiberboard, Resin, Technological Properties Three Layered Fiberboard, Urea-Formaldehyde

1. INTRODUCTION

Medium density fiberboard (MDF) is a wood-based panel which is made from fine wood fibers with resin under heat and pressure. It is one of the most commonly used wood-based panels in the furniture industry due to its favorable properties such as good mechanical properties and surface quality, and good machinability. In conventional particleboard manufacture, surface layers consist of fine particles; the core layer consists of coarse particles. However, in conventional MDF production there is only one mat forming process, such that the surface and core layers consist of the same mixture of wood fibers [1]. In the furniture industry, the surfaces of MDF should be smooth and stable for direct painting or laminating [2,3]. By contrast, the core layer can be formed with coarse fibers when the MDF panel is faced with decorative laminate or melamine paper. The fiber size in the core layer does not directly affect the surface quality of the MDF when the panel is overlaid with melamine paper or other decorative laminates. However, the core layer should be made from the fine fibers when the MDF panel is profiled by panel processing machines such as profile wrapping machines.

The objective of this study was to transfer benefits of three-layered particleboards to dry-process MDF manufacture by using coarse fibers and, thus, less energy and less cost-intensive fibers as core layer material. In this study, the face layers of the MDF panels were prepared from commercial size wood fibers, while the core layer was prepared from the coarse fibers. This was because three-layer MDF panels having fine fibers in the surface layers have better surface appearance than three-layered particleboard. The fiber production capacity of the defibrator can be increased as the gap distance between the defibrator discs is increased, which also improves energy savings in the defibrator.

In the particleboard production, the amount of resin is lower than that of surface layers. This is because the fine particles are used in the face layers of the particleboard while the coarse particles are used in the core layer. As the total surface area of the particles increase, the amount of the resin increases. For this reason in this study, the amount of the resin was gradually decreased in the core layer since the coarse fibers was used in the core layer.

In this study, three-layered MDF panel design was developed, which was a similar structure to three-layered particleboard. The technological properties of three-layered MDF panels containing coarse fibers in the core layer were investigated. The resin content was decreased from 10.5 to 6.5% (by weight) while the resin content was kept constant in the surface layers (10.5 wt%) in the MDF production. The surface/core layer ratio of the MDF panels was 50/50 wt%. The physical and mechanical properties of the MDF panels were determined according to European standards and the results of each MDF group were compared with each other.

2. MATERIALS AND METHODS

Wood Fibers

The wood fibers were produced using a thermo-mechanical refining process without any resin application at Kastamonu Integrated Wood Company, Gebze, Turkey. Two different fiber types (*Pinus sylvestris* and *Fagus orientalis* Lipsky), were produced using *Pallmann* defibrator. Steaming parameters of the defibration process applied to the all fibers were kept constant at 170 °C, 8 bar, and 4 min. The pine wood fibers to be used in surface layers were obtained at 0.4 mm defibrator gap distance while the coarse beech wood fibers were obtained at 0.8 mm defibrator gap distance. Prior to MDF production, the wet fibers in the plastic bags were transported to the faculty of forestry, Istanbul University. The fibers were then dried in a laboratory dryer until 2-3% based on the oven-dry weight of wood fiber. *A hundred fibers were randomly obtained from the coarse fibers and then their length and thickness were measured. The average length and thickness of the coarse beech wood fibers used in the core laye were 11.5 mm and 0.73 mm while they were 4.9 mm and 0.5 mm for pine wood fibers in the face layers, respectively.*



Figure 1. A: Fine wood fibers (pine) in face layers of MDF. B: Coarse wood fibers (beech) in core layer.

Resin

A commercial liquid E1 grade urea-formaldehyde (UF) resin with 55% solid content was supplied by Kastamonu Integrated Wood Company, Gebze, Turkey. Ammonium chloride (NH₄Cl) solution with 20% solid content was used as hardener for the UF resin.

Preparation of MDF Panels

Three-layered mats for the MDF panels consisted of a central layer (core) and two outer layers were manufactured under laboratory conditions. Both surfaces are made of fine fibers (pine wood), while the core were produced from the coarse fibers (beech wood). The core layer/surface layer ratio was kept constant for all MDF formulations, which was 50/50 wt%. 1% hardener based on the resin solid content was added into the resin. According to target density of the three-layered MDF panel, the surface and core layer particles were separately placed in a drum blender. For the surface layers, 10.5 wt% UF resin based on the oven dry weight of wood fibers was applied with an air-atomized metered spray system for 5 min to obtain a homogenized mixture. As for the core layer, the resin content was gradually decreased from 10.5 to 6.5 wt%. The amount of the surface and core particles of the MDF panels were separately weighed and distributed evenly by hand into a 400 mm 400 mm forming box. A second such plate was laid on the top while both were covered with siliconized paper to prevent adherence between panel and plates. After cold pre-pressing, the mats were transferred to the hot press, operated in plate position control mode. Hot pressing temperature, maximal specific pressure and total press time were 190 °C, 3.5 N/mm², and 8 min, respectively. Target panel thickness and density were 10 mm and 700 kg/m³, respectively. Three replicate panels were prepared from each fiber type. Prior to sample cutting, the panels were allowed to cool and edges were trimmed. Test specimens were conditioned in a climatic chamber at 20 °C and 65% relative humidity for 2 weeks before testing. The experimental design of the MDF panels are given in Table 1.

Table 1. Experimental design

MDF type	Face layer ratio (%)	Core layer ratio (%)	Resin content in the face layer (weight %)	Resin content in the core layer (weight %)
A	50	50	10.5	10.5
B	50	50	10.5	9.5
C	50	50	10.5	8.5
D	50	50	10.5	7.5
E	50	50	10.5	6.5

Determination of Physical and Mechanical Properties

Physical and mechanical properties of the three-layered MDF panels were determined according to European Norms (EN). One day thickness swelling test were performed on the 15 specimens with dimensions of 50 mm x 50 mm x 10 mm according to the EN 317 [4]. Bending strength and modulus of elasticity of the 12 MDF specimens with dimensions of 250 mm x 50 mm x 10 mm (6 // and 6 \perp to the MDF surface) were tested according to the EN 310 standard [5]. Internal bond test (EN 319 [6]) and surface soundness (EN 311 [7]) was performed on the ten specimens with dimensions of 50 mm x 50 mm x 10 mm according to the. The density of the specimens with dimensions of 50 mm x 50 mm x 10 mm according to the EN 323 [8]. The linear and thickness variations of the MDF panels were determined in conformance with EN 318 standard [9]. According to EN 318, linear and thickness variations of fiberboards, between two equilibrium moisture contents, are calculated as a percentage of the initial specimen length and thickness.



Figure 2. Production of three-layer MDF panels at the laboratory

Statistical Analysis

The effect of surface/core layer ratio on the physical and mechanical properties of the MDF panels was evaluated using analysis of variance (ANOVA; $p < 0.05$). Significant differences among the mean values of MDF types were determined using Duncan's multiple range test.

3.RESULTS AND DISCUSSION

The physical properties of the MDF panels are presented in Table 2. The average density of the MDF panels was found to be 697-700 kg/m³. The thickness swelling and dimensional changes of the MDF specimens were significantly affected by the resin content in the core layer. As the resin content decreased from 10.5 to 6.5 wt% in the core layer, all the thickness swelling and dimensional changes in the changing relative humidity increased. The significant differences in the group averages are presented in Table 2. As the resin content decreased from 10.5 to 9.5 wt%, there was no significant decreases (34.2 to 36.7%)

in the thickness swelling values as well dimensional changes (Table 2). Another result was that there was no significant difference as the amount of the resin was decreased by 1 wt% in the core layer. The dimensional stability of the MDF specimens in changing relative humidity conditions were affected by the resin content in the core layer. As the resin content decreased from 10.5 to 6.5 wt%, the linear contraction (LC) of the MDF specimens increased from 0.15 to 0.33%. As for the thickness shrinkage (TSh), it increased from 2.36 to 4.36% as the amount of resin decreased from 10.5 to 6.5 wt% (Table 2). A similar trend was observed for the linear expansion (LE) and thickness swelling (TS) of the MDF specimens as the relative humidity increased from 65 to 85%. The highest dimensional stability was found in the specimens having the highest resin content (10.5 wt%) while the lowest dimensional stability was found in the specimens having 6.5 wt% resin content.

Higher porosity, more free space between particles, enables faster penetration of water between particles. As the amount of the resin was decreased in the core layer, the resin does not entirely cover the particles, hence water can easily penetrate into the particles. Easy penetration of water into micro voids and micro fractures results in greater thickness swelling and a higher swelling stress. Due to the presence of water, particles tend to regain the position prior to pressing. The interaction between water (moisture) and particleboard wood leads to the development of swelling stresses that cause the “separation” of the particles within the panel and hence the failure of the resin bond between particles [10].

Table 2. Some physical properties of the three-layered MDF panels.

MDF code	Density (g/cm ³)	Thickness swelling (24 h) (%)	Dimensional changes in changing relative humidity at 20 °C			
			Relative humidity (65 to 30% at 20°C)		Relative humidity: (65 to 85% at 20 °C)	
			LC _{65 to 30} (%)	TSh _{65 to 30} (%)	LE _{65 to 85} (%)	TS _{65 to 85} (%)
A	696 (21)	34.2 (1.8) a	0.15 (0.01) a	2.36 (0.2) a	0.14 (0.02) a	2.25 (0.2) a
B	698 (17)	36.7 (2.4) ab	0.18 (0.03) a	2.85 (0.2) ab	0.17 (0.03) ab	2.54 (0.3) ab
C	695 (13)	40.8 (3.0) bc	0.22 (0.02) b	3.15 (0.4) b	0.19 (0.02) b	3.01 (0.4) b
D	697 (20)	43.4 (2.7) cd	0.27 (0.03) c	3.94 (0.3) c	0.25 (0.03) c	3.78 (0.2) c
E	700 (24)	49.2 (3.2) d	0.33 (0.04) d	4.36 (0.5) c	0.30 (0.04) d	4.20 (0.3) d

LC: linear contraction. TSh: thickness shrinkage. LE: linear expansion. TS: thickness swelling. Groups with same letters in column indicate that there is no statistical difference ($p < 0.05$) between the specimens according to Duncan's multiply range test.

The mechanical properties of the MDF specimens are given in Table 3. All the mechanical properties decreased with resin content in the core layer. However, as the amount of the resin content was decreased from 10.5 to 8.5 wt%, the bending strength and modulus of elasticity in bending, and surface soundness did not decrease significantly. This could be related to the fact that surface layers of the MDF affects bending properties. Since the resin content in the face layers as kept constant (10.5 wt%), the bending strength and modulus of elasticity did not significantly decreased until 8.5 wt% resin content in the core layer. As for the internal bond strength, it did not decrease significantly as the amount of the resin decreased from 10.5 to 9.5 wt%. Decreasing resin content most affected internal bond strength. As known, the resin significantly affects of the mechanical properties of wood-based panels [11,12]. Surface layers directly affect the bending properties of the materials.

Table 3. Some mechanical properties of the three-layered MDF panels

MDF code	Bending strength (MPa)	Modulus of elasticity (MPa)	Internal bond strength (MPa)	Surface soundness (MPa)
A	17.25 (1.09) a	2149.4 (134.7) a	0.56 (0.06) a	1.28 (0.08) a
B	17.01 (0.92) a	2085.6 (126.5) ab	0.54 (0.06) ab	1.20 (0.11) ab
C	16.62 (1.02) ab	2012.0 (102.8) ab	0.50 (0.04) bc	1.12 (0.15) abc
D	15.82 (0.71) b	1882.8 (116.1) b	0.47 (0.03) c	1.04 (0.96) bc
E	14.31 (0.74) b	1740.5 (98.5) c	0.41 (0.04) d	0.93 (0.14) c

Groups with same letters in column indicate that there is no statistical difference ($p < 0.05$) between the specimens according to Duncan's multiply range test.

4. CONCLUSIONS

The results showed that the physical and mechanical properties of the MDF panels were negatively affected by the decreased resin content. Decreasing resin content most affected internal bond strength as compared to the bending properties. There was no significant difference in the properties of MDF panels as the resin content decreased from 10.5 to 9.5 wt%. The resin content in the core layer of MDF panels can be decreased without significantly decreasing the physical and mechanical properties of the MDF.

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BIOGRAPHY

Major focus of Nadir Ayırlımıs has been on physical, mechanical, and thermal properties of wood-based panels and natural fiber reinforced thermoplastic composites. He have focused on the utilization of waste materials to produce high value added materials. Use of nanocellulose in wood resins are of interest. He have published more than 120 SCI papers for 10 years. I have performed International Research Joint Projects with different Universities located in USA, Germany, S. Korea, Slovenia.

Fuel Characteristics of Rice Plant

Pravin Kumar SAHU¹, Khageshwar Singh PATEL²

Abstract

India is one of the world's largest producers of rice ≈ 100 M. There are ≈ 20000 varieties of rice in India of which ≈ 4000 are cultivated. Rice straw is the vegetative part of the plant, which is burned and left on the field before the next ploughing or used as a feed for livestock. Rice straw is a major forage in rice-producing areas. The burning of rice residues causes severe air pollution in some regions. The outermost layer of the paddy grain is the rice husk, also called rice hull. At least 80, 20 and 30 M rice grain, husk and straw are produced in the country. In this work, their fuel properties in the terms of gross calorific value(GCV) are described. The GCV of rice grain, husk and straw derived from 20 different plants was ranged from 4900 – 7150, 4520 – 6800 and 4810 – 6910 kcal kg⁻¹ with mean value ($p = 0.05$) of 5748 \pm 253, 5299 \pm 245 and 5646 \pm 195 kcal kg⁻¹, respectively. The weight loss of 5.0 – 9.0% due to volatile matter (including moisture) in the straw and husk material over temperature range of 50 – 150 °C was observed. The weight loss of materials 49 – 52 % in the straw and husk material due to decomposition of hemicelluloses, cellulose and lignin over temperature range of 150 – 500 °C was marked.

Keywords: Rice; Husk; Straw; Calorific Value; Proximate Parameters

1. INTRODUCTION

Rice (*Oryza sativa*), a member of grass family (Poaceae) is a tropical plant associated with the wet and humid climate. Globally, two major varieties of rice are grown viz. *Oryza sativa indica* and *Oryza sativa japonica*. The dehulled rice grain is covered by an outermost layer called pericarp and such rice with pericarp is called brown rice. It is a staple crop, rich in carbohydrate with poor in protein content. Brown rice is rich in some vitamins mainly Thiamine and B1. Rice straw is used as cattle feed, thatching roof and in cottage industry for preparation of hats, mats, ropes, sound absorbing, etc. Rice husk is used as animal feed, for paper making and as fuel source. India is one of the world's largest producers of rice 100 M. There are 20000 varieties of rice in India of which 4000 are cultivated. The type of rice grown in different parts of India depends on the weather, soil, structure, characteristics and purposes. The period of maturity for rice varies between 130 to 160 days, depending on the kind of rice and the area in which it is grown. Rice straw is the vegetative part of the rice plant, which is burned and left on the field before the next ploughing, ploughed down as a soil improver or used as a feed for livestock [1]. Rice straw is a major forage in rice-producing areas. The burning of rice residues causes severe air pollution in some regions. The alternative, residue incorporation into the soil, in turn causes methane emissions from rice fields, contributing to climate change. The outermost layer of the paddy grain, rice husk and straw were sparingly used as a source of renewable energy [2] – [7]. Several varieties of rice are grown in central India, differing in life time, yield of grain, straw and husk. In this work, the calorific value of rice of 20 different varieties of grown in Chhattisgarh state, India is described. The effect of proximate parameters i.e. bulk density, moisture and ash content and yield of rice grain in the calorific value are discussed.

¹ Corresponding author : School of Studies in Environmental Science, Pt ,Ravishankar Shukla University, Raipur 492010, CG, India. sahu.pravin89@gmail.com

² School of Studies in Chemistry, Pt ,Ravishankar Shukla University, Raipur 492010, CG, India. patelkhageshwarsingh@gmail.com

2. MATERIAL AND METHODS

2.1 Study area and sampling

Twenty different rice grains and respective straws and roots were collected from different 20 rice fields in December 2015 from Raipur area (21° 15' 0" N, 81° 37' 48" E). The samples were air dried for 5 days. Thereafter, they were dried for 2 days in oven at 50 °C for 2 days. The husk from rice grain was separated manually. They were crushed into particles of < 0.25 mm for the pellet formation.

2.2 Analysis

The bulk density (BD) was determined by dividing the mass with the volume of the capsule [8]. The moisture content of the samples were analyzed by heating it at 105±2 °C till constant weight was observed [9]. The ash content of the materials was determined by heating the sample at 600 °C for 4 hr [10]. The gross calorific value (GCV) of the sample was determined experimentally using a Digital Microprocessor Based Bomb Calorimeter UTS 1.34, Advance Research Instruments Co., New Delhi as described in the literature [11]. The GCV was calculated by using the following equation:

$$GCV = \{We. \Delta T\} - \{W1(4.18)+W2(0.335)\}/M$$

Where, GCV, M, We, W1, W2 and ΔT represent gross calorific value of species (kcal kg⁻¹), weight of sample, water equivalent, weight of cotton thread, weight of fuse wire and rise in temperature, respectively. A Mettler Thermogravimetric Analyzer-TGA-2 was used to scan the chromatogram at heating rate of 20 °C min⁻¹. The IBM SPSS Statistics 23 was used for the statistical and cluster analysis in the present work [12].

3. RESULTS AND DISCUSSION

3.1 Physical parameters of rice

The physical characteristics of 20 rice is summarized in Table 1. The husk and straw are yellowish in color unlikely to rice grain which is white colored. The value of cultivation period, height of rice plant, yield of rice grain and straw was ranged from 110 – 160 day, 90 – 130 cm, 40 – 57 Q ha⁻¹ and 14 – 19 Q ha⁻¹ with mean value (p = 0.05) of 128±6 day, 109±5 cm, 49±2 Q ha⁻¹ and 16±1 Q ha⁻¹, respectively. The husk fraction in rice grain (n=20) was ranged from 24 – 32% with mean value of 27±1%. The mass of single grain of 20 rice was varied from 15 – 38 mg with mean value (p = 0.05) of 27±3 mg, respectively. Among them, the highest grain size mass was obtained with the Basmati rice. The correlation matrix of physical parameters for rice is presented in Table 2. The yield of rice grain had a partial negative correlation with plant height and cultivation period unlikely to straw yield. The yield of grain, husk and straw showed a partial positive correlation among themselves. The weight of single rice particle had a fare correlation with the cultivation period.

Table 1. Physical characteristics of rice

S. No.	Type	Cultivation Period, day	Height of rice plant, cm	Grain yield Q ha ⁻¹	Husk yield Q ha ⁻¹	Straw yield Q ha ⁻¹	Single grain weight, mg
1	Shankh	135	110	50	13	17	29
2	Sai ram	120	110	55	13	18	15
3	1001	140	105	55	14	18	30
4	1010	110	100	55	15	17	28
5	1008	130	100	50	12	15	27
6	52-4	140	115	50	13	18	32
7	Basmati	160	130	40	12	16	38
8	Sonali	110	120	45	13	16	17
9	HMT	135	120	40	11	14	31
10	Dabang	110	110	45	11	15	22
11	Kanak sarna	135	120	45	12	14	33
12	Sarna	140	110	50	13	17	30
13	Mahamaya	130	110	57	15	19	30
14	Saubhagya	120	120	45	11	16	18
15	Sarathi	120	105	50	14	16	17
16	Swarn masi	125	110	45	11	15	30
17	MT-13	125	100	50	13	15	30
18	Maheshwari	130	90	50	14	15	28
19	Pusa	130	95	50	15	15	28
20	IR-64	110	90	45	11	14	23

Table 2. Correlation matrix of physical parameters

	H	CP	GY	HY	SY	GM
H	1					
CP	0.4	1				
GY	-0.11	-0.64	1			
HY	0.05	-0.37	0.69	1		
SY	0.18	0.15	0.32	0.56	1	
GM	0.76	0.15	-0.15	0.05	-0.05	1

H = Height, CP = Cultivation period, GY = Grain yield, HG = Husk yield, SY = Straw yield

3.2 Bulk density

The bulk density (BD) is an important parameter of rice plant for subsequent processing and energy production as shown in Table 3. The BD value for rice grain, husk and straw (n = 20) was ranged from 1100 – 1500, 525 – 834 and 450 – 710 kg m⁻³ with mean value (p = 0.05) of 1253±44, 648±35 and 571±34 kg m⁻³, respectively. The BD value was found to increase in following order: straw < husk < rice grain as shown in Figure 1. Among them, the BD of husk and straw had a fare correlation (r = 0.70).

Table 3. Bulk density of rice materials, kg m-3

S. No.	Rice	Grain	Husk	Straw
1	Shankh	1100	600	500
2	Sai ram	1300	650	600
3	1001	1367	734	700
4	1010	1250	625	530
5	1008	1267	584	560
6	52-4	1390	550	500
7	Basmati	1200	660	450
8	Sonali	1167	625	460
9	HMT	1150	525	520
10	Dabang	1267	734	640
11	Kanak sarna	1500	625	530
12	Sarna	1250	684	530
13	Mahamaya	1167	550	510
14	Saubhagya	1180	534	560
15	Sarathi	1267	675	650
16	Swarn masi	1250	750	640
17	MT-13	1400	700	680
18	Maheshwari	1167	834	710
19	Pusa	1250	700	560
20	IR-64	1170	625	580

3.3 Moisture content

The moisture content (MC) of rice materials are summarized in the Table 4. The moisture presents in rice as bulk and physically or chemically bound water. Low moisture results in improved density and durability of the fuel [13]. The most techniques need a small amount of moisture to "soften" the biomass for compaction. The physically and chemically bound water of rice grain, husk and straw (n=20) was ranged from 5.1 – 7.9, 3.8 – 7.1 and 2.4 – 4.7% with mean value ($p = 0.05$) of 6.0 ± 0.3 , 5.7 ± 0.3 and $4.7 \pm 0.2\%$ with mean value ($p = 0.05$) of $3.3 \pm 0.3\%$. The higher hydroscopic index of rice grain or husk than respective the straw was marked, Figure 1. A partial correlation ($r = 0.39$) of the husk MS with the straw was observed.

Table 4. Moisture content of rice materials, %

S. No.	Rice	Grain	Husk	Straw
1	Shankh	6.2	6.4	3.2
2	Sai ram	5.6	6.0	3.3
3	1001	5.1	6.4	2.8
4	1010	6.9	6.2	2.5
5	1008	6.1	5.1	3.3
6	52-4	5.4	5.7	3.8
7	Basmati	5.8	7.1	4.7
8	Sonali	5.8	5.9	3.3
9	HMT	5.6	5.8	3.4
10	Dabang	5.8	4.6	2.7
11	Kanak sarna	5.6	5.4	3.6
12	Sarna	5.8	5.2	3.2
13	Mahamaya	7.9	6.2	3.6
14	Saubhagya	6.6	5.6	3.5
15	Sarathi	5.2	5.2	2.6
16	Swarn masi	6.8	6.2	2.4
17	MT-13	5.8	6.4	3
18	Maheshwari	6.7	3.8	2.9
19	Pusa	5.6	4.6	2.7
20	IR-64	5.8	5.4	2.7

3.4 Gross calorific value

The most important fuel property is calorific value, and is used to calculate the competitiveness of a processed fuel in the market situation [14]. The energetic content of the rice material is measured in the term of gross calorific value (GCV), representing the absolute value of the specific energy of combustion in calorie, for unit mass of a rice sample burned in presence of oxygen in a calorimetric bomb under the specific condition as shown in Table 5. The GCV of rice grain, husk, straw and root was ranged from 4630 – 6210, 4520 – 6800 and 4810 – 6910 kcal kg⁻¹ with mean value ($p = 0.05$) of 5387 ± 220 , 5299 ± 245 , 5646 ± 195 and 4835 ± 195 kcal kg⁻¹, respectively. A slightly higher GCV for straw sample was recorded, may be due to presence of higher energetic carbons as shown in Figure 1. The GCV of the husk and straw of the present studies was found to comparable to the GCV of the rice materials reported in the other regions [2] – [7].

Table 5. Calorific value of rice materials, kcal kg⁻¹

S. No.	Rice	Grain	Husk	Straw
1	Shankh	5260	5090	5820
2	Sai ram	6010	5580	5860
3	1001	6160	5190	5980
4	1010	4910	5130	6140
5	1008	5660	5410	5530
6	52-4	6180	4780	5450
7	Basmati	5380	4520	4810
8	Sonali	5350	5150	5260
9	HMT	5180	4980	5180
10	Dabang	5410	5720	5600
11	Kanak sarna	6210	5420	5260

12	Sarna	5180	5660	5270
13	Mahamaya	4630	4790	5480
14	Saubhagya	4900	4630	5340
15	Sarathi	5320	4950	5720
16	Swarn masi	4800	4870	5660
17	MT-13	6110	5880	6020
18	Maheshwari	4930	6800	6910
19	Pusa	5150	6220	5900
20	IR-64	5000	5210	5720

3.5 Ash residue

Inorganic constituents i.e. bound cations, inorganic salts and minerals make up the ash present in or on the surface of rice [15]. The ash residue (AR) of rice grain, husk and straw samples ($n = 20$) is presented in Table 6. Value of grain, husk and straw were ranged from 1.2 – 2.1, 14 – 21 and 10 – 19% with mean value ($p = 0.05$) of 1.5 ± 0.1 , 18 ± 1 and $14 \pm 1\%$, respectively. The highest AR value for husk was marked, may be due to higher silica content as shown in Figure 1.

Table 6. Ash residue of rice materials, %

S. No.	Rice	Grain	Husk	Straw
1	Shankh	1.5	19	14
2	Sai ram	1.4	19	14
3	1001	1.3	18	13
4	1010	1.8	16	11
5	1008	1.5	20	17
6	52-4	1.3	18	14
7	Basmati	1.6	21	19
8	Sonali	1.5	18	15
9	HMT	1.4	19	16
10	Dabang	1.2	16	12
11	Kanak sarna	1.3	19	15
12	Sarna	1.4	19	16
13	Mahamaya	2.1	16	12
14	Saubhagya	1.9	16	12
15	Sarathi	1.3	15	11
16	Swarn masi	2	17	12
17	MT-13	1.3	18	13
18	Maheshwari	1.8	14	10
19	Pusa	1.6	15	11
20	IR-64	1.7	16	12

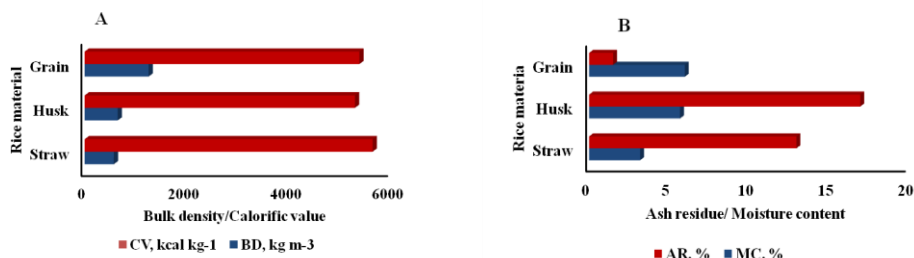


Fig. 1. Proximate and calorific value of rice material

3.5 Correlation matrix

The correlation matrix of GCV with proximate parameters is presented in Figure 2. The correlation analysis of the GCV with proximate parameters is of tremendous importance for proper selection of biomass for specific purpose due to dependence of heat value on moisture content and chemical composition of rice materials. The GCV had fare positive correlation with the BD unlikely to the MC and AR. Similar trend of the GCV with the MC and AR in the case of the husk and straw is observed as shown in Figures 2.

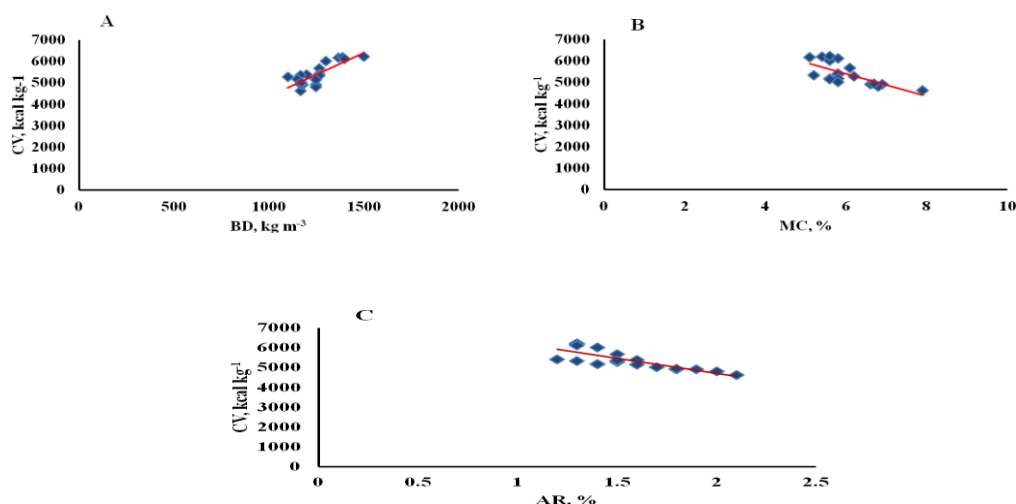


Fig. 2. Correlation of calorific value of rice grain with proximate parameters

3.6 Cluster analysis

The elemental composition (i.e. C, H, N and O) of rice materials is varied with respect to species, geographical and climate condition and harvesting methods. Hierarchical cluster analysis was used to produce a dendrogram, using group-average linkage clustering based on proximate parameters, Figures 3. In rice grain, a single group was appeared due to slight variation in the GCV. However, in the husk and straw, two groups were formed. The rice no. 18 – 19 and 1 – 2 were included into Group-I and -II, respectively. Overall, the highest GCV for the 1008 grain, Pusa husk and Maheshwari straw was recorded.

3.7 Volatile and carbon

The TG-DGA chromatogram for Sarna straw, husk and root is shown in Figures 4. The weight loss of 9, 5 and 8% due to volatile matter (including moisture) in the straw, husk and root material over temperature range of 50 – 150 °C was recorded. The weight loss of 52, 49 and 64% in the straw, husk and root material due to decomposition of hemicelluloses, cellulose and lignin over temperature range of 150 – 500 °C was observed. The residue (i.e. fixed carbon and ash) content in the straw, husk and root material was marked to be 39, 46 and 28%, respectively. The ash residue determined by the oxidation method in the straw, husk and root was found to be 16, 19 and 17%, respectively. The fixed carbon in the straw, husk and root evaluated was 23, 27 and 11%, respectively. The low fixed carbon content making it tend to prolong cooking time by its low heat release [16]. The higher the fixed carbon content the better the charcoal produced because the corresponding calorific energy is usually high [17].

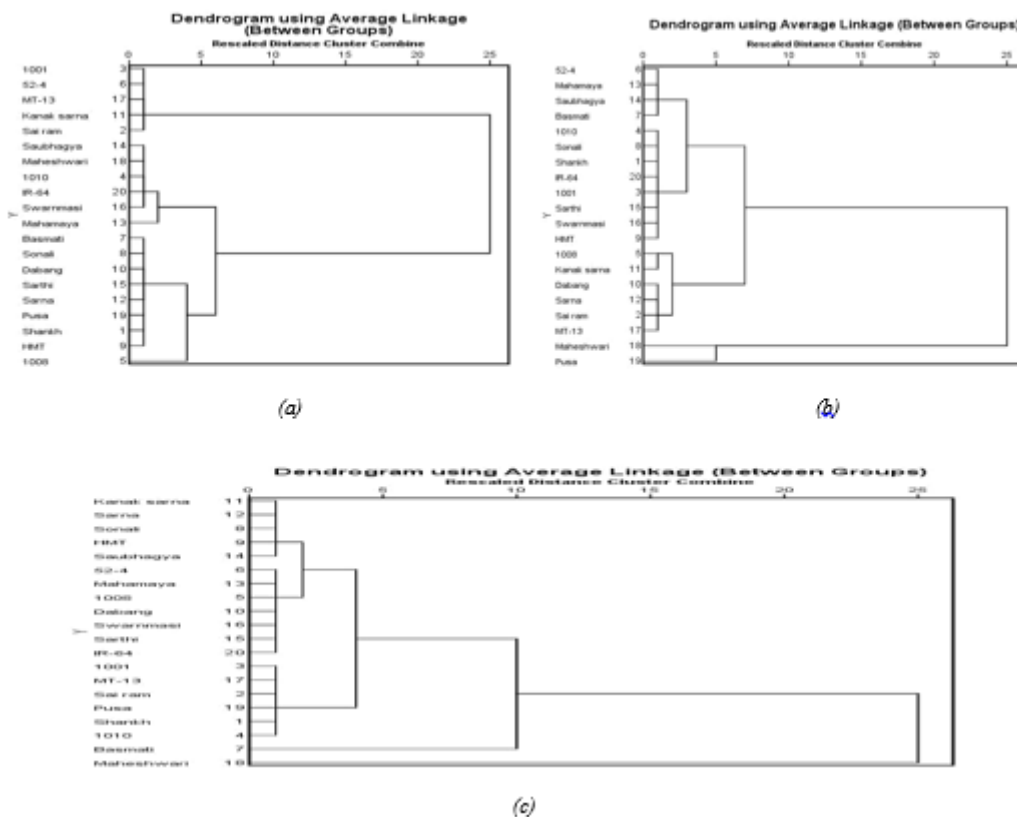


Fig. 3. Dendrogram for (a) rice grain, (b) husk samples and (c) straw samples

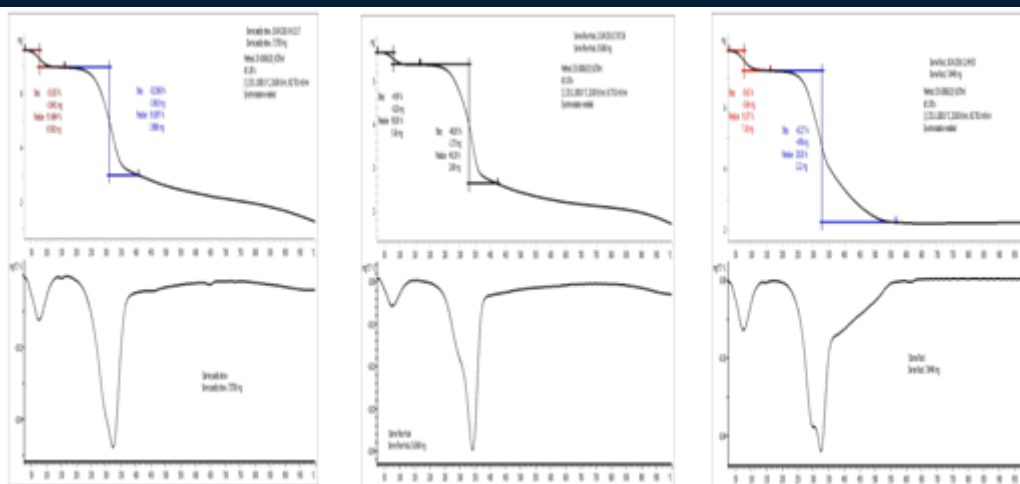


Fig.4. TG-DGA chromatogram for Sarna (a) straw sample, (b) husk sample and (c) root sample

3.8 Energy fluxes

At least 100 M ton rice grain per year is produced in India. The husk and straw waste generated are 27 and 33 M ton every year. The GCV for rice grain, husk and straw is 5390, 5300 and 5650 kcal kg⁻¹, respectively. The energy flux produced by rice grain, husk and straw in the country is expected to be 4.1x10⁸, 1.4 x10⁸ and 1.8 x10⁸ Mcal, respectively. The total energy flux generated by rice plants in the country is 7.4x10⁸ Mcal or 3.1x10⁹ MJ every year.

4. CONCLUSIONS

The GCV of the rice plant was found to decrease from the grain to root, due to increase in AR content. The rice Geno types do not influence significantly the GCV of the plant. The annual energy stock for the grain, husk and straw estimated is 4.1x10¹⁰, 1.4 x10¹⁰ and 1.8 x10¹⁰ Mcal, respectively.

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A Cross-Sectional Study About The Respiratory Health Of Workers Who Environmentally Exposed Cement Dust

Hulya GUL^{1*}, Savas KAMBUR²

Abstract

The cement industry leads to significant occupational and environmental health problems in developing countries. In this study, we aimed to investigate functional capacity changes in the respiratory system according to the working environment conditions of a cement sector employees. This cross-sectional study was conducted among 178 male workers between November 21st, 2016, and March, 30th, 2017, from a cement plant with a total of 334 employees. Data on socio-demographic characteristics, occupational history, chronic diseases, smoking habits, alcohol consumption, and respiratory symptoms were collected using a questionnaire during an interview with employees who worked in the production department. At the same time, respiratory function capacities of workers were evaluated by performing respiratory function tests and examining exposures. The average age of the exposed group was 36.73±6.7 and 73.59% of the employees had been working in the same cement factory for 5 years. Of the subjects, 46.1% were smokers, 42.7% consumed alcohol, and the mean body mass index (BMI) was 26.92±3.93 kg/m². There was no relationship between forced vital capacity (FVC), forced expiratory volume (FEV1), FEV1/FVC values, BMI, alcohol use, smoking, and chronic diseases, but a statistically significant relationship with the duration of working time was revealed ($p < 0.05$). Over time, there was a decrease in the functioning capacities of the workers' respiratory systems in the cement industry. In order to preserve these capacity decreases against future adverse health consequences, it would be proper to control dust particle concentrations, use personal protective equipment, and perform "respiratory function test" (RFT) at regular intervals.

Key words: Cement industry, Environmental and Occupational health, Respiratory system

1. INTRODUCTION

Cement industry workers are of great importance in terms of employment. Turkey is the second in the world and the first in Europe in clinker production, which is the primary material of cement production, and the number of employees in the cement industry has increased over the years. Dust emanating during the conversion of clinker into cement gets inhaled to the respiratory zone of the workers and leads to occupational respiratory system diseases. The increase in the employment of workers in the cement industry has increased the interest of researchers in their working environment conditions [1-7]. Being affected by the ambient cement conditions up to the last stage of packaging causes different health problems in the employees' different body systems. Especially in the cement industry, dust and dust-related diseases occur in the workplace, in the immediate vicinity, and in people living in the environment as a result of the dust created at all the stages of production and emissions after heat treatment for meeting high heat demand. Employees in the cement industry are affected by different factors caused by the increase of concentrations of heavy metals, furans, dioxins, and greenhouse gases, which are caused by the burning of fossil fuels used in the process and during the clinker production of cement required for production.

In evaluating the occupational exposures of cement sector employees, findings from studies that include the respiratory system, heart, liver, and circulatory system assessments in addition to physiologic capacity measurements, will contribute a proactive approach [8-13]. Physiologic capacity assessments as well as environmental and employee demographic data in diagnosing occupational respiratory system diseases, such as it is in the diagnosis of all occupational diseases, are of great importance. The most frequently used test to make these evaluations is the "respiratory function test" (RFT). This tests play an important role in both evaluating the employees' functional capacities and also for monitoring how much they are affected through exposure to the environment. It is important to show changes in forced vital capacity (FVC), forced expiratory volume (FEV1) and FEV1/FVC from the most frequently used parameters in respiratory function capacity measurements in terms of environment and occupational health. As a result of these tests, the decrease in functional capacity of the respiratory system over time indicates that these people are affected by workplace and environmental factors.

^{1*} Corresponding author E-mail: hulyagul@istanbul.edu.tr Istanbul University, Istanbul Faculty of Medicine, Istanbul, Turkey

² Gedik University Social Sciences Institute Occupational Health and Safety, Istanbul, Turkey

In this study, we aimed to investigate the employees' respiratory health problems by examining respiratory system capacities of male employees in the cement sector.

2. MATERIAL AND METHODS

This cross-sectional research was performed on 178 people who worked in the production department from a total of 334 employees in a cement factory between November 25th, 2016, and March 30th, 2017. The research began after the necessary ethical permits were approved. Exposure status of employees was examined by taking the Thorax Association Occupational and Environmental Lung Disease Evaluation Form into account. Respiratory capacities of employees were evaluated using a respiratory function test with a "MIR SpiroLAB3" respiratory function meter calibrated by considering daily temperature, pressure, and humidity values. At least three measurements were made for each worker and their averages were evaluated. The FEV1, FVC, and FEV1/FVC values obtained from the test results were uploaded to the SPSS 21.0 package program. Homogeneity of the data was shown by performing a normality test. The relationship between working time, body mass index (BMI), alcohol use, smoking, history of chronic illness, and the respiratory capacities of employees were examined statistically. The significance relations on variables categorized among themselves were tested by conducting Chi-square tests. The level of statistical significance was taken as $p < 0.05$.

3. RESULTS AND DISCUSSION

Table 1 shows the demographic characteristics taken from the questionnaire given to the employees. Tables 2, 3, and 4 show the level of significance of the relationship between the total working time of employees, BMI, alcohol, chronic illnesses, smoking, and RFT. As shown in the tables, the decline in the respiratory function capacities of the cement sector employees over the years due to working environment factors was statistically significant. The finding that this decrease in capacity was not affected by smoking, alcohol, BMI, and chronic diseases was statistically significant.

Table I. Demographic characteristics of the cement sector employees

Parameter		n	%
Age (years)	≤ 25	1	0,6
	26 -34	88	49,5
	35-45	62	34,8
	≥46	27	15,1
Weight (kg)	≤ 59	3	1,7
	60-79	78	43,9
	80 – 89	57	32,0
	≥90	40	22,5
Length (cm)	≤159	-	-
	160 – 169	47	26,4
	170 – 179	102	57,3
	≥180	29	16,3
BMI (kg/m ²)	≤19,9	4	2,2
	20-24,9	45	25,3
	25-29,9	97	54,5
	≥30	32	18,6
Smoking	No	82	46,1
	Yes	96	53,9

Alcohol use	No	102	57,3
	Yes	76	42,7
	≤8 year	18	5,9
Education	8-12 year	90	29,3
	≥High school	70	22,8
Chronic Disease	No	169	94,9
	Yes	9	5,1

Table II. Relation of FEV1 value with some variables

		FEV1			Significance	
		<3,0	3,00 – 3,72	≤4,5	Chi-square	p
Working Time	<5years	6	6	35	12,547	0,002*
	≥5years	8	53	70		
Alcohol Use	Yes	5	19	52	4,934	0,085
	No	9	40	53		
Smoking	Yes	11	29	56	3,979	0,137
	No	3	30	49		
Chronic Disease	Yes	0	4	5	1,130	0,568
	No	11	55	100		
BMI (kg/m ²)	0-19	2	0	0	16,005	0,100
	20-24,9	4	14	27		
	25-29,9	4	34	59		
	≥30	4	11	17		

Table III. Relation of FVC value with some variables

		FVC			Significance	
		<3,85	3,85 - 4,45	>4,45	Chi-square	p
Working Time	<5years	11	3	33	9,054	0,011
	≥5years	32	34	65		
Alcohol Use	Yes	15	13	48	3,519	0,572
	No	28	24	50		
Smoking	Yes	24	20	52	0,091	0,955

	No	19	17	46		
Chronic Disease	Yes	4	1	4	2,236	0,327
	No	39	36	94		
BMI (kg/m ²)	0-19	2	1	1	4,583	0,917
	20-24,9	10	10	25		
	25-29,9	22	20	55		
	≥30	9	6	17		

Table IV. Relation of FEV1 / FVC value with some variables

		FEV1/FVC (%)					Significance	
		<30	31-50	51-70	71-80	≥81	Chi-square	p
Working Time	<5years	-	-	-	4	43	13,811	0,001
	≥5years	-	-	-	49	82		
Alcohol Use	Yes	-	-	-	18	58	2,353	0,125
	No	-	-	-	35	67		
Smoking	Yes	-	-	29	67	-	0,019	0,891
	No	-	-	24	58	-		
Chronic Disease	Yes	-	-	-	2	7	0,259	0,611
	No	-	-	-	51	118		
BMI (kg/m ²)	0-19	-	-	-	0	4	7,076	0,215
	20-24,9	-	-	-	10	35		
	25-29,9	-	-	-	32	65		
	≥30	-	-	-	11	21		

The present study investigated relationships between respiratory function tests and some personal risk factors among men who worked in the production departments of a cement factory. There was only statistical significance between working time and FEV1, FVC, FEV1/FVC parameters. There was no significant statistical difference between FVC, FEV1, FEV1/FVC values and BMI, alcohol use, smoking, and chronic diseases. The findings of the present study were similar to studies in the related literature.

In a multi-national study, Nordby et al. demonstrated that exposure to dust in cement production plants was associated with airway symptoms as well as reduced dynamic lung volumes [14]. Their results support the hypothesis that exposure to dust in cement production may lead to respiratory symptoms and airway obstruction. Siyoum et al. found that the prevalence of respiratory symptoms was 66.2% in cement factory workers and 31.2% in civil servants with a significant difference [15]. Meo et al. aimed to determine the effect of long-term exposure to cement dust on lung function in non-smoking cement mill workers. A significant reduction was observed in the mean values of FVC, FEV1, peak expiratory flow (PEF), and maximal voluntary ventilation (MVV) in cement mill workers who had worked in the cement industry for more than 10 years compared with their matched un-exposed group [1]. Mwaiselage et al. showed that cement workers seemed to be at high risk of developing chronic respiratory symptoms and chronic obstructive pulmonary disorder (COPD), probably caused by cumulative total dust exposure independent of smoking habits [17]. Gizaw et al. found that chronic respiratory symptoms were highly prevalent among workers of a cement factory [18]. The findings of Rafeemanesh et al. showed that occupational exposure to cement dust could be a

significant factor of respiratory system dysfunction [19]. Thepakorn et al. found that ventilatory respiratory function values (FEV1 and FVC) were slightly lower for roofing cement workers compared with unexposed group [20].

The limitations of the study were the lack of personal and indoor air measurements in the factory environment for the exposed group. Further studies searching of environmental measurement reports and consultation with physician to objective corroboration must be carried out in the cement factories.

4. CONCLUSIONS

Chronic respiratory diseases seen in the cement production industry represent a public health problem in developing countries. Considering the working time in the cement sector, this study revealed an increase in respiratory function capacity decreases over the first five to over five years. Regulations of the working environment in the cement sector will reduce the frequency of employees developing occupational respiratory diseases, but there will also be an examination opportunity regarding both the amount of decrease in occupational respiratory system capacities and the adequacy of the measures taken, as well as RFT evaluations before starting work and periodic examinations. This will decrease the rate of occupational respiratory system diseases by considering all possible risk factors. Measuring environmental exposures in the cement sector to check for possible dust particle exposure, providing employees and managers with RFT tests for occupational respiratory diseases, and providing awareness training on early diagnosis will be beneficial in terms of protecting employees and environmental health.

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BIOGRAPHY

Hulya Gul has been working in the Department of Public Health, Istanbul Faculty of Medicine, Istanbul University. She got her PhD degrees in preventive oncology and public health from Istanbul University Faculty of Medicine in 1995 and 2002, respectively. She studied two term at the Occupational Studies Section of the National Cancer Institute, NIH in the USA. She has been actively involved in research on environmental, occupational health and epidemiology. She is the author of more than 100 papers in national and international scientific journals and conference proceedings.

The Influence of CNT-E Glass Hybrid Composites on Composition of Sea Water

Mustafa TASYUREK^{1*}

Abstract

The aim of this study is to examine effect of the nanocomposite pipes to sea water after being used as a transport pipeline in aqueous and under sea systems. Glass/epoxy pipes are produced by the filament winding method and have $[\pm 55]_3$ fiber orientations. Multi-walled carbon nanotubes (MWCNTs) are used as nano reinforcement element.

Test specimens were stored in seawater for 2, 3, 4, 6 and 9 months as well as dry condition. In the study, it was compared with glass reinforced plastic (GRP), the reference materials, thanks to With CNT reinforcement in certain percentages. Physical and chemical effects of CNT on seawater have investigated with pH, conductivity, temperature, turbidity and hardness values of water for each material. Obtained conclusions were evaluated with various help of pictures and graphs and also, original inferences are made. According to these inferences, it has been achieved that; CNTs reinforced structures led to degradation in seawater, depending on time. Consequently, it can be said that; the four months period can be acceptable as critical threshold.

Keywords: Carbon Nanotubes, Sewater Composition, Sea Pollution

1. INTRODUCTION

In recent years, carbon nanotubes have begun to be preferred as additional reinforcing components in conventional fiber-reinforced composites to improve the fiber-matrix interface. There is a great potential for reinforcing matrix materials with nano-sized materials to increase the life of glass fiber reinforced plastics under mechanical load. It is better understood how nano technology is indispensable for many areas in the coming years. The products obtained by nanotechnology make easier people's lives in various fields such as automotive, aviation, medicine, defense, textile, energy, electronics, mechatronics and food. One of them is the transportation sector. Public and private sector infrastructure investments realized in recent years have significantly improved logistics services. Pipelines are the most economical way to transfer fluids such as water, oil, and natural gas to another. When compared to railways, it is less expense per transferred quantity and it has higher transport capacity. Pipelines are also used to transport liquids, such as drinking and irrigation water, over long distances. Such pipelines are useful for transporting water in rugged land or to protect the water from evaporation, contamination or environmental effects. One of the problems in composite materials is the lack of adhesion at the interface required for load transfer. This problem can be solved by reinforcing the matrix with carbon nanotubes due to the interface allows stress transfer to the matrix reinforcing member.

Wherever possible, the pipeline can be constructed over the ground. Pipelines are located 1 meter below the ground at Areas where urbanization is increasing or potentially hazardous areas for the environment. Pipelines can also be built under the sea. However, despite all these features being wished to be improved, the pollution of the sea may mean that. Sea pollution is a part of environmental pollution. Urban pollution, industrial pollution, pollution from solid wastes, agricultural and animal pollution are among the factors that cause sea pollution (24). For this reason, while industrial developments are planned, the future effects of materials should also be taken into account.

Thousands of substances mix into the sea through production and use of materials for energy production. The direct and indirect effects of the substances thrown on the seas can result in environmental pollution and the death of the living things. Producers, consumers, refutations and activities of the creatures in the ecosystem consisting of many living and non-living creatures are influenced by the physical and chemical properties of the environment. So the properties of the materials used in over sea and in-sea works are extremely important. In this context, a considerable increase is seen in the number of academic studies on sea water in recent years. While some of these studies are based on water improvement, treatment and anti-pollution properties (1-4), others have focused on the effects of materials on sea water (5-7), tribological properties (8-9) and improving their

^{1*} School of Civil Aviation, Selcuk University, Konya, Turkey

mechanical properties (10-12). In addition to these, studies involving direct interaction of carbon nanotubes with seawater have also been carried out (13-14).

Rhee et al. (2004) applied the compression test to seawater-impregnated carbon-epoxy composite specimen (15). They stressed that the test conditions increase the elastic modulus, fracture strength and fracture elongation. Chiou and Bradley (1995) performed a carbon-epoxy plate edge delamination test in their study (16). After the expose to seawater absorption, they repeated the tests. Accordingly, they emphasized that seawater absorption does not significantly change the elongation energy dissipation rate. Gellert and Turley (1999) reported that the bending strengths of glass fiber reinforced polymer sheets used in marine applications increase in the water absorption result in seawater dipping aging operation (17).

Sari (2010) investigated the effect of sea water on fatigue behavior of composite pipes after impact damage (18). Emphasized that the maximum deflection, total absorbed energy and maximum force values of water impregnated specimens were greater than that of the samples tested under dry conditions. Calik (2010) investigated the effect of sea water on the impact behavior of glass fiber-epoxy layered composite platter (19). Absorbed energy, maximum contact force, maximum collapse and change in the maximum contact time have been examined depending on the time of standing in seawater up to nine months. Deniz (2011) examined the effect of sea water on impact behavior and post-impact compressive strength (20). They reported that; three months about composite materials waiting in seawater is critical time for all impact characteristics. In a similar study, Deniz and Karakuzu (2012), investigated the impact behavior of unreinforced glass fiber-epoxy composite pipes under the influence of sea water and they have reported that the stored time in seawater does not make a significant change on impact characteristics (21).

Ng et al. investigated the potential of using carbon nanotubes in marine applications (22). They counted structural strengthening and free coating structural health monitoring, high performance wire/cable and lubrication applications as the recommended application areas. They also argued that such studies would be potentially appropriate and useful in the integration of nanotechnology applications on renewable energy for marine applications.

While using technology, taking advantage of it without disturbing the conditions are important for protecting the natural life of the seas. Protection of the seas benefiting from many areas such as transportation, food, transport means protection of animals from there. This is the protection of humanity. The aim of this study is to investigate the effect of nano reinforcement on the physical properties of water under conditions of standing in seawater of GRP pipes reinforced with CNT.

2. MATERIALS AND METHOD

2.1. Carbon Nanotube

The physical properties of the multi-walled carbon nanotube used in the study are given in Table 1. The elemental analysis of CNTs is also shown in Table 2.

Table 1. properties of the CNT

Properties	Values
Outer diameter	< 8 nm
Inner diameter	2-5 nm
Purity	> % 95
Length	10-30 micron
Specific Surface Area	500 m ² /g
Electrical Conductivity	> 100 S/cm
Volumetric Density	0.27 g/cm ³

Table 2. Elemental analysis of CNT

Compounds	Content %
Carbon (C)	97.44
Aluminum (Al)	0.19
Clor (Cl)	1.03
Cobalt (Co)	1.10
Sulfur (S)	0.24

2.2. Sea Water

The sea water they were waiting in the samples was taken from Antalya-Cyprus line from eastern Mediterranean. The main components in seawater are given in Table 3.

Table 3. Sea Water Components (Doganay and Ulcay 2007)

Rate	component
Chloride	19000 mg/l
Sodium	10500 mg/l
Magnesium	1270 mg/l
Sulfur	880 mg/l
Calcium	400 mg/l
Potassium	380 mg/l
Bromide	65 mg/l
Carbon	28 mg/l
Strontium	13 mg/l
Boron	5 mg/l
TOTAL	34,4 g/l

2.3. Production of nano material

In the production of the samples, 17 micron diameter Vetrotex 1200 single E glass and Epikote 828 XA epoxy resin produced from Ciba Geigy Bisphenol A and epichlorohydrin were used. The amount of hardener was determined as 44% by weight. Ultrasonic mixing method has been preferred in order to obtain homogeneous mixture. As a result, a six layer nanocomposite material with a wall thickness of 2.2 mm was obtained. The full image of the test samples during production is given in Fig 1. The samples were cut to the required size for the split disc test before being immersed in seawater. The holding of the test samples in seawater is shown in Fig 2.



Figure 1. Production of CNT reinforced nanocomposite tubes by filament winding method (23).



Figure 2. CNT-reinforced test specimens immersed in seawater

3. EXPERIMENTAL

In this study, the effect of CNT on characteristics of seawater was investigated as a result of the physical change in the structure of the material affected by sea water.

Electrical conductivity is a measure of the ability of water to conduct electric current. Water conductivity is influenced by the presence of dissolved inorganic materials that (-) charged anions such as chloride, nitrate, sulfate, phosphate; and (+) charged cations such as Na, Mg, Fe, Ca and Al. When salt concentration in the water increases, the electrical conductivity increases. It is observed that the conductivity value of sea water increases with time when CNT reinforced GRP material starts to hold in sea water. When you look at the Figure 3, it is understood that the critical period is four months. It is seen that the measurement results for the first three months are close to the pure sea water measurement result.

Salinity value of sea water increased after two months as seen in Figure 4. This value has reached the maximum value from four months. The 4th month is also a critical point for salinity of nano-reinforced material stored seawater.

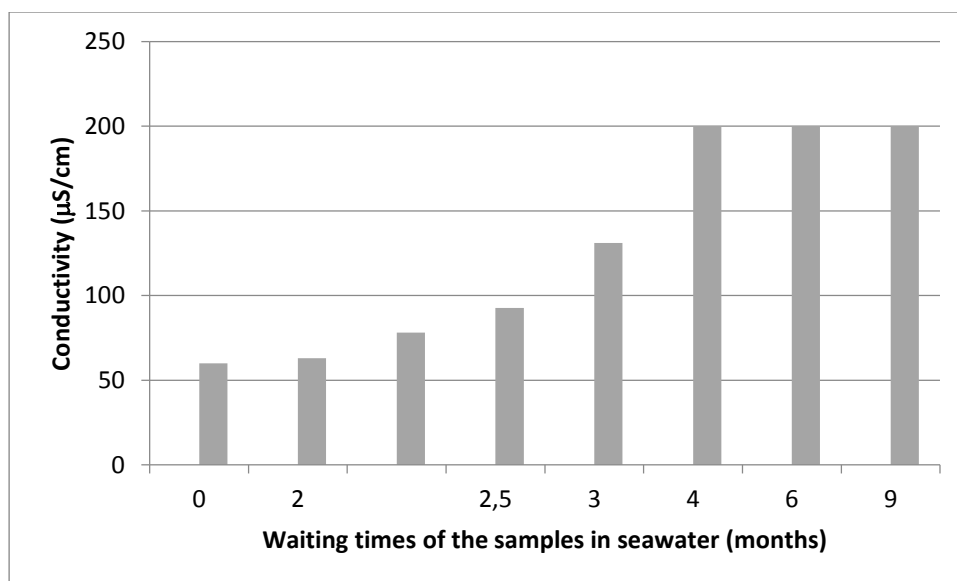


Figure 3. Time-dependent effect of nanocomposite samples on the conductivity of sea water

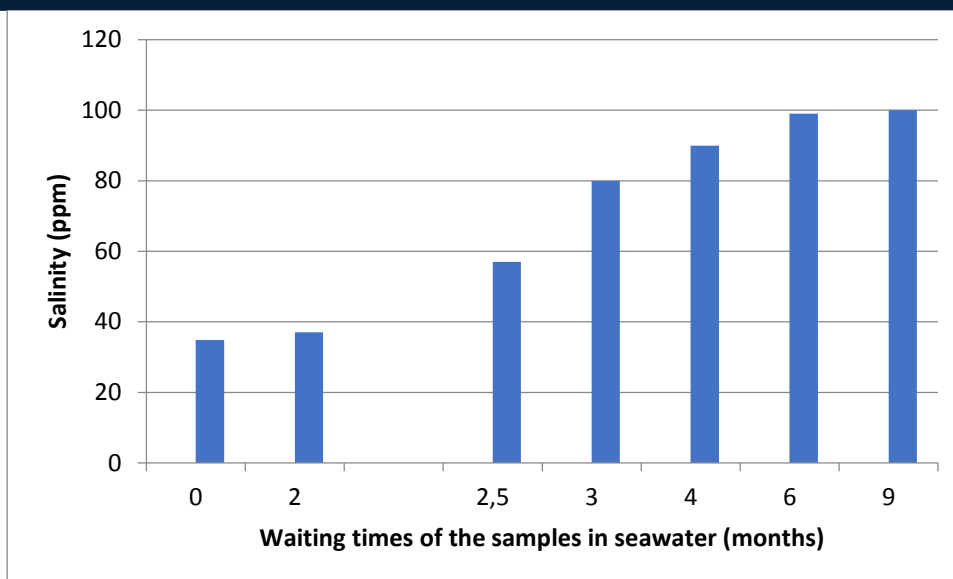


Figure 4. Time-dependent effect of nanocomposite samples on the salinity of sea water

Atmospheric gases dissolve in sea water and reach all depths through mixing processes and flows. The most common gases at the atmosphere and in the sea are nitrogen, oxygen and carbon dioxide. Since the number of biological activity and live life depends on the concentration of oxygen and carbon dioxide, they play a very important role in the seas.

Oxygen sources of sea water are diffusion of air through the water surface and usually plant photosynthesis. It is likely that a decrease in the amount of dissolved oxygen over time in seawater because of the test conditions do not simulate living conditions. In addition, the solubility of oxygen in water decreases with the increase in salinity. Each increase of 9000 mg/L in salinity reduces the solubility of oxygen in pure water by 5%. Similar behavior is observed under artificial experimental conditions as shown in Fig 5.

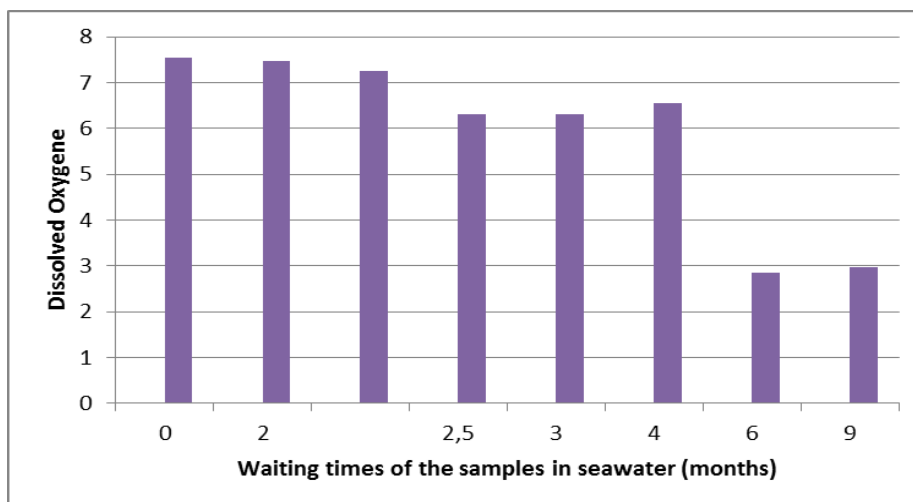


Figure 5. Time-dependent effect of nanocomposite samples on the amount of dissolved oxygen in the sea water

Sea water values are an important element in salty water. Over time, living creatures in water can accumulate components from sea water and rescue their lives healthier. Besides, the living creatures leave wastes and by-products at a certain rate to the aquarium water after the daily feeding. As a result of this, while the pH value of the water decreases, the general alkalinity of the water also tends to fall down. If the aquarium conditions are taken into account, a slight increase in the pH value will occur when the lighting is on. In dark environments, the amount of CO₂ increases and the pH value decreases. In addition, the closure of the invisible living organisms'

breathing in the water is also effective in decreasing the pH value. (see. Figure 6.) As time progressed, waste sediments mixed with water reduced the clarity of water they have led to a darker environment.

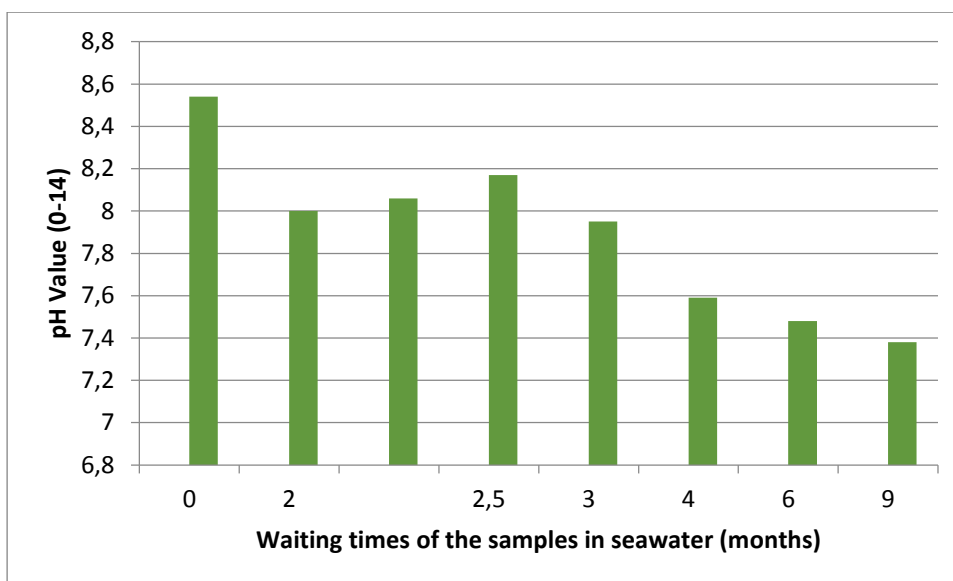


Figure 6. Time-dependent effect of nanocomposite samples on the pH values of the sea water

The data obtained from the turbidity level experiments are given in Fig 7. According to this, the turbidity of sea water did not exceed 1 NTU level for the first three months. The original turbidity of sea water has hardly changed in the first two months. The level of turbidity that tripled after 4th month showed a huge increase in the following months. Values of 3.5 NTU in six months and 4 NTU in nine month proves that the carbon nanotube is separated from the main structure and mixed with sea water and physically affected sea water. For this reason, coating of the inner and outer surfaces of the samples can minimize the undesired effects on the water.

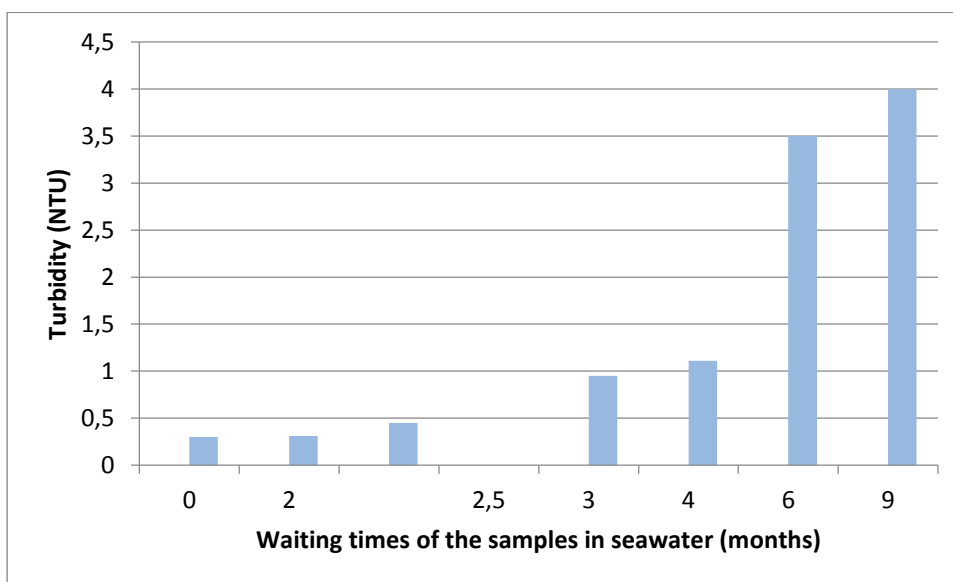


Figure 7. Time-dependent effect of nanocomposite samples on the turbidity of the sea water

4. CONCLUSION

In this study, multi-walled carbon nanotube reinforced epoxy / glass fiber composite material produced was produced by filament winding method. The samples were kept in a waiting tank with seawater for nine months for the specified periods.

The effect of nanocomposite pipes in water systems and underwater systems as a transport element has been examined. The results and suggestions are as follow:

- All investigated properties of seawater were affected depending on time.
- Water conductivity started to increase after two months. At month 4, it reached max level.
- Salinity value also exhibited similar behavior to conductivity. It reached three times in 4th month.
- Water turbidity is in acceptable level for the first four months and it has increased about ten times since 6th month.
- The pH value has started to decrease from the third months and the dissolved oxygen amount started to decrease from the fourth month.

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Eco-Friendly Fertilizer Characteristics Of Some Turkish Lignites And Potential Of Using In Agricultural Sector

Nazan YALCIN ERIK^{1*}, Faruk AY²

Abstract

Recently, a lot of progress have been obtain towards progress on the quality and quantity in agriculture. The advances and development in agriculture depend on mechanisation and the development on the soil characteristic which also help to increase the product efficiency. This study aims to determine some Turkish low rank coal samples for applications in the agricultural sector and assesses the suitability of a certain coal either as soil conditioner or as raw material for manufacturing organic fertilizers. They improve the soil structure and improve physical properties of soil by increasing the exchange capacity and buffering qualities, promoting the chelation of many elements and making these available to plants. Humic substances can ameliorate negative soil properties; improve the plant growth and nutrients uptake. Twenty-six samples of subbituminous coal obtained from several Turkish coal deposits such as Arguvan, Cayirli, Artova and Zile, Kangal-Gemerek-Divrigi were studied. When optimum parameters were used, the most promising samples for utilization are the coal samples from Arguvan, Artova and Zile, since they yielded high HA contents (≥ 30 wt). Although the Artova and Arguvan samples display high HA contents, they are also rich in S and release Fe, which might be threatening for the plants.

Keywords: Coal, fulvic acid, humic substances, humic acid, organic fertilizer, Turkey

1. INTRODUCTION

People have tried different techniques and supportive products to increase the agricultural productivity and to get higher quality. In this context, the usage of chemical fertilizers is the most leading methods for decades. By means of this technics, the plant provides many nutrients necessary for them. However, especially in the production phase, because of the additional cost and polluting the groundwater, rivers and lakes, the chemical fertilizers have also become a current problem in terms of environment and ecology with their harmful sides. For this reason, new techniques have also started to be investigated to increase vegetative productivity, which is not harmful for both environment and the livings.

Organic materials are important soil additives to improve soil physical, chemical and biological properties. It has been scientifically proved that fulvic and humic acid, the most important organic component of the soil, make important effects to the growth of the plant materials in terms of physical, chemical and microbiologically [1]. These natural components have supported the plant yield and quality, by increasing the flowering and the root and stem development, providing more water and air from the soil. At the same time, as well as economic benefits, humic and fulvic acids have been helped to protect the environment by increasing the effectiveness of the chemical fertilizers and inhibiting the excessive fertilizer usage [2, 3]. This is important to sustain the productivity of soils particularly in semi-arid regions (such as Turkey) where there is low input of organic materials. Therefore, usage of organic-based materials has gained importance within the last few years for sustainable agriculture and preventing soil degradation.

^{1*} Corresponding author: Cumhuriyet University, Department of Geological Engineering, 58140, Sivas, Turkey.
nyalcin@gmail.com

^{2 2} Cumhuriyet University, Department of Antropology, 58140, Sivas, Turkey.

Due to Turkish agricultural lands have alkaline reaction (85%), and are poor in terms of organic matter (94%), and has a chalky structure (58%), insufficient water storage results in mudslide together with soil loss with erosion and quality impairment in vegetative production, depending on the insufficiency of the elements (phosphorus, potassium, iron, and zinc) feeding the plant [3]. In many regions in Turkey, especially in Central Anatolia, the organic matter content of soils has fallen below 2 or 1 %. For this reason, the agricultural production in such areas must be supported with fertilizer.

Humic acids and their salts, derived from coal and other natural sources, which have modes of action similar to synthetic fertilizer, have been evaluated as potential eco-friendly soil fertilizer. The advantage of humic substances is the refractory nature of their chemical structures that makes them more resistant to microbial attacks. However, at the end of a certain period of time, no matter how much fertilizer is used, the danger of desertification is also in question because it will be difficult to get the soil productivity. Since the addition of sufficient amount of organics fertilizers to whole lands of the country is not possible, it has been determined that productivity potentials might be increased by applying the lower amounts of humic and fulvic acids, which is active fraction of organic matter and humus, when compared to organic fertilizers. The structure of the organic fertilizer consists of humus containing humic and fulvic acid, which is the result of the microorganism action [4, 5, 6].

Humic substances are the most widely found organic components on the Earth crust. These are a general category of naturally occurring, biogenic, heterogeneous organic matters that can generally be characterised as being yellow to black in colour, of high molecular weight and refractory. These components form most of the organic ingredient of soil, peat and natural waters, they effect the process of genesis of fossil fuels, and play a major role in the global carbon cycle. In the same time humic substances (especially humic acids) may be regarded as a valuable item which may found various uses for different purposes and their industrial production and application is growing. Humic and fulvic acid are present in the composition of the all organic materials in the nature. However, with the ratio ranging between 40% to 90%, organic material containing the highest amounts of humic and fulvic acid is brown coal, with its other name "leonardit". At present, low-rank coals are used for the production of HA, which are in the form of alkali-soluble humate salts or as N-rich coal HA (ammonium nitrohumates) [5, 6].

In our country, there is low-quality lignite (20-40% humic and fulvic acid of composition) to be used in the production of 5 million tons of leonardite, which has more than 40% of humic and fulvic acid and 7-8 million tons of solid and liquid K-Humate. However, because the leonardit having these properties and low-quality lignites have an energy amount of 800-1000 kcal/kg, they do not provide any economical returns and are removed as mine waste material. But, when assessed these materials having an estimated reserve of 12-13 million tons as resources of leonardit, solid and liquid humic-fulvic acid in agricultural lands, soil productivity can be increased and soil loss with erosion can be decreased [5, 6]. All of these will result in an increase in the vegetative production and economic benefits. In this study, it has been aimed the determination of humic components of some Tertiary aged and low-quality coals and their usage in agricultural lands.

Experimental

For this study, 26 samples were collected from the tops to the bases of the seams in the various coal fields (Arguvan-Malatya, Cayirli-Erzincan, Artova-Tokat, Zile-Tokat, Kangal-Sivas, Gemerek-Sivas, Divrigi-Sivas). These samples were taken from along ~ 1 m lines using the channel-sampling technique. Coal-quality data (total moisture, ash, volatile matter, fixed carbon, gross calorific value) were obtained using an IKA 4000 adiabatic calorimeter; elementary contents were determined using a LECO analyzer. For the determination of humic acids (HA) and fulvic acids (FA) contents a method combining the procedures proposed by ISO 5073 (1985) and the International Humic Substances Society [7] was followed.

2 RESULTS AND DISCUSSION

Proximate and Ultimate analysis

Moisture, ash yields and pH values of bulk samples are listed in Table 1. Most of the samples reveal ash yields between 20 and 50 wt.% and are very low-grade coals. The majority of the samples show an acidic to slightly acidic character (pH 4.5–7.4); samples Arguvan and Artova are strongly acidic (pH < 4.5), whereas samples Zile, Cayirli, Kangal, Gemerek, and Divrigi display neutral pH values (6.6–7.4).

The total C contents range from 42.52–80.2 wt.% (Table 1), with the majority of the samples showing contents greater than 50 wt.%. The H and N contents range from 3.46–5.79 wt.% and up to 2.1 wt.%, respectively. Sulphur contents range from 2.0–6.3 wt.%.

Humic substances content

Humic substances (HS) are the most widespread natural organic compounds. These are complex organic compounds and have endurance to degradation. Humin (HU) and Humic acid (HA) generally represent the major fraction of HS and appear to display similar analytical characteristics and chemical structures.

Table 1. Some proximate ve ultimate analyses results of investigated coal samples.

Area	Moisture (db) wt%	Ash (db)wt%	C wt. %	H wt. %	N wt. %	S wt. %
Arguvan	23.3	32.28	43.25	3.46	1.1	6.3
Cayirli	10.38	14.43	80.20	3.95	1.5	2.0
Artova	29.69	43.43	57.1	4.34	1.1	3.6
Zile	25.75	47.97	53.98	4.28	1.2	4.7
Kangal	43.22	22.11	42.52	5.79	2.1	5.3
Gemerek	31.09	17.45	65.66	4.03	1.8	4.0
Divrigi	10.68	24.04	60.02	4.32	1.0	5.6

HA occur naturally in low-rank coals and can account for an important fraction of the organic matter. The HS contents of the studied coals are shown in Table 2. The HA contents range between 4.12 and 57.55wt.% with Cayirli coal sample shows the lowest value, due to the higher rank (Ro; 0.61). The highest HA content was measured in Artova coal sample. Fulvic acid (FA) contents range between 3.2 and 33.33 wt.%. In general, the Cayirli coal samples show the lowest HS contents (Table 2). The total concentrations of HA and FA in the studied samples indicate that, coal samples of Arguvan, Artova, Zile areas contain the highest amount of HS (HA+FA>50 wt.%, on a dry basis).

Table 2. Humic substance composition of the investigated coal samples.

Area	Humic Acid (wt. %)	Fulvic Acid (wt. %)	pH	Humic Substances (wt. %)
Arguvan	39.70	12.10	2.3	51.8
Cayirli	4.12	3.20	6.0	7.32
Artova	57.55	15.12	2.4	72.67
Zile	45.28	12.84	5.4	58.12
Kangal	21.45	23.55	6.7	45.00
Gemerek	5.30	33.33	7.1	38.63
Divrigi	8.60	11.33	7.4	19.93

3.RESULTS AND DISCUSSION

The usage in the agricultural areas of the low-quality coals which is economically not very valuable is very important in terms of the prevention of the environmental hazards by minimizing the usage of chemical fertilizers.

At the same time, this kind of material can improve the quality of soil and contribute the plant growth and yields. Coal samples used in this study had occurred in similar precipitation conditions and geological age range. But, it has been seen that humic composition is different depending on the effect of coalification degree to the precipitation conditions or the type of organic material during the precipitation together with the physicochemical conditions and the tectonic activity. The most promising samples for utilization are the coal samples Arguvan, Artova and Zile, since they yielded high HA contents (≥ 30 wt). Although the Artova and Arguvan samples display high HA contents, they are also rich in S and release Fe, which might be threatening for the plants. Additionally, samples with pH values between 6 and 7 (Cayirli, Kangal, Gemerek, Divrigi samples), could be applied in heavily degraded, acidic soils such as mine spoils; this can promote the biotic activities.

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Iron speciation in surface waters by new ion-imprinted sorbents

Mariya Mitreva¹, Ivanka Dakova², and Irina Karadjova³

Abstract

Iron exists in surface waters in different physical and chemical forms. In order to provide a better understanding of the interactions of individual processes and the response of ecosystems to varying iron speciation the development of procedure for the determination of the most reactive, kinetically labile Fe(II) and Fe(III) is actual task in environmental analytical chemistry.

The aim of the present study was synthesis and characterization of new Fe(II) ion-imprinted sorbents (Fe(II)-IIPs) and their application for Fe(II)/Fe(III) speciation in surface waters. Fe(II)-IIPs were synthesized by precipitation copolymerization of methacrylic acid (functional monomer), trimethylolpropane trimethacrylate (crosslinking agent) and 2,2'-azobisisobutyronitrile (initiator) in the presence of different template species – Fe(II) complexes with 4-(2-pyridylazo)resorcinol, salicylic acid or 2,2'-bipyridine. The structure and morphology of the polymer particles obtained were characterized using SEM and BET analyses. The optimization experiments showed quantitative sorption of both Fe(II) and Fe(III) on the surface of Fe(II)-IIPs at pH 7–8, however selective sorption of only Fe(II) could be achieved in the presence of fluoride ions as a masking agent for Fe(III). Analytical procedure for the determination of Fe(II) and Fe(III) in surface waters was developed and characterized.

Keywords: Fe(II) ion-imprinted sorbents, Fe(II), Fe(III), speciation, surface waters

1. INTRODUCTION

Iron is widely distributed in nature and is one of the most important elements in environmental and biological systems. It may be present in surface waters as dissolved ferrous (Fe(II)) and ferric (Fe(III)) ions, complexed with inorganic or organic ligands, and as colloidal and particulate forms containing either or both oxidation states [1]. The environmental and biological effects of iron depend on its oxidation state, solubility and the degree of complex formation. Iron is not normally considered a toxic element, but it becomes toxic when accumulated, especially when present as free ion [2]. Generally, Fe(II) is considered to be more toxic than Fe(III) because it may cause cell degeneration [3]. Due to changing properties of the different iron forms, it is highly critical to gain information not only on the total content of the metal, but also about its speciation [4]. A large number of techniques for determination and speciation of Fe have been developed commonly based on spectrophotometric, electrochemical and chromatographic methods or non-chromatographic separations followed by highly sensitive instrumental detection [5]. Nevertheless, sample pretreatment prior to measurement is often demanded due to the low iron concentrations or matrix interferences observed. Recently, more attention has been paid to solid phase extraction (SPE) because it offers several advantages such as performance simplicity, low solvent consumption, minimization of sample volumes, high enrichment factor, good reproducibility and flexibility [6]. However, it should be noted that the extraction efficiency and selectivity of this technique is strongly dependent on the sorbent material used.

During the last years ion-imprinted polymers (IIPs), as selective sorbents for a particular chemical form of the given element, have received much attention [7]. The high selectivity of IIPs can be explained by the polymer memory effect toward the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination number, charge and size [8]. Numerous studies on IIPs and their application for selective preconcentration and separation of ferrous [9] and ferric [10-13] ions have been also reported. According to authors' knowledge, IIPs have never been used for Fe(II)/Fe(III) speciation in water samples.

The aim of the present study was synthesis and characterization of new Fe(II) ion-imprinted sorbents (Fe(II)-IIPs) and their application for Fe(II)/Fe(III) speciation in surface waters. Fe(II)-IIPs were synthesized by precipitation copolymerization of methacrylic acid (MAA) as a functional monomer, trimethylolpropane trimethacrylate (TMPTMA) as a crosslinking agent and 2,2'-azobisisobutyronitrile (AIBN, initiator) in the presence of different template species – Fe(II) complexes with 4-(2-pyridylazo)resorcinol (PAR), salicylic acid (SA) or 2,2'-bipyridine (BP). Critical comparison between

¹ National Centre of Public Health and Analyses, Sofia 1431, Bulgaria, m.mitreva@ncpha.government.bg

² Corresponding author: University of Sofia "St. Kliment Ohridski", Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria, i.dakova@chem.uni-sofia.bg

³ University of Sofia "St. Kliment Ohridski", Faculty of Chemistry and Pharmacy, Sofia 1164, Bulgaria, karadjova@chem.uni-sofia.bg

extraction efficiencies, adsorption capacities, and selectivity's of the three types Fe(II)-IIPs and non-imprinted (NIP) polymer gels are presented. Finally, analytical procedure for the determination of Fe(II) and Fe(III) in surface waters was developed based on both the high selectivity of Fe(II)-IIP toward Fe(II) and Fe(III) in the presence fluoride anions as masking agent.

2. MATERIALS AND METHODS

2.1. Materials

All reagents were of analytical-reagent grade and all aqueous solutions were prepared in high-purity deionized water (DW) (Millipore Corp., Milford, MA, USA). The stock standard solutions of Cu(II), Cd(II), Fe(III), Mn(II), Pb(II) and Zn(II) (1000 µg/mL) were Titrisol (Merck, Germany), in 2% HNO₃. For the preparation of aqueous Fe(II) solutions, (NH₄)₂Fe(SO₄)₂·6H₂O (Sigma-Aldrich Co. LLC., USA) was used. A stock solution of 100 mg/L Fe(II) was daily prepared by dissolving the required amounts of Fe(II) salt in 100 mL of DW. Working standard solutions were daily prepared by appropriate dilution with DW.

4-(2-Pyridylazo)resorcinol (PAR, as Na salt), salicylic acid (SA), 2,2'-bipyridine (BP), MAA, TMPTMA, 2,2'-azo-bis-isobutyronitrile (AIBN) (Merck, Darmstadt, Germany) and acetonitrile (ACN) (Labscan, Dublin, Ireland) were used without further purification. The pH was adjusted with NH₄OH or HNO₃. Deionized water was used in all experiments.

2.2. Apparatus

The Flame AAS measurements were carried out with a Perkin Elmer Model AAnalyst 400 atomic absorption spectrometer in air/acetylene flame. Instrumental parameters were optimized according to the Instrument Manual.

A scanning electron microscope (SEM, JEOL JSM-5500, Tokyo, Japan) was used for the determination of the microbead shape and size.

Specific surface area and pore size distribution were measured through nitrogen adsorption-desorption isotherms at 77 K using a Brunauer-Emmett-Teller (BET) analyzer (Quantachrome NOVA 1200, Quantachrome UK Ltd. England).

A microprocessor pH meter (Hanna Instruments, Portugal) was used for pH measurements.

A centrifuge EBA 20 (DJB Labcare Ltd., England) was used to separate micro particles and extracted metal ion solution in batch experiments.

2.3. Preparation of Fe(II)-IIPs

The imprinted polymer materials were synthesized as described earlier with minor modification [14]. As template species (0.04 mmol) the complexes of the imprinted ion (Fe(II)) with PAR, SA, or BP were used, as shown in Figure 1. Fe(II)-IIPs were prepared via dispersion copolymerization using ACN (8 mL) as solvent, AIBN (6 mg) as initiator, MAA (0.18 mmol) as functional monomer and TMPTMA (0.30 mmol) as crosslinking agent at T=60 °C for 24 h. Four type copolymer gels were prepared: (i) imprinted with Fe(II)-PAR complex (named Fe(II)-PAR-IIP); (ii) imprinted with Fe(II)-SA complex (named Fe(II)-SA-IIP); (iii) imprinted with Fe(II)-BP complex (named Fe(II)-BP-IIP) and (iv) non-imprinted (blank) polymer (named NIP) synthesized in the same way as described above, in the absence of template. They were recovered by centrifugation, washed with ACN to remove unreacted monomers and other ingredients. Fe(II) was eluted from the produced polymer networks by several elution steps using 4 M HNO₃ as eluent. Then IIPs were dried in a vacuum oven at 60 °C.

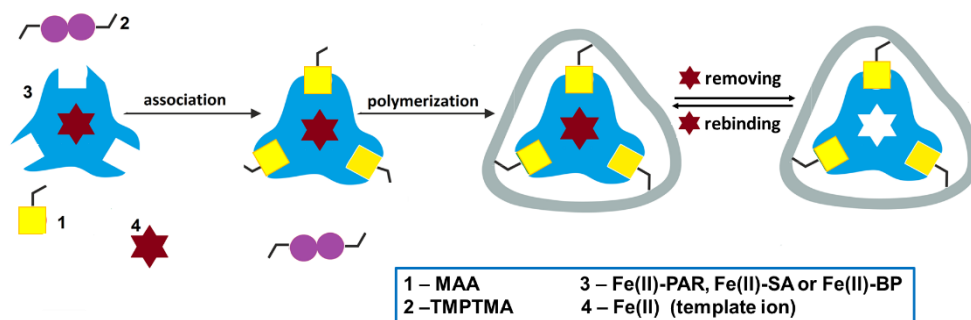


Figure 1. Scheme of the Fe(II)-IIP preparation

2.4. Solid-phase extraction of Fe(II)

A portion of standard solution containing 5 µg Fe(II) was added to a 10 mL test solution and adjusted to a desired pH value. Polymer gel particles of ca. 50 mg were added to this solution and stirred with an electric shaker for 30 min. The suspension was centrifuged at (5000 rpm), supernatant removed and the polymer gel washed twice with DW. The Fe(II) was eluted from the polymer particles with 5 mL 4 M HNO₃. Iron content in the effluate (supernatant after sorption) and eluate solutions was determined by FAAS.

2.5. Selectivity experiments

A 10 mL aqueous solution containing 0.5 µg/mL of Fe(II)/Cd(II), Fe(II)/Cu(II), Fe(II)/Fe(III), Fe(II)/Mn(II), Fe(II)/Pb(II) or Fe(II)/Zn(II). The mixture was shaken (250 rpm) at pH 7 for 30 min. The retained Cd(II), Cu(II), Fe(II), Fe(III), Mn(II), Pb(II) and Zn(II) were desorbed from the polymer gel particles with 5 mL 4 M HNO₃ was treated with the Fe(II)-IIPs or NIP (50 mg) at pH 7 and stirred for 30 min with an electric shaker. The Cd(II), Cu(II), Fe(II), Fe(III), Mn(II), Pb(II) and Zn(II) were eluted from the polymer gel with 5 mL 4 M HNO₃. The concentration of metal ions in the eluate was measured by a FAAS system.

2.6. Extraction efficiency and selectivity characteristics

The degree of sorption (D_s , %) of metal ions is defined as:

$$D_s, \% = [(A_i - A_{eff}) / A_i] \times 100, \quad (1)$$

where A_{eff} (µg) is the cation amount in the effluate solution after extraction by copolymer gels from a solution with a total cation amount A_i (µg).

The degree of elution (D_E , %) of adsorbed Fe(II) ions was calculated using equation:

$$D_E, \% = (A_{el} / (A_i - A_{eff})) \times 100, \quad (2)$$

where A_{el} (µg) is the amount of metal cations in solution after elution process

The distribution coefficient (D) is defined as:

$$D = (A_i - A_{eff}) / A_{eff} \quad (3)$$

The selectivity coefficient ($S_{Fe(II)/Me}$) is calculated by:

$$S_{Fe(II)/Me} = D_{Fe(II)} / D_{Me}, \quad (4)$$

where $D_{Fe(II)}$ and D_{Me} are the distribution coefficients for Fe(II) and Fe(III), Cd(II), Cu(II), Mn(II), Pb(II) or Zn(II), respectively.

The maximum adsorption capacity of the Fe(II)-IIPs is defined as the amount of the adsorbed Fe(II) ions per gram of the copolymer gel.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Fe(II)-IIP and characterization studies

Fe(II)-IIPs were synthesized by “trapping” technique, i.e. complexes between target metal ion and non-vinylated chelating agent get were trapped inside the polymer matrix during the polymer formation. In this case, preparation of Fe(II)-IIPs included several steps (Fig. 1). At the first one the prepolymerization complex is formed by non-covalent interactions between the functional monomer (MAA) and the template Fe(II) ion chelated by appropriate ligand. At the second step the copolymer network is formed by the dispersion cross-linking copolymerization of the prepolymerization complex with the TMPTMA as a cross-linking agent. Finally as a third step, Fe(II) ions were removed from copolymer network prepared leaving behind some specific binding sites with functional groups in a predetermined orientation and cavities with special size of templates.

In the present investigation, initially three types of Fe(II)-IIPs were synthesized using varying template species: complexes of Fe(II) with BP (N-containing ligand), SA (O-containing ligand) or PAR (N,O-containing ligand) to observe the chelating ligand type effect on the properties of the prepared polymer gels. The SEM micrographs of prepared Fe(II)-PAR-IIP and NIP are presented in the Fig. 2. It is seen that the synthesized NIP particles are in the shape of spheres (Fig. 2a). The surface structure and morphology of the Fe(II)-imprinted sorbent is different - Fe(II)-PAR-IIP is in the form of bigger aggregates of irregular particles (Fig. 2b). Analogous micrographs are obtained for Fe(II)-BP-IIP and Fe(II)-SA-IIP. Rough surface of ion imprinted polymers as compared to the non-IIP suggests that cavities were formed on the sorbent surface after template removal [5].

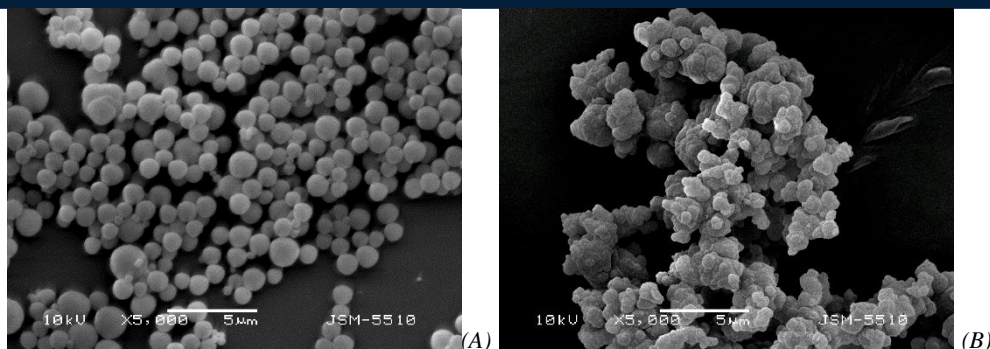


Figure 2. Scanning electron micrograph of NIP (A) and Fe(II)-PAR-IIP (B) particles at a $\times 5000$ magnification

The specific surface area for the Fe(II)-IIPs and NIP were determined from nitrogen adsorption–desorption isotherms. The three imprinted polymers, Fe(II)-PAR-IIP, Fe(II)-SA-IIP and Fe(II)-BP-IIP, have similar surface areas ($34 \text{ m}^2/\text{g}$, $29 \text{ m}^2/\text{g}$ and $28 \text{ m}^2/\text{g}$, respectively), while NIP has higher surface area ($80 \text{ m}^2/\text{g}$). These typical results after imprinting are explained with the incorporation of Fe(II)-chelating ligand complexes in polymer network which causes a certain filling of the pores and reduced adsorption of N_2 [16].

3.2. pH influence on the extraction efficiency of Fe(II) with different types of Fe(II)-IIPs

The acidity of the solution is the most critical parameter controlling the degree of sorption of metal ions because the pH value affects both the metal binding sites on the adsorbent surface and the metal chemistry in the solution. The pH-dependence (in the range 3–9) of the degree of sorption (D_s , %) of the three Fe(II)-IIPs and NIP sorbents is presented in Fig. 3 and shows that D_s values achieved for imprinted polymer gels are well above those for the non-imprinted sorbent. The quantitative sorption of Fe(II) ions on the Fe(II)-BP-IIP, Fe(II)-SA-IIP and Fe(II)-PAR-IIP, was achieved at pH 7, while for the NIP the maximal degree of sorption was 60 %. Evidently, the specific interaction between chelating agents (BP, SA or PAR) and Fe(II) ions does not take place in the case of NIP, thus explaining the observed lower degree of sorption. The degree of sorption for all studied sorbents decreased at $\text{pH} > 7$ most probably related to the partial hydrolysis of the ferrous hydroxide. Finally, the pH 7 was selected as optimal for the SPE of Fe(II) by Fe(II)-IIPs and NIP in the further investigations.

3.3. Capacity and adsorption isotherms

The sorption capacity of the imprinted and non-imprinted polymer gels were determined after saturation of the sorbents with the Fe(II) ions under optimum conditions at room temperature (Fig. 4). For this purpose, increasing amounts of metal ions were added to a 50 mg polymer gel and the total metal sorbed was measured by FAAS after elution with 4 M HNO_3 . The determined maximum adsorption capacities of Fe(II)-PAR-IIP, Fe(II)-BP-IIP, Fe(II)-SA-IIP and NIP are 46.4 , 39.6 , 32.2 and $28.2 \text{ } \mu\text{mol Fe(II) per g sorbent}$, respectively. As it might be expected the adsorption capacity of Fe(II)-IIPs are higher than non-imprinted polymer gels, which indicated that the cavities created after removal of template in Fe(II)-IIPs are more complementary to the imprinted ion in size, shape and chemical functionality. These results demonstrated that the imprinting effect of the prepared sorbents is obvious and depend on the type of chelating ligand. The comparison between sorption capacity values of the three types of Fe(II)-IIPs shows that copolymer gels with chelating agent PAR

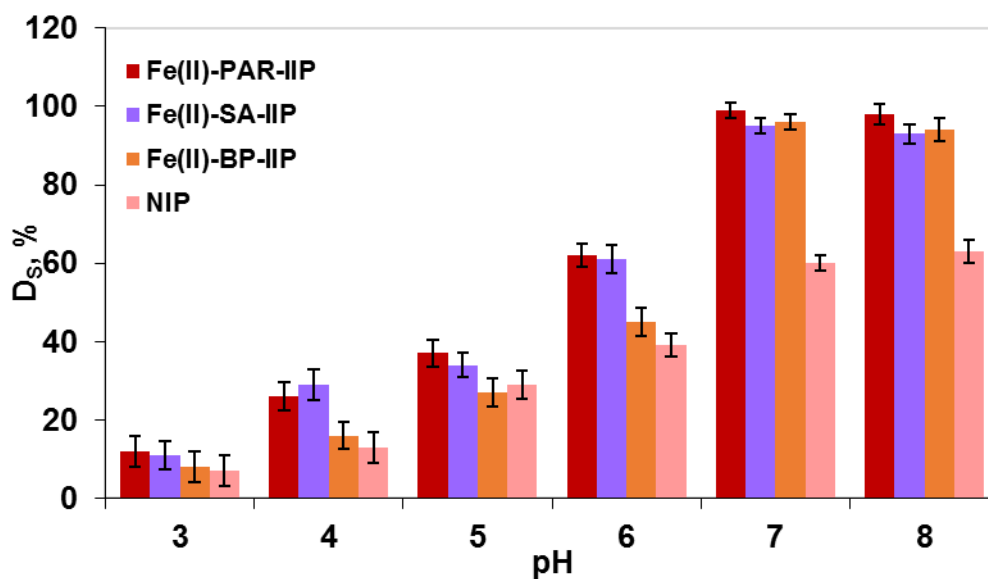


Figure 3. pH-dependence of the degree of sorption of Fe(II) ions with Fe(II)-IIPs and NIP

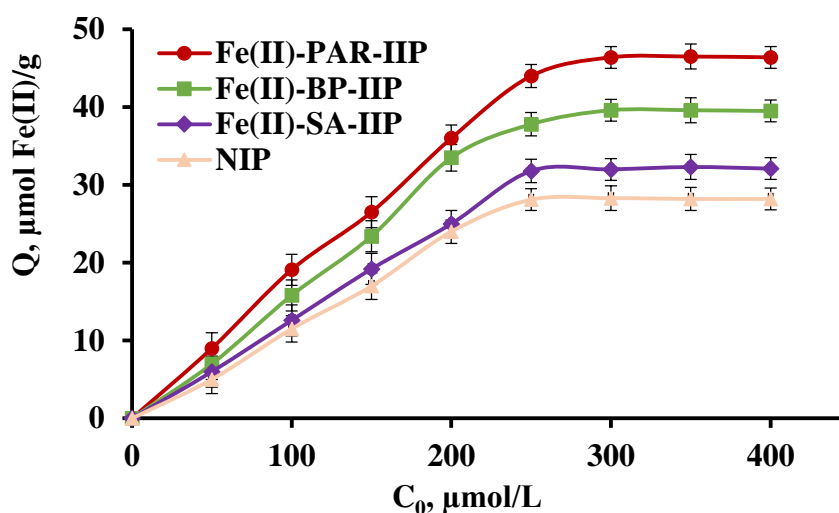


Figure 4. Experimental sorption isotherms for Fe(II) sorption onto the Fe(II)-PAR-IIP and NIP at temperature 25 °C

have the highest capacity toward Fe(II) ions. Therefore the Fe(II)-PAR-IIP was selected as optimal for the SPE of Fe(II) by Fe(II)-IIPs and NIP in the further investigations.

3.4. Optimization of the sorption/desorption conditions for Fe(II) preconcentration

The influence of various parameters (eluent volume and concentration as well as sorption and desorption time) on the solid phase extraction efficiencies of Fe(II)-PAR-IIP were investigated.

In order to elute iron adsorbed on the loaded Fe(II)-PAR-IIP particles nitric acid and EDTA at different concentration

levels (0.5–4 M for HNO₃ and 0.1–0.5 for EDTA) were tested. Quantitative elution was achieved using 4 M HNO₃. The effect of the eluent volume on the iron desorption was investigated in the range of 2–10 mL 4 M HNO₃. The full extraction efficiency of Fe(II) was reached when the adsorbed Fe(II) was eluted with 5 mL 4 M HNO₃.

The kinetics of the Fe(II) sorption and desorption were investigated in a batch system with 50 mg of Fe(II)-PAR-IIP particles for 5–60 min. It was established quantitative sorption was reached for 20 min. The Fe(II) ions could be quantitatively eluted for 40 min.

3.5. Selectivity experiments

The competitive ion recognition studies were performed in order to investigate the adsorption selectivity of the synthesized Fe(II)-PAR-IIP sorbent toward selected metals like Cd(II), Cu(II), Fe(III), Mn(II), Pb(II) and Zn(II). The experiments were carried out with Fe(II)-PAR-IIP and NIP in batch mode at pH 7. Figure 5 and Table 1 summarize the degree of sorption (D_s), distribution coefficients (D) of the metal ions, selectivity coefficient ($S_{Fe(II)/Me}$) of the sorbents between Fe(II) and Cd(II), Cu(II), Fe(III), Mn(II), Pb(II) and Zn(II) ions and the relative selectivity coefficient (ρ) between the Fe(II)-PAR-IIP and NIP. Although some ions have similar ionic radii, the same charge, and high affinity toward the PAR ligand, significant differences in their extraction characteristic D_s (Figure 5), were observed. The results indicated higher selectivity of Fe(II)-PAR-IIP toward Fe(II) even in the presence of competitors Cd(II), Cu(II), Mn(II), Pb(II) and Zn(II) ions. The D_s Fe(II)-PAR-IIP sorbent toward Fe(II) were largest and decreased in order Fe(II) > Cu(II) > Cd(II) > Zn(II) > Pb(II) > Mn(II) due to the coordination-geometry selectivity of the sorbent which could provide the ligand groups arranged in a suitable way required for coordination of Fe(II).

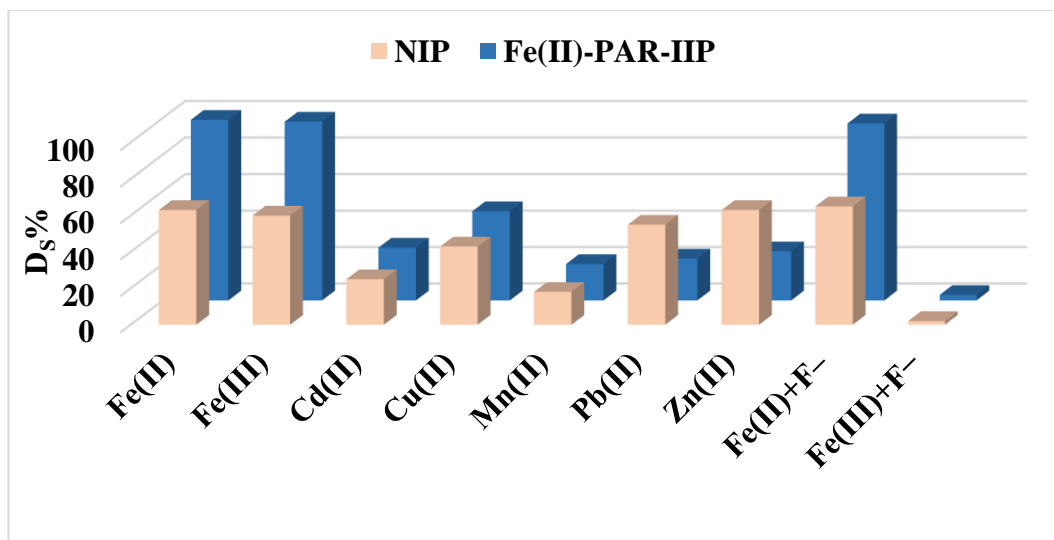


Figure 5. Degrees of sorption (D_s %) of template and competitive ions with Fe(II)-IIP and NIP (three parallel experiments)

The high values of the relative selectivity coefficients $\rho(S_{Fe(II)/Me})$ convincingly demonstrated superiority of Fe(II)-PAR-IIP sorbent over NIP (Table 1). However the results presented in Table 1 showed that Fe(II)-PAR-IIP exhibits the lowest selectivity toward Fe(III) ions ($S_{Fe(II)/Fe(III)}=2$). This result might be explained by the same stoichiometry of the complexes of Fe(II) and Fe(III) with PAR. To increase the selectivity of the sorbent was used masking agent which forms stable complexes with one of the studied species. As far as Fe(II) do not form fluoride complex selective quantitative retention of Fe(II) in the presence of fluoride ions was observed (Figure 5). The degree of sorption of Fe(II) in the presents of fluoride anions was $99 \pm 2\%$, while this value for Fe(III) was 3%. The selectivity of the Fe(II)-PAR-IIP toward Fe(III) ions increased remarkably $S_{Fe(II)/Fe(III)}=3201$, as shown in Table 1.

Table 1. Distribution (D), selectivity ($S_{Fe(II)/Me}$) and relative selectivity coefficients $\rho(S_{Fe(II)/Me})$ of Fe(II)-PAR-IIP and NIP for Fe(II)

Me ion	Fe(II)-PAR-IIP	NIP	$\rho(S_{Fe(II)/Me})$
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	<i>D</i>	<i>S_{Fe(II)/Me}</i>	<i>D</i>	<i>S_{Fe(II)/Me}</i>	
Fe(II)	99		1.8		
Fe(III)	49	2	1.5	1	2
Cd(II)	0.4	242	0.3	5	48
Cu(II)	1	103	0.8	2	51
Mn(II)	0.3	396	0.2	8	49
Pb(II)	0.3	331	1.2	1	331
Zn(II)	0.4	268	1.7	1	268
Fe(II) + F ⁻	32	3	1.9	1	3
Fe(III) + F ⁻	0.03	3201	0.02	83	38

3.6. Application of the method

The extraction characteristics of synthesized Fe(II)-PAR-IIP assumed that it can successfully be used for determination of Fe(II) and Fe(III) in surface water samples. To evaluate the possibility of absorption of ionic species of Fe(II) and Fe(III) and their kinetically labile complexes were tested EDTA and humic acids, which forming stable complexes with both species in a concentration range close to that encountered in the environment. The results obtained for $D_s < 1\%$ (Table 2) unambiguously show that there is no sorption of their complexes with EDTA and humic acids.

Table 2. Degree of sorption (D_s) of Fe(II) and Fe(III) ions at SPE with Fe(II)-PAR-IIP

Ion	$D_s, \%$				
	EDTA		Humic acids		
	0.01 M	0.05 M	0.5 mg/L	1 mg/L	2 mg/L
Fe(II)	< 1	< 1	< 1	< 1	< 1
Fe(III)	< 1	< 1	< 1	< 1	< 1

To evaluate the extraction efficiency of Fe(II)-PAR-IIP for determination of Fe(II) and Fe(III) in surface waters were carried out experiments with low mineral river waters. The experiments were performed with real samples of surface waters with the addition of known concentrations of Fe(II) and Fe(III). The following procedure was applied: 50 mg sorbent, 4 μ g of Fe(II) and Fe(III) and 1 mL 0.1 M NH₄F were added to 10 mL river water, pH adjusted to 7 and stirred for 20 min to complete the Fe(II) sorption process. Under these conditions Fe(III) are bound in complex with the fluoride ions, which should not be expected to be adsorbed on Fe(II)-PAR-IIP. After centrifugation, the content Fe(III) was measured in effluate by electrothermal AAS (ETAAS). The sorbent particles were washed with DW and the adsorbed Fe(II) was eluted with 5 mL 4 M HNO₃ with continuous stirring for 40 min. The content of Fe(II) was determined in the eluate by ETAAS. Recoveries for both Fe species and for all river water samples were between 95 and 98%.

Analytical characteristics of developed procedure for Fe(II)/Fe(III) speciation were defined by 5 parallel analyses of low mineral river water samples. The results obtained by using ETAAS can be summarized as follow: LOD and LOQ calculated according to the 3σ and 10σ criteria are 0.05 μ g/L and 0.15 μ g/L for Fe(II) and 0.2 μ g/L and 0.6 μ g/L for Fe(III), respectively. The relative standard deviation varied in the range 4–9% for Fe(II) and 6–8 % for Fe(III) at concentration of 0.2–100 μ g/L.

4. CONCLUSIONS

In the present work a new Fe(II) imprinted sorbents were successfully synthesized by a precipitation copolymerization. The composition, structure and morphology of the polymer particles obtained were characterized using SEM and BET analyses. The optimal pH range for the quantitative sorption of Fe(II) and Fe(III) was between 7–8, however without any selectivity between Fe(II) and Fe(III). Selective quantitative sorption of Fe(II) was achieved in the presence of

Fe(III) masked as fluoride complex in the same pH range 7–8. The application of Fe(II)-PAR-IIP for the determination of Fe(II) and Fe(III) in surface waters was developed and characterized.

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