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CONTACT

Yildiz Technical University
Environmental Engineering Department, 34220 Esenler
Istanbul – Turkiye
Web: https://dergipark.org.tr/en/pub/ert
E-mail: ert@yildiz.edu.tr

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Research Article

An experimental study on release mechanism of iron and manganese from sediments to the water column in reservoirs

Buse VURAL[1], Şebnem ELÇI[1,*], Hatice Eser ÖKTEN[2]

[1]*Izmir Institute of Technology, Department of Civil Engineering, Izmir, Turkey*
[2]*Izmir Institute of Technology, Department of Environmental Engineering, Izmir, Turkey*

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ABSTRACT

Iron and manganese accumulation in drinking water reservoirs is a challenging issue and should be controlled to prevent their adverse effects on human health. Accumulation of these elements not only clogs pipeline systems but also causes stains on fixtures and laundry. Also, high concentrations of iron and manganese may lead to various health problems when ingested. This study focuses on the release mechanism of iron and manganese from sediments to the water column in reservoirs and investigates methods to prevent this release. Effects of hypoxia, hypolimnetic aeration, alkalinity of water, and thermal stratification on iron and manganese concentrations were investigated through laboratory experiments. Experiments done simulating the water column showed that hypoxia caused more dissolution of ferrous iron when compared with that of manganese. Accordingly, aeration of the water column in hypoxic conditions lead to a significant decrease in ferrous iron concentrations (in our case reaching zero). However, manganese and total iron levels were not affected by the aeration of the water column. Alkalinity level of the water column was observed to have a great effect on the solubility of iron and manganese. Concentrations of total Fe and total Mn measured for acidic (pH = 5) conditions were considerably greater than concentrations measured at neutral conditions. As for alkaline (pH = 11) conditions, the opposite was observed with measured concentrations of total Fe and total Mn being lower than the ones measured for neutral conditions. Thermal stratification had an enhancing effect on the solubility of both iron and manganese ions. While aeration of the stratified water column slightly decreased the concentrations of Total Fe and Mn, it had a greater impact on decreasing Fe^{2+} concentrations.

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***Corresponding author.**
*E-mail address: sebnemelci@iyte.edu.tr

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INTRODUCTION

Behavior of metals in reservoirs is influenced by the composition of sediment bed, suspended sediment composition, and water chemistry, which controls the rate of adsorption and desorption of metals to and from sediments. Since a natural degradation process for eliminating the excess metals does not exist, they are often absorbed by the sediments. As a result of accumulation of metals in underlying sediments, concentration of metals in sediments may be much higher than the water column above it. In general, sediment composed of fine sand and silt have higher levels of adsorbed metals than quartz, feldspar, and detrital carbonate-rich sediments [1]. Metals also have a high affinity for humic acids and organic matter [2].

Iron and manganese are two similar elements that commonly exist in Earth's crust. Iron is the most widely found element together with manganese in water supplies. These two elements are found frequently in water systems that use groundwater. Water, infiltrating through soil or rock, may dissolve iron and manganese that are inherently present in the solid material. Moreover, iron pipes may leach and cause high concentrations of iron in water. On the other hand, surface water generally does not contain large amounts of iron or manganese. Considering the reservoirs, varying iron and manganese speciation may be observed in the water column. While Fe^{2+} and Mn^{2+} ions are mostly soluble in water, when enough oxygen is supplied, they are converted to insoluble Fe^{3+} and Mn^{4+} ions, precipitating towards sediments underlying the hypolimnetic water layer.

Thermal stratification generally occurs during summer months due to the heating of the upper layers of the water column. Once thermal stratification occurs, it is generally accompanied by a lack of oxygen in the hypolimnetic zone. Under anoxic conditions, iron and manganese are soluble in water and these soluble elements may accumulate in the hypolimnion. Moreover, organic residues tend to sink to hypolimnion and due to microbial degradation of these organic residues in sediments, remaining oxygen is depleted. Anoxic or anaerobic microbial degradation tends to change the pH of sediment and eventually of hypolimnion towards acidic conditions. It may lead to several adverse results such as failure of meeting the drinking water quality standards, aquatic problems such as fish kills, cloggings of the pipeline system, stains on fixtures and laundry, etc. Due to these adverse effects, water intake depth needs to be adjusted in drinking water reservoirs to minimize the iron and manganese concentrations along with suspended solids concentration.

Previous studies pointed out iron and manganese occuring naturally as oxidized, insoluble forms in bed sediments of thermally stratified reservoirs ([3], [4]). Conditions during stratification may lead to reductive dissolution of iron and manganese from sediments to the water column [5]. Although previous studies investigated effects of hypolimnetic aeration on the metal concentrations, the combined effect of pH, metal oxidation mechanisms and mixing in the water column and sediments at the reservoir scale still remains unknown.

As stated by other researchers [6], hypolimnetic aeration alone might not be sufficient to remove manganese from the water column. Since the abiotic oxidation rate of manganese is pH-dependent, lakes and reservoirs having slightly acidic conditions (pH 5.6 to 7.5) may experience critical manganese problems. In another study [7], authors investigated the impact of oxygenation on manganese concentrations and they found that soluble manganese levels increased when oxygenation was turned off and the upper sediment became anoxic. After several weeks of anoxic conditions, they also observed a higher release of Mn^{2+} ions from the sediment. However, they stated that the diffusive flux of manganese from the sediment also increased in response to the oxygenation which contradicted their previous remarks.

Manganese preparation mechanisms with the perspective of adsorption onto suspended solids and microbial oxidation of Mn was studied in Lake Biwa [8]. Concentration of dissolved manganese, Mn^{2+}, decreased at pH > 7 by microbial oxidation in aerobic water samples maintained in the laboratory. In the end, it was observed that autoclaving, irradiation with ultraviolet light, filtration of water samples and the addition of NaN_3 prevented Mn^{2+} precipitation. Besides, in the suspended solid, the adsorption of Mn^{2+} was appreciable at pH > 7 and it reached equilibrium point within the minimum 30 minutes. When the Mn^{2+} oxidation rate was compared with Mn^{2+} adsorption rate, it was much slower. In different parts of the lake, for example, bottom water, river mouth or sediment surface, subsequent slow oxidation mediated by bacteria and initial adsorption of Mn^{2+} might be required for the Mn^{2+} precipitation mechanism process.

Oxygenation systems could decrease soluble manganese concentrations by increasing dissolved oxygen levels, subsequently causing manganese oxidation and adsorption to other particles, resulting in precipitation to the sediment ([4], [9]). These researchers also pointed out that oxygen dynamics and biogeochemical processes were variable at the sediment-water interface and thus changes in the sediment oxygen uptake rate might occur. In these studies, the influence of oxygenation on sediment-water fluxes of manganese was also unclear. Thus, for accurately describing the processes controlling elements' concentrations, the governing mechanism must be further studied for good management practices of drinking water supply reservoirs.

World Health Organization (WHO) set the maximum allowable concentration limits for Fe and Mn as 0.3 mg/l and 0.1 mg/l, respectively. Iron deposits in various part of the brain were known to be related to risks for Alzheimer's disease [10]. Overconsumption of manganese also affects the brain, leading to increased movement abnormalities [11]. Removing Fe and Mn from water withdrawn from lakes or reservoirs by oxidation and filtration techniques is especially difficult and expensive, and thus in situ treatment is preferred in most cases. A common application for in-situ treatment is hypolimnetic aeration, which increases dissolved oxygen while preserving thermal stratification in water bodies. In many reservoirs, the aeration systems are accepted as the sole solution for improving the water quality for better management strategies. When dissolved oxygen (DO) concentration increases in hypolimnion, oxidized iron and manganese species precipitate to bottom sediments. However, bottom sediments may release metals as a result of the combined effects of DO concentration, pH, and microbial activity, which need further research in order to elucidate the whole mechanism. In this paper, we aim to investigate the processes that control concentrations of Fe and Mn, facilitating the good management practices for drinking water supply reservoirs.

METHODOLOGY

Preparation of Iron and Manganese Solution

Iron and manganese solutions from ferrous chloride tetrahydrate ($FeCl_2.4H_2O$, Sigma Aldrich) and manganese (II) sulfate monohydrate ($MnSO_4.4H_2O$, Sigma Aldrich) were prepared for sediment spiking, respectively and were used as sources of Mn^{2+} and Fe^{2+}. In total, 12.18 grams of $MnSO_4.4H_2O$ and 10.68 grams of $FeCl_2.4H_2O$ were used to prepare a solution. Iron and manganese concentrations of the prepared solution were 3 g/L each.

Experimental Setup

Two identical glass water tanks (1 m × 0.4 m × 0.5 m), with 200 L capacity were used to examine the effects of hypoxia, aeration, alkalinity and thermal stratification on iron and manganese concentrations (Fig. 1). To simulate sediments in a water supply reservoir, sediment size composition observed in Tahtali Reservoir, Turkey was used as the reference. Thus, sediments consisting of 60 % sand and 40 % silt and clay were obtained by sieve analysis. For each experiment, a total of 1.2 kg sediment was distributed homogeneously to a container and then mixed with 300 mL of prepared stock solution to form a firm creamy paste. The contaminated sediment container was always placed at bottom of the tank slowly in order to avoid any unintended mixing.

Figure 1. Water tank used in experiments.

Dissolved oxygen (DO), pH, and temperature were monitored via a multimeter (HQ40D, Hach Lange). The multimeter was calibrated and the probes were rinsed with DI water and dried before and after each analysis. All samples were kept at +4 °C prior to analysis. All samples were analyzed using a spectrophotometer (UV-2600, Shimadzu) (Fig. 2). At the beginning of each analysis, the wavelength of the device was set to 265 nm for total Fe, 295 nm for Mn, and 255 nm for Fe^{2+}. Total Fe, Fe^{2+}, and Mn analyses were conducted following the spectrophotometric methods (Hach Lange) specified by the manufacturer (see DOC316.53.01053, DOC316.53.01049, DOC316.53.01058).

Experiments

Tap water was analyzed for total iron and manganese concentrations, which were 0.003 mg/l and 0.001 mg/L, respectively. Total Fe and Mn analyses for the bare sediment also showed negligible results (total Fe = 0.001 mg/l; Mn = 0.0015 mg/L). The release mechanism of Fe and Mn from sediments to the water column was investigated in a series of experiments grouped in three categories (Table 1).

For all experiments, the first sample was collected as soon as the contaminated sediment container was placed at the bottom of the tank (0 hour) and the rest of the samples were collected at 2, 6, 12, 24, 36, 48, 72 and 96 hours, while dissolved oxygen (DO), pH and temperature measurements were conducted simultaneously. Water samples were taken from 5 cm above the sediment surface.

The first experiment represented the reference case. The aim was to observe iron and manganese release from the sediments to the water column under normal conditions. In the rest of the experiments, the starting conditions were representing hypoxia. Following the filling of the water tank with tap water, *Elodea canadensis*, a common waterweed, which is known to consume high rates of oxygen in a short time, was used to create hypoxia in the water tank (Fig. 3). It is an aquatic plant native to most of North America, with average lengths between 20 and 30 cm. Its numerous overlapping, dark green, translucent, and minutely toothed leaves are about 1 cm long and 2–3 mm wide. It was selected for its ability to consume oxygen rapidly in the dark, simulating the depths of a reservoir. Hence, the water tank with waterweed was covered with black nylon to prevent sunlight and air diffusion to the tank. The tank stayed covered with black nylon for about 4 days until the DO level of 5 mg/l was reached. When the desired DO level was achieved, the nylon cover was removed from the tank. For experimental runs 3 and 7, aeration of 60 L/h was applied. In many reservoirs, aeration of the water column is accepted as the sole solution for improving the water quality for better management strategies. It can increase dissolved oxygen while preserving thermal stratification in water bodies. The third and seventh experiments aimed to investigate how aeration in the hypolimnium affects the dissolution of Total Fe, Fe^{2+}, and Mn. As it was the case for the second experiment, hypoxia was maintained using Elodea plants. The purpose of the fourth experiment was to show how acidic water conditions affected iron and manganese solubility in the case of hypoxia. The tank was filled, and the plant was placed to create hypoxia in the tank. To reach a low level of pH, HCl was used. HCl solution was prepared and poured to the tank gradually to adjust the pH of water around 5. In the fifth experiment, to achieve alkaline water conditions, NaOH solution was added to the water tank slowly until the pH of water reached 11. The sixth and the seventh experiments aimed to investigate the effects of thermal stratification on the solubility of iron and manganese. Stratification in the water tank was achieved through an electric heater placed at the top of the tank. Electric heater was kept running until a temperature profile representing thermal stratification was obtained (Fig. 3). In experiment 6, after the

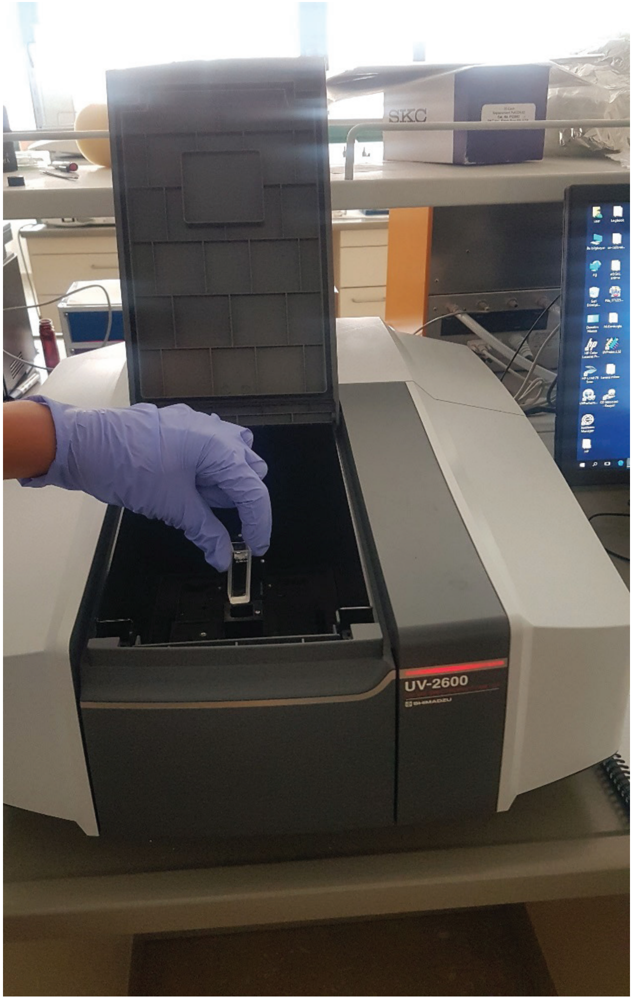

Figure 2. Insertion of the cell holder to the spectrophotometer.

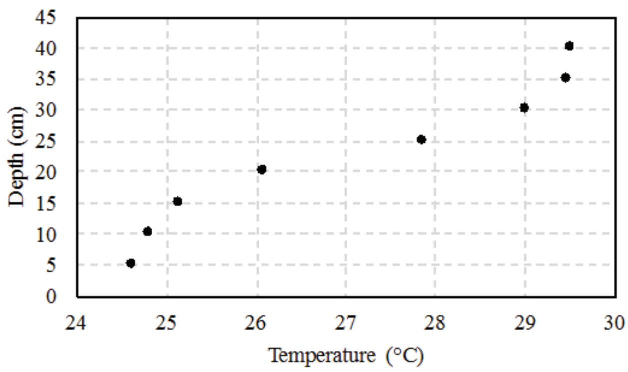

Figure 3. Vertical temperature profile obtained after heating of the water column.

Table 1. Summary of studied conditions

Experiment #	Oxygen level	Aeration rate (l/s)	pH	Stratified/Mixed	Oxygen level	Group #
1	Oxic	–	7	Mixed	Oxic	1
2	Hypoxia	–	7	Mixed	Hypoxia	
3	Hypoxia	60	7	Mixed	Hypoxia	
4	Hypoxia	–	5	Mixed	Hypoxia	2
5	Hypoxia	–	11	Mixed	Hypoxia	
6	Hypoxia	–	7	Stratified	Hypoxia	3
7	Hypoxia	60	7	Stratified	Hypoxia	

water column was stratified, the Elodea plant was used to achieve hypoxia and the water tank was covered with black nylon. When the DO reached around 5, the plant was removed and the polluted sediment was placed to the bottom of the tank. The seventh experiment simulated the case where aeration would be effective in a stratified reservoir experiencing hypoxia. Thus, this last experiment aimed to investigate how aeration affects the dissolution of Total Fe, Fe^{2+}, and Mn in the joint case of stratification and hypoxia.

RESULTS AND DISCUSSION

Representing the reference scenario, values of DO and pH stayed pretty much the same for 96 hours where temperature values slightly increased after 12 hours adjusting to ambient temperature in experiment 1 (Fig. 4a). Concentrations of Total Fe and Fe^{2+} increased in the first two hours, then both decreased slowly until the end of 96 hours (Fig. 4b). Manganese showed a different behavior than iron. While its concentration decreased sharply during the first two hours, it followed a smoother decrease for the following 48 hours. All three parameters stabilized after 60 hours.

In the second experiment, through prevention of photosynthesis, the plant was forced to consume the DO in the water column which was approximately 7.5 mg/l. The experiment started when DO concentration reached a value of 5 mg/l. During the second experiment, the temperature did not vary significantly and stayed around 24°C, and so did pH, fluctuating within the values of 7.5–8.2 as it was observed during the first experiment. Dissolved oxygen (DO), however, increased from its initial value of 5 mg/l to 7.8 mg/l (Fig. 4c). Created hypoxia in the water column caused more dissolution of Fe^{+2} in the water column (Fig. 4d). In fact, at the end of the second experiment, the concentration of Fe^{+2} in the water column doubled as compared to the first experiment. Created hypoxia caused more dissolution of manganese in water although this increase was trivial as compared to the increase of Fe^{2+}.

During experiment 3, the water column was aerated at a flow rate of 60 L/hr using an air diffuser designed for aquariums. As expected, aeration led to a faster increase of DO levels from 5 mg/l to 7.9 mg/l as compared to non-aeration cases (Fig. 4e). Aeration caused a significant decrease of Fe^{+2} concentration reaching zero. We believe aeration did not eliminate the formation of reduced Fe^{+2} instead pushed the oxic-anoxic boundary to the sediments. Total manganese and iron levels were not affected by the aeration of the water column when their levels were compared with the results of the second experiment where aeration was not applied (Fig. 4f). In contrast to iron, manganese oxidation kinetics are slower, and manganese persists in the water column longer after initiation of hypolimnetic aeration (Gantzer et al., 2009).

In experiment 4, the pH increased from 5 to 6 in 24 hours and then remained at 6 for the following 72 hours (Fig. 4g). An increase in DO concentration from 5 mg/l to 8 mg/l during the experiment was observed. There was no considerable change in water temperature. When the results of acidic water conditions (Fig. 4h) were compared with the results of neutral water conditions (Fig. 4d), concentrations of total Fe, Fe^{2+}, and total Mn in the acidic water were considerably greater than the neutral conditions. Manganese concentration in the water column reached to 0.770 mg/L at the end of the 96 hours where its counterpart for the neutral conditions was only 0.229 mg/L. Similarly, Fe^{2+} concentration in the water column reached 0.220 mg/L at the end of the 96 hours whereas it was 0.096 mg/L for the neutral conditions.

In experiment 5, the pH decreased from 11 to 10 in 24 hours and then remained around 10 for the following 72 hours (Fig. 4i). Also, as it was the case in the previous experiment, DO increased from 5 mg/l to 8 mg/l and no significant variation of temperature was observed. Total Fe, Fe^{2+} and total Mn concentrations showed a considerable decrease in alkaline water conditions (Fig. 4j). In fact, total Mn concentration decreased to 0.174 mg/L at the end of four days whereas this value was 0.770 mg/l for acidic and 0.261 mg/l for neutral conditions.

Variation of the water quality parameters during the sixth experiment is given in Figure 5a. The pH values fluctuated between 7 and 8. Temperature values also fluctuated around 29°C, higher than the previous experiment due to heating of the water column. DO concentrations increased from 5 mg/l to 7.5 mg/l during the experiment, as was the case in the previous experiments. The results showed that the solubility of both iron and manganese were significantly higher in stratified conditions as compared to the mixed water column (Fig. 5b). The values of total Fe, Fe^{2+}, and total Mn concentrations were 0.282 mg/l, 0.199 mg/l, and 0.781 mg/l at the end of the sixth experiment whereas at the end of the second experiment they were 0.112 mg/l, 0.096 mg/l, and 0.261 mg/l, respectively.

In the seventh experiment, pH values fluctuated between 7.5 and 8.1, temperature values were around 29°C due to heating of the water column, and DO concentrations increased from 5 to 7.6 (Fig. 5c). Results showed that the solubility of both iron and manganese were significantly higher in stratified conditions as compared to the mixed water column (Fig. 5d). Aeration of the water column had a slight effect on lowering the concentrations of total Fe, Fe^{2+} and total Mn.

Time variation of monitored total iron (Fig. 6a), ferrous ion (Fig. 6b), and total manganese (Fig. 6c) concentrations at the water column measured at 5 cm above the sediment

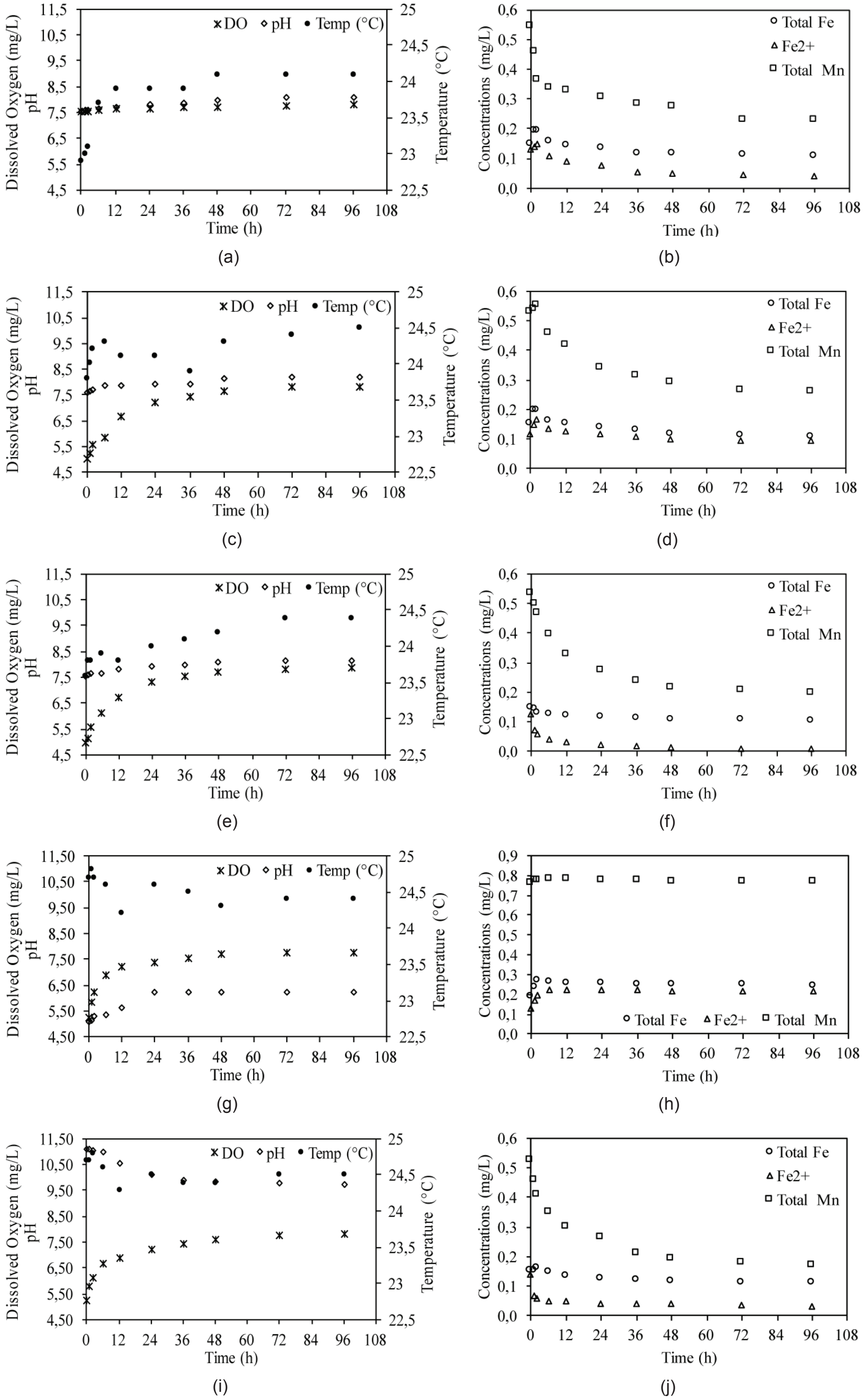

Figure 4. Variation of DO, pH, and temperature during the experimental runs 1 (a), 2 (c), 3 (e), 4 (g), 5 (i). Variation of Total Fe, Fe^{2+} and Total Mn in experimental runs 1 (b), 2 (d), 3 (f), 4 (h), 5 (j).

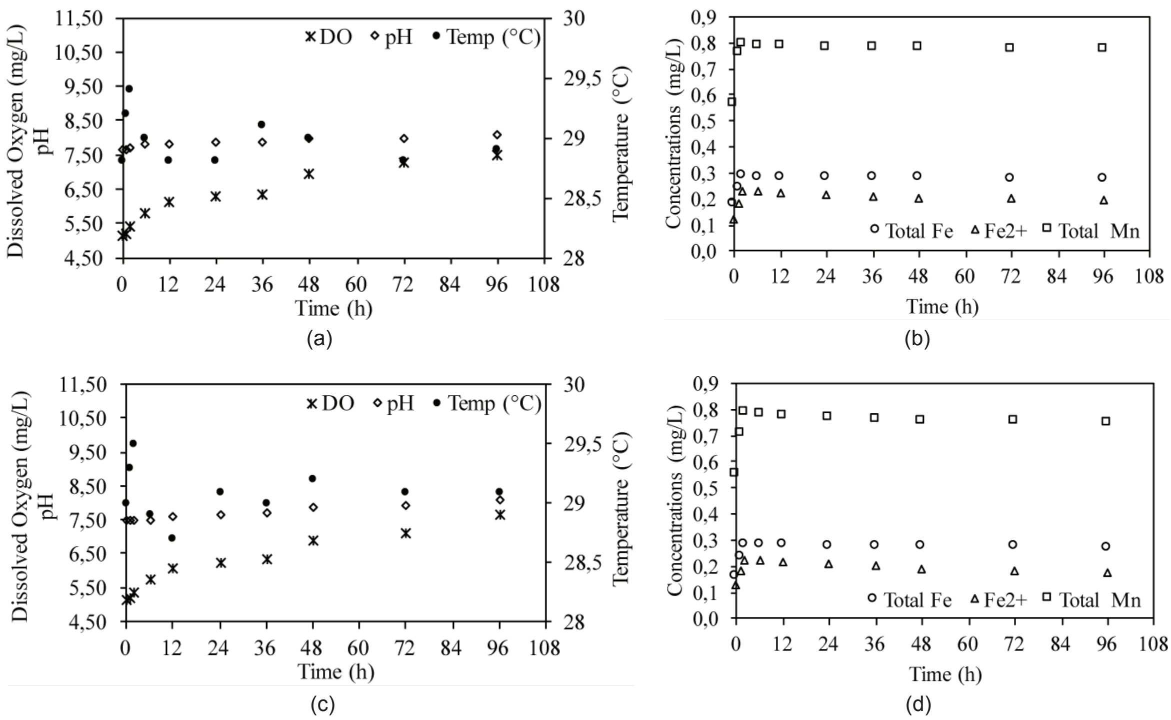

Figure 5. Variation of DO, pH, and temperature during the experimental runs 6 (a) and 7 (c). Variation of Total Fe, Fe^{2+} and Total Mn in experimental runs 6 (b) and 7 (d).

container was presented for all seven experiments. As stated by other researchers (Munger et al., 2016), hypolimnetic aeration alone might not be sufficient to remove manganese from the water column. Because the abiotic oxidation rate of manganese is pH-dependent, lakes and reservoirs might experience critical manganese problems due to slightly acidic conditions (pH 5.6 to 7.5). Increasing DO levels may decrease soluble Mn concentrations by facilitating manganese oxidation, adsorption to other particles and ultimately precipitation to the sediment ([4], [9]). Researchers also pointed out that oxygen dynamics and biogeochemical processes were variable at the sediment-water interface and thus changed in the sediment oxygen uptake rate may occur. In these studies, the influence of oxygenation on sediment-water fluxes of manganese is also stated as unclear. Even in oxic conditions, sediments may continue releasing elements as reported by other researchers ([4], [7]).

CONCLUSIONS

Present study investigated the release mechanism of iron and manganese from the sediments to the water column and was expected to serve as a guide for better management practices under the increasing stresses related to climate change and urbanization. The processes which control concentrations of iron and manganese become complicated when these stresses result in unfavorable conditions such as hypoxia and high acidity levels. Hypoxia, which occurs in reservoirs following nutrient-induced algae production and formation of thermally stratified layers, is observed in many reservoirs around the world. Reservoirs in Turkey, including the Tahtali Reservoir, are no exception since warming of the water bodies in summer is a common phenomenon and unfortunately nutrient inputs occur mostly due to agricultural activities. Thus, deterioration of water quality in water supply reservoirs is a current and crucial issue to tackle. Aeration, which is preferred as a water quality improvement method by many professionals around the world, is selected for this analysis and the release mechanisms of the iron and manganese were investigated under aeration of the water column. Finally, the acidity of the reservoirs that was highly affected by urbanization and its deteriorating effects was considered for the analysis. Release mechanisms of iron and manganese from the sediments to the water column were studied under different acidity conditions of the water column.

Main findings of this study were summarized as:

1) Hypoxia increased Fe^{+2} concentration in the water column. It resulted in more dissolution of manganese in the water column as well, however, this increase was trivial as compared to the increase of Fe^{2+}.
2) Aeration of the water column caused significant decrease of Fe^{+2} concentrations (in this case

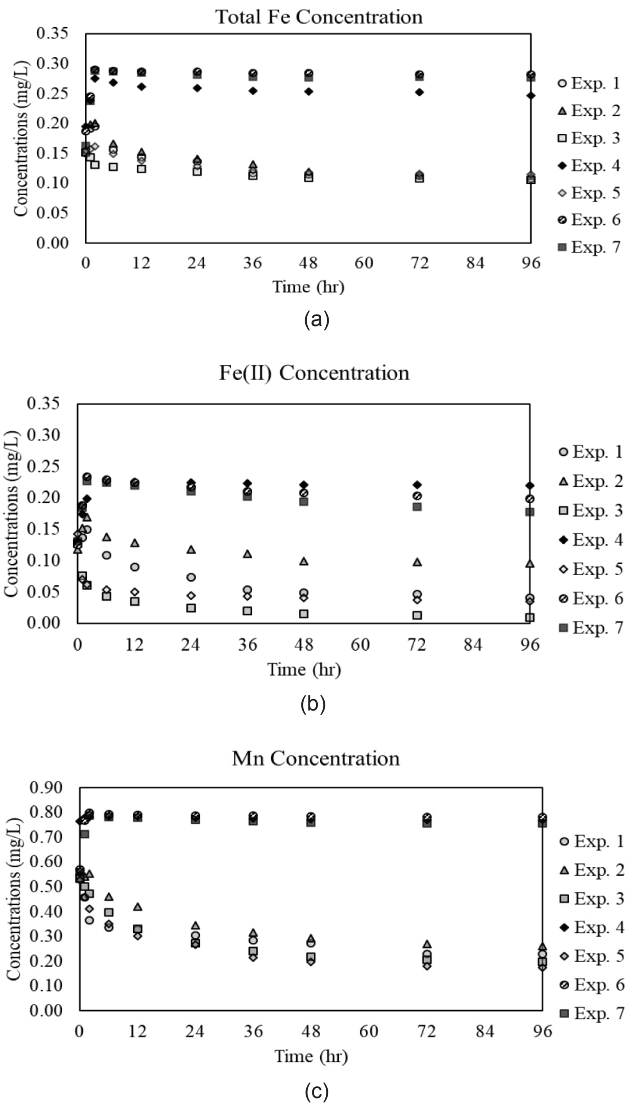

Figure 6. Comparison of total iron (a), ferrous iron (b), and total manganese (c) concentrations in seven different experiments.

reaching to zero). We believe aeration did not eliminate the formation of reduced Fe^{+2} instead pushed the oxic-anoxic boundary to the sediments. This is not the case for manganese and total iron levels were not affected by the aeration of the water column.

3) It was observed that acidity level of the water column had a great effect on the solubility of iron and manganese. When the results of acidic water conditions (pH = 5) were compared with the results of neutral water conditions (pH = 7), the concentrations of total Fe, Fe^{2+}, and total Mn in the acidic water were considerably greater than the neutral conditions. According to the results, all total Fe, Fe^{2+} and total Mn concentrations showed a considerable decrease in alkaline water conditions. Manganese concentration in the water column reached 0.770 mg/L at the end of the 96 hours where this value was observed as 0.229 mg/L for the neutral conditions. Similarly, Fe^{2+} concentration in the water column reached 0.220 mg/L at the end of the 96 hours where this value was observed as 0.096 mg/L for the neutral conditions. Alkaline water conditions (pH = 11) had an opposite impact on total Fe, Fe^{2+}, and total Mn concentrations, lowering the concentrations observed during the neutral water conditions.
4) Solubility of both iron and manganese increased in stratified conditions as compared to the mixed water column. Aeration of the stratified water column had a slight effect on lowering the concentrations of total Fe, Fe^{2+} and Mn.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Deposit refund system for beverage containers as a best practice example for recycling maximization

Erdem GÖRGÜN*[1], Kardelen Afrodit ADSAL[1], Aybike MISIR[2], Eyüp Vural AYDIN[3], Çağdaş Evrim ERGÜN[4], Nihan KESKİN[2], Aynur ACAR[5], Şeyla ERGENEKON[6]

[1]Department of Environmental Engineering, İstanbul Technical University, İstanbul, Turkey; [2]IO Environmental Solutions R&D Co., İstanbul, Turkey; [3]İstanbul PPPCOE, İstanbul, Turkey; [4]Ergün Çevre, Ankara, Turkey; [5]TÜÇEV, İstanbul, Turkey; [6]Ergenekon Consulting, İstanbul, Turkey

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ABSTRACT

Packaging waste has a detrimental impact on the pollution of the ecosystem unless it is not managed properly. Many countries try to solve this problem by collecting beverage packaging before it gets mixed with other wastes and sends the beverage packaging to recycling facilities. In order to reproduce a packaging material, in the exact same form and quality as the materials produced from the raw material, the quality and status of the used material become rather important. Therefore, a specific method, among others, becomes prominent for the re-collection of the used beverage packaging, before these become wasted and contaminated. This system is called the "Deposit Refund System (DRS)". In the DRS, each beverage packaging shall have a certain deposit value and with each purchase, the consumer shall pay that deposit value in addition to the product price. This system leads the way to a clean and effective collection of recyclable beverage packaging. The aim of this study is to draw attention to the importance of packaging waste, to introduce the Deposit Return System, which is the best management method of used beverage packaging in the world, and to introduce the reader to the main lines of the deposit return system we have developed for Turkey. In this study, we have researched the best practices of DRS and examined the implementation of the system. The methodology we used included a detailed examination of all the administrative, technical and economic processes necessary for the sustainable implementation of the subject. The success of the system depends on a clear structuring and outlining of the relationships, duties, authorities, and responsibilities of each stakeholder. Accordingly, the legal framework shall set forth a comprehensive framework, in order to regulate all procedures and principles relating to the DRS. The main outcome of the study is to determine the advantages of implementing the DRS in Turkey, for beverage packaging waste management. In addition, we analyze the governance models of DRS, where the DRS is run by an Operator. We examine the alternative governance models, such as state-owned and Public-Private Partnership (PPP) models other than "non-profit organization model" which is common in EU countries. We further elaborate on the financial sustainability of the PPP projects and how to create "bankable projects". As an innovative model for the DRS, we created a well-structured finance model with a resilience revenue stream in the PPP option for long-term public services. The DRS is one of the best implementation mechanisms for the separate collection of packaging waste. In the countries where DRS is applied, recycling rates

***Corresponding author.**
*E-mail address: gorgune@itu.edu.tr

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reach up to 98% for beverage containers [1]. DRS in Turkey can increase recycling rates up to 70% for PET, glass, and aluminum materials. This outcome leads more efficient and closed-cycle source management. The New Circular Economy Action Plan by the EU aims to design the entire life cycle of products while promoting circular economy processes, fostering sustainable consumption, and aiming to keep resources available as much as possible in the EU's economy. Lastly, we also considered and examined other environmental benefits of the DRS in Turkey.

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INTRODUCTION

Human consumption behavior is the main parameter for environmental pollution. Especially now in today's globalized world, using fast-moving consumer goods has become more widespread, eventually resulting in a significant increase in waste generation. This increase is ominously caused by the packaging wastes, especially with its implicit economic value.

The materials used in the packaging industry are plastics, metal, glass, paper, wood, and composites. The food and beverage packaging, which commonly uses plastic, metal, glass and composite materials has a market share amounting to approximately 70% in the overall packaging sector [1]. In 2018, 1,167.5 billion liters of packaged beverages were consumed worldwide [2] while 1,292 billion liters in 2020 [3].

As can be seen from the figures, the waste generated by the consumption of beverage products has increased in recent years. The beverage industry mainly uses plastics, metal, glass, paper, wood and composites as packaging materials. Some of these materials can be recycled and reused as raw materials in packaging production process, instead of virgin materials. The replacement of recycled materials enables to conserve the resources which are mostly consumed in fast-moving sectors. However, quality of the recycled materials is an important parameter to realize the replacement. The recycled materials must sustain a certain quality standard for replacement and this depends on the condition of the materials after their usage. The collection methods may have positive and negative impacts on the condition of the materials. Therefore, separate collection mechanisms for recyclable materials should be provided, in order to keep the quality of such products at a certain level.

DEPOSIT REFUND SYSTEM

The Deposit Refund System ("DRS") is a recycling system in which consumers pay a small deposit value for beverage containers, which can be refunded upon return of the used container to a collection point. DRS is very important for achieving circularity, resource management and clean collection of the materials. The clean collection of the materials enables to sustain high quality in recycled materials.

DRS is one of the methods to perform Extended Producer Responsibility ("EPR"). EPR is a policy approach under which producers are given a significant responsibility – financial and/or physical– for the treatment or disposal of the post-consumer products [4]. DRS has been implemented in more than 40 countries around the world as a part of the EPR policy and has achieved considerably high recycling rates.

Figure 1 shows the operation of the DRS; the flow of deposits, fees, beverage containers and information in general. According to EPR, producers finance the system to reach the recycling targets which are defined by the governments. Retailers are one of the most important stakeholders of the systems since they serve as collection points to which the customers can return empty containers. The DRS Operator, on the other hand, manages, controls, and operates the system.

The governance of the DRS Operator may differ from country to country. In the most common implementations, the DRS Operator is a non-profit organization which is founded by producers and retailers. However, there are few examples in which the DRS Operator is a governmental organization. In Table 1, stated below, different implementations of the DRS across Europe are shown. As it can be seen from the table, most of the countries have a centralized operating system and the operations are carried out by the Non-Profit Organizations. Nevertheless, in Germany, although the system operator is a Non-Profit Organization, the operating system is decentralized. On contrary, Croatia has a centralized operating system like many others but the system is operated by a Governmental Organization.

The return (recycling) rates of European Countries under the DRS are stated in the Figure 2, below. The figure demonstrates that Germany has the highest return rate with 98%. Even though Estonia has the lowest return rate, it still has a considerable rate of 83% [6]. The main reason of reaching a higher return rate with the DRS is motivation of the consumers to receive the deposit that they paid. When the consumers pay a deposit in addition to the product price, they are more motivated to bring empty containers in order to receive the deposit back.

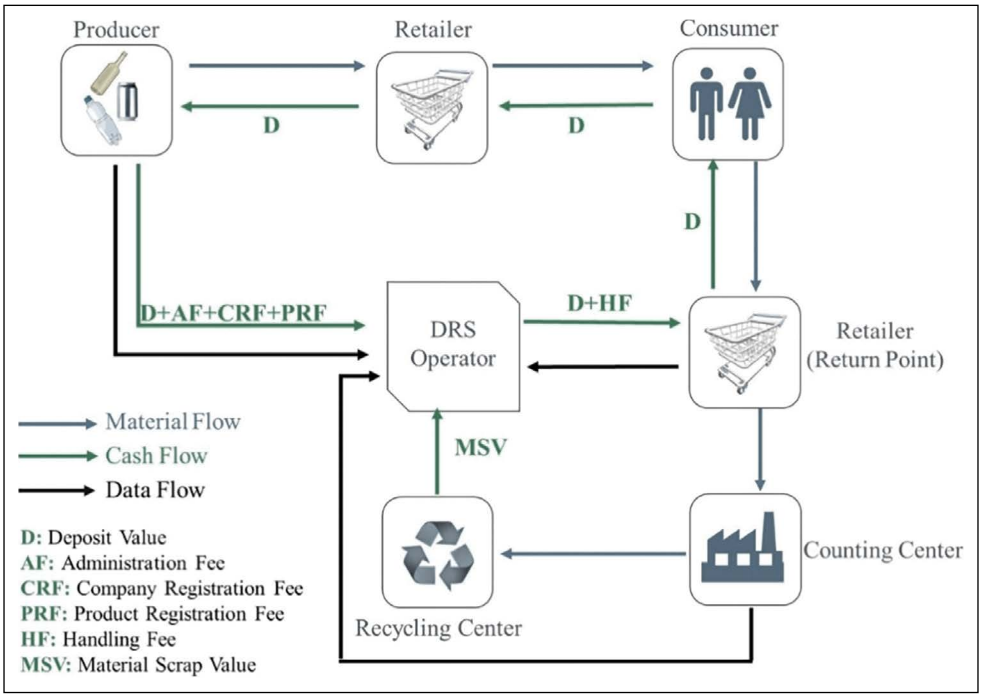

Figure 1. Flow of deposit, fees, containers, and information in the general drs [5].

DRS is not only a beneficial model for achieving the high recycling targets, but also, it has various economic and environmental benefits. The waste management cost of local authorities may decrease with the implementation of the DRS. Apart from the cost reduction, recyclable materials do not lose their material value in the containers where

Table 1. Implementation of the DRS in European countries [6]

Country	Mandate enacted	Mandate Implemented	Operating system	Included material
Estonia	2004	2005	Centralized (Non-Profit Organization)	Plastic (mainly PET), metal (aluminum/steel), glass
Sweden	1982, 1991	1984 (Metal), 1994 (PET)	Centralized (Non-Profit Organization)	PET, metal
Croatia	2005	2006	Centralized (Governmental Organization)	Plastic (predominantly PET), metal (aluminum/tinplate), glass
Denmark	2000	2002	Centralized (Non-Profit Organization)	Plastic (predominantly PET), metal (aluminum), glass
Iceland	1989	1989	Centralized (Non-Profit Organization)	Plastic (predominantly PET), metal (aluminum), glass
Finland	Not Available	1996 (Metal), 2008 (PET), 2012 (Glass)	Centralized (Non-Profit Organization)	Plastic (predominantly PET), metal (aluminum), glass
Lithuania	2014	2016	Centralized (Non-Profit Organization)	Plastic, metal, glass 0.1 L – 3 L
Norway	1997	1999	Centralized (Non-Profit Organization)	Plastic (predominantly PET, HDPE), metal (aluminum/tinplate)
Netherlands	2003	2005	Centralized (Non-Profit Organization)	Plastic (>0.5l predominantly PET)
Germany	1991	2003	Decentralized (Non-Profit Organization)	Plastic (predominantly PET), Metal (aluminum), glass

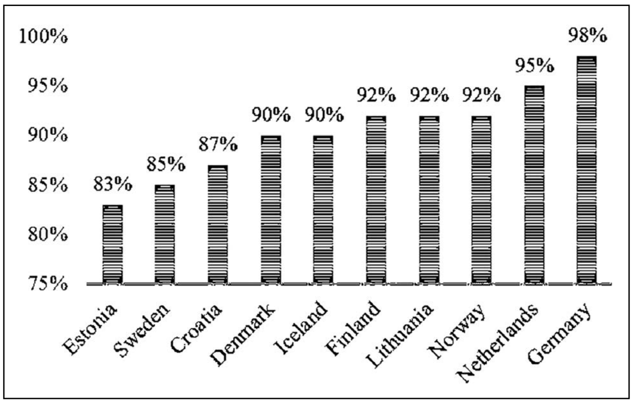

Figure 2. Return rates in European countries where DRS is applied [6].

they are mixed with municipal organic waste in the landfill facilities. Such materials can be recycled into high-quality materials with a source separation model. The source separation is significantly important for the recycling industry. The scrap material must sustain a certain quality level in order to be used as raw material for production. Currently, Turkey cannot implement source separation model effectively. For this reason, Turkey imports scrap plastic, glass, and aluminum from Europe to run the high-tech recycling facilities. In 2019, Turkey spent around 665 million, 10.7 million and 1.040 million Turkish Lira to import plastic, glass, and aluminum scraps respectively [7]. After the implementation of the DRS, the import rate of recyclable materials is expected to decrease as a result of the high return rates of used beverage containers achieved by the system.

MATERIAL AND METHODS

In this study, initially, the implementation of the Deposit Refund System in other countries was analyzed in detail [6, 8]. The research involved the analysis of administrative, technical and economical processes of the system in different countries. Then, necessary data were collected from the Ministry, relevant stakeholders and literature. After analyzing the collected data, it was made available for the Turkey-specific DRS setup as a result of a series of meetings with the Ministry and relevant stakeholders.

In administrative analysis, the governance models, stakeholders and their responsibilities were examined. In technical study, collection methods of beverage containers, beverage container materials and beverage types included in the system, container monitoring, data security, method for the refund of deposit to the consumers (manually or via Reverse Vending Machines) were examined. In economic analysis, all revenues, operational and initial investment costs of the DRS were analyzed.

After that, the most effective and ineffective system alternatives were searched and system requirements for Turkey were determined by taking the results of Turkey Deposit Refund System Project (TÜDİS), which was performed by the Ministry of Environment and Urbanization, as a reference [9]. While determining the social, environmental, and economic benefits of the implementation of the DRS in Turkey, the findings of the TÜDİS Project have been utilized. What makes the study unique is the analysis of Public Private Partnership (PPP) model in order to provide the most sustainable financial structure and the most effective system suggestion for the DRS. Finally, the best available Deposit Refund System structures are set out in the study.

RESULTS AND DISCUSSION

The system has numerous benefits which could be achieved in consideration of several factors. First of all, the governance structure should be constituted well. Responsibilities must be shared between stakeholders properly. Producers must have responsibilities to establish and finance the DRS. Hence, they must pay some fees to the DRS. Retailers must be responsible to collect empty containers from the consumers. For this reason, retailers' operations also play a key role in the DRS because reaching the recycling targets depends on the rate of consumers' return. HORECAs (hotel-restaurant-café) must also collect beverage containers which are included in the DRS separately. It is also important to raise the awareness of the consumers who have a significant role in reaching the target rates of collection and achieving clean collection of beverage containers.

There are two options for collection: Manual collection and collection with Reverse Vending Machines (RVMs). In manual collection, beverage containers are accepted from consumers by retail staffs. The retailers scan the barcode of containers with cash registers or handsets for counting of containers. When the RVMs are used for the return of containers, consumers can refund the deposit via machines. Most of the RVMs compact the PET and metal containers inside the machine. Glasses are kept without being broken.

There are two options for refund of the deposit value to the consumers. Depending on the consumer's preference, the deposit value corresponding to the return of packaging is paid to the consumer in cash or a voucher equal to the deposit value can be provided to the consumer to be used in the same store for another purchase.

Control of the DRS operations and material-data-finance flow are other significant elements of a successful DRS. Material-data-finance flow can be monitored through a well-designed software.

Revenues of the DRS can be classified as one-time revenues and constant revenues. The product registration fee and the company registration fee are one-time revenues whereas the administration fee, material scrap value and the unre-

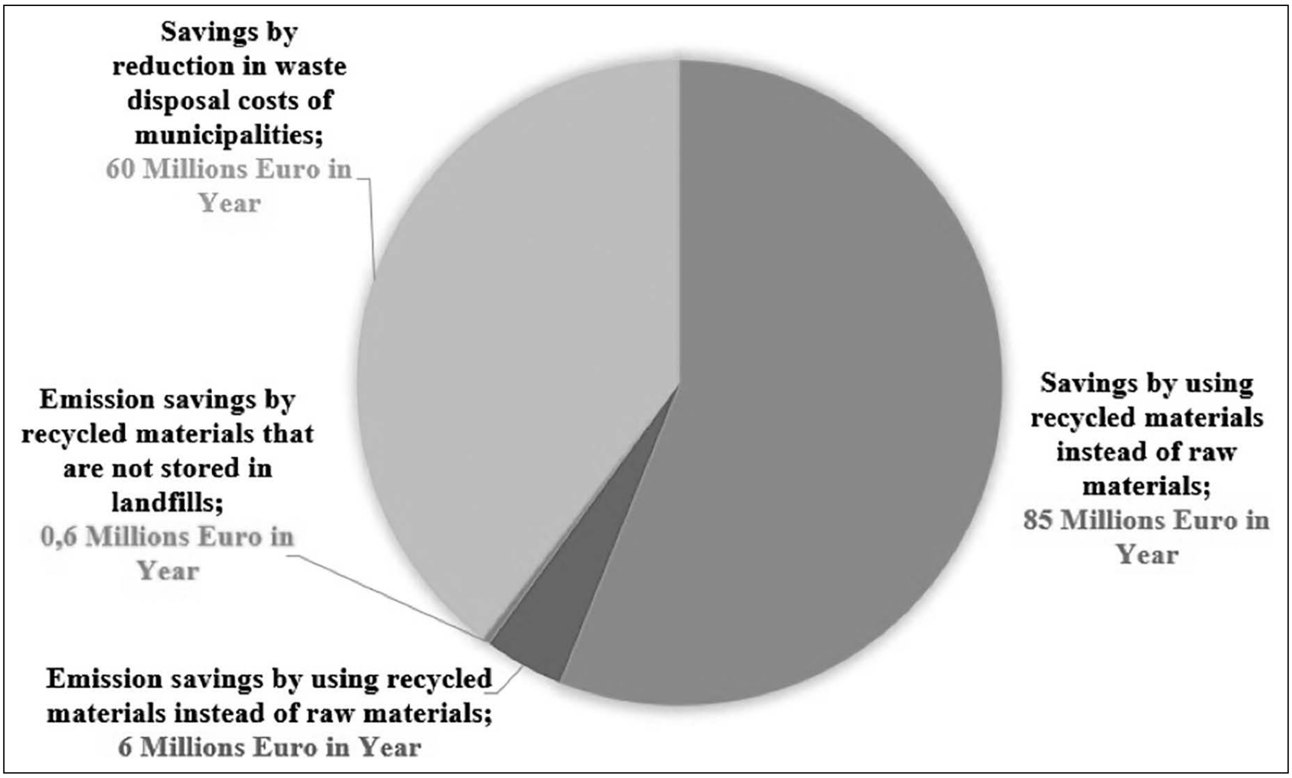

Figure 3. Estimated economic benefits of the DRS for Turkey in the first implementation year [9].

deemed deposit value are constant revenues. Costs of the DRS can be separated into two main parts: Investment costs and operational costs. Investment costs are incurred while building the counting centers and setting up the Reverse Vending Machines. Operational costs are generally classified as logistic costs, handling fees and other operational costs (central admin system, label, DRS bag).

System efficiency is an important factor to provide a sustainable DRS. System efficiency depends on required timing to implement the DRS, the balance between revenues and costs of the system and used technologies during investment and/or operation period and so on. At this point, it could be said that the Public-Private-Partnership (PPP) model is more advantageous than other governance models.

Public-Private Partnership (PPP) Model for the DRS

PPP model has many advantages for public projects. Under the PPP model, projects are realized with the involvement of private sector investors and financial institutions. Management tools can be used effectively in the PPP model and thus, many innovations can be made to monitor the market [10].

Firstly, the private sector can act faster. The best available technologies can be used in the investment and/or operation period. Secondly, the private sector provides excellent performance for profitability. Therefore, system can be more recoverable and efficient. In PPP model, all risks are shared between the public and the sector. It is also possible to access the best practice in PPP projects to benefit from the project more effectively and in a more innovative way in order to increase the quality of the service. For a successful implementation of the DRS under the PPP model, there are preliminary issues, which must be dealt with as demonstrated below:

- The existing legal infrastructure must be identified to determine deficiencies (if necessary).
- The areas included in the projects, the stakeholders who will take responsibility during the operation phase, how the process will be controlled and how the service will be monitored by the state, should be planned.
- An effective monitoring and coordination mechanism must be ensured in order to detect inefficiencies in time and to reduce the costs incurred.
- Internal capacity must be developed for the continuity and sustainability of the PPP projects and for an effective control and coordination by the institutions.
- It is essential to work with independent consultants to develop the PPP project and to carry it to the project implementation phase.
- All stakeholders must be informed and engaged in every step of the PPP Project. (This is extremely important for the success of the project as it has been identified in many exemplary projects.)

Economic and Environmental Benefits of the DRS

DRS has many economic and environmental benefits since it is one of the best ways for the separate collection of beverage containers. With the DRS, beverage containers can be collected without being mixed with other waste. Therefore, their economic value for sale does not decreases caused by any contamination. Accordingly, the waste management service fees decrease. Beverage containers are not thrown to the municipal waste containers at curbsides. Materials are saved and resource recovery is provided.

Mining activities to obtain virgin materials will be reduced. Since the required material can be collected with the DRS, there will be no need to import waste material. The recycled material will be used in new production.

Turkey imports waste PETs to use in textile and plastic industry. If the DRS is implemented in Turkey, it is assumed that the import rate of used raw material will decrease by 42%. With this way, the current deficit can be reduced as well. Furthermore, with the reduction in carbon emission, saving of raw materials and decrease in the waste disposal cost of municipalities many economic benefits can be provided. Figure 3 shows the estimated economic benefits of the DRS for Turkey within the first implementation year [9].

In addition to the economic benefits stated above, there are also several environmental benefits of the DRS for Turkey, which are listed below:

- Decrease in sea, land and air pollution,
- Reduction of approximately 1 million tons of waste annually,
- Reduction of carbon emissions,
- Extension of landfills' lifespan due to a decrease in the amount of waste being sent to landfills,
- Saving and effective use of raw materials and resources,
- Decrease in fossil fuel-based energy consumption in packaging production,
- Development of technology and capacities of recycling facilities in Turkey [9].

Lastly, it must be noted that, with the implementation of the DRS, 6 of the Sustainable Development Goals of the United Nations Development Program (UNDP) can be achieved. These goals are, namely Decent Work and Economic Growth (Goal 8); Industry, Innovation and Infrastructure (Goal 9); Responsible Consumption and Production (Goal 12); Climate Action (Goal 13); Life Below Water (Goal 14) and Life on Land (Goal 15). UNDP has aimed to ensure resource conservation, ecosystem prevention and sustainability in each stage of mining, production, logistic and consumption. Therefore, it is very important to achieve these goals in order to contribute to sustainable growth and to leave a better planet for future generations.

CONCLUSION

The implementation of the DRS, which enables the efficient use of country resources, is environmentally and economically vital for Turkey. In this sense, the system must be well-structured and constructed on a strong governance model. Under the PPP model, the system will be developed in a more effective, profitable and innovative way with the involvement of the private sector and financial institutions in the realization of the project. By establishing a strong infrastructure for the system, the waste management and separate collection of the waste at source will be improved as well. In line with the circular economy principles, it is anticipated that the bottle-to-bottle recycling will be enabled and resource efficiency will reach the highest level in general. Furthermore, the implementation of the DRS will also contribute to the achievement of the Sustainable Development Goals of the UNDP in Turkey.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Textile wastewater treatment by uv/fenton-like oxidation process using Fe-Cu doped pumice composite

Deniz İzlen ÇİFÇİ*, Süreyya MERİÇ

Department of Environmental Engineering, Tekirdağ Namık Kemal University, Çorlu Engineering Faculty, Tekirdağ, Turkey

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ABSTRACT

In this study, Fe-Cu-Pumice (Fe-Cu-P) composite was prepared to attempt it for UV/Fenton-like treatment of biologically treated textile wastewater by means of COD and color removal. SEM-EDX analysis showed that Fe-Cu-P composite contained Fe and Cu at 3.5% of each one. More than 95% color (RES-436, RES-525, RES-620) removal could be achieved using 3 g/L Fe-Cu-P in the Fenton-like process. The removal of COD and absorbances at Abs-254 nm and Abs-280 nm increased up to 5 g/L Fe-Cu-P concentration. In addition, the highest COD, Abs-254 nm and Abs-280 nm removal could be achieved at 250 mg/L H_2O_2 concentration pH 3. The removals of COD, Abs-254 nm and Abs-280 nm were obtained to be 63.7%, 66.3% and 72.9%, while the removals of RES-436, RES-525 and RES-620 were observed as 92.9%, 96.7% and 98.1%, respectively at optimum doses of catalyst (5 g/L Fe-Cu-P), oxidant (250 mg/L H_2O_2) and pH 3 after 3 h oxidation at room temperature.

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INTRODUCTION

The textile industry, one of the largest industries worldwide, has the highest water consumption [1]. Since textile wastewater has high stability and low biodegradability, includes toxic dyes, treatment by conventional wastewater treatment processes is difficult [2, 3], thus advanced oxidation processes (AOPs) have gained importance. Among advanced oxidation processes, Fenton process is one of the most favoured one as it provides advantageous such as high efficiency, inexpensive, low reaction time, and easy application [4, 5]. On the other hand, Fenton oxidation has also some disadvantages such as excessive iron sludge. Thus, coating iron oxides on composites have been developed for AOPs applications [6, 7]. Studies have been carried out on dye or organic matter removal with Fenton-like and Photo Fenton-like oxidation processes by iron coated materials such as activated carbon, zeolite and clay and it was stated that these processes improved removal of dye or organic matter [4, 7, 8]. Dükkancı et al. (2010) reported a 100% removal of 100 mg/L Rhodamine 6G dye after 45 min of Fenton-like oxidation using a 1 g/L CuFeZSM-5 zeolite catalyst and 40 mmol H_2O_2 amounts at pH 3.4 [9]. The best Reactive black 5 (RB5) dye removal was obtained as 89.2% with 0.5 g/L catalyst of iron (III) oxide doped on rice husk ash and 4 mM H_2O_2 at pH 3 and 100 mg/L initial RB5 concentration

***Corresponding author.**
*E-mail address: dicifci@nku.edu.tr

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by Fenton-like oxidation [10]. In addition, it was stated that the iron doped on materials such as zeolite and clay showed very good stability, and the iron concentration in treated wastewater was below 2 mg/L, which is the discharge standard in the EU directive [11, 12].

Having a high specific surface area and porous structure, pumice has been widely used for dye and metal adsorption [13]. Successful and remarkable results have been obtained in dye removal using the Fenton-like oxidation process with the synthesized magnetic iron coated pumice [14]. Furthermore, Fenton-like oxidation process proved the maximum COD, UV_{254}, UV_{436}, UV_{525} and UV_{620} removals to be 79.7%, 92.7%, 91.7%, 95.6% and 98.2% respectively using 7.5 g magnetite pumice composite catalyst at 500 mg/L H_2O_2, pH 3 during 120 min oxidation for a wastewater originated from a textile chemicals production industry [15].

However, the use of pumice bi-metal coated with Fe and Cu in the UV/Fenton-like oxidation process has not been studied so far that the aim of this study is to investigate the treatment of a biologically treated textile wastewater by Fenton-like oxidation process. For this purpose, the effect of Fe-Cu-P composite concentration, H_2O_2 concentration and pH on UV/Fenton like process performance was assessed in terms of COD, absorbances at 254 nm and 280 nm and color (RES-436, RES-525, RES-620) removal.

MATERIALS AND METHODS

Materials

The chemicals namely $CuSO_4.5H_2O$ (Cat No: 1.02790), hydrogen peroxide (H_2O_2 35% wt, Cat No: 1.08600), $FeCl_3.6H_2O$ (Cat No: 1.03943), NH_3 (25%, Cat No: 1.05422), $FeSO_4.7H_2O$ (Cat No: 1.03965), HCl (Cat No: 1.00314), HNO_3 (Cat No: 1.00456) and NaOH (Cat No: 1.06462) were purchased from Merck. All aqueous solutions were prepared using bidistilled water.

Treated Textile Wastewater

Biologically treated textile wastewater was collected from a dyeing and finishing textile industry located in Corlu, Tekirdag, Turkey. The sample kept at refrigerated (+4°C) without adding any conservative during analysis.

Synthesis of Fe-Cu-Pumice Composite (Fe-Cu-P)

Pumice was obtained from Nevşehir, Turkey. The particle size of pumice powder ranged from nano to micron (0–125 microns). $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ were first dissolved in 200 mL distilled water with the molar ratio of 2 between Fe^{3+} and Fe^{2+} in the solution according to literature [16, 17]. $CuSO_4.5H_2O$ was added into solution. Final Fe:Cu:Pumice ratio was adjusted to 5:5:100 as weight basis. An amount of 100 g pumice was added to this solution and the pH of the solution was adjusted to 9.5 by adding 6 N NaOH. The solution was ultrasonicated for 15 min and heated at 70°C for 1 hour. A 5 mL NH_3 solution was added into and stirred for 24 hours at room temperature. After 24 hours, composite was rinsed with distilled water for several times to remove dissolved ions from composite. Finally, the composite catalyst was dried at 105°C.

UV/Fenton-Like Oxidation Experiments

The UV/Fenton-like experiments were carried out in a UV Photoreactor equipped with ten UV-A light lamps (Philips, 8W, 350 nm wavelength). 3x2 lamps were positioned at left and right sides and 4 lamps were positioned on the top of the reactor. The lamps were switched off for 15 min as the dark adsorption process before starting the experiments. The experiments were carried out in 200 mL treated textile wastewater samples at a constant room temperature (25°C). pH was adjusted to the desired values by dosing 1 M NaOH and 1 M H_2SO_4. The effects of composite concentration, pH, H_2O_2 concentration on the process efficiency were studied ranging their values at the intervals of 1–5 g/L, 2–4 and 75–250 mg/L respectively.

Analysis

The wastewater samples were characterized for chemical oxygen demand (COD), total suspended and volatile solids (TSS and VSS), conductivity (WTW Cond 3210 Set 1 (2005), total khejdahl nitrogen (TKN) and ammonia-nitrogen (NH4-N), alkalinty, and pH (WTW pH 315i) parameters according to Standard Methods [18]. Absorbances at 254 nm and 280 nm and color (RES-436, RES-525, RES-620) were measured with a UV-Vis spectrophotometer (Shimadzu UV-2401) using 1 cm path length quartz cuvettes. Due to the aromatic nature of some organic compounds in wastewater, especially double bonds and aromaticity were characterized by Abs-254 nm and Abs-280 nm measurement, respectively [19].

Fe-Cu-Pumice composite was characterized by scanning electron microscope (SEM)-energy dispersive X-ray analyzer (EDX). FTIR analysis was performed using Bruker VERTEX 70 ATR in the range of 400–4000 cm^{-1}. The pH_{pzc} of the composite was determined according to the literature [20].

RESULTS AND DISCUSSION

SEM Analysis

SEM analysis and EDX profile of Fe-Cu-P composite are given in Figure 1. It is seen that Fe-Cu-P has irregular character. EDX spectrum of Fe-Cu-P composite showed that oxygen and silisium were the major elements. Fe-Cu-P mainly contains 50.9% O, 23.3% Si, 5.2% Al, 1.3% K, 12.5% Na, 0.22% Ca, 3.5% Fe and 3.5% Cu. It can be seen from Figure 1b that nano iron and copper particles were successfully doped on the surface of pumice as confirmed by EDX spectrum that Fe and Cu contents were at 3.5% in Fe-Cu-P

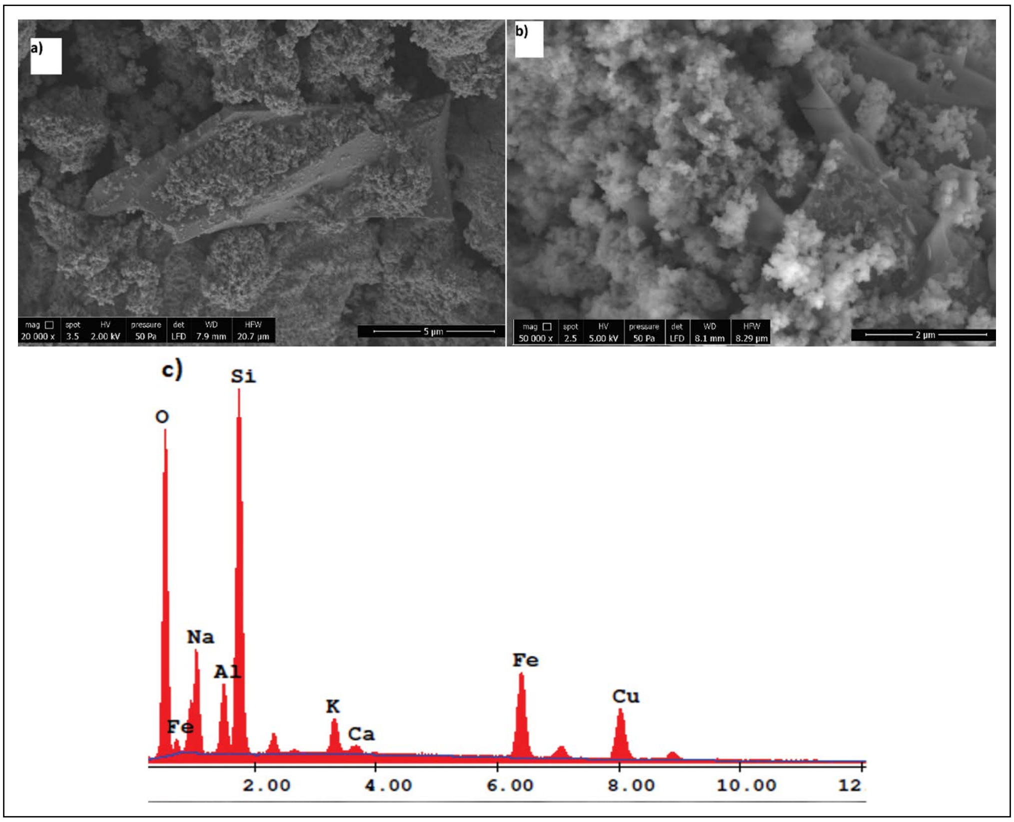

Figure 1. SEM images of Fe-Cu-P composite (a) 20000X (b)50000X (c)EDX analysis.

composite (Fig. 1c). The success of Fe and Cu coating on pumice in this study confirmed the study by Su [21] that coated zeolite with Fe and Mn metals for Fenton like oxidation of Reactive Brilliant blue dye.

FTIR analysis of Fe-Cu-P is given in Figure 2. At 995 cm^{-1} as the strongest peak is the Si-O-Si or Si-O-Al stretching vibration in pumice [22, 23]. The peak observed at 617 cm^{-1} is thought to be caused by Fe-O bond vibration [24, 25]. In addition, the peaks at 437 cm^{-1} and 617 cm^{-1} could also be due to Cu-O bonds [26, 27].

The pH_{pzc} is important to evaluate surface charge of the composite synthesized. If the solution pH is lower than pH_{pzc}, composite surface is positive and this provides a high adsorption capacity of anionic pollutants. On the contrary, if the pH of sample is above than the pH_{pzc}, surface of composite can be negative charged and this provides the increasing adsorption of cationic pollutants [20]. The value of pH_{pzc} was measured to be 5.87 and 10.09 of P and Fe-Cu-P composite, respectively. High value of pH_{pzc} of Fe-Cu-P composite gained affinity of a wide range anionic pollutions for adsorption.

Characterization of Biological Treated Textile Effluent

Characterization of the sample is given in Table 1. COD and color values need further removal according to Zero Discharge Hazardous Chemicals Limits [28].

Table 1. Characterization of biological treated textile wastewater

Parameter		Unit	Biological treatment effluent
pH		-	7.74
Conductivity		Ms/cm	4.2
Alkalinity		mg $CaCO_3$/L	251±1.3
TSS		mg/L	115±7.1
TVSS		mg/L	80±5.7
COD		mg/L	246±4.5
TKN		mg/L	67±7.5
Ammonia Nitrogen		mgNH_4-N/L	37±3.4
Abs-254 nm		Abs	3.544
Abs-280 nm		Abs	2.848
	RES-436	Abs	0.66
Color	RES-525	Abs	0.852
	RES-620	Abs	0.468

Effect of Fe-Cu-P Concentration on UV/Fenton-Like Process Efficiency

The effect of Fe-Cu-P composite amount on the removal of Abs-254 nm and Abs-280 nm is given in Figure 3. As can be seen in Figures 3a and 3b, Abs-254 Abs-280 significantly decreased by increasing catalyst dose. Above 2 g/L catalyst dose, both Abs-254 and Abs-280 gradually decreased up to 1.5 oxidation time and after that time the absorbances started to decrease down during 3 h oxidation time. The highest Abs-254 (66.3%) and Abs-280 (68.6%) removal was ob-

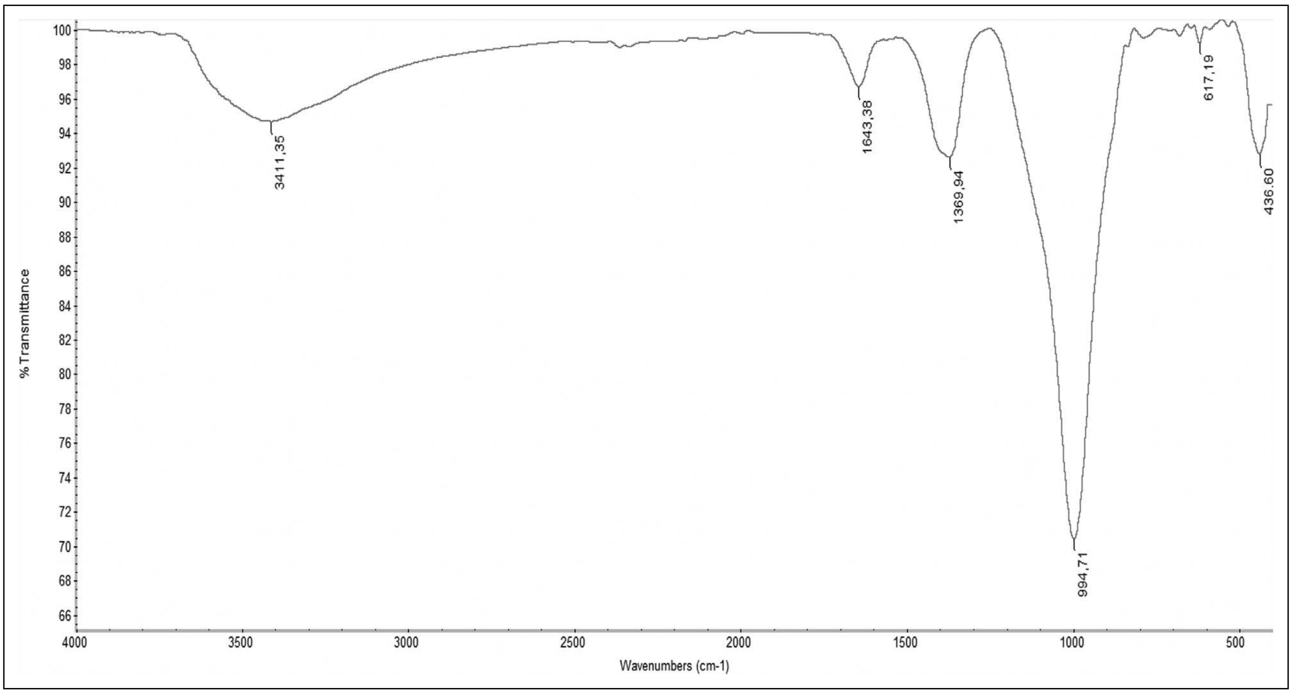

Figure 2. FTIR analysis of Fe-Cu-P composite.

tained with 5 g/L Fe-Cu-P composite dose at pH 3 and 250 mg/L H_2O_2. The effect of Fe-Cu-P amount on color removal (RES-436, RES-525 and RES-620) is given in Figure 4. The color (RES-436, 525 and 620) remained low in 1 g/L Fe-Cu P amount. RES-620 removal was seen to be similar in 2–5 g/L Fe-Cu-P amounts and over 98% removal was achieved. RES-525 and RES-620 removals were similar when Fe-Cu-P amounts of 4 and 5 g/L were used. After 3 hours of oxidation at 5 g/L Fe-Cu-P, the removal of RES-436, RES-525 and RES-620 were obtained as 95.6%, 98.7% and 98.9%, respectively.

The removal of COD using different Fe-Cu P amounts was given in Figure 5. While color removals were observed close at 2–5 g/L Fe-Cu P amounts, COD removal increased as the amount of Fe-Cu P increased in parallel with Abs-254 nm and Abs-280 nm removals. When increasing the amount of Fe-Cu-P composite from 4 to 5 g/L, the COD removal efficiency incremented from 53.7% to 63.7%, respectively. Not only organic matter removal but also aromatic structure degradation could be achieved in the treatment of textile wastewater by Fenton-like oxidation using Fe-Cu-P composite. Since the highest Abs-254 nm, Abs-280 nm and COD removal efficiencies were obtained at 5 g/L Fe-Cu-P, the optimum Fe-Cu-P amount was determined to be 5 g/L. Comparing with the previous literature, the removal of absorbance, color and COD was obtained lesser than the study that used 7.5 g of magnetite pumice composite as catalyst [15].

Effect of H_2O_2 Concentration on UV/Fenton-Like Process Efficiency

The changes of Abs-254 nm and Abs-280 nm removals depending on time and varying H_2O_2 concentration in the range of 75–250 mg/L, were given in Figure 6. While Abs-254 nm and Abs-280 nm removals were not observed below 150 mg/L H_2O_2 concentration, Abs-254 nm and Abs-280 nm removals improved from 19.2% to 66.3% and 36.0% to 72.9%, respectively when the H_2O_2 concentration was increased from 150 mg/L to 250 mg/L. At 250 mg/L H_2O_2 concentration, Abs-254 nm and Abs-280 nm removals continued for 2 hours, and no significant change in removals was observed after 2 hours of oxidation.

Similar removals of RES-436, RES-525 and RES620 were observed at all H_2O_2 concentrations. The RES-620 removal increased over 90% after 2 hours of oxidation, while RES-436 and RES-525 removals enhanced to above 90% after 2.5 hours (Fig. 7).

In parallel with Abs-254 nm and Abs-280 nm removals, COD removal was also achieved above 150 mg/L H_2O_2 concentration (Fig. 8). Altogether, the removal of Abs-254 nm and Abs-280 nm were obtained as 66.3% and 72.9% respectively at 250 mg/L H_2O_2 which were lower than a previous study [15].

Effect of pH on Textile Wastewater Treatment Using UV/Fenton-Like Process Efficiency

The changes of Abs-254 nm and Abs-280 nm obtained with different pH values at 5 g/L Fe-Cu P amount and 250 mg/L H_2O_2 concentration are given in Figure 9. As seen in the figure, Abs-254 nm and Abs-280 nm removal was dropped at pH 2 and 4 values, and when the pH was increased from 2.5 to 3, Abs-254 nm removal enhanced from 57.7% to 66.3% and Abs-280 nm removal increased from 65.0% to 72.9%.

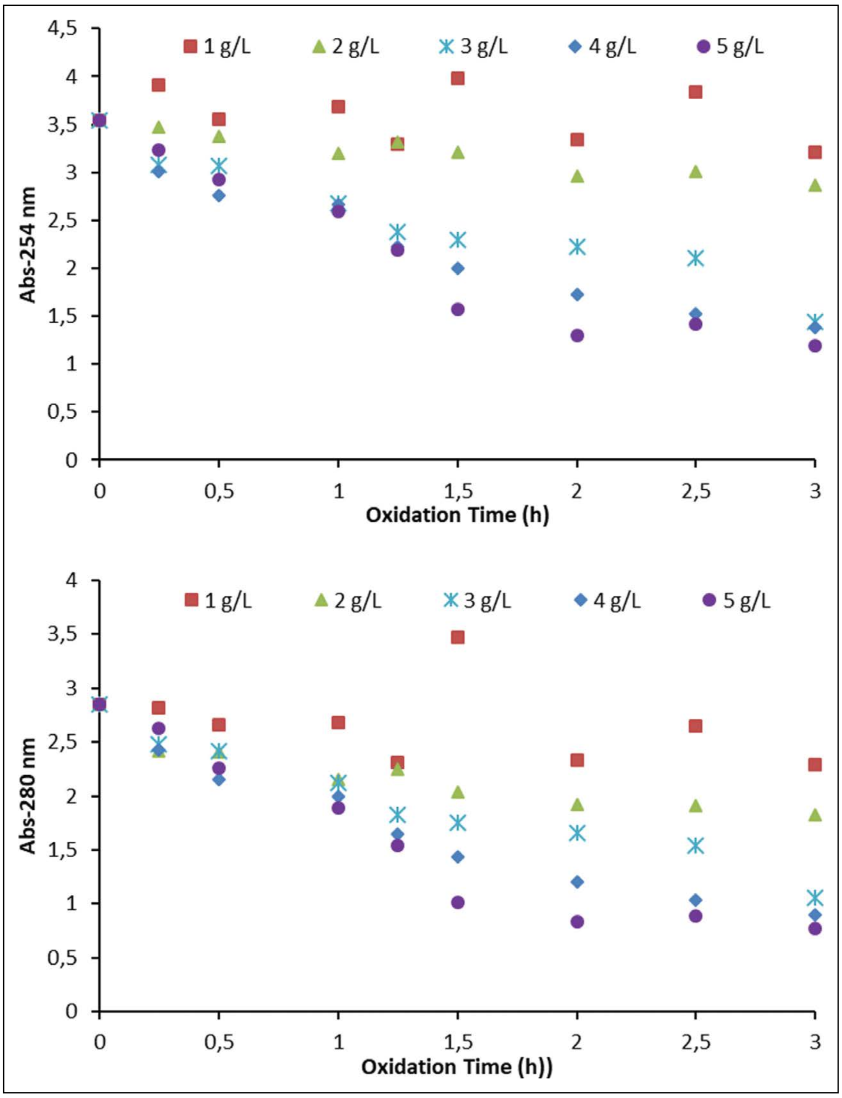

Figure 3. Effect of Fe-Cu-P catalyst amounts on the removals of Abs-254 nm and Abs-280 nm (pH: 3, H_2O_2 concentration: 250 mg/L)

Although the color removals (RES-436, RES-525 and RES-620) were similar in the pH range of 2–3, the removal of all colors at pH 4 values decreased (Fig. 10). RES-436, RES-525 and RES-620 removals were continued for 2 hours in the pH range of 2–3, and after 2 hours of oxidation, color removal as RES-436, RES-525 and RES-620 was observed over 90% between pH 2–3. RES-436, RES-525 and RES-620 removal were 92.9%, 96.7% and 98.1% at pH 3 after 3 hours oxidation. Both color and aromatic substance removals could not observed at pH 4. Although color removal observed at pH 2, aromaticity removal was low at Abs-280 nm and no removal was achieved at Abs-254 nm.

The COD removal at different pH values is given in Figure 11. Although the color removal as RES-436, RES-525 and RES-620 were similar in the pH range of 2–3, it was seen that the removal of COD, Abs-254 nm and Abs-280 nm gradually increased as pH increased from 2 to 3. The COD removal increased from 16.4% to 63.7%, when the pH was enhanced from 2 to 3 and 50.2% of COD could be achived at pH 2.5. In this study, optimum pH was obtained as 3 and this is generally the case in Fenton oxidation because H_2O_2 and HO. redox potentials decrease with increasing pH and H_2O_2 stability decreases at higher pH values [4]. In addition, iron hydro-complex which has the more photoactive properties become to dominate at near pH 3, as the pH increases less photo-active iron species begin to active and dominate [29, 30].

Kinetic Evaluation of UV/Fenton-Like Process

The first order kinetic values obtained in this study are given in Table 2. The k_1 values for Abs-254 nm and Abs-280 nm were calculated with the data obtained in the first 2 hours as there was no significant change in Abs-254 nm

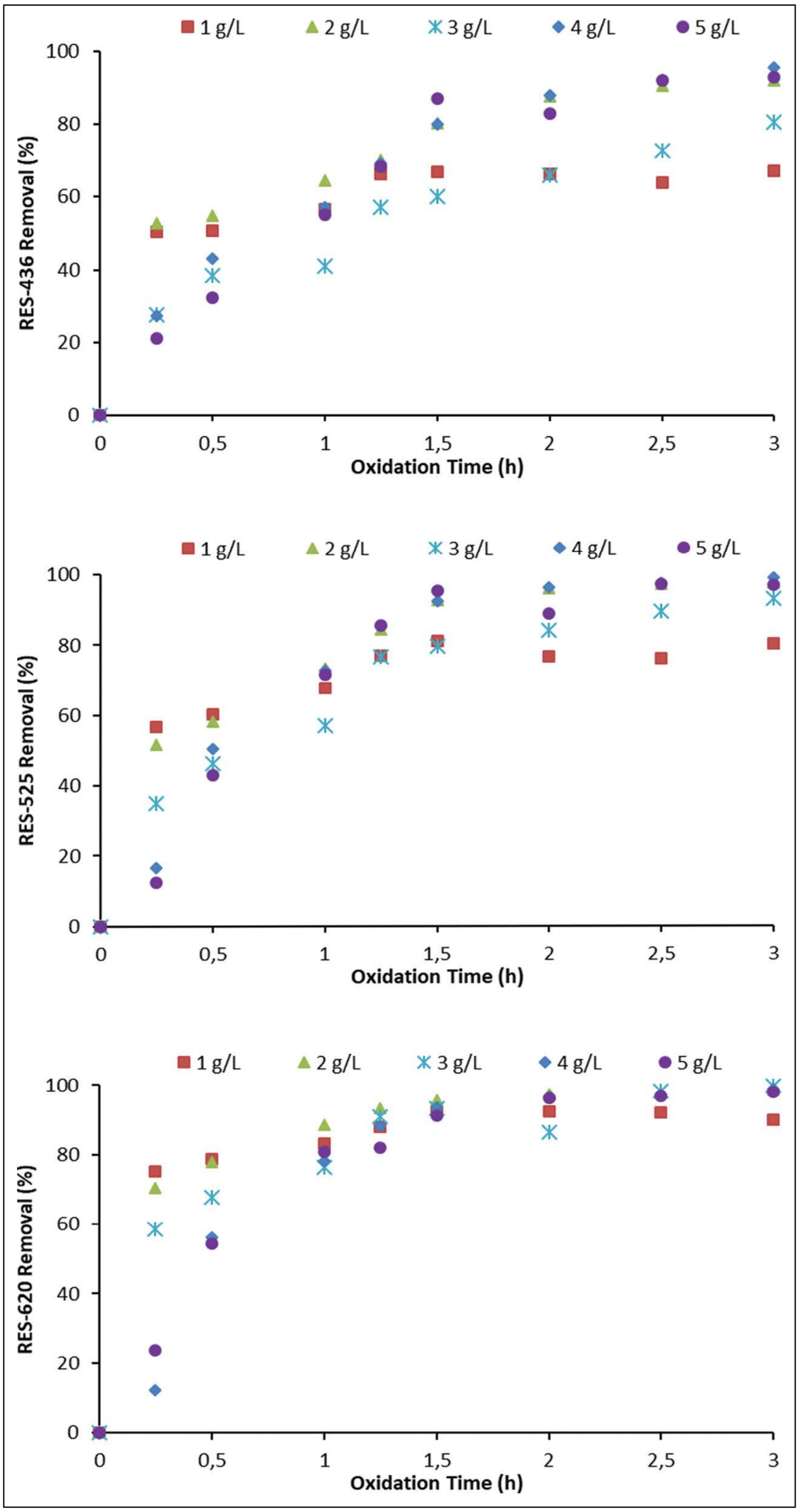

Figure 4. Effect of Fe-Cu-P amounts on color (RES-436, RES-525 and RES-620) removal (pH: 3, H_2O_2 concentration: 250 mg/L)

and Abs-280 nm in the 2–3 hours interval. With the same reason k_1 was calculated from the data obtained within the first 1.5 hours as the removal of RES-436, RES-525 and RES-620 occurred within the first 1.5 hours [14, 29]. Above a 90% removal of RES-436, RES-525 and RES-620 could be achieved at 5 g/L Fe-Cu-P composite concen-

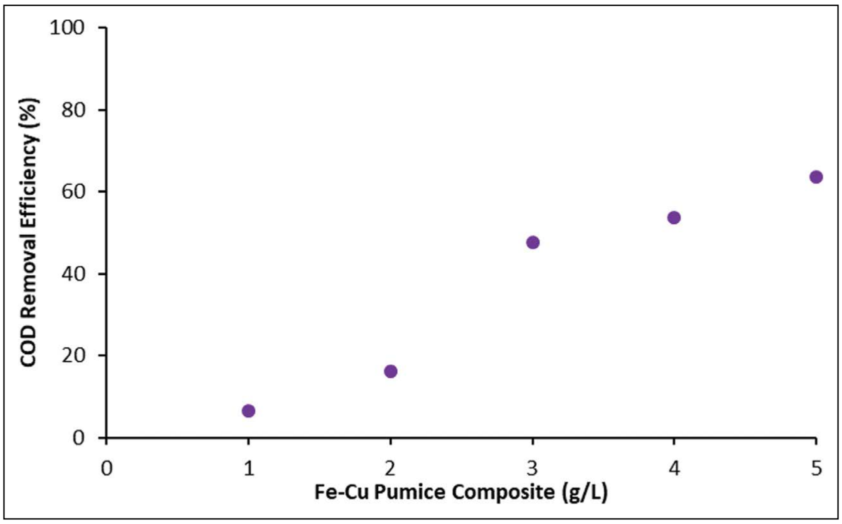

Figure 5. COD removal at varying amount of Fe-Cu-P composite (pH: 3, H_2O_2 concentration: 250 mg/L, oxidation time: 3h)

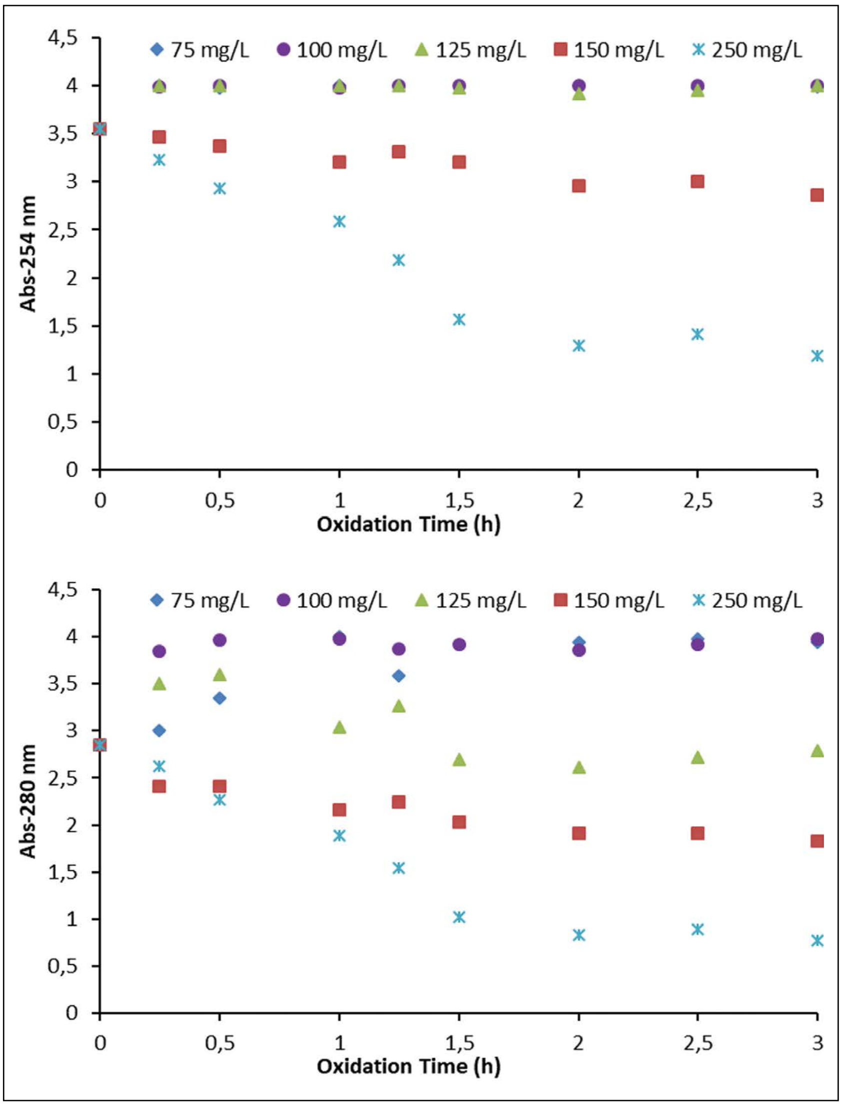

Figure 6. Effect of H_2O_2 concentration on absorbance removal (Abs-254 nm and Abs-280 nm) (pH: 3, Fe-Cu-P concentration: 5 g/L)

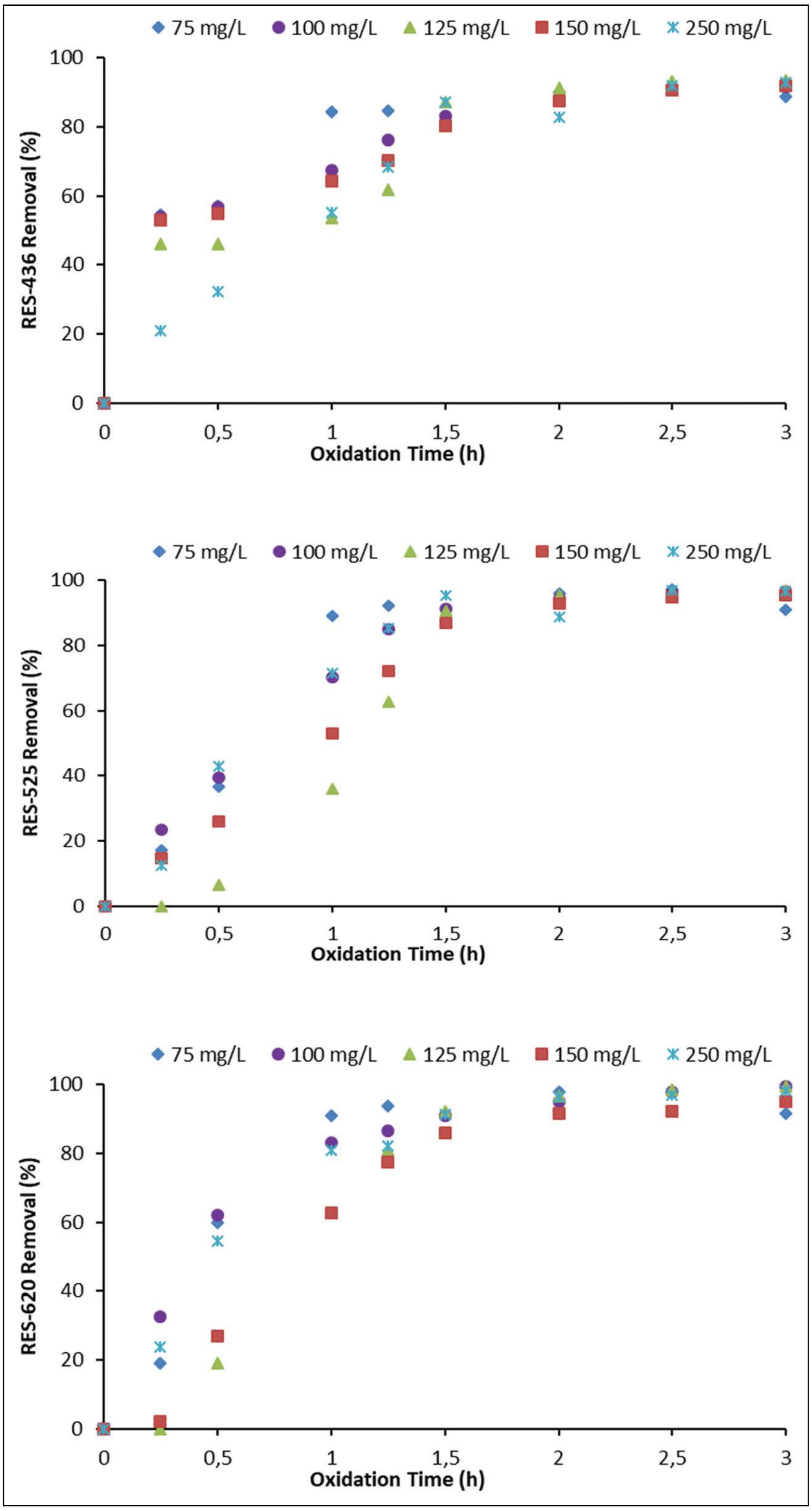

Figure 7. Effect of H_2O_2 concentration on color (RES-436, RES-525 and RES-620) removal (pH: 3, Fe-Cu-P concentration: 5 g/L)

tration, 250 mg/L H_2O_2 concentration and pH 3 after 1.5 hours degradation. Mahamallik and Pal found over a 92% of decolorization when textile wastewater was oxidized with photo Fenton process using 10 g/L Co-SMA (Co(II) adsorbed surfactant-modified alumina) catalyst, 37.9 mM H_2O_2 after 1 hour of oxidation [31].

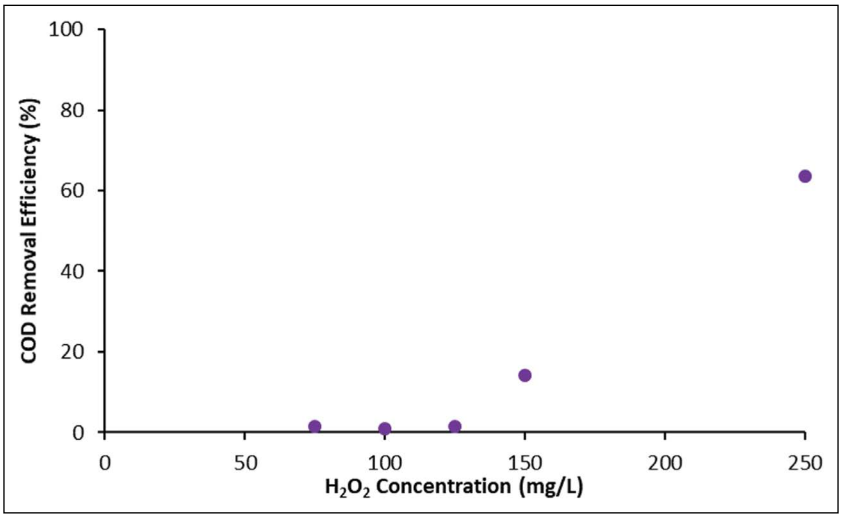

Figure 8. COD removal at different H_2O_2 concentration (pH: 3, Fe-Cu-P concentration: 5 g/L, oxidation time: 3h)

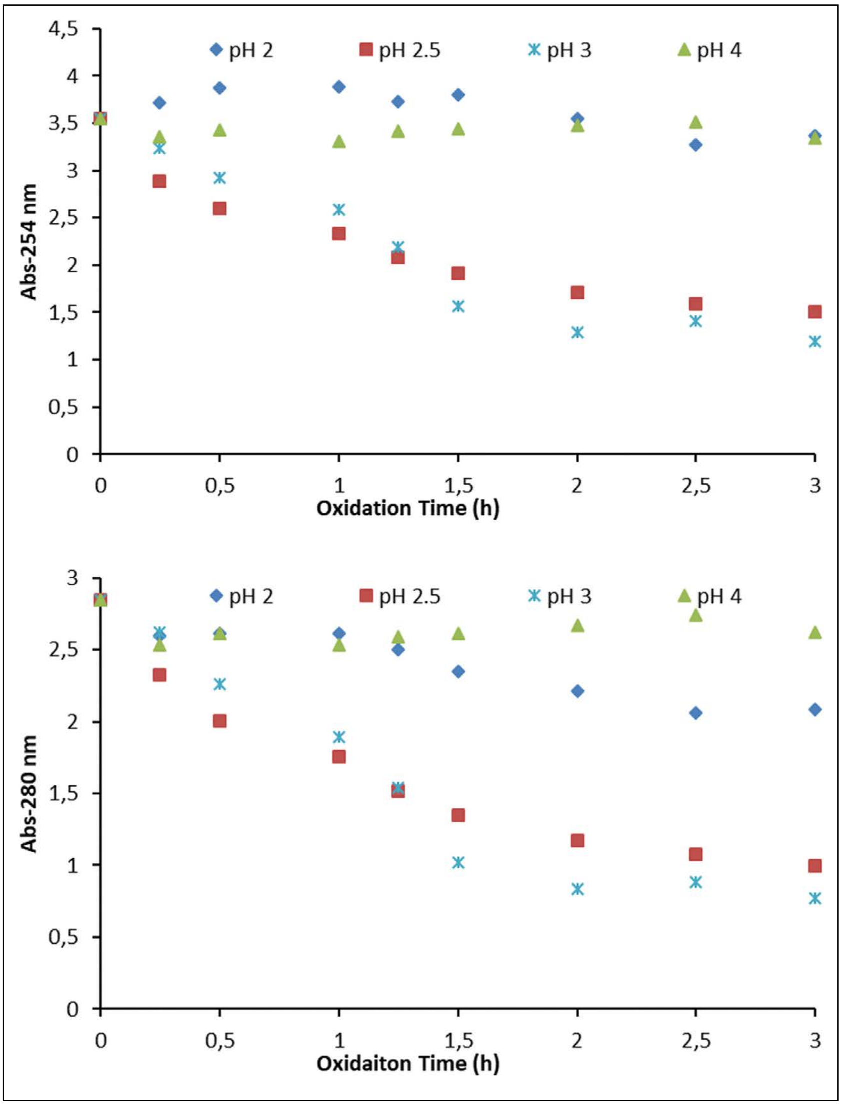

Figure 9. Effect of pH on the removals of Abs-254 nm and Abs-280 nm (Fe-Cu-P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L)

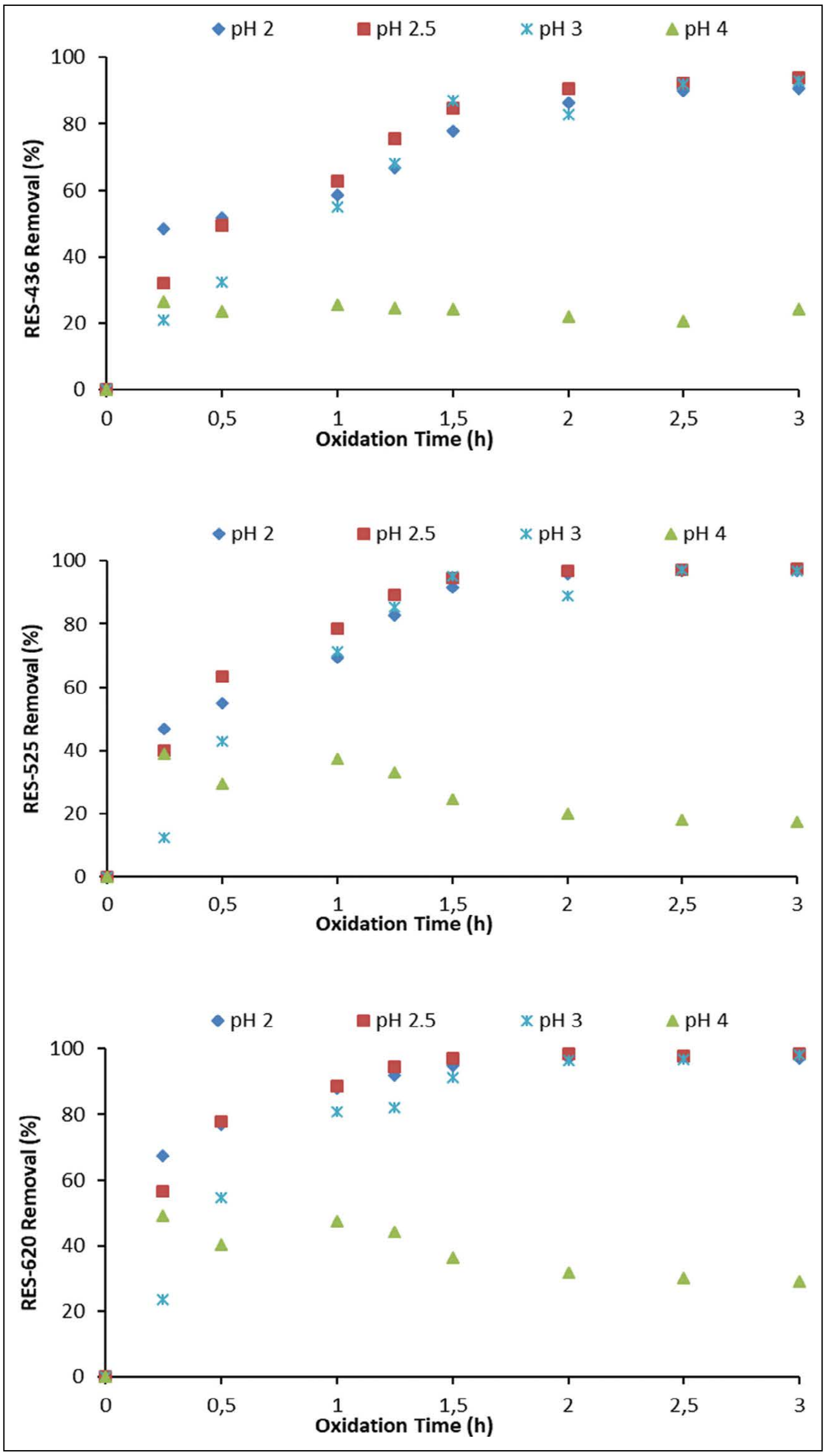

Figure 10. Effect of pH on (a) RES-436, (b) RES-525 and (c) RES-620 removals (Fe-Cu P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L)

Assessment of Treatment with UV/Fenton-Like Process

Standardized industrial wastewater discharge limits by the Zero Discharge of Hazardous Chemicals Program (ZDHC) are given in Table 3. The COD concentration of treated textile wastewater decreased from 246 mg/L to 78 mg/L with UV/Fenton-like proses using Fe-Cu-P composite catalyst in this study. According to ZDHC limits, this textile wastewater is in the progressive part as seen in Table 3 [28]. In addition, RES-436, RES-525 and RES-620 values of the treated textile wastewater with UV/Fenton-like were obtained as

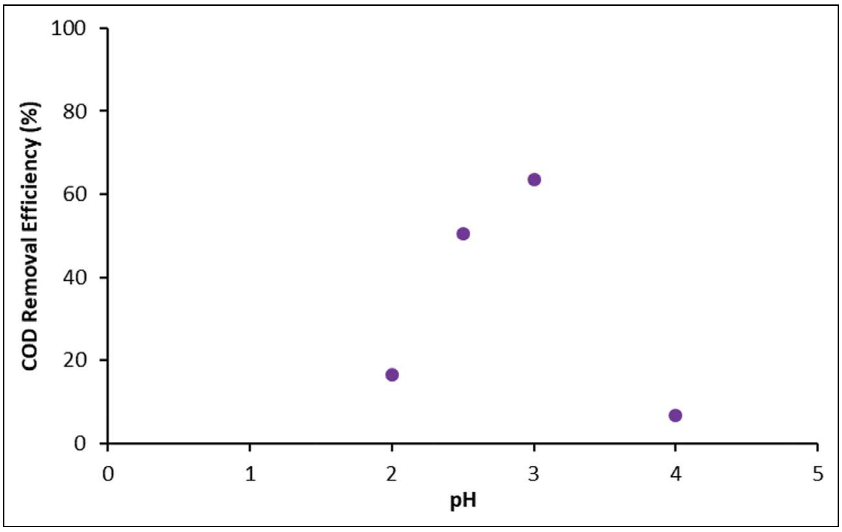

Figure 11. COD removal at different pH values (Fe-Cu-P concentration: 5 g/L, H_2O_2 concentration: 250 mg/L, oxidation time: 3h)

Table 2. Kinetic parameters of UV/Fenton-like proses

Parameter	k_1	R^2
Abs-254 nm	0.3246	0.9731
Abs-280 nm	0.3735	0.9762
RES $_{436}$ (m^{-1})	0.5704	0.9852
RES $_{525}$ (m^{-1})	0.6738	0.9798
RES $_{620}$ (m^{-1})	0.6895	0.8886

Table 3. Characterization of UV/Fenton-like treated wastewater and ZDHC limits

Parameter	Biological treated wastewater	Fenton treated wastewater	ZDHC limits [14]		
			Foundational	Progressive	Aspirational
COD (mg/L)	246	78	150	80	40
RES $_{436}$ (m^{-1})	66.0	4.7	7	5	2
RES $_{525}$ (m^{-1})	85.2	2.8	5	3	1
RES $_{620}$ (m^{-1})	46.8	0.9	3	2	1

4.7 m^{-1}, 2.8 m^{-1} and 0.9 m^{-1}, respectively, and these values also comply with the discharge limits in the progressive class [28]. As a result, treated textile wastewater complies with the ZDHC progressive discharge limits, however it needs additional treatment for compliance with the aspirational class [28].

CONCLUSIONS

In this study, the treatment of biologically treated textile wastewater with the prepared Fe-Cu pumice composite (containing 3.5% Fe and 3.5% Cu) by UV/Fenton-like oxidation was investigated. A high color removal (RES-436, RES-525 and RES-620) was achieved at 3–5 g/L Fe-Cu-P concentration, 125–250 mg/L H_2O_2 concentration and pH 2–3 range. However, the conditions that can provide the highest COD, Abs-254 nm and Abs-280 nm removals were obtained at 5 g/L Fe-Cu-P and 250 mg/L H_2O_2 concentrations and at pH 3. As a result of the study, it has been observed that UV/Fenton-like oxidation process using the Fe-Cu-P is a very suitable process in terms of obtaining color and organic matter removal of biologically treated textile wastewater before discharging to the receiving environment.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Undrained shear strength of polypropylene fiber reinforced alluvial clay

Eylem ARSLAN, İrem DÜZEN, Hasan Fırat PULAT*, İnci DEVELİOĞLU

Department of Civil Engineering, İzmir Katip Çelebi University, İzmir, Turkey

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ABSTRACT

Construction of civil engineering structures on weak soil without taking necessary precautions may be risky. Alluvial soil that has not completed its geological formation has a high void ratio and contains organic material therefore, the strength properties of these soils should be examined carefully. In this study, the undrained shear strength (cu) behavior of natural and polypropylene (PP) fiber-reinforced alluvial clays was investigated with a laboratory Vane shear test. To examine the moisture content effects on cu behavior of alluvial clay, samples were prepared in 0.50 liquid limit (LL), 0.75 LL, and LL water contents. The PP fibers used were 6 and 18 mm long, they mixed with soil 0.1, 0.5, and 1% by dry weight of the sample. The Vane shear tests were performed at two different depths to investigate the overburden pressure effect. The increase in water content caused a significant decrease in cu. The laboratory results indicated that the cu of PP reinforced (1% and 18 mm PP) alluvial clay deposits prepared in 0.5LL, 0.75LL, and LL water contents were 56.6, 20.7, and 8.4 kPa, respectively. The increase in PP fiber content increased the cu of alluvial clay deposits. The length of fiber was directly proportional to cu values. The effect of fiber was more pronounced in long fiber added samples. The cu of natural and 1% fiber reinforced (6 mm and 18 mm) samples prepared in the same water content were 27.4, 29.1, and 55.7 kPa. The cu increased with increasing penetration depth.

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INTRODUCTION

Shear strength is one of the essential geotechnical parameters used in the design procedure of geotechnical constructions like retaining walls, foundations, and embankments, and is determined using a variety of laboratory and in-situ tests. Due to the action of rapid loading (or unloading) on clayey soils, the water content and the volume of the soil remain constant, and excess pore water pressure is generated. In such a case, the shear strength is called the undrained shear strength (cu). Undrained shear strengths are influenced by several factors including sample disturbance, anisotropy, over consolidation ratio, deformation state, strain rate, and sample size. The determination of this parameter is significant, and it can be measured by using a variety of laboratory and in-situ tests. In laboratory conditions, Unconsolidated-Undrained (UU) triaxial, Unconfined Compression (UCS), and Vane Shear Tests (VST) can be conducted to define this parameter. Besides, it can be determined from field VST and calculated by empirical

***Corresponding author.**
*E-mail address: hfirat.pulat@ikcu.edu.tr

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correlations using SPT – CPT data. Among these, the VST is the most effective and suitable method for specifying the undrained shear strength of very soft-hard clays in terms of being a cheaper and quicker method compared to the complexed mechanism of the triaxial shear test or time-consuming in-situ tests. It is also recommended by ASTM D4648 [1] as an effective tool to examine the strength of anisotropy in both directions of soil samples. The VST which can be performed either in the laboratory or in the field is commonly used for measuring the undrained strength of undisturbed, fully saturated clay and cohesive soils at low shear strength due to its simplicity, speed, and relative cost [2–4]. Although it has many advantageous features, there are a limited number of studies in the literature regarding VST. Wilson et al. [5] researched the effect of several factors such as vane rotation rate, insertion disturbance, soil anisotropy, and structure on the vane-measured strength of soft clays and they reported the main information about the factors affecting the interpretation of VST values. They concluded that the resistance developing during the VST in soft clays is affected by these mechanisms and more mechanical properties of soil can be retrieved through the test.

Many reinforcement methods have been applied in the previous studies to alter the undesirable engineering properties of problematic soils such as organic soils, soft clays, loose sands, alluvial deposits. Improvement of the engineering properties of the soil by adding randomly distributed fibers has started at least 5000 years from now [6]. In most geotechnical engineering projects, using fiber-reinforced soils attracts attract more attention and approval. The mixing fibers into the soil increase the shear, compressive, and tensile strength reduces the swelling and brittleness. Currently, many researchers have examined the behavior of reinforced clays by using discrete fibers [7–13].

The advantages of this material are low cost, easy to execute, and has a high melting point. Also, polypropylene does not react or absorb the soil moisture because it is a chemically inert and hydrophobic material [7].

The determination of the undrained shear strength of low permeability soils is an interesting subject and has been studied by many researchers in various methods. Furthermore, there are many studies concerning the improvement of strength properties of soils using different types of additives. Ozkul and Baykal [8] studied the impact of the fiber on the undrained shear strength of the kaolinite clay. Consolidated – undrained (CD) triaxial tests were performed with clay and clay – fiber samples. The tire fiber was mixed with 10% by dry weight of clay. The samples were prepared in two different compaction energies (standard and modified). Three different confining pressures (100, 200, and 300 kPa) were applied. It was observed that undrained shear strength values increased with the tire fiber addition for both compaction energies. The undrained shear strength was between 100 and 485 kPa for standard compaction, between 440 and 1080 kPa for modified compaction. Mollamahmutoglu and Yilmaz [14] investigated the shear strength behavior of polypropylene fiber reinforced high plasticity clay. The consolidated – undrained (CU) triaxial tests were performed on fiber-reinforced clay with contents of 0.1, 0.2, 0.3, and 0.4% by dry weight of soil. The specimens were prepared in accordance with the maximum dry unit weight and optimum moisture content. The test results revealed that cohesion decreased, internal friction angle increased with the fiber content increasing. Cohesion values were ranged between 28–212 kPa, the internal friction angle took values from 4.9^0 to 21.4^0. Pradhan et al. [11] inspected the change in shear strength of the soil reinforced with polypropylene fibers. The strength characteristics of fiber-reinforced soil, as well as unreinforced soil, were investigated by using several tests such as California Bearing Ratio (CBR), unconfined compression, and direct shear tests. The test results proved that the peak and residual shear strength of soil samples are increased concerning the inclusion of randomly distributed polypropylene fibers. Maliakal and Thiyyakkandi [9] used randomly distributed coir fibers to better understand the effect on the shear strength of clay by conducting a series of consolidated – undrained triaxial tests. It was reported that the inclusion of fibers increased the shear strength of clay remarkably, therefore it is convenient to mix soil with fibers in-situ conditions. Yilmaz [15] analyzed the fly ash and polypropylene fiber effect on the strength behavior of Ankara clay. The clay soil was mixed with fly ash (10 and 30%) and polypropylene fiber (1%). Unconsolidated – undrained triaxial tests were conducted with 28 days of cured samples. When the polypropylene fiber was added, undrained shear strength values increased from 115.3 to 124.3 kPa for 0% fly ash, from 180.2 to 260.2 kPa for 10% fly ash, from 246.2 to 266.2 kPa for 30% fly ash. Diab et al. [13] analyzed the undrained shear strength behavior of clay blended with natural hemp fibers. The fibers were mixed with soil 0.5, 0.75, 1.0, 1.25 and 1.5% by dry weight of soil. The unconsolidated – undrained triaxial tests were conducted to specify undrained shear strengths. The specimens were prepared in different water contents (14, 18, and 20%) with Standard Proctor compaction energy. The undrained shear strength values were determined between 160 and 880 kPa. Also, the test results revealed that when the fiber content increased up to 1.25% more strength is gained, yet less is obtained with the water content increases.

In the literature, researchers have studied the relation between water content and undrained shear strength of different types of soils. Mohamad et al. [16] examined moisture content effect on the undrained shear strength of older alluvium soil that is widely spread in Malaysia. It was concluded that the increase in water content has a great impact on the reduction of shear strength. The cohesion values of dry and saturated samples were reported to decrease from

21.04 kPa to 9.54 kPa. Kuriakose et al. [17] studied to obtain a relation between the undrained shear strength of clays and the water content. Laboratory Vane shear tests were conducted with clay samples obtained from four different sites (Parur, Kumbalam, Maradu, Elamkulam). They generated two correlations in-between Water Content Ratio (WCR) – undrained shear strength and liquidity index (IL) – undrained shear strength. According to test results, the undrained shear strength decreased as the water content increases.

A very limited number of studies have investigated the change in the undrained shear strength with respect to depth. Bartetzko and Kopf [18] studied how porosity and undrained shear strength of marine sediments are affected by depth. The values of undrained shear strength were evaluated by an automated Vane shear system, hand-held Torvane, and pocket penetrometer in Ocean Drilling Program (ODP) site. At the end of the test, the undrained shear strength values were found between 0 – 439 kPa. When the depth increased, the undrained shear strength values increased, and porosity decreased. Li et al. [19] observed the change of undrained shear strength with depth. The data were collected from four different sites (Port Huron, Baton Rouge, Kringalik Plateau, Ontario). The results showed that undrained shear strength improved with the increase in depth. Researchers proposed four different correlations for the undrained shear strength with respect to both depth and effective unit weight.

When the studies about the fiber-reinforced soil's behavior are investigated, it is commonly concluded that fiber should be long enough to activate fiber-soil interaction since the fabric of the composite does not allow such an interaction in short lengths. In another case, if the fiber diameter is smaller than the grain size by at least one order of magnitude, fibers may slip during the deformation, thus they cannot take any load [20, 21]. A number of studies have revealed that the increase in shear strength of soils can be enhanced further by longer fiber additions. In general, the length of fibers in the aforementioned studies was ranged between 6–25 mm [22–24]. The chosen fiber lengths were selected according to the dimension of the soil sample used in the study. Since Standard Proctor Mold in the study is large enough to allow a homogeneous mixing area of fiber-soil mixture, it is decided to use fiber length up to 18 mm.

Cigli-Balatcik (Izmir, Turkey) is a newly developing region that generally contains alluvial clay soils under the quick-undrained loading condition due to the rapidly increasing demand on the constructions. Thus, the objective of this study is to investigate undrained shear strength characteristics of natural and polypropylene (PP) fiber-reinforced alluvial clays taken from this region. The laboratory VSTs were conducted using two different lengths (6 mm and 18 mm) of polypropylene fibers with different ratios (0.0, 0.1, 0.5, and 1.0% by dry weight). To investigate the water content effects on undrained shear strength, samples were prepared and tested in three different water contents (LL, 0.75LL, and 0.5LL). Overburden pressure was also taken into account and tests were performed at two different depths (2H and 3H). The undrained shear strength behavior of natural and reinforced alluvial clays was defined with 126 VSTs. Test results were statistically analyzed by the methods of two-way ANOVA and the Student–Newman–Keuls as a post hoc test to search for the relationship between variables and undrained shear strength.

Figure 1. The top view from the region of Cigli – Balatcik.

MATERIALS AND METHODS

Alluvial Clay Deposit

Alluvial clay deposits were obtained from Cigli – Balatcik region located at the north of Izmir, surrounded by Menemen from the north, the Gulf of Izmir from the south (Turkey). The alluvial clay samples were taken from a construction site at Izmir Kâtip Celebi University (Fig. 1). Alluvial deposits have a broad spectrum in terms of both the condition and the type of the soil. According to the mechanical properties, alluvial deposits are classified as the so-called transition soils or intermediate soils. Alluvial deposits containing a significant amount of organic matter carried by a stream have high porosity. They have a low bearing capacity so that they are considered problematic soil in geotechnical engineering.

Polypropylene Fiber

Synthetic fibers are commonly used to improve the strength of soil or concrete by a micromechanical interaction mechanism between particles [7, 20]. The monofilament fibers

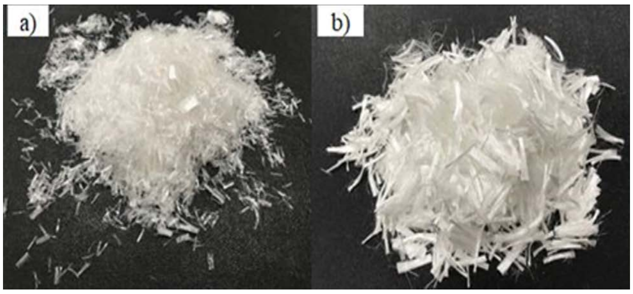

Figure 2. (a) 6 and (b) 18 mm polypropylene fibers.

used for sample preparation are commercially available synthetic polypropylene fibers. The fiber lengths were 6 mm and 18 mm, the diameter was 0.023 mm, and the specific gravity was 0.91. PP fibers used in the laboratory tests have been shown in Figure 2.

Physicochemical and mechanical properties obtained from the manufacturer company for polypropylene fibers are summarized in Table 1.

Polypropylene fibers were added to alluvial deposits at 0.1, 0.5, and 1% by dry weight. The content of fibers in soil samples is calculated by using Equation 1.

$$\rho_f = {W_f}/{W_s} \quad (1)$$

where ρf represents the fiber-reinforced ratio, W_f and W_s indicate the weight of fiber and air-dried soil, respectively. In this study, ρ_f values were chosen as 0, 0.1, 0.5 and 1%, variables, and the sample properties were summarized in Table 2.

Since the fibers are hydrophobic chemically, they need only be mixed long enough to ensure the dispersion in material [24].

Table 1. The physicochemical and mechanical properties of PP fibers

Type	Properties
Fiber type	Monofilament
Material	100% virgin PP
Appearance	Individual fiber
Cross-section	Round
Specific gravity	0.91
Softening point (°C)	150
Melting point (°C)	160
Length (mm)	6 & 18
Young modulus (MPa)	3000 – 3500
Tensile strength (MPa)	600 – 700
Alkali effect	Stable
Color	Transparent

Table 2. The variable parameters in the study

PP length (mm)	ρf (100%)	Moisture content	Penetration depth
6 and 18	0.0	0.50LL	2H/3H
		0.75LL	2H/3H
		LL	2H/3H
	0.1	0.50LL	2H/3H
		0.75LL	2H/3H
		LL	2H/3H
	0.5	0.50LL	2H/3H
		0.75LL	2H/3H
		LL	2H/3H
	1.0	0.50LL	2H/3H
		0.75LL	2H/3H
		LL	2H/3H

Geotechnical Index Properties

The geotechnical index properties of alluvial deposits were designated by laboratory tests following ASTM Standards. To define the liquid limit of alluvial clay, the Casagrande device was used, and the Multipoint method (Method A) was followed according to ASTM D4318 [25]. The water content at which a 3.2 mm diameter soil sample crumble while rolling between the two fingers is called the plastic limit of the soil and in this study, it was determined with the traditional hand rolling method which is detailly defined in ASTM D4318 [25]. Besides, the Standard Proctor test was conducted to find the water content and dry unit weight at the optimum compaction effort. The compaction curve of the alluvial clay deposit was determined according to the ASTM D698, Method A [26]. The identification of specific gravity of alluvial soil samples was determined based on ASTM D854 [27] instructions utilizing a water pycnometer. Therefore, the density or phase relationships of soil samples could be determined. The classification of alluvial deposits was specified by interpreting grain size distribution analysis according to ASTM D2487 [28], Unified Soil Classification System (USCS).

Vane Test

The laboratory VSTs were performed to determine the undrained shear strength of natural and PP reinforced alluvial deposits based on ASTM D4648 [1].

Sample Preparation

Natural and fiber-reinforced alluvial clay samples were prepared in 0.5LL, 0.75LL, and LL moisture contents. To obtain uniform and consistent samples same procedures were applied such as mixing, placement, rodding, compaction and smoothing. Mixtures were prepared in a benchtop laboratory mixer with 4.7 lt capacity. Polypropylene was added and mixed thoroughly using a mechanical mixer at a speed of 142 rpm for 15 min to prevent clumping (local aggregation) and balling and to obtain homogeneous fiber-reinforced soil. Standard Proctor molds having 10.3 cm diameter and 11.6 cm height with a compaction effort of 596 kj/m^3 were used to achieve predetermined unit weight values. The samples were prepared with a similar compaction procedure such that the unit weights remained within a certain range (16–18 kN/m^3). Since fibers are not able to absorb water, the added

Table 3. Guide for spring detection [30]

Spring No.	General soil description	Maximum shear stress (kN/m^2)
1	Very soft (Weakest)	20
2	Soft	40
3	Soft to firm	60
4	Firm (Stiffest)	90

Table 4. Geotechnical index properties of alluvial deposits

Geotechnical indices	Results
Liquid limit (LL), %	58.6
Plastic limit (PL), %	27.5
Plasticity index (PL), %	31.1
Specific gravity, (G_s)	2.58
Fine content (-No.200), %	91
Max. dry unit weight ($\gamma_{dry,max}$), kN/m^3	15.4
Optimum moisture content (w_{opt}), %	26.8
Unified Soil Classification System (USCS)	CL

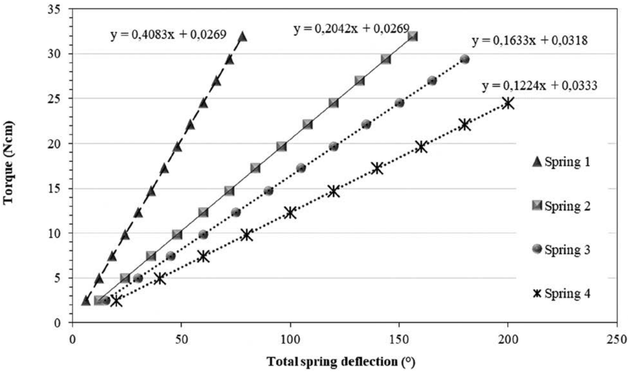

Figure 3. Calibration curves of springs.

fiber amount did not affect the available unit weight. The degree of saturation value of the samples in LL, 0.75LL, and 0.5LL water contents were determined as 98.14, 96.82, and 95.31% respectively. To prevent moisture loss, Vane tests were conducted immediately after samples were prepared.

The Arrangement of the Vane Apparatus

Vane device consists of many parts such as spring, Vane blade, vertical shaft, hand knob, pointer, circular graduated scale, and secondary scale. The number of torsion springs shall be chosen according to the probable soil strength as it is indicated in Table 3.

After the trial tests, spring No.4 was concluded to be suitable for alluvial soils. The spring was calibrated to ensure proper operation of the Vane device by following the instructions suggested by ASTM D4648 [1]. At the end of the calibration process, the calibration curve for each spring was plotted and from that curve, the spring constant values were determined (Fig. 3).

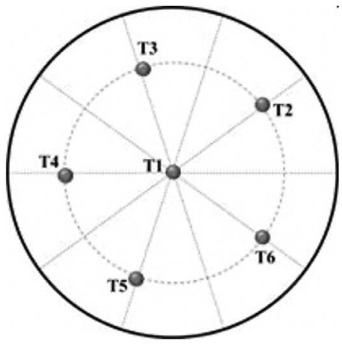

Figure 4. Test points configuration of samples.

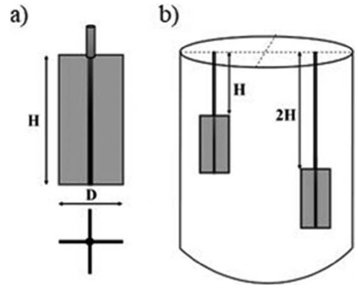

Figure 5. (a) Miniature Vane blade geometry (b) penetration depths of Vane blades (2H and 3H).

Testing of Samples

Undrained shear strengths of reconstituted (remolded) specimens were determined by using a miniature vane test device according to Method A (Conventional Calibrated Torque Springs). Six points were selected on the surface of the sample (T1, T2, T3, T4, T5, and T6). The configuration of the test points is shown in Figure 4.

According to the ASTM D4648 [1], the Vane must be penetrated the sample at least twice the height of the blade. In other words, the depth of penetration should be twice the height of the Vane blade at a minimum. Experiments were performed at two different depths (2H; [T1, T2, T4] and 3H; [T3, T5, T6]) to investigate the effects of penetration (overburden pressure) on undrained shear strength. Miniature Vane blade geometry has shown in Figure 5a. The penetration depths were selected as 2 and 3 times of Vane blade height measured from the top of the mold surface by taking care of its possible minimum value as recommended in the ASTM D4648 [1] and schematically demonstrated in Figure 5b.

The experiment starts by inserting the Vane blade to the desired point in the sample (2H or 3H). The initial reading is recorded and then the handle is rotated counterclockwise to apply torque to spring at a constant rate of 60 to 90°/min. (Fig. 6). The upper part of the spring starts to rotate at a constant speed, while the lower part remains constant. Torque and angular displacements are saved every 5 seconds and recorded with the video camera to prevent misreading. When the applied torque passes the shear resistance of the soil, the bottom of the spring starts to rotate [1]. The record-

Figure 6. Test points and test steps.

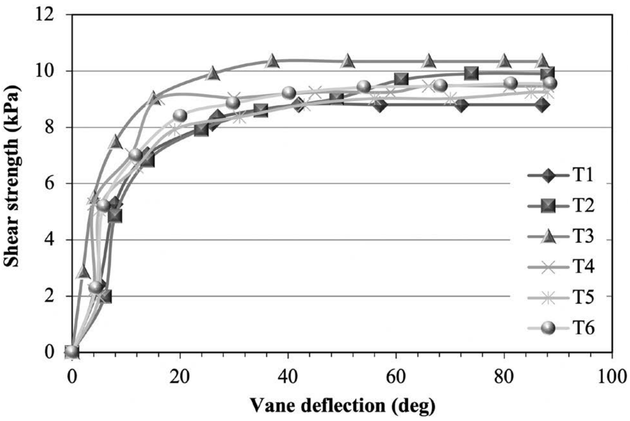

Figure 7. The undrained shear strength – Vane deflection relation of natural samples.

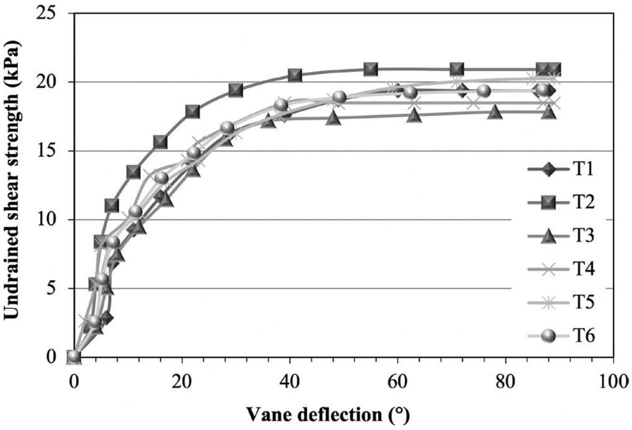

Figure 8. The undrained shear strength – Vane deflection relation of PP reinforced samples.

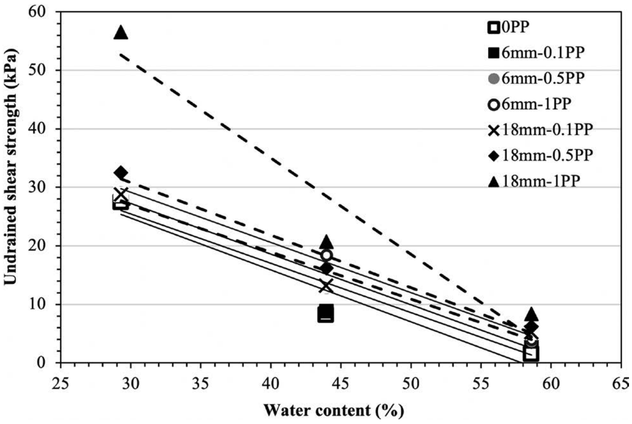

Figure 9. The undrained shear strength – water content relation of natural and reinforced alluvial soil.

ing continues until the spring deflection remains constant. This procedure is followed for six test points with different depths. The test points and test steps are shown in Figure 6.

The data obtained from the torque displacement scale and spring deflection angle were converted into torque values by multiplying the angle with the spring constant (Equation 2).

$$T=k\times\Delta \quad (2)$$

where: T = torque applied (Nm), k = spring constant (Nm/°), Δ= spring deflection (°). The undrained shear strength (c_u) of the soil was calculated by Equation 3.

$$c_u = T/K \quad (3)$$

where: cu = Undrained Shear Strength (Pa), K = Vane blade constant (m^3), $K = \pi r D^2 \times (\frac{H}{2} + \frac{H}{6})$

Statistical Analysis

The VST results are analyzed statistically by using two-way ANOVA (SPSS 12.0, SPSS GmbH, Germany) and the Student–Newman–Keuls methods. Significant differences between groups were stated at p-values at least <0.05. (*p<0.05, **p<0.01, ***p<0.001).

RESULTS AND DISCUSSIONS

In this part, the geotechnical index properties of alluvial clay obtained from laboratory tests were given. The laboratory Vane shear test results were summarized for natural and PP added samples. Also, the test results were supported by statistical analysis.

Geotechnical Index Properties Results

The geotechnical index properties of alluvial clay deposits were determined with laboratory tests according to ASTM Standards. The test results are displayed in Table 4. The particle size distribution analysis and consistency limits test results revealed that the soil can be categorized as low plasticity clay (CL) according to USCS.

Vane Shear Test Results

In this study fiber length, water content, fiber content, and penetration depth were examined as factors affecting the undrained shear strength behavior of alluvial clay deposits. A total of 126 experiments were performed with 18 natural and 108 reinforced samples. Undrained shear strength - Vane deflection relation has shown in Figures 7 and 8. Curves were plotted for six different test points and two different depths (2H; [T1, T2, T4] and 3H; [T3, T5, T6]). Since the VSTs were performed with reconstituted (remolded) alluvial clay samples, peak shear stress was not observed.

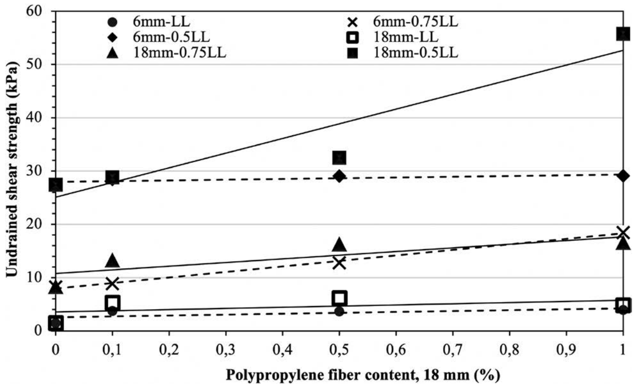

Figure 10. The undrained shear strength – PP fiber content relation of natural and reinforced alluvial soil.

Thus, the maximum shear stress was equal to ultimate shear stress and tests were terminated at 90^0 deflection.

The PP fiber effect on the undrained shear strength behavior of alluvial clay deposits can be compared with Figures 7 and 8. The average undrained shear strength of the natural alluvial sample prepared in 0.75 LL water content was 9.14 kPa (Fig. 7). On the other hand, the average undrained shear strength of reinforced alluvial samples (0.5% PP) prepared in the same water content was 18.80 kPa (Fig. 8). The undrained shear strength behavior of fine-grained soil is directly related to water content [17, 29–32]. The undrained shear strength-water content relation of natural and PP reinforced alluvial soils is presented in Figure 9. The test results clearly showed that when the water content increased, a significant decrease in undrained shear strength was obtained. The undrained shear strengths of PP reinforced (1% and 18 mm PP) alluvial clay deposits prepared in 0.5LL, 0.75LL, and LL water contents were 56.6, 20.7, and 8.4 kPa, respectively. This can be explained that in fine-grained soils, intermolecular bond in-between water causes cohesion of particles [33, 34]. Therefore, cohesion varies with soil water content, particle size, and compaction of soils. When the water content is raised, the adhesion decreases due to the further separation of the clay particles, thereby reducing the shear strength. Similarly, as the soil particles start to come closer, owing to continuous reduction in water content, the bonding between solid particles builds up and contributes to the shear resistance of soil in friction [31, 35].

To improve the undrained shear strength properties of alluvial clays polypropylene reinforced fibers were used with three different contents and results are demonstrated in Figure 10. The test results have stated that when the polypropylene fiber content is raised, the undrained shear strength of alluvial clay deposits has increased, too. As the soil is sheared, fibers extended in the soil body, which increases the tensile strength of the PP fiber reinforced soil and increases the shear strength because of the extensible nature of the fibers [36–38]. Discrete fibers in a randomly distributed position lock the soil grains together and form a single coherent matrix that helps

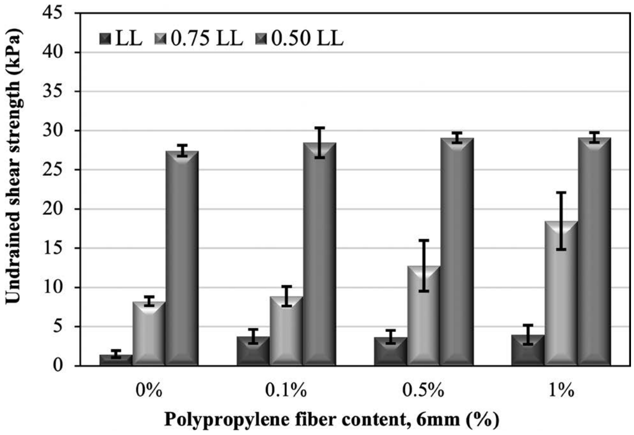

Figure 11. Undrained shear strength of alluvial deposits reinforced with 6 mm PP fiber.

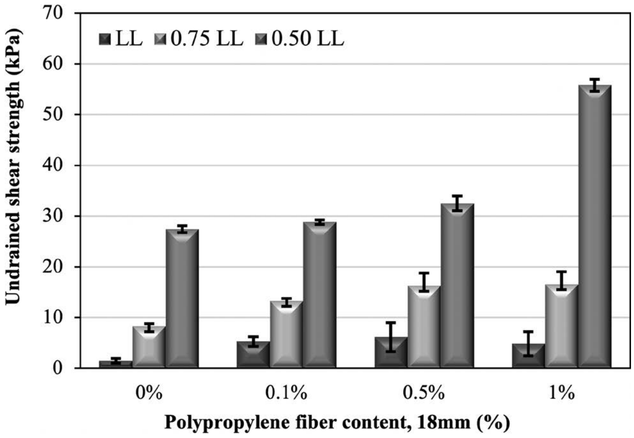

Figure 12. Undrained shear strength of alluvial deposits reinforced with 18 mm PP fiber.

limit the displacement of the particles. The grooves and pits formed on the fiber surface are thought to form a lock and improve the interaction between the soil matrix and the PP fiber surface. The effect of interlocking is more pronounced when fiber content has risen so that an increase in the shear strength of samples with a high fiber content is obtained [12]. Especially in samples with low water content (0.5LL), the fiber of 18 mm length played a more effective role than 6 mm length on undrained shear strength. The undrained shear strengths of natural and 1% fiber reinforced (6 mm and 18 mm) samples prepared in the same water content (0.5LL) were 27.4, 29.1, and 55.7 kPa, respectively.

The undrained shear strengths of natural and fiber-reinforced samples prepared at different moisture contents and various fiber contents have been shown in Figures 11 and 12. The test results indicated that the water content crucially influenced the undrained shear strength. The increase in moisture content adversely affects the undrained shear strength. The test results were indicated that the PP fiber effectively influenced the undrained shear strength parameter.

The positive impact of PP fiber additive on undrained shear strength was more evident in long fiber samples. While the undrained shear strength of natural alluvial clay was 27 kPa, samples with 6 mm and 18 mm long PP fibers in 1% were 29 kPa and 56 kPa, respectively. After compaction, the PP fiber is covered with interconnected soil particles. Some of the particles are bonded to the PP fiber surface after the fiber has been pulling out. This shows that in the shearing procedure of soil, the interface of the soil structure is disturbed and disconnected. Therefore, the interface friction is highly dependent on the resistance shown by soil particles to rotation and regulation when shear occurs [39, 40].

The VSTs were performed at two different depths to examine the influence of overburden pressure on the undrained shear strength. The test results revealed that the undrained shear stress improved with increasing penetration depth. The penetration depth was more effective in samples with high water content. In other words when the overburden pressure increased the undrained shear strength is increased too (Fig. 13).

The samples with high water content have higher undrained shear strength increases due to penetration depth. The undrained shear strength of natural samples prepared in LL water content, tested at 2H and 3H depths were 1.47 kPa and 2.42 kPa, respectively.

According to 126 VST results useful correlations were derived between effective overburden stress (γ'z) – undrained shear strength (c_u) and moisture content (w) – undrained shear strength (c_u). These correlations were given in Equation 4 and Equation 5.

$$c_u = 0.14 \times \gamma \times z + 13.3 \quad (4)$$

$$w = 104.88 \times c_u^{-0.37} \quad (5)$$

Statistical Analysis Results

In this study, each sample was tested at least three times to check repeatability and obtained test results were statistically analyzed. The undrained shear strength of natural alluvial clays decreased with increasing water content. These results were supported by statistical analysis ($c_{u(LL)}$ [1.47±0.46; p<0.001], $c_{u(0.75LL)}$ [8.23±0.55; p<0.001], $c_{u(0.5LL)}$ [27.43±0.67; p<0.001] kPa. Test results have clearly shown that polypropylene fiber reinforcement positively affected the undrained shear strength of the sample prepared in the same water content. Additionally, the PP fiber was more effective in samples with high water content ($c_{u(6mm\_0.1\%)}$ [3.74±0.88; p<0.001], $c_{u(18mm\_0.1\%)}$ [5.28±0.0.96; p<0.001].

Literature Comparison

When the results of the current study are compared with the studies conducted in the literature [40–42], it was observed that the undrained shear strength tends to increase with the addition of polypropylene fiber (Fig. 14). It was also found that the increase was sharply up to certain fiber content, then a less increase.

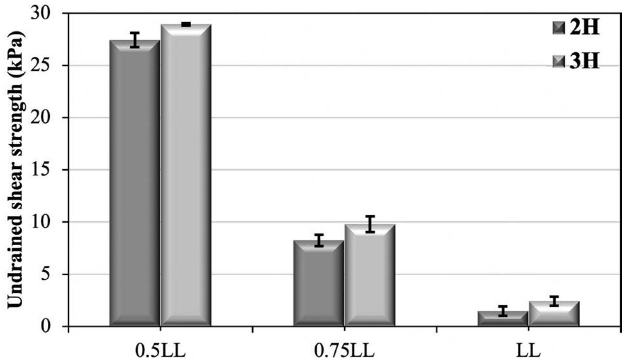

Figure 13. Undrained shear strength of natural alluvial deposits at depth 2H and 3H.

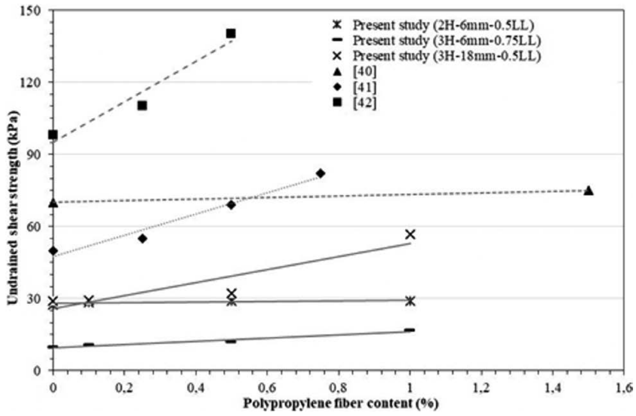

Figure 14. Comparison of literature and current study results.

In addition, it was observed that the increase in undrained shear strength was higher in studies using soils with high plasticity [41–42]. On the contrary, in studies using soils with low plasticity (i.e., present study), the increase in undrained shear strength was found to be slightly less [40].

CONCLUSIONS

In this study, the undrained shear strength behavior of natural and PP fiber-reinforced alluvial clay deposits obtained from Balatcik – Cigli (Izmir, Turkey) was investigated. VSTs were performed considering the effects of water content, fiber length, fiber content, and penetration depth on the undrained shear strength. Firstly, the effect of water content on the undrained shear strength was examined for natural alluvial deposits. Afterward, the soil was improved by the addition of two different lengths of PP fiber with a variety of proportions in specified water contents. A total of 126 experiments were performed with 18 natural and 108 reinforced samples. Test results were supported by statistical analysis. The laboratory test results indicated that,

- The increase in water content caused a significant decrease in undrained shear strength. The undrained shear strengths of PP reinforced (1%- and 18-mm PP) alluvial clay deposits prepared in 0.5LL, 0.75LL, and LL water contents were 56.6, 20.7, and 8.4 kPa, respectively.
- The increase in polypropylene fiber content increased the undrained shear strength of alluvial clay deposits. The interlocking effect increases with increased fiber content, which leads to an increase in the shear strength of samples with high fiber content.
- Especially in samples with low water content (0.5LL), the fiber of 18 mm length played a more effective role than 6 mm length on undrained shear strength. The undrained shear strengths of natural and 1% fiber reinforced (6 mm and 18 mm) samples prepared in the same water content (0.5LL) were 27.4, 29.1, and 55.7 kPa, respectively.
- The undrained shear strength increased with increasing penetration depth. The penetration depth was more effective in samples with high water content. The undrained shear strength of natural samples prepared in LL water content, tested at 2H and 3H depths were 1.47 kPa and 2.42 kPa, respectively.
- The length of fiber was directly proportional to undrained shear strength values. The effect of fiber was more pronounced in long fiber added samples.
- The equations derived from test results can be used to determine the undrained shear strength in the preliminary design stage of the projects.
- Statistical analysis results confirmed the consistency of the test results.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Comparison of the meteorological drought indices according to the parameter(s) used in the Southeastern Anatolia Region, Turkey

Gözde Nur AKŞAN[1], Ülker Güner BACANLI[2]

Faculty of Engineering, Civil Engineering Department, Denizli, Turkey

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ABSTRACT

Southeast Anatolia Region, where Turkey's summer-winter differences were experienced as a region, was preferred in this study. Daily precipitation and daily temperature data for the 1950–2019 period were provided for analysis. However, due to data deficiencies, Adiyaman, Batman and Kilis stations were worked in the 1959–2019 period and Sirnak station in the 2000–2019 period. All data have been tested for homogeneity.
According to the parameters used in this study, comparisons were made between the indices. It is divided into 4 according to the parameters used. Although the parameter used is the same, each index has drawn different results due to time differences. Dry results were obtained across the entire station from the methodology of the EDI (as used daily rainfall data). In addition, due to the low precipitation in the index, dry results were obtained in the RAI. Normal results were obtained with other precipitation-based drought indices.
According to EDDI results, the driest month is April. During the 12-month seasonal period, only 5 months have passed in the form of no drought.
According to SPEI and RDI values, normal results were achieved at all stations. Moderately and severely dry conditions sometimes occur, extremely dry have rarely been seen. RDI has been identified to have a more drought duration than SPEI.
According to PCI and HTC (based on precipitation and temperature), EDI and RAI results (precipitation-based), the region is dominated by drought. When viewed on a station-by-station basis, drought has been observed at stations in the borders.

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INTRODUCTION

Drought is a natural disaster that causes the deterioration of hydrological, biological [1], economic [2], and social balance [3]. It is very difficult to indicate the beginning and end of the drought. Because drought gradually shows its effects and continues for long periods of time. It doesn't happen suddenly, like natural disasters like floods, storms, etc. It is one of the highest cost disasters in the world, with an average annual loss of $8–10 million [2].

***Corresponding author.**
*E-mail address: ugbacanli@pau.edu.tr

Although it is difficult to fully identify drought, it can be classified as a meteorological, agricultural, hydrological, and socioeconomic drought [4, 5]. 1) Meteorological drought occurs due to below-normal precipitation. 2) Agricultural drought occurs because of intense but less frequent precipitation or above-normal evaporation. All these harm plant production and plant development. 3) Then, hydrological drought occurs in aquifers, lakes, and reservoirs when river stream flow falls below long-term average levels. 4) Finally, socioeconomic drought occurs because of associating the supply and demand of some economic goods or services with meteorological, hydrological, and agricultural drought elements [6].

Drought indices provide comprehensive information for drought analysis. Drought indices are used to determine the beginning and end of the drought event, to monitor its change over time, to determine the severity of the drought, and to evaluate the drought.

Several drought indices have been developed to detect complex events such as droughts. Station-based drought models such as the Standardized Precipitation Index (SPI) [7], Aridity Drought Index (AI) [8], Percent of Normal Precipitation Index (PNPI) [9] and Reconnaissance Drought Index (RDI) [10] are among the most used models. Drought indecencies are markers that numerically and conceptually show information such as drought-related violence, duration, amplitude. These also categorize drought parameters.

Many research studies have conducted studies to compare drought indices. For example, there are many studies that compare index where only precipitation is used as parameters [11–13]. It is available in studies where indices with similar formulas are used [14]. There are also many studies comparing SPI and SPEI, where the same classification is used [15–18].

In this study, a drought study was conducted using meteorological data (precipitation, temperature and potential evapotranspiration). Southeast Anatolia Region, where the total annual rainfall in Turkey is low, the average annual evaporation is multi and the average annual temperature is high, has been selected. Meteorological data between 1950 and 2019 were used. The data were first tested for homogeneity. Meteorological droughts are important for monitoring drought and reducing its dangers because meteorological droughts occur first. For this purpose, China Z Index (CZI), Effective Drought Index (EDI), Percent of Normal Precipitation Index (PNPI), Rainfall Anomaly Index (RDI), Standardized Precipitation Index (SPI), Weighted Anomaly Standardized Precipitation (WASP), Z-Score Index (ZSI), Evaporative Demand Drought Index (EDDI), De Martonne Aridity Index (AI), Pinna Combinative Index (PCI), Hydro-Thermal Coefficient of Selyaninov (HTC), Standardized Precipitation Evapotranspiration Index (SPEI) and Reconnaissance Drought Index (RDI) in meteorological drought were used in the study. Comparisons were made between indices divided into four groups according to the parameters used.

MATERIALS AND METHODS

Study Area and Data

Southeastern Anatolia region, one of the 7 regions of Turkey, was selected as the field of study. The region is located within the 38° 6′ 22″ North and 41° 19′ 43″ East area. Southeast Anatolia Region is 8% of Turkey's territory. It is equivalent to an area of 59.176 km². It is found from the Southern Taurus Mountains in the north to Iraq and Syria in the South. Fig 1 shows the map where the boundaries are set.

In this study, 9 stations in Southeastern Anatolia region of Turkey were studied. Drought analysis was performed on stations from 1950–2019. Daily and monthly precipitation (mm) and monthly temperature (°C) data were used from meteorological data. This data was obtained from the General Directorate of Meteorology. Potential evapotranspiration (PET) was obtained using temperature data. Many methods are available to achieve potential evapotranspiration. In this study, Thornthwaite method (mm) was preferred. Due to their incomplete data at some stations, there are differences in the observation intervals at those stations. Adiyaman, Batman and Kilis stations 1959–2019 period and Sirnak station 2000–2019 period was worked. Diyarbakir, Gaziantep, Kilis, Mardin, Siirt and Sanliurfa stations were worked in 1950–2019 period.

The type of climate that dominates the region is the terrestrial climate. When looking at Fig 2, the station with the most rainfall is Adiyaman, while the station with the least rainfall is Sanliurfa. The highest annual temperature average station belongs to Sanliurfa station. June, July, and August are very dry in the region. When examined monthly, it can be said that the months with the most precipitation are December and January, and the month with the least rainfall is August.

In addition, it can be said that the average annual rainfall values of the stations belonging to the provinces that make up the borders of the country are lower than the stations inland. This can be attributed to the position of the stations on the parallels.

Homogeneity Test

The concept of variance analysis used in statistics is the general name of a group of methods that contain many statistical methods. The simplest form of variance analysis

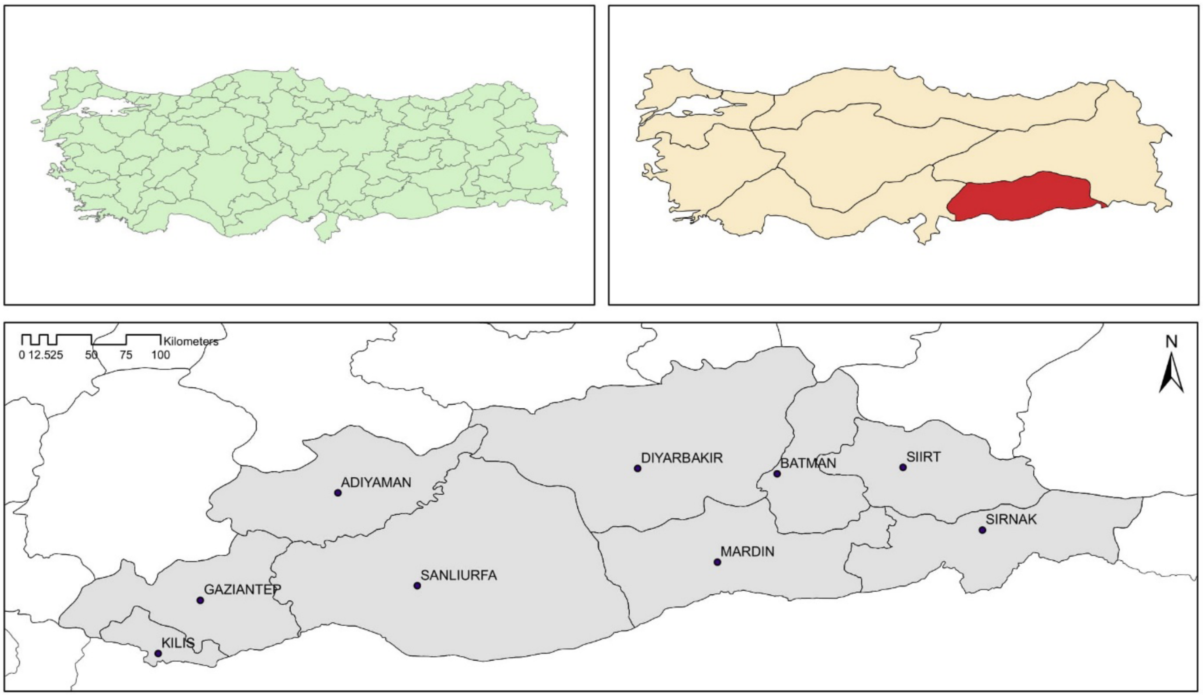

Figure 1. The location of Southeastern Anatolia Region in Turkey.

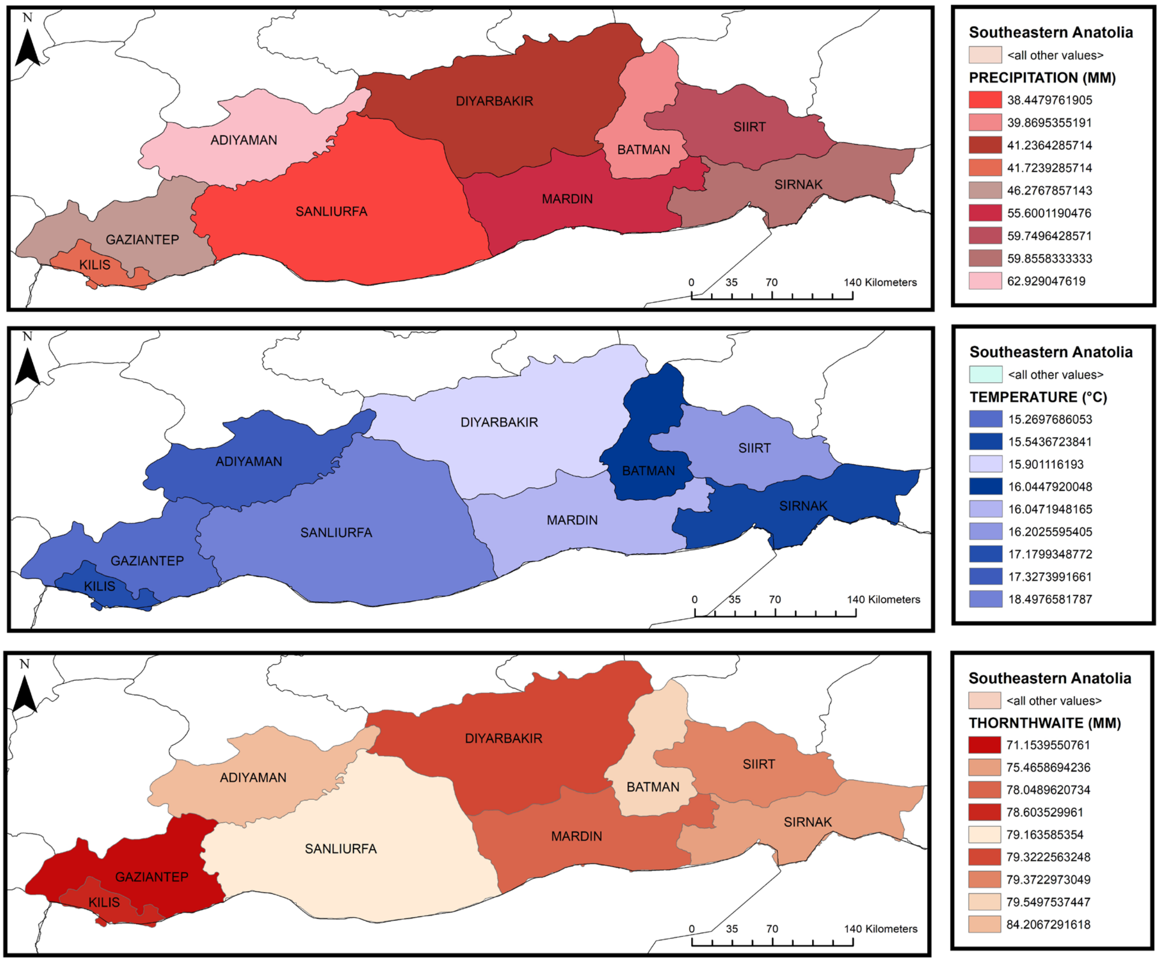

Figure 2. Average annual precipitation, average annual temperatures and average annual Thornthwaite distributions of stations.

		TEMPERATURE					THORNTHWAİTE					PRECİPİTATİON				
		Sum of Squares	df	Mean Square	F	Sig.	Sum of Squares	df	Mean Square	F	Sig.	Sum of Squares	df	Mean Square	F	Sig.
ADIYAMAN	Between Groups	421.064	57	7.387			23655.944	57	415.017			410092.846	69	5943.375		
	Within Groups	60603.541	629	96.349	0.08	1.00	4142969.955	629	6586.598	0.06	1.00	4357279.950	770	5658.805	1.05	0.37
	Total	61024.605	686				4166625.899	686				4767372.796	839			
BATMAN	Between Groups	1978.866	60	32.981			44902.218	60	748.370			89374.213	60	1489.570		
	Within Groups	70473.135	671	105.027	0.31	1.00	4132553.223	671	6158.798	0.12	1.00	1220215.838	671	1818.503	0.82	0.83
	Total	72452.001	731				4177455.440	731				1309590.051	731			
DIYARBAKIR	Between Groups	511.570	69	7.414			22358.895	69	324.042			91119.584	69	1320.574		
	Within Groups	88917.236	770	115.477	0.06	1.00	4910798.009	761	6453.085	0.05	1.00	1450440.282	770	1883.689	0.70	0.97
	Total	89428.806	839				4933156.905	830				1541559.865	839			
GAZIANTEP	Between Groups	692.245	69	10.033			22391.350	69	324.512			111298.123	69	1613.016		
	Within Groups	66888.874	770	86.869	0.12	1.00	3265329.080	761	4290.840	0.08	1.00	1972948.214	770	2562.270	0.63	0.99
	Total	67581.120	839				3287720.429	830				2084246.337	839			
KILIS	Between Groups	453.358	60	7.556			14375.063	60	239.584			113750.795	69	1648.562		
	Within Groups	48546.930	671	72.350	0.10	1.00	2988833.638	671	4454.298	0.05	1.00	1573426.514	770	2043.411	0.81	0.87
	Total	49000.287	731				3003208.701	731				1687177.309	839			
MARDIN	Between Groups	701.914	69	10.173			25853.939	69	374.695			259718.462	69	3764.036		
	Within Groups	78040.400	770	101.351	0.10	1.00	4339366.151	761	5702.189	0.07	1.00	3338206.028	770	4335.333	0.87	0.77
	Total	78742.314	839				4365220.091	830				3597924.490	839			
SIIRT	Between Groups	685.103	69	9.929			29241.164	69	423.785			207774.276	69	3011.221		
	Within Groups	82428.006	770	107.049	0.09	1.00	4670843.472	761	6137.771	0.07	1.00	3009762.344	770	3908.782	0.77	0.91
	Total	83113.109	839				4700084.636	830				3217536.620	839			
SANLIURFA	Between Groups	537.357	69	7.788			29062.570	69	421.197			123389.004	69	1788.246		
	Within Groups	74358.232	770	96.569	0.08	1.00	4630891.559	761	6085.271	0.07	1.00	1719719.133	770	2233.401	0.80	0.88
	Total	74895.588	839				4659954.129	830				1843108.137	839			
SIRNAK	Between Groups	98.192	19	5.168			3709.022	19	195.212			67750.850	19	3565.834		
	Within Groups	22123.601	220	100.562	0.05	1.00	1170987.977	220	5322.673	0.04	1.00	965041.042	220	4386.550	0.81	0.69
	Total	22221.792	239				1174696.998	239				1032791.892	239			

Figure 3. ANOVA test results of stations.

is one-way variance analysis, in other words, One-Way ANOVA. One-Way ANOVA is used to analyze how arguments interact between themselves and their effects on the dependent variable.

According to the ANOVA test, the H_0 hypothesis for homogeneity testing is accepted because the value "Sig." is Sig..>0.05 in all data groups (Fig 3). In other words, it can be said that "the variances of groups with 95% confidence are homogeneous."

Drought Indices Where Only Precipitation Data are Used

There are several indices in the meteorological drought, which has an input parameter precipitation. The calculation of these indices requires a specific classification (Table 1).

China Z Index (CZI) is based on Wilson–Hilferty's cube root transformation [22]. It has been observed that the precipitation data to be used in the index complies with the Pearson type III distribution. [11, 12]. China's National Climate Center developed CZI in 1995 as an alternative to the Standardized Precipitation Index (SPI) [21]. The CZI value is calculated as follows,

$$CZ_{ij} = \frac{6}{C_{si}}\left(\frac{C_{si}}{2}\varphi_{ij} + 1\right)^{1/3} - \left(\frac{6}{C_{si}}\right) + \left(\frac{C_{si}}{6}\right) \quad (1)$$

$$C_{si} = \frac{\sum_{i=1}^{n}(x_{ij} - \overline{x}_i)^3}{n \times \sigma_i^3} \quad (2)$$

$$\varphi_{ij} = \frac{x_{ij} - \overline{x}_i}{\sigma_i} \quad (3)$$

Where i is a time scale and can be equal to 1, 2, 3,..,72 months, and j is the current month. C_{si} = coefficient of skewness and n = the total number of months in the record, φ_{ij} = standardized variate, also called the Z-Score, and x_{ij} = precipitation of *j* month for period i, $\bar{x}_i$ = average of the precipitation of *j* month for period *i*, φ_{ij} = Standard deviation of the precipitation of j month for period i.

Effective Drought Index (EDI)

Unlike other drought indices, Effective Drought Index (EDI) uses data in the daily time period [23]. Initially, EDI was developed to monitor drought status in the daily time step [12, 24, 25]. It is suitable for the study of both meteorological and agricultural droughts, as the calculations include daily data. Calculate the EDI value:

$$EP_i = \sum_{n=1}^{i}\left[\frac{\sum_{m=1}^{n} P_m}{n}\right] \quad (4)$$

$$DEP = EP - MEP \quad (5)$$

Table 1. Dry and wet categories of various drought indices where only precipitation data are used based on the index value [19–21]

Class	CZI	EDI	PNPI	RAI	SPI	WASP	Z–Score
Normal	–1 to +1	–0.7 to +0.7	>80	0 to 2	–1 to +1	–1 to +1	–1 to +1
Slight Dry	–	–	70 to 80	–	–	–	–
Moderately Dry	–1 to –1.5	–0.7 to –1.5	55 to 70	–2 to 0	–1 to –1.5	–1 to –1.5	–1 to –1.5
Severely Dry	–1.5 to –2	–1.5 to –2.5	40 to 55	–4 to –2	–1.5 to –2	–1.5 to –2	–1.5 to –2
Extremely Dry	≤–2.0	≤–2.5	<40	>–4	≤–2.0	≤–2.0	≤–2.0

China Z Index (CZI)

$$EDI = \frac{DEP}{SD(DEP)} \tag{6}$$

Where i is the period over which precipitation is summed. P_m shows the rainfall from m days ago (Eq. 4). Thus, the EP shows 365 days of precipitation. Mean EP (MEP) for each calendar day. Calculate the DEP, which is the difference between the EP and MEP (Eq. 5). The EDI account is obtained by dividing the DEP into the standard deviation of DEP [25, 26]. EDI and SPI use similar drought severity classification.

Percent of Normal Precipitation (PNPI)

Percent of Normal Precipitation (PNPI) was defined by [9] as a normal percentage of precipitation. It can be calculated in daily, weekly, monthly, seasonal, and annual time series. Precipitation data must be in accordance with the time series to be calculated. It is required to have at least 30 years of data to calculate the normal period. PNPI is calculated as following,

$$PNPI = \frac{P_i}{p} \times 100 \tag{7}$$

Where P_i is the precipitation in time increment *i* for in each year (mm), and P is average precipitation for the study period (mm) (Eq. 7) [27].

Rainfall Anomaly Index (RAI)

Rainfall Anomaly Index (RAI) was started by Van Rooy in the early 1960s [28]. This index is based on monthly or annual precipitation data.

$$\text{If } P > \overline{P} \text{ then } RAI = 3\left(\frac{P - \overline{P}}{\overline{\overline{m - P}}}\right) \tag{8}$$

$$\text{Else } P < \overline{P} \text{ then } RAI = -3\left(\frac{P - \overline{P}}{\overline{\overline{x - P}}}\right) \tag{9}$$

In Eq. 8 and 9, P is annual precipitation, $\overline{P}$ is average of 30 years of precipitation, the average of $\overline{m}$ 10 precipitation values occurring in $\overline{x}$ average of at least 10 precipitation values occurring during the period [29].

Standardized Precipitation Index (SPI)

The Standardized Precipitation Index (SPI) method, which converts the precipitation parameter into a single numerical value to describe the drought of regions with different climates, was first developed by [7]. SPI is obtained by dividing the difference between precipitation and the average in a selected time frame into standard deviation.

$$SPI = \frac{x_i - \overline{x}}{\sigma_x} \tag{10}$$

x_i the observed precipitation value, the average of the x_i precipitation series, and the standard deviation of series σ_x (Eq. 10). The resulting SPI values show a trend that increases and decreases linearly with the lack of precipitation [30]. To consider, the impact of precipitation deficiency on different water sources, different time periods such as 1..., 3, 24 months are determined in which changes in indices will be observed. SPI is one of the most studied drought indices among drought indices [31].

Weighted Anomaly Standardized Precipitation (WASP)

Weighted Anomaly Standardized Precipitation (WASP) was developed by [20] to monitor rainfall in the tropics within 30 degrees from the equator. Grilled uses monthly precipitation data at a resolution of 0.5° × 0.5°. It is based on 12-month overlapping totals of standardized monthly precipitation anomalies.

$$WASP_N = \frac{1}{\sigma_{WASP_N}} \times \sum_{i=1}^{N}\left(\frac{P_i - \overline{P_l}}{\sigma_i} \times \frac{\overline{P_l}}{\overline{P_A}}\right) \tag{11}$$

$\underline{Pi}$ and P_A monthly and annual precipitation here, $\overline{P_l}$ and $\overline{P_A}$ monthly and annual precipitation climatology, σ_i is the standard deviation of monthly precipitation and σ_{WASP_N} is the standard deviation of Weighted Anomaly Standardized Precipitation (WASP) (Eq. 11) [13].

Z-Score Index

Z-Score Index is compared to Standardized Precipitation Index (SPI). However, it is more similar to China Z Index (CZI). Precipitation data is not required to match gamma distribution or Pearson Type III distribution. It has been involved in many studies [12, 32].

$$ZSI = \frac{P_i - \overline{P}}{SD} \quad (12)$$

Here $\overline{P}$ average monthly precipitation (mm); P_i precipitation (mm) in the specific month and the SD shows the standard deviation at any time (Eq. 12) [33].

Drought Indices Where Only PET Data are Used

Evaporative Demand Drought Index (EDDI)

Since it is done via E_0, index results can be obtained by more than one method (Thornthwaite, Blaney-Criddle, Penman-Monteith, Hargreaves-Samani etc.) [14]. The calculation steps are similar to Standardized Precipitation Evapotranspiration Index (SPEI) [34].

$$P(E_{oi}) = \frac{i - 0.33}{n + 0.33} \quad (13)$$

$$EDDI = W - \frac{C_0 + C_1 W + C_2 W^2}{1 + d_1 W + d_2 W^2 + d_3 W^3} \quad (14)$$

Values of constants; C_0 = 2.515517, C_1 = 0.802853, C_2 = 0.010328, d_1 = 1.432788, d_2 = 0.189269, d_3 = 0.001308 (Eq. 14). If $P(E_{oi}) \leq 0.5$ then $W = \sqrt{-2In[P(E_{oi})]}$; $P(E_{oi}) > 0.5$ then $W = \sqrt{-2In[1 - P(E_{oi})]}$ [34]. EDDI within our climatology period (1950–2019), n = 70 (Eq. 13). The EDDI results obtained require a classification (Table 2).

Drought Indices Where Temperature and Precipitation Data are Used

De Martonne Aridity Index (AI)

De Martonne Aridity Index (AI) was found by [36]. Aridity is effective in climate and has emerged from a lack of humidity. It can also be calculated monthly or on an annual period. However, there are two different calculations.

Table 2. Dry and wet categories of various drought indices where only PET data are used based on the index value [34].

USDM drought category	Description	EDDI percentiles
D_0	Abnormally dry	70–79
D_1	Moderate dry	80–89
D_2	Severe dry	90–94
D_3	Extreme dry	95–97
D_4	Exceptional dry	98–100

Table 3. Dry and wet categories of various drought indices where temperature and precipitation data are used based on the index value [35]

Climate classification	Values of IDM	PCI	HTC
Dry	<10	<10	<0.3
Semidry	10 to 20	10 to 20	0.30 to 0.6
Mediterranean	20 to 24	20 to 24	0.6 to 0.8
Semi-humid	24 to 28	24 to 28	0.8 to 1.0

$$I_{DM} = \frac{P}{T + 10} \quad (15)$$

$$I_M = \frac{12P'}{T' + 10} \quad (16)$$

Eq. 15 performs annual calculations, while eq. 16 performs monthly calculations. The drought values obtained because of these formulas are classified according to Table 3. P expresses the annual precipitation value (mm), T expresses the annual temperature value. P' and T' represent the average monthly precipitation and temperature [35, 37].

Pinna Combinative Index (PCI)

The Pinna combinative index (*Ip*) was developed by Pinna [35].

$$I_p = \frac{1}{2}\left(\frac{P}{T + 10} + \frac{12P'_d}{T'_d + 10}\right) \quad (17)$$

P and T represent the annual mean precipitation and temperature. P'_d and T'_d are the mean values of precipitation and air temperature of the driest month (Eq. 17). Many studies have been carried out on this index [35, 38].

Hydro-Thermal Coefficient of Selyaninov

The Selyaninov's hydrothermal coefficient (HTC), developed by [39]. Calculated using the following formula,

$$HTC = \frac{P}{\sum_{T>10} \frac{T}{10}} \quad (18)$$

where P is the sum of precipitation amounts (mm) and T is the sum of temperatures (°C) for the months (Eq. 18).

Table 4. Dry and wet categories of various drought indices where PET and precipitation data are used based on the index value [10, 40]

Class	SPEI	RDI
Normal	−1 to +1	−1 to +1
Moderately Dry	−1 to −1.5	−1 to −1.5
Severely Dry	−1.5 to −2	−1.5 to −2
Extremely Dry	≤−2.0	≤−2.0

Drought Indices Where PET and Precipitation Data are Used

Standardized Precipitation Evapotranspiration Index (SPEI)
SPEI was originally developed by [40] to assess agricultural drought severity, considering plant evaporation and meteorological drought. SPEI is expressed as the difference (D_i) between monthly or weekly potential evapotranspiration (PET_i) and precipitation (P_i). This difference (D_i) is the surplus or lack of water for the analyzed month (i).

$$D_n^k = \sum_{i=0}^{k=1}(P_{n-i} - PET_{n-i}), \quad n \geq k \tag{19}$$

$$SPEI = W - \frac{C_0 + C_1 W + C_2 W^2}{1 + d_1 W + d_2 W^2 + d_3 W^3} \tag{20}$$

P and PET are calculated for i month. In different Dk series, k is the timescale for the month and n is the calculation number. D cannot be calculated in the case of $k > n$ (Eq. 19). Values of constants; C_0 = 2.515517, C_1 = 0.802853, C_2 = 0.010328, d_1 = 1.432788, d_2 = 0.189269, d_3 = 0.001308 (Eq. 20). If $P \leq 0.5$ then $W = \sqrt{-2In[P]}$; $P > 0.5$ then $W = \sqrt{-2In[1-P]}$. P is the probability of higher values of D. Many studies have been carried out on this index [41].

Reconnaissance Drought Index (RDI)

Reconnaissance Drought Index (RDI) was found by Tsakiris and Vangelis of the National Technical University of Athens / Greece [10]. There are two new expressions in the form of Normalized RDI and Standardized RDI.

$$\alpha_k^{(i)} = \frac{\sum_{j=1}^{k} P_{ij}}{\sum_{j=1}^{k} PET_{ij}} \tag{21}$$

$$RDI_n^{(i)} = \frac{\alpha_k^{(i)}}{\bar{\alpha}_k} - 1 \tag{22}$$

$$RDI_{st}^{(i)} = \frac{y_k^{(i)} - \bar{y}_k}{\sigma_{yk}} \tag{23}$$

Here, P_{ij} and PET_{ij} provide precipitation and potential evapotranspiration of the y-pearl month of the x-pearl year (Eq. 21). In the formula , $\alpha_k^{(i)}$'s value was found to be satisfactory able to track both lognormal and gamma distributions at different timescales and over a wide range of locations [42, 43]. The $\bar{\alpha}_k$ parameter is the average of $\alpha_k^{(i)}$ values calculated for n years of data. In eq. 23; , arithmetic means and σ_{yk} standard deviation.

The SPEI and RDI results obtained are divided into the same classification (Table 4). The results provide information about the region.

RESULT AND DISCUSSIONS

There are many drought indices in meteorological drought. However, many parameters such as precipitation and temperature vary from the location of each station. In addition, drought indices use different classifications due to the parameters used. As a result of the analysis, the obtained index values are divided according to drought categories. It has been tried to show which category the region is in.

Drought Indices Where Only Precipitation Data are Used
The result of frequency analyses of the CZI, EDI, PNPI, RAI, SPI, WASP, and Z-Score indices using the same drought classification are shown in Fig 4. Only classification by dry category was made. First, it can be said that similar results have been achieved in 9 stations. This shows that there is not much difference between the precipitation at the stations.

The index with extremely dry results is the EDI. This result may be due to the index's use of daily precipitation value, unlike other indices. RAI is the index where the severe dry category is maximum at each station. This result is due to the lack of precipitation in stations most of the time. Moderately dry, all stations have a certain percentage of drought. However, it belongs to Adiyaman and Gaziantep stations with a maximum value of 21%. At both stations, this value belongs to the RAI index. The sightly dry class contains only values for the PNPI index. This classification is available in Table 2.

The indices where normal results are lowest at all stations are EDI and RAI. From here, according to the RAI and EDI indices, it is the conclusion that the Southeast Anatolia Region is dry. According to these indices, the region can be said to be severely drought.

Drought Indices Where Only PET Data are Used
The EDDI values obtained monthly are averaged for each month and the value for that month was obtained. Fig 5 shows the mapping of the monthly averages of the EDDI at

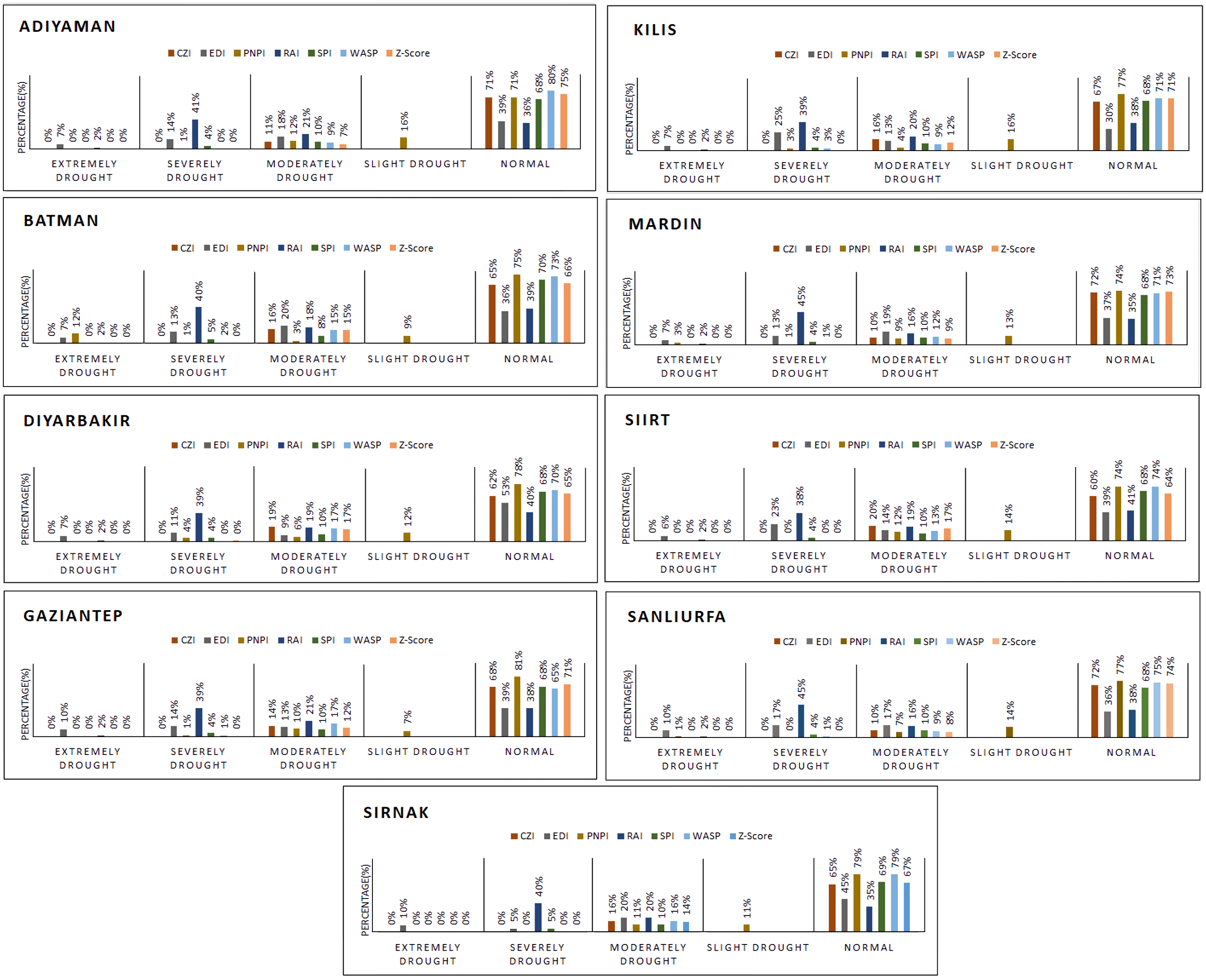

Figure 4. Frequency analysis of drought indices using only precipitation.

stations by Spline method (ARGCIS). Drought is observed from April to October, according to the results. Between December and February, minor variations were observed between the stations. It can be said that there are many seasonal differences on the border of the region.

November and March include a pass. The month dominated by Level 0 is January, while the month dominated by Level 4 is July.

Drought Indices Where Temperature and Precipitation Data are Used

The percentage results of the AI, PCI and HTC drought indices using the two parameters are seen in Fig 6. The results are based on annual formulas. According to the results, the Sanliurfa station is dry with a value of close to 90% in the maintenance of PCI and HTC indices. On a drought basis, it can be said that Batman came after Sanliurfa. The AI drought index showed lower results in drought across the region than the other two indices.

The AI drought index has more semi-humid values. According to the PCI and HTC indices, the region is a drought zone.

Drought Indices Where PET and Precipitation Data are Used

The RDI drought index is divided into Normalized RDI and Standardized RDI. However, because SPEI is a standardized value, comparing it to RDIs gives more accurate results. SPEI and RDI values were calculated at short (1 and 3 months), medium (6 months), and long (9 and 12 months) timescales, and drought analysis were performed. Fig 7 shows the results of the SPEI and RDIs drought indices of Diyarbakir station in graphs. There is also a more detailed representation of the values between 1950 and

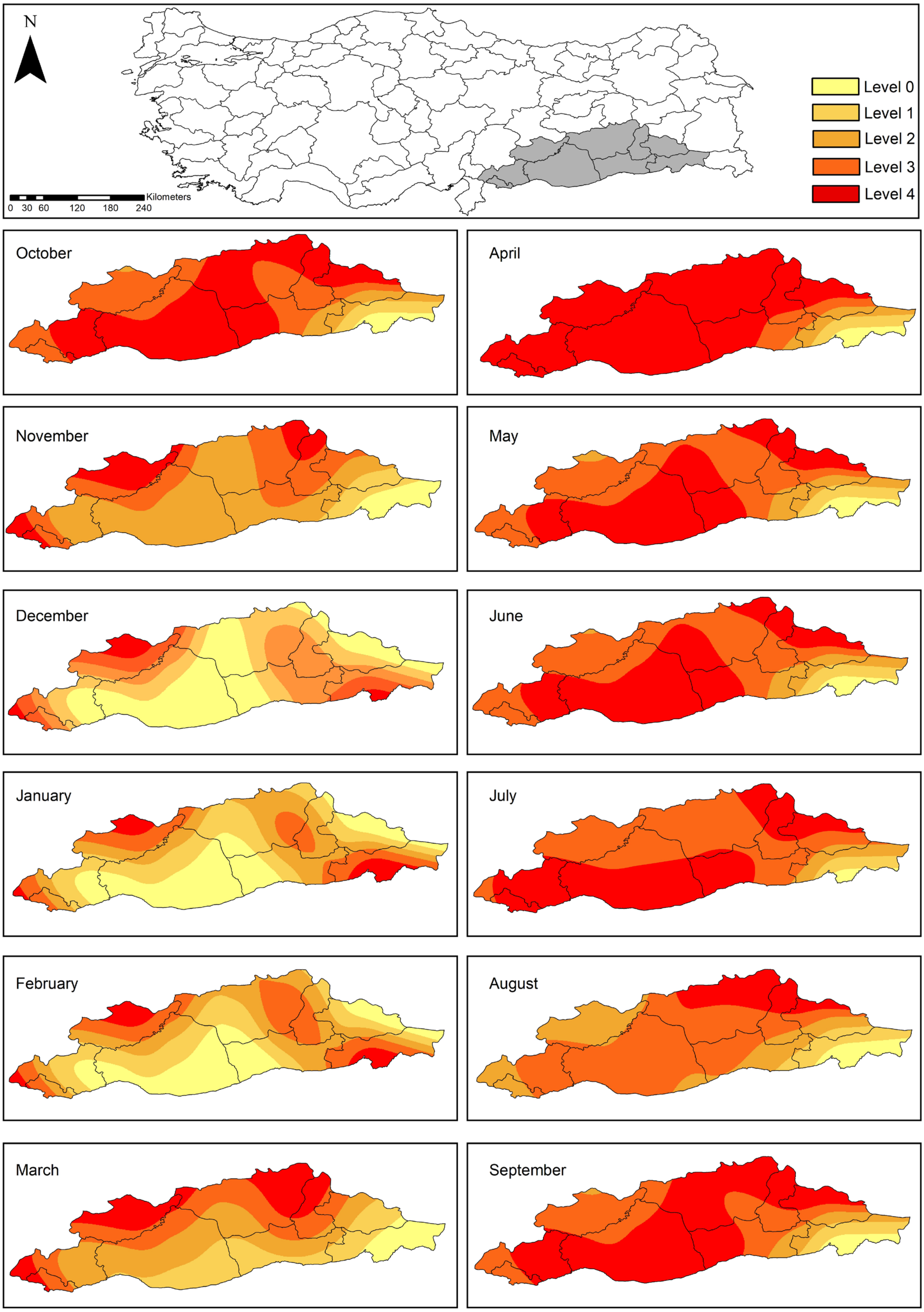

Figure 5. Monthly map of drought indices using only PET value by Spline method.

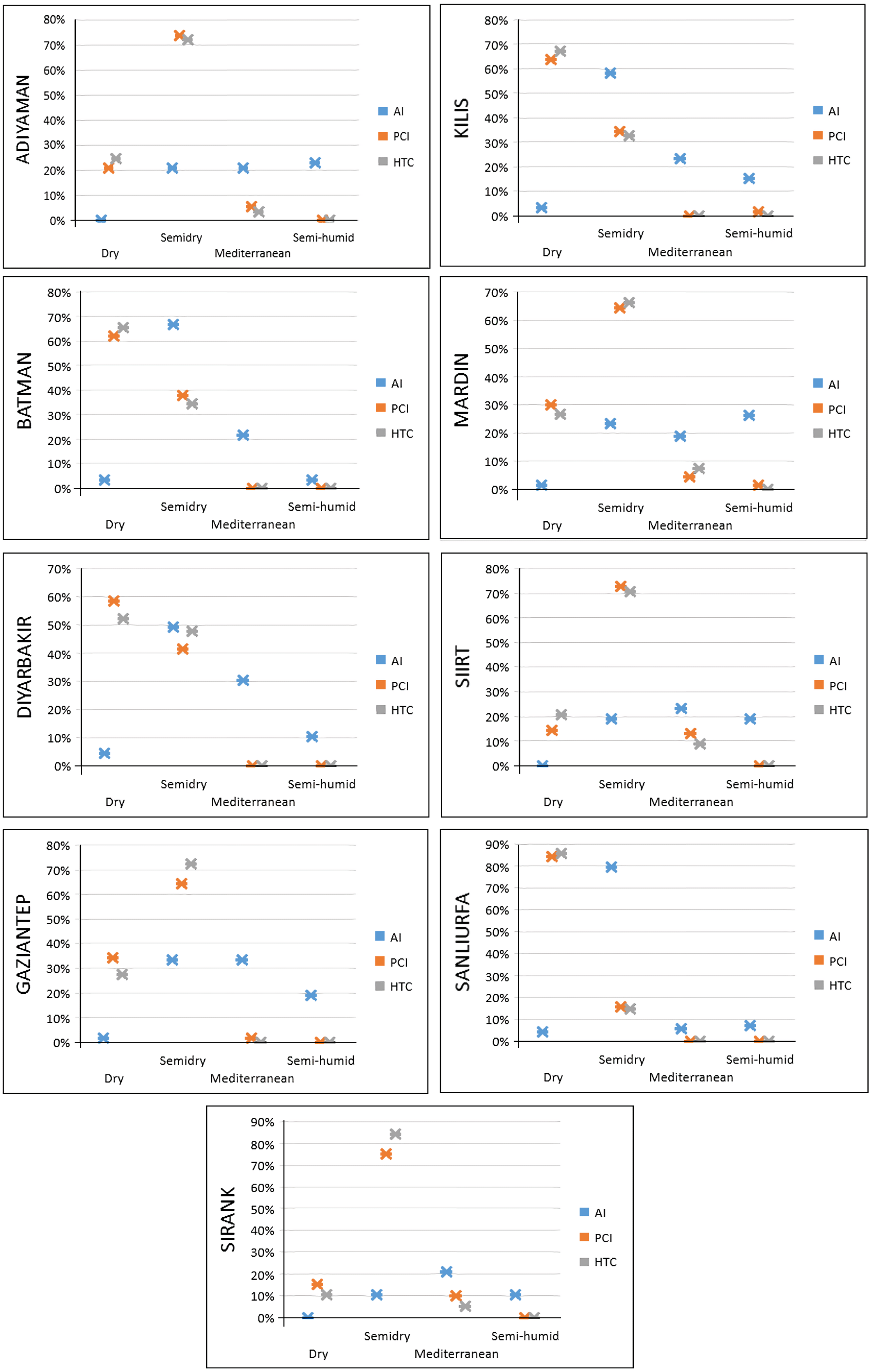

Figure 6. Frequency analysis of drought indices using precipitation and temperature.

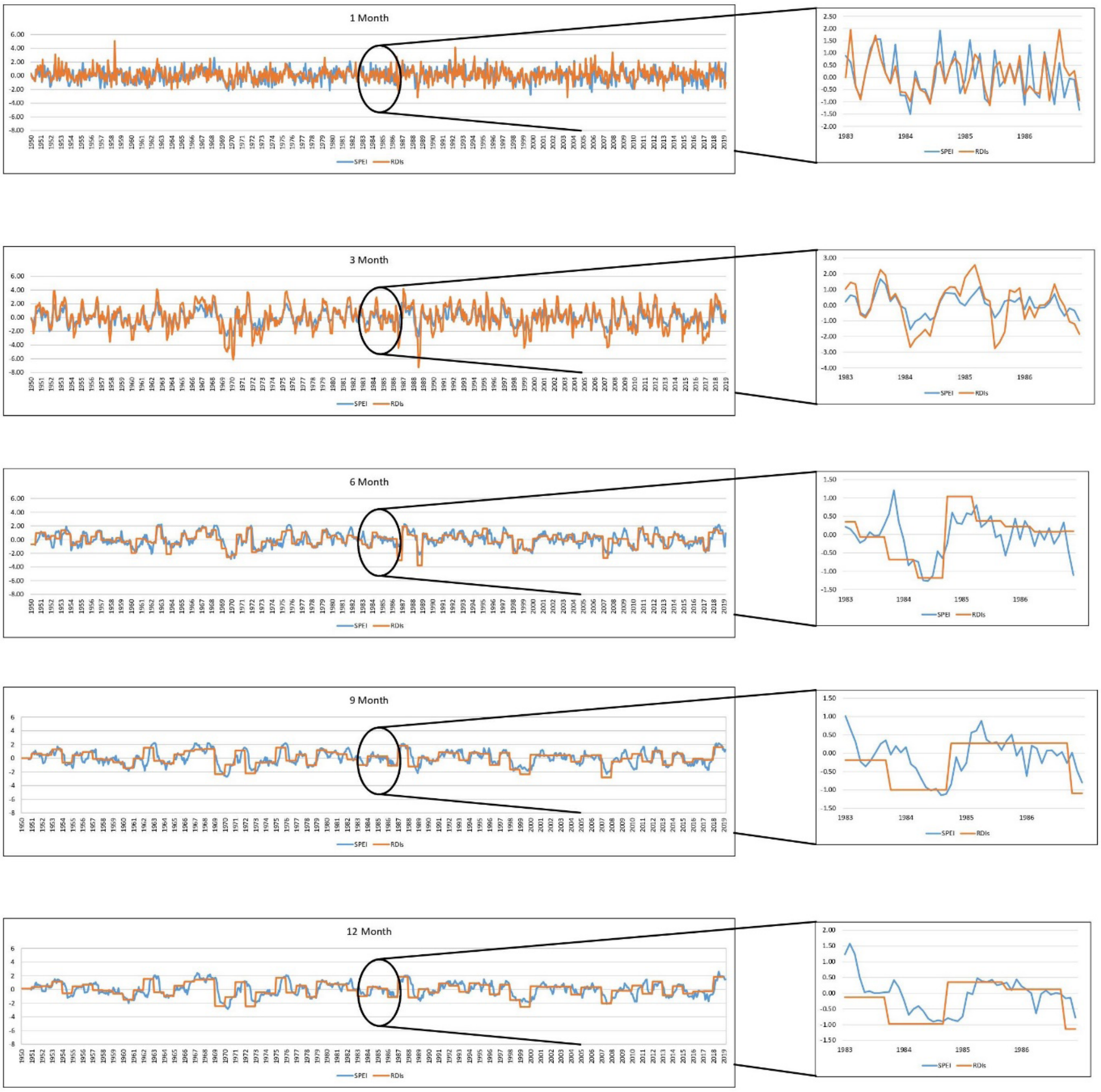

Figure 7. SPEI and RDI at different timescales in Diyarbakir.

2019 between 1983 and 1986 in the chart. According to the results, the frequentness of 1-month values and the frequentness of 12-month values vary.

CONCLUSION

Drought cannot be fully defined due to its mixed structure and effects. That is why it has been suffered for a long time. From simple approaches to mixed approaches, this has contributed to the development of the progressively evolving drought indices.

In this study, it covers a long period of 70 years between 1950 and 2019 for the Southeast Anatolia Region. Drought analysis was tried using meteorological drought indices. Given the drought indices, it can be concluded that there are differences between both seasonal variations and the parameters used. The objective is to sort the indices by separating the indices according to the parameters in which they are used. Thus, comparing the indices with each other gives more accurate results. In addition, the role of each method in drought detection will be determined. It is also intended to determine the most appropriate drought index for the region.

It is seen that the methods partially detect the drought that occurred in the period 2006 – 2009, which occurred throughout the country and caused large agricultural crop and economic loss, especially in the Southeastern Anatolia Region.

- Drought indices where only precipitation is used have high dry values on a percentage basis compared to normal values. According to the drought results applied for 70 years, normal values are currently prevailing in the region. However, it is observed that the dry values are increasing. RAI is the largest number of dry results between the indices. PNPI is also classified as 5 droughts, unlike other indices. As a result of these analyses, it was determined that SPI-originated indices (CZI, Z-Score and others) are reliable and accurate indices for drought analysis, and it was concluded that other indices may not yield very reliable results.
- In drought indices where only PET is used, it has been determined that dry months are more than normal months. Drought has an impact in most months. The months of April and July can be said in the months of the dry.
- Different results occur in drought instances where both precipitation and temperature are used. According to the PCI and HTC drought index, drought has been experienced, while AI says the drought may be just starting. In the indices in this drought classification, weedy results were achieved more dryly than others.
- Firstly, 5 different reference periods of 1, 3, 6, 9 and 12 months were determined for the total amount of rain per month. Potential evapotranspiration amounts were then obtained by Thornthwaite method by using monthly average temperatures, and these potential evapotranspiration amounts were divided into 5 different reference periods: 1, 3, 6, 9 and 12-month periods. In drought indices where both precipitation and PET are used, drought has generally been observed in both indices for at least 1 month. In SPEI, maximum drought was observed at all stations with a 3-month frequency. In RDI, maximum drought was observed at all stations with a 3-month frequency.

Differences are observed when looking at the drought rates obtained from the stations' annual and monthly drought indices. These differences are because the stations experience summer droughts, with rainfall falling mostly during the winter and spring months.

With this study, the approach created for the Southeast Anatolia Region is based on the meteorological drought index. Researchers tried to conduct spatial analysis of drought and determine the stations affected by drought in the study area, which is important for water resources and agriculture.

As a result, this study can be further expanded by including climate elements such as humidity, temperature, precipitation type, evaporation, wind, sunbathing intensity, etc. Relations between drought and these variables can be revealed. The effects of all climate elements on drought should be investigated and methods should be developed to fore-tell the drought.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Assessment of strength and abrasion resistance of elasto-plastic fiber reinforced concrete using geopolymer based recycled aggregates

Abdelaziz MOHAMED[1,*], Orhan CANPOLAT[1], Mukhallad M. AL-MASHHADANI [2]

[1] *Yildiz Technical University, Faculty of Civil Engineering, Civil Engineering Department, Davutpasa Campus, Istanbul, Turkey*
[2] *Istanbul Gelisim University, Faculty of Architecture and Engineering, Civil Engineering Department, Avcilar Campus, Istanbul, Turkey*

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ABSTRACT

Recycled aggregates and geopolymer binders are green materials contributing to the sustainability of the planet. We investigated the performance of geopolymer concrete using recycled aggregates (fly ash (FA) and ground granulated blast furnace slag (GGBS)) related to their mechanical properties. Geopolymer concrete were prepared by mixing 50% low calcium fly ash, 50% GGBS, sodium hydroxide and sodium silicate solution, Coarse aggregate (Natural coarse aggregate, Recycled coarse aggregate), Fine aggregate (Crushed Sand, Riverbed Sand) and elastoplastic fibers. Recycled aggregate used was obtained locally from Istanbul, Turkey. To explore the efficiency of recycled aggregate, during the production of geopolymer concrete, partial replacement of recycled coarse aggregate with natural aggregate was made in 10, 20, 30, and 40%. To compare the results, geopolymer concrete containing 100% natural aggregates was made. Since concrete gains strength with time after casting, On Day-28 and Day-90, the compressive strength, split tensile strength, and flexural strength of those geopolymer based concrete were examined. Results of the test showed that the compressive strength of 28 and 90 days w.r.t. different ratios was 26.8, 25.3, 24.2, 23.1, 23 MPa, and 30.2, 28.1, 27.0, 25.2, 25.0, 23.0 Mpa respectively, while split tensile strength was 1.9, 1.5, 1.5, 1.4, 1.4 MPa and 2.0, 1.9, 1.9, 1.6, 1.5 MPa respectively, and the ultimate flexural strength of tested beams were in the range of 3.53 to 4.54MPa. Although the general performance of the produced samples was showing a decrement with the increasing ratio of recycle aggregates, the obtained results indicated that using recycled aggregate is up to some extent of 30% is beneficial in terms of strength.

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***Corresponding author.**
*E-mail address: f1318022@std.yildiz.edu.tr

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INTRODUCTION

With the increase of environmental concerns related to production and usage of ordinary cement-based reinforced concrete, scientists have been vigorously engaged with investigating prospects of utilizing alternative materials to address these concerns [1,2]. To decrease this problem Geopolymer is regarded as an inventive construction material and it had impressive interest from researchers around the world [3]. Consuming geopolymers fabricated by industrial byproducts to replace cement completely or partially can decrease cement consumption, hence dropping CO_2 emissions [4]. On the contrary, Recycled aggregate extracted from recycled concrete can consume accumulated construction byproducts and save non-renewable materials and land resources. The amalgamation of the two materials can protect the environment and save resources [5]. Trying to decrease the reliance on customary concrete constituent materials, which are fast consuming it is found that the alternative concrete composing materials such as recycled aggregate, fly ash and granulated blast furnace slag can contribute strength and durability to the concrete [6,7,8]. On the other hand, the annual production of cement in the world is estimated 1.6 billion tons which contributes 1.6 billion tons of CO_2 into the environment. In other words, cement industry is counted as the major CO_2 emission source, which generates 5–7% of entire CO_2 in the globe [9,10,11]. This amount of carbon dioxide release is projected to cause the climate change. According to performance and mechanical properties of fly ash and slag based geopolymer concrete with recycled aggregate instead of Portland cement-based concrete could contribute strength development. But further increasing recycled aggregate contents in both recycled aggregate concrete and geopolymer recycled concrete, the strength was decreased steadily. the low water availability between old mortar and aggregate causes the formation of weaker (ITZ) interfacial transition zone. The controlling factor for recycled aggregate geopolymer concrete strength failure is projected to be caused the weaker link of ITZ [12]. Through microstructure analysis it is proved that two factors owing to strength weaken, was increased recycled aggregate and the structure of interfacial transition zone (ITZ) [13].It is proved that making 10% replacement of recycled concrete aggregate of natural aggregate the compressive strength plus split tensile strength increased. Furthermore, curing ambient condition for 10% replaced recycled aggregate of natural aggregate in geopolymer concrete, the flexural strength showed good result over compressive strength [14].In this study, geopolymer fabricated from the combination of GGBFS and FA will be used as a binder and RA was partially replaced in NA. This study explores the mechanical and durability properties of elastoplastic fiber reinforced GPC with RA.

MATERIALS AND METHODS

In this study we investigated 5 series of geopolymer mixes. Mixes were conducted with the inclusion of 0.4% ratio of elasto-plastic fiber (EP) and the properties of EP is given in table 2. Also, through the whole mixes recycled aggregate was replaced of natural aggregate in different percentages of 10%, 20%, 30% and 40% by weigh. The first mix containing same proportion of compositions to other four mixes but 100% natural aggregate, was casted as a control sample. Also, for the fabrication of each mixture total binders used contains Fly ash, GGBFS, Sodium silicate and Sodium hydroxide Both were acquired from a Chemicals Company called Merck in turkey. The weight ratio of FA and GGBFS was contained an equal weight ratio of 50% FA and 50% GGBFS. Fly ash used in the study was sourced from Cates electrical production Inc., a thermal power plant located in a northern city in Turkey called Çatalağzı/Zonguldak and has a specific gravity of 1.96 g/cm^3 while the GGBS material used in this study was obtained from a cement company in Bolu Turkey that has specific gravity of 2.91g/cm^3. The chemical compositions of FA and GGBS are listed in Table 1.

In the experiment, cube molds of (100×100×100) mm, cylinder molds of (100×200) mm and Beam molds of (100×100×500) mm were used. Molds were oiled with grease to ease the demolding process. Firstly, dry materials namely, No.1 Natural coarse aggregate, No.2 Natural coarse aggregates, No.1 and No.2 Recycled coarse aggregate and fine crashed sand aggregates attained from DÖKMAK Foundry Industry which is in Darıca-Gebze/Kocaeli. with fly ash and GGBFS were mixed for at least 2 min properly, and then, chemicals which were prepared one day prior to use were added along with fibers and mixed for 3 more min. To achieve a better workability MasterGlenium51 supplied by BASF Türk Kimya San. ve Tic. Ltd. Şti. based in Turkey was added. Owing to physical design of the mixer drum each mixture was casted in three batches.

Table 1. Chemical composition of fly ash and slag (%).

Chemical composition	Amount (%)	
	GGBS	Fly ash
SiO_2	40.55	54.08
Al_2O_3	12.83	26.08
Fe_2O_3	1.10	6.681
CaO	35.58	2.002
MgO	5.87	2.676
SO_3^{-2}	0.18	0.735
Na_2O	0.79	0.79
Cl^-	0.0143	0.092
LOI (loss of ignition)	0.03	1.36

Table 2. Elasto-plastic fiber (EP) properties

Type of Fiber	Length (mm)	diameter (mm)	Width (mm)	Slenderness (Lf/de)	Tensile strength (MPa)	Elastic modulus (GPa)	Shear modulus (pa)
EP	40	0.78	1.1	51.3	450	3.6	1.28

RESULTS AND DISCUSSION

Three parameters of compressive, splitting tensile strength and flexural strength were investigated in 28 and 90 days. The test results are shown in Figures 1 and 2. After examining both 28- and 90-days it is noted that as the recycled aggregate proportions increased, strength results were found to be decreased. The reduction degree was found to be significant in the case of 30% and 40% replacement of the recycled aggregate. However, 10% and 20% caused insignificant reduction in strength. the combination of binders was 50% GGBS and 50% fly ash having 0.45 W/B ratio. This combination exhibited an excellent performance in mechanical properties but decreased the workability for the replacement beyond 20%. As expected, geopolymer with natural aggregates showed higher strength than the geopolymer concrete with recycled aggregate, existed cracks in recycled aggregate are the main defects causing the lower strength in compliance with Wangetal. [15]. Also, the void volume is high and existed calcium hydroxide in old and new interfacial zones in recycled geopolymer is an agent of effect in strength [16]. The highest compressive strength was achieved in 28 days specimens result was 26.8 MPa which is mix one and mix 5 found to be the lowest strength having only 23.0 MPa. While for the 90 days results mix one performed the highest strength which is 30.2 MPa also the lowest was mix 5 which is 25.0 MPa. Highest splitting tensile strength in 28 days was mix 1 which is 1.92 MPa and lowest -was mix 5 which is 1.39 MPa and for 90 days test results mix 1 showed highest result which is 1.96 MPa while lowest was mix 5 which is 1.5 MPa. Highest flexural strength result of 28 days test result was exhibit by mix 2 which is 3.48 MPa and lowest was M5 which is 2.11 MPa, for 90 days highest result performed by mix 5 which is 4.54 MPa and lowest was mix 1 which is 3.53 MPa. Also, for durability one of the parameters explored was abrasion. Abrasion resistance of measured specimens was assessed in terms of weight loss. The test of abrasion resistance measurement was conducted in compliant with BS EN 13892-3:2014 [17], which determines horizontal abrasion resistance of concrete surfaces. Results showed that natural aggregates resulted in less weight loss compared to recycled aggregate this may be caused by the increase of void content

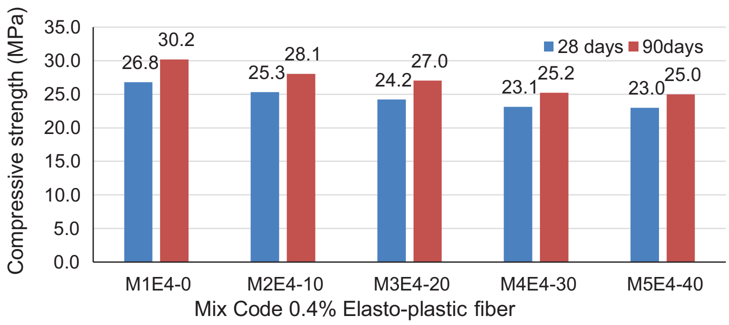

Figure 1. Compressive strength results.

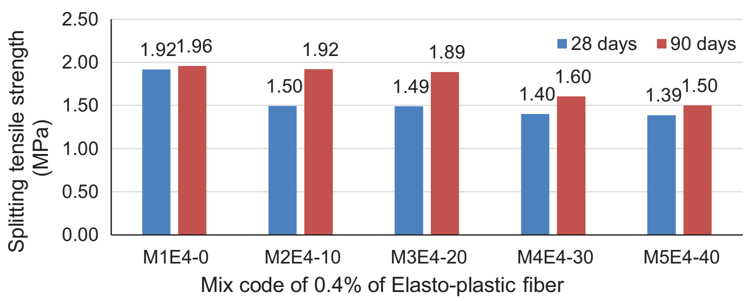

Figure2. Splitting tensile Strength results.

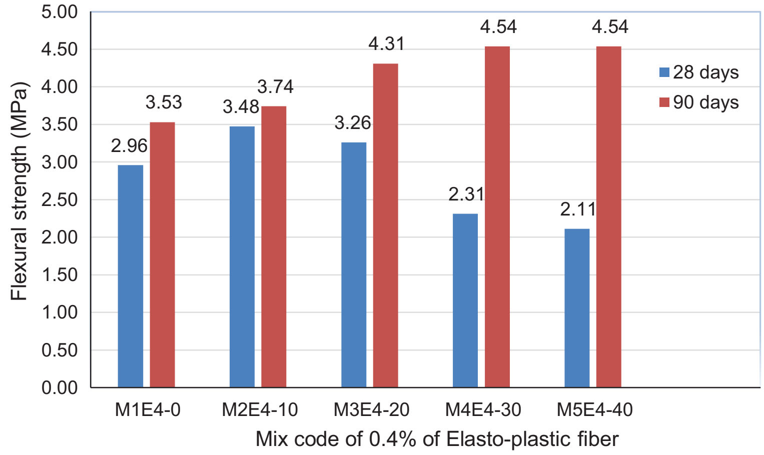

Figure 3. Flexural strength results.

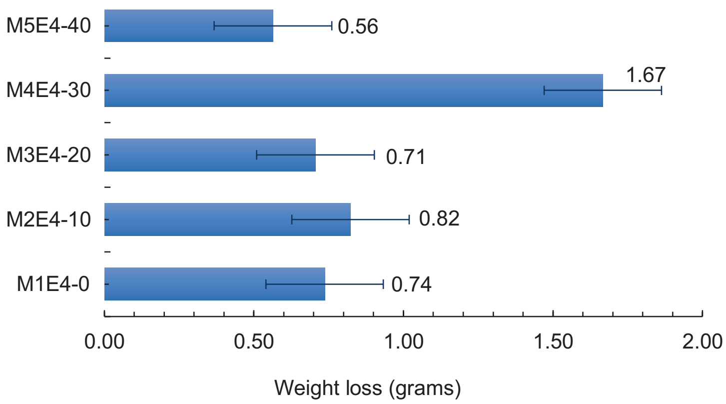

Figure 4. Average weight loss due to abrasion for 0.4% fiber inclusion.

and porosity that exists inside the recycled aggregates that weakened its wear-resisting strength [18, 19].

CONCLUSIONS

This experiment was conducted with fly ash and GGBS based geopolymer concrete with different proportions of recycled aggregate reinforcing with elasto-plastic fibers, after performing compressive, splitting and flexural tests following conclusions can be accounted:

- Using recycled aggregates in the geopolymeric matrix up to a certain limit is feasible in terms of utilizing wastes and by-product materials, thus, creating a sustainable binding material is achievable.
- Using non-cementitious binders such as GGBS and fly ash instead of ordinary Portland cement (OPC) in the matrix could result in improved strength of the recycled aggregates geopolymer concrete.
- based on the research results to achieve excellent mechanical properties and workability the incorporation of Fly ash and GGBS binder having 1:1 ratio with 0.45 water-binder ratio can give promising geopolymer concrete.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Effects of Saharan dust cloud water in the remediation of soil having high heavy metal content

Vildan Zülal SÖNMEZ[1,2*], Emine Elmaslar ÖZBAŞ[1]

[1]*Istanbul University-Cerrahpasa, Department of Environmental Engineering, Istanbul, Turkey*
[2]*Düzce University, Department of Environmental Engineering, Düzce, Turkey*

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ABSTRACT

Studies revealed that the precipitation from the Saharan Desert brings on a natural fertilizer effect on the plants, contributing to the growth of plants during daytime. In this study, the effectiveness of the Saharan dust has been investigated in the remediation of soil, which has been a very low pH value and high concentrations of various metals. The effects of using the solution obtained by dilution of Saharan dust (as namely Saharan dust water) and Saharan dust on the development of Phaseolus vulgaris and the amount of metal passing to the plant were investigated. It was observed that no plant growth occurred when no remediation was provided on the soil. When metal amounts penetrating the plant was considered, lower metal concentrations were determined in the plants growing with mixtures in which Saharan dust was added and which were irrigated with Saharan dust water compared to mixtures in which compost was added and which were irrigated with Saharan dust water. It was observed that irrigation with Saharan dust water and/or addition of Saharan dust was making the soil suitable for the growth of the plant by increasing its pH in a similar way as adding compost. It was seen that the compost and Saharan dust, and that the solution obtained by Saharan dust water were enabling remediation in soil containing high amounts of metal and having an acidic character at a level as to enable plant growth, and are causing a decrease in the amounts of heavy metal penetrating the plant.

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INTRODUCTION

Many studies have reported that heavy metal contamination of soil is likely to cause risks and harm to humans and ecosystems (for example, when we are exposed to contaminated soil, food chain or groundwater) [1–6]. Heavy metal concentrations in soil can significantly diverge in uncontaminated soils because of considerable differences in the geochemical compositions of rocks. However,

***Corresponding author.**
*E-mail address: zulal.sonmez@iuc.edu.tr

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contamination that cause from many sources is likely to lead to toxicity as the result of the growth of a high level of heavy metal concentrations in soil organisms and sensitive plants [7]. Mobility and toxicity of heavy metals in soil are determined by their chemical properties, concentrations and availability [8]. Organic substance, clay mineral, pH and oxidation/reduction status are among the features of soil, are parameters which is likely to alter the solubility and mobility of toxic metals [9]. Moreover, the alteration of these parameters is likely to impact the mobility of heavy metals and influce the usage area of soil by transforming the chemical forms of toxic metals, particularly as the change in pH increases in alkaline direction, heavy metals may be immobilized in soil gradually [10]. Several methods in remediating metal-polluted soils occur, such as physical,chemical and biological methods. Most physical and chemical methods (e.g., encapsulation and vitrification) are costly, and they do not prepare the soil proper for plant growth [11]. We should note that the yield strength of soils may be increased using soil remediators in the remediation of contaminated soils. Many materials such as sewage sludge, tree wastes, tea industry wastes, humic acid, straw, farm manure, compost, chicken manure, humus, pumice, hazelnut shell, sawdust are used in the reclamation of contaminated soils [12–14]. Sahara Desert, which is the largest desert of the world with a surface area of 9.149.000 km^2 at the north of Africa Continent, provides a large part of the dust at the northern hemisphere. It is known that dust of annually 80 million tons –arising from the large Sahara Desert at the north of Africa- is being carried to Amazon Region through winds, and contributes to the growth of plants there. Turkey is close to significant deserts of the world as per its location, and each year about 20 million tons of dust transportation is being realized to Turkey from these deserts through the winds as per its latitude values. It has been revealed by the researches made that red sands are being carried to Turkey from the Grand Sahara, Arabia, Iran and Syria deserts [15, 16]. It has been revealed that these precipitations – which were initially considered as contaminating the environment- are causing natural fertilizer effect on the plants, especially in case of their realization during day time, and are contributing to the growth of plants [16]. Dust coming from the Sahara Desert can start many reactions once contact with cloud water, and it results in the formation of decreased iron (Fe^{2+}), oxalate and various basic amino acids. Microorganisms can be propagated using these products [17].

In this study, the effects of irrigation with dust transported from Sahara Desert (is named as Saharan dust) in the remediation of soil contaminated by heavy metals was searched. It was selected green bean (Phaseolus vulgaris) that could be easily adapt to environmental conditions. Moreover, it was tried to determine the soil remediator feature of Saharan dust by the use of Saharan dust instead of compost. Thus, it was tried to determine the role of irrigation with Saharan dust on the growth of plants against the removal of heavy metal toxicity in contaminated soil. This study is the first study in the literature in which Saharan dust was used as a soil remediator in the reclamation of soils contaminated with heavy metals.

MATERIALS AND METHODS

In this study, Municipal Solid Waste (MSW) Compost samples were acquired from Istanbul Solid Waste Recycling and Composting Facility in Turkey. The soil sample (S1) used in the present study was collated from a rural area in Trabzon. The other soil sample (S2) used in this study was a commercial soil (brand of the soil; TROPIKAL). Saharan dust samples that were obtained from southern Tunisia near Tozeur were used.

Characterization of Soil and Compost Samples

Distilled water was added to the samples at a ratio of 5:2 (v/w) to determine the pH values of the compost samples. The measurement of pH values was performed using a pH meter after being mixed by a magnetic mixer for 10 minutes [18]. The pH values of the soil samples were determined in a water suspension 1:2.5 sample: solution ratio and in KCl 0.1 N [19]. A Jenway 3051 pH meter and SIS electrode were used for the determination of the soil's and compost's pH.

The percentages of C, H and N in the compost and soil samples were determined using an elemental analyzer at the Environmental Engineering Department of Istanbul University- Cerrahpasa. Samples were dried at 50°C for 24 hours and ground to a fine powder in a quartz mortar before elemental analysis. The equipment specifications included Thermo Scientific Flash 2000 CHNS Analyzer, temperature: 900 °C; mobile gas He; burning gas O_2.

Soil and compost samples were air-dried and then sieved to pass a 2 mm mesh for determination of total Ni, Fe, Cu, Cd, Zn, Pb and Mn concentrations. The "Microwave Solubilization Method" was used to determine the total metal concentrations of the soil and compost samples [20]. Accuracy was regularly checked by reference digests of standard reference soils (SRM 2711, CMI7004). The analytical precision, which was measured as relative standard deviation, was between three and 5%.

To investigate the immediately available elements, the concentrations for Ni, Fe, Cu, Cd, Zn, Pb and Mn, 2 grams were obtained from each air-dried sample. For the samples, 20 mL was added from 0.01 N $CaCl_2$ solution, and it was then shaken for three hours. Extracts were filtered using a 0.45 μm membrane. Metal concentrations in filtrates were identified [21].

In the identification of potentially available elements, 50 mL of the solution, having a pH value of 4.95 and comprising 0.5M ammonium acetate and 0.02M EDTA, was added to 5-grams air-dried samples. After shaking for one hour, they were centrifuged at 700 rpm for 15 minutes. Extracts were filtered using a 0.45 μm membrane filter. After this, the metal concentrations in filtrates were identified [21].

The EPA Method 1311 was used for the TCLP (toxicity characteristic leaching procedure) leaching test. Soil samples and distilled water (the pH value was adjusted to 4.93 with acetic acid) were mixed at a ratio of 1:10. They were shaken at 250°C for 18 hours at 30 rpm. After the extraction, the mixture was centrifuged at 2000 rpm for 15 minutes. Then, the extracts were filtered using a 0.45 μm membrane filter. Metal concentrations was determined on these filtrates [21].

Metal concentrations of extracts that were obtained at each stage were measured using AAS (Perkin Elmer AAS 400).

Studies with Plant

In this study, compost at ratios of 25% and 50% (v/v) was added to the S1 and S2 soil samples. In the experiments that were performed in parallel, irrigation was made with distilled water and with water obtained by diluting the Saharan dust and by keeping it under day light (this water will be identified with the abbreviation SDSS in this study). In this respect, when the literature is examined, there are studies on the effects of simulated "cloud water" produced by diluting the Saharan dust on plant growth [22]. Moreover, Saharan dust at ratios of 25% and 50% (v/v) was added to the S1 sample, and irrigation was made with the water of Saharan dust. On the other hand, mixtures -obtained by the addition of only compost and only Saharan dust, and by the addition of compost to Saharan dust at ratios of 25% and 50% (v/v)- were prepared, and irrigation was made with distilled water (each pot was watered with 30 ml of distilled water every two days). Seeds of previously germinated green bean *(Phaseolus vulgaris)* plant were added to these mixtures (1 plant was planted in each 300 ml beaker), and the growth of plants was observed. By the end of 30 days' growth period, the plants were harvested, and their heights and weights were measured. After the harvest, the pH values of soil mixtures were measured. Moreover, the samples used and the abbreviations of the samples are given in Table 1. In this study, the aim of adding compost and the Saharan dust to the soil at 25% and 50% rates is to utilize the method which was defined in Kubatoğlu's 1994 study [23], to investigate the effects of soil improvers added to the soil on the development of the plant.

For Saharan dust water (SDSS), 200 g of dried, sieved (30 mesh) and homogenized Saharan dust soil samples were mixed with 2000 ml of deionized water. It was illuminated Saharan with 500-Watt halogen light having a wavelength spectrum of 380–800 nm at a constant temperature (20°C) to simulate the encapsulated dust within a cloud droplet during the day time. Plant samples were first washed with tap water, and then two times with distilled water. The samples were then dried in an incubator at 60°C. AAS (Perkin Elmer AAS 400) device at Yıldız Technical University

Table 1. Samples used and the abbreviations of the samples

Sample	Abbreviation	Sample	Abbreviation
Soil 1 + 0% Compost + irrigated with distilled water	S1-C0-d	Soil 2 + 25% Compost + irrigated with distilled water	S2-C25-d
Soil 1 + 25% Compost + irrigated with distilled water	S1-C25-d	Soil 2 + 50% Compost + irrigated with distilled water	S2-C50-d
Soil 1 + 50% Compost + irrigated with distilled water	S1-C50-d	Soil 2 + 0% Compost + irrigated with Saharan dust water	S2-C0-s
Soil 1 + 0% Compost + irrigated with Saharan dust water	S1-C0-s	Soil 2 + 25% Compost + irrigated with Saharan dust water	S2-C25-s
Soil 1 + 25% Compost + irrigated with Saharan dust water	S1-C25-s	Soil 2 + 50% Compost + irrigated with Saharan dust water	S2-C50-s
Soil 1 + 50% Compost + irrigated with Saharan dust water	S1-C50-s	Compost + 0% Saharan Dust+ irrigated with distilled water	C-s0-d
Soil 1 + 25% Saharan dust dust + irrigated with Saharan dust water	S1-s25-s	Compost + 25% Saharan Dust + irrigated with distilled water	C-s25-d
Soil 1 + 50% Saharan dust dust + irrigated with Saharan dust water	S1-s50-s	Compost + 50% Saharan Dust + irrigated with distilled water	C-s50-d
Soil 2 + 0% Compost + irrigated with distilled water	S2-C0-d	100% Saharan Dust + irrigated with distilled water	s100-d

Environmental Engineering Laboratories was used to determine Ni, Fe, Cu, Cd, Zn, Pb and Mn concentrations in plant samples. Before AAS analysis, plant samples were prepared for analysis by applying a microwave dissolution procedure (by adding 10 mL HNO_3 into 1 gram sample). Using the reference soil, the accuracy of the measurement results was checked. Reference soil NCS Certified Reference Material NCS ZC73002 was used. Analytical precision measured as relative standard deviation is between 5% and 6%. In this study, all experiments and analyzes were repeated three times. The results were presented as mean values and standard deviations.

Statistical Analysis

A Mann-Whitney U Test was used to find out whether there was a difference in irrigation types and soil types. All analyses were conducted using the significance level 0.05 using the SPSS v20 software (IBM, USA).

RESULTS AND DISCUSSION

In Table 2, the characteristics of compost, Soil 1 and 2 and Saharan dust, which were used in the study, were presented. When pH values in Table 2 were compared with the values in Table 3, it was observed that Soil 1 was very high acidity as its pH value was 3 and that it was defined as "toxic for all the products". It was observed that the pH value of Soil 2 is 7 (Table 2). In this case, Soil 2 was defined as "all products may grow" in terms of pH value (Table 3). As the pH value of Saharan dust was measured as 7.5, it was observed that it could be classified as "most products may grow" as per Table 3.

When the literature is considered, it has been specified in the studies that the high (7.0 and more) and low (lower than 6.5) degree of the pH value of soil are affecting the plant growth, the effectiveness of plant's nutrient in soil and intake of nutrient by the plants. The pH values required for the optimum growth of each plant are different. However, it has been specified that the maximum intake of most of the nutrients of the plant is being realized at pH values in between 5.5 and 6 [24]. Soil 1 is an infertile soil as its pH is much lower than the normal values, and it can be said that the growth of any plant is impossible on it.

When values in Tables 2 and 3 were compared, it was observed that S1 might be defined as "organic mineral soil" in terms of organic substance and that S2 might be defined as "medium" as per the classification in Table 3.

When the results in Table 4 are examined, it is seen that the Ni concentration determined by TCLP for Soil 1 is very, very low. In a similar manner, the potentially available and immediately available concentrations of Ni in S1 were also very low (Table 4). Fe concentration was determined as 4165±2.20 mg/kg in S1 (Table 2). Considering the TCLP test results, it can be said that a very small part of the Fe determined in S1 is in the form defined as toxic (Table 4). It was observed that the highest concentration among the determined Fe forms was the potentially available form (961.50±0.2 mg/kg) (Table 4). It was observed that 128.30±0.1 mg/kg of the total Cu concentration in S1 was in the toxic form determined by TCLP (Table 4). The total amount of Cd in S1 was measured as 134±0.2 mg/kg (Table 2). It was observed that the Cd concentration, which could be defined in the toxic (TCLP) form, was very low compared to its potentially avaliable and immediately available concentrations (Table 4). When the concentrations of Zn, Pb and Mn in TCLP, potentially and immediately available forms were examined, it was observed that their

Table 2. Characterization of soil and compost samples

Parameter	Unit	Compost	Soil 1	Soil 2	Saharan dust
pH		7.9±0.01	3±0.01	7.00±0.01	7.5±0.01
C	%	11.07±0.001	0.1±0.0002	3.42±0.0001	2±0.0002
N	%	0.28±0.001	ND*	0.545±0.001	0.01±0.001
H	%	ND	0.76	0.95	ND
OM	%	1.36±0.001	28.4±0.02	1.83±0.001	ND
Ni	mg/kg	36±0.002	20.14±0.002	2±0.001	ND
Fe	mg/kg	11000±25.20	4165±2.20	5200±2.50	6.64±0.01
Cu	mg/kg	200±0.3	3515±2.2	48.89±0.02	ND
Cd	mg/kg	1±0.001	134±0.2	ND	ND
Zn	mg/kg	380±0.40	25901±22.55	125±0.2	ND
Pb	mg/kg	80±0.01	3553±1.52	ND	ND
Mn	mg/kg	320±0.15	140±0.22	110±0.20	18.48±0.001

*ND: Not Dedected, ±Standard deviation

Table 3. The relation in between pH degree and growth of products [25] and Classification of soil in terms of organic substance [26]

The relation in between pH degree and growth of products 25			Classification of soil in terms of organic substance 26	
pH	Reaction of Soil	Effect on the Product	Organic Substance (%)	Classification
3	Very high acidity	Toxic for all the products	<0.5	Very poor
4	Strong acidity	Toxic for most of the products	0.5–1	Poor
5	Medium acidity	Toxic for some products	1–2	Medium
6	Slight acidity	All the products may grow	2–5	Rich
7	Neutral	All the products may grow	5–10	Very rich
8	Slight alkaline	Most products may grow	10–20	Very much rich
9	Medium alkaline	Toxic for many products	20–50	Organic – mineral soil
10	Strong alkaline	Toxic for all the products		

Table 4. The results of immediately and potentially available elements' experiments and TCLP leaching test for S1

Metal forms	Ni (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
TCLP (soil 1)	0.1822±0.001	82.40±0.3	128.30±0.1	1.913±0.001	710.50±0.3	39.26±0.01	1.917±0.001
Potentially A.E. (soil 1)	0.7265±0.001	961.50±0.2	440.20±0.2	7.460±0.002	2563.00±22.20	916.00±0.2	5.055±0.001
Immediately A.E. (Soil 1)	0.3788±0.001	143.45±0.3	255.45±0.1	4.745±0.001	1578.50±9.35	66.10±0.01	2.946±0.002

±Standard deviation

concentrations in the form which be assessed as toxic were very low compared to the other forms (Table 4).

When Table 5 was examined, it was observed that the C (%), N (%) and OM (%) contents of both soil samples increased with the addition of compost. With the addition of Saharan dust to the S1 soil sample, it was determined that there was a decrease in the OM (%) value, since OM could not be detected in the Saharan dust (Table 5).

The metal amounts measured in the mixtures in the beakers by the end of the study were given in Table 6. The highest Fe, Zn and Pb concentrations were determined in S1, which was irrigated with Saharan dust water (Table 6). When the results in Table 6 relevant to plant growth were examined, it was observed there was no plant growth in S1, which was irrigated with Saharan dust water. Moreover, it was observed that the pH value of that soil sample was 4.5 (at a pH value being toxic for most of the products) (Table 3). It was determined that the highest Ni and Mn concentrations were in the S2 mixture in which 50% compost was added and which was irrigated with distilled water (Table 6). The highest Cd concentration was measured in S1, which was irrigated with distilled water.

When the pH values measured by the end of the study in the mixtures in beakers were examined, it was observed that the pH value of soil was increasing as per the increasing added compost amount. When Saharan dust was added to S1, it was observed that the pH value of soil was increasing (Table 8). When compost was added to Soil 1, and when it was irrigated with the water obtained from Saharan dust, it was observed that the metals amounts in soil except Ni and Mn were decreasing along with the increase of added compost amount (Table 6). The reason for this is that the amount of Fe and Mn in the Saharan dust is lower than that of S1. Also, Saharan dust does not contain Cu, Cd, Zn, Pb and Ni (Table 2).

As a result of the experiments conducted with the S1 sample, it was observed that the concentrations of metals except Ni and Fe were decreasing when compost was added to the S1 sample and when it was irrigated with distilled water (Table 6). This situation may arise from the amount of Ni

Table 5. Nutrient content of mixtures

Sample	C(%)	N (%)	H (%)	OM (%)
S1-C25	2.84	0.07	0.57	21.39
S1-C50	5.59	0.14	0.38	14.88
S1-s25	0.58	0.0025	0.57	21.3
S1-s50	1.05	0.005	0.38	14.2
S2-C25	5.33	0.48	0.71	1.71
S2-C50	4.48	0.41	0.48	1.6
C-s25	8.8	0.21	NM	1.02
C-s50	6.54	0.15	NM	0.68

Table 6. Metal amounts in soil samples

Sample	Ni (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
S1-C0-d	19±0.01	27938±20.20	883±3.45	110±3.45	31800±10.40	4603±12.40	134±11.55
S1-C25-d	18±0.01	26050±12.30	4850±2.80	722±3.45	20338±27.35	3350±18.80	182±9.85
S1-C50-d	20±0.01	30275±11.00	14938±12.25	59±0.02	163623±18.70	2490±5.55	150±3.40
S1-C0-s	19±0.02	34950±15.30	7138±8.60	96±0.01	22275±30.20	4980±25.00	172±1.50
S1-C25-s	30±0.01	31650±32.40	4650±10.30	49±0.01	15688±15.80	3713±14.40	194±7.90
S1-C50-s	32±0.01	26325±25.70	3863±9.85	42±0.02	14263±13.25	3650±9.80	218±4.75
S1-s25-s	26±0.02	24762±22.20	3281±11.15	49±0.01	12881±20.85	3340±6.55	177±3.45
S1-s50-s	16±0.01	16268±22.20	1422±7.45	15±0.01	6899±13.45	1450±3.40	132±10.05
S2-C0-d	ND	5155±9.15	33±0.01	ND	111±5.45	ND	57±0.01
S2-C25-d	24±0.01	6235±13.35	154±5.05	ND	322±3.85	501±4.95	231±12.20
S2-C50-d	44±0.01	10868±17.40	159±3.45	ND	327±4.45	79±0.01	295±17.40
S2-C0-s	ND	1585±8.45	38±0.01	ND	162±8.90	4.5±0.01	49±0.01
S2-C25-s	34±0.01	8648±3.50	144±6.70	ND	278±12.40	70±0.01	278±13.35
S2-C50-s	29±0.02	7833±9.80	146±9.80	ND	787±18.50	42±0.01	259±16.55
C-s0-d	35±0.01	10800±20.00	200±7.40	ND	378±4.20	77±0.02	312±8.40
C-s25-d	34±0.01	8988±18.50	109±6.50	ND	325±2.80	56±0.01	239±4.40
C-s50-d	33±0.02	9788±14.40	76±2.50	ND	212±3.65	46±0.01	200±8.75
s100-d	17±0.01	4725±5.50	4.5±0.2	ND	145±6.40	20±0.01	97±0.01

±Standard deviation

and Fe in compost being higher than the amount of compost samples (Table 2). When Saharan dust was mixed with S1, and when it was irrigated with water obtained from Saharan dust, it was observed that the concentrations in the soil of all the metals were decreasing once the amount of Saharan dust added to S1 increases (Table 6). The finding suggests that the cause of it may be that these metals in the Saharan dust are either in very few amounts or not even available (Table 2). When S1 soil containing heavy metals in high concentrations and S2 soil, which is suitable soil for plantation, were examined concerning the metal concentrations they contain, it was seen that there is a statistically significant difference between the concentrations of Fe, Cu, Cd, Zn, Pb metals ($p < 0.05$). When the two soil types were compared, there was no statistically significant difference between the Mn concentrations in the soils ($p > 0.05$). After the growth of the plants, the metal concentrations in them were examined according to the soil type they grow in, and a statistically significant difference was found in Fe, Cu, and Zn concentrations among the plants grown in different soil types ($p < 0.05$).

As a result of the measurement of metal concentrations in plants, it was observed that the metal amounts in the plant were decreasing (expect Ni and Pb) as the added amount of Saharan dust increases. These results were similar to the results measured in S1 and Saharan dust mixtures (Table 6 and 7). When Table 7 is examined, it was observed that while the pH of Soil 1 was 3, it was reaching to pH values of 6–7 by the addition of compost. In the same manner, it was observed that again pH values of 6–7 were reached when Saharan dust was added to S1 (Table 8). It has been provided in the literature that a suitable pH value for the growth of green bean plant is 5.5–6.7 [27]. For this reason, it is being thought that the green bean plant is unable to grow in soils and soil mixtures where the pH is 5 and less.

When metal amounts measured in the plant were considered, it was observed that the green bean plant did not grow in beakers containing only S1 (both when irrigated with distilled water, and when irrigated with water obtained from Saharan dust). It was observed that plant growth was realized by the addition of compost to S1. When 50% (v/v) compost was added to Soil 1, and when irrigation was made with the water obtained from Saharan dust, it was observed that the growth of plant is much better compared to irrigation with distilled water (while 6 cm plant height and about 1 gr plant weight were measured in irrigation with distilled water, 20 cm plant height and about 2 gr plant weight was measured as the result of irrigation with water obtained from Saharan dust) (Table 8). Depending on the soil type, a statistically significant difference was found in the growth of plants in different soil types (only when evaluated concerning plant height) ($p < 0.05$). When S1 was mixed with Saharan dust at ratios of 25% (v/v) and 50% (v/v), and when irrigation was made with the water obtained from

Table 7. Metal amounts in plant samples

Sample	Ni (mg/kg)	Fe(mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
S1-C0-d	The plant did not grow.					
S1-C25-d	1.25±0.001	288±10.55	54±0.01	2428±20.85	13±0.01	172±4.80
S1-C50-d	19±0.01	332±4.40	61±0.01	273±5.55	40±0.01	120±3.60
S1-C0-s	The plant did not grow.					
S1-C25-s	The plant did not grow.					
S1-C50-s	1.5±0.001	370±8.90	181±4.45	886±6.75	131±15.50	126±9.45
S1-s25-s	13±0.01	585±4.70	85±0.01	361±4.50	ND	83±0.01
S1-s50-s	14±0.01	327±2.35	40±0.02	212±2.80	19±0.01	77±0.01
S2-C0-d	1.25±0.002	167±6.60	27±0.02	125±4.85	ND	100±10.55
S2-C25-d	11±0.02	227±4.30	36±0.01	222±3.45	ND	78±0.01
S2-C50-d	19±0.01	184±3.40	40±0.01	179±5.50	ND	93±0.01
S2-C0-s	ND	191±1.25	20±0.01	175±6.80	5.5±0.001	94±0.02
S2-C25-s	13±0.01	161±5.50	25±0.02	138±4.40	ND	56±0.01
S2-C50-s	7.3±0.001	201±6.80	30±0.01	191±3.60	5.1±0.001	56±0.01
C-s0-d	13±0.01	196±12.80	19±0.01	107±12.80	78±0.01	38±0.02
C-s25-d	5.75±0.001	253±17.40	21±0.02	151±15.00	ND	46±0.02
C-s50-d	6.5±0.001	159±5.65	23±0.02	139±14.90	ND	53±0.01
s100-d	8.75±0.001	184±3.90	26±0.02	100±10.00	85±0.01	34±0.01

ND:not dedected ±Standard deviation

Saharan dust, it was observed that values similar to ones in which 50% (v/v) compost was used were obtained in terms of plants' height and weight (Table 8). However, when the comparison was made according to the type of irrigation (what the plants were irrigated with) ($p > 0.05$), a statistically significant difference could not be found between the level of growth and the heavy metal concentrations in the plants.

In experiments in which S2 was used, it was observed that all the metal concentrations in soil were increasing along with the increase of compost amount added to S2 and when irrigation was made with distilled water. When compost was added, and irrigation was made with the water obtained from Saharan dust, it was observed that lower amounts of the increase were occurring compared to irrigation with distilled water despite the increase of metal concentrations in soil along with the increase of added compost amount (Table 6). It was observed that the growth of plant was worsening when irrigation was made with distilled water as the compost amount added to the S2 sample increases. When irrigation was made with water obtained from Saharan dust, it was again observed that the best plant growth was in the sample in which compost was not added. However, it was determined that addition of 50% (v/v) compost was yielding to better results in terms of plant growth compared to the addition of 25% (v/v) compost (Table 8).

It was determined that Ni and Cu amounts in the plant were increasing in irrigation with distilled water as the amount of compost added to S2 increases and that Fe and Zn were at higher values in the plant samples growing in S2 in which 25% (v/v) compost was added compared to other soil samples (Table 7). There are many studies in the literature in which compost has positive effects on the growth of plant [12, 13, 28]. Moreover, there are studies in the literature regarding the usability of compost in the remediation of soils which are contaminated with heavy metals or which have high heavy metal content [13, 19, 29, 30]. Desert dust is nutrimental for some plants, but it is not being possible to say that all desert dust is nutrimental at the same level. Even the desert soil, which gets wet with the rains and enters the soil, enriches the soil, bacteria and mushrooms, increases the fertility of the soil and acts as an almost natural fertilizer [16]. In laboratory environment, dust and sands from different desert areas were compared by Saydam (2002) [22], and it was determined that Saharan dust was the most fertile among them. When studies in the literature are considered, there are studies which specify that water obtained from Saharan dust has positive effects in growing plants as if like a fertilizer [16, 17]. When the results in Tables 5, 6 and 7 are examined, it is being seen that the compost and Saharan dust and that the solution obtained by diluting the Saharan dust are enabling remediation in soil containing high amounts of

Table 8. pH values of samples by the end of the study, and heights and weights of plants

Sample	pH	Plant Height (cm)	Plant Weight (gr)
S1-C0-d	3	The plant did not grow.	The plant did not grow.
S1-C25-d	6	5	1.978
S1-C50-d	7	6	0.978
S1-C0-s	4.5	The plant did not grow.	The plant did not grow.
S1-C25-s	5	The plant did not grow.	The plant did not grow.
S1-C50-s	6	20	1.830
S1-s25-s	5	19	1.750
S1-s50-s	6	20.5	1.600
S2-C0-d	6	22	1.978
S2-C25-d	6	7.5	0.920
S2-C50-d	6	7.6	0.970
S2-C0-s	7	34	2.550
S2-C25-s	7.2	18.75	1.688
S2-C50-s	7.4	23	2.288
C-s0-d	8	2	0.724
C-s25-d	7.8	2	0.647
C-s50-d	7.6	6	0.821
s100-d	7.5	1	0.753

metal and having an acidic character. It has been observed that the compost and Saharan dust and that the solution obtained by diluting the Saharan dust affects the plant growth positively and leads to a decrease in the amount of heavy metals penetrating the plant.

CONCLUSIONS

In this study, the effects of using the solution obtained by diluting Saharan dust and Saharan dust as a soil conditioner on the development of the bean plant were investigated. At the same time, the change in the amount of metal passing from soil to plant was also investigated. It was worked under the same conditions with the commercially sold S2 for the purpose of control. Moreover, the effects of irrigation with distilled water and irrigation with water obtained from Saharan dust on the plant growth and the penetration of metals to the plant were examined. It was observed that no plant growth occurred when no remediation was made on S1. It was observed that the best plant growth for S1 was occurring in mixtures in which Saharan dust was added and which were irrigated with water obtained from Saharan dust. When metal amounts penetrating the plant was considered, lower metal concentrations were determined in the plants growing with mixtures in which Saharan dust was added and which were irrigated with Saharan dust water compared to mixtures in which compost was added and which were irrigated with Saharan dust water. In the experiments, it was observed that in the soil in which 50% Saharan dust was added, although the amount of the Saharan dust added was increased, the amount of Ni and Pb transferred to the growing plants increased. With the addition of the Saharan dust, the heavy metal concentrations in the soil decreased in proportion to the amount of the Saharan dust added (there is considered to be a decrease due to the dilution in the metal density in the soil). Despite this observation, there was no decrease in the amount of metal transferred from the soil to the plant consistent with the decrease in the metal ratio in the soil. This circumstance shows us that although the heavy metal concentrations in the soil decreased due to dilution as a result of the addition of the Saharan dust to the soil, this dilution was not effective in the metal concentrations detected in the plant. Also in the control sample, it was observed that plant growth was better in soils irrigated with water obtained from Saharan dust. Moreover, the metal concentrations determined in plants growing in beakers containing control soil (S2) which were irrigated with water obtained from Saharan dust are lower than the metal concentrations determined in plants growing in beakers which were irrigated with distilled water. It was observed that irrigation with Saharan dust water and/or addition of Saharan dust was making S1 suitable for the growth of plant by increasing its pH in a similar way as adding compost.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Assessment of domestic water quality in coastal region of Ilaje Akoka, Lagos state

Adebola DARAMOLA, Ese EBHUOMA, Victoria AKINYEMI

Department of Geography, University of Lagos, Akoka, Yaba, Lagos, Nigeria

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ABSTRACT

Coastal regions are surrounded by water yet often have limited access to potable water. These regions are usually at the receiving end of indiscriminate dumping of industrial and domestic waste water. Using the co-production approach, some issues observed by residents with available water were noted. These were investigated by undertaking a laboratory analysis examining selected physico-chemical properties (colour, pH, Tds, Hardness, Iron and Manganese) of water from different sources. Results revealed that none of the sources produced water completely within acceptable limits. Sachet water which is widely taken as the safest source, had a pH value of 5.3 which makes it more acidic than is acceptable. Manganese which could lead to neurological disorder over a long period of exposure was found to be present at 0.7mg/l and 0.25mg/l in water from well and water trucks respectively. All other elements have relatively insignificant health implications yet are important for acceptability by consumers and system maintenance. Constant water system monitoring and treatment especially in such coastal area, provision of mini-water treatment plants and appropriate water storage practices were recommended accordingly.

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INTRODUCTION

Water is essential to life and human health, economic development, food, security, poverty reduction and sustainable ecological functions [1]. Continuous increase in the world's population is expected to consequentially intensify the demand for potable water for domestic use, food production and other competing uses. Poor sanitation systems amongst other factors, has aggravated the contamination of surface and groundwater resources in most developing countries ([2], [3], [4]).

Coastal regions are surrounded by water yet often have limited access to potable water. Most of them are usually at the receiving end of indiscriminate dumping of industrial and domestic waste water. In the coastal region of Southwestern Bangladesh, nearly one fourth of the population lack access

***Corresponding author.**
*E-mail address: adedaramola@unilag.edu.ng

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to potable water in spite of their proximity to water bodies. [5] Indeed [6] examined water quality of this region and found levels of arsenic, salinity and a multitude of contaminants above Bangladesh's drinking water standard and WHO guideline values. This, they connected to the occurrence of various skin and intestinal diseases such as dysentery, fever and diarrhea in the region. [7] also investigated various water sources in six costal districts of Ghana where they found that residents rely considerably on surface water, pipe borne water, rainwater, bottled and sachet water for drinking. They further established the generally poor quality of water in the region and speculated that there may be substantial elevated risk of childhood diarrhea and other water borne infectious diseases.

The inability of the Nigerian government to provide adequate portable water for her citizen has left the public, drinking water from unreliable sources. Various households and communities have therefore taken several adaptive measures to alleviate this stress [8]. In the coastal area of Ilaje-Bariga, community, Lagos Nigeria, various water consumption practices have been adopted according to varying levels of water availability. Despite being surrounded by water, the inhabitants are compelled to obtain drinking water from various sources such as boreholes, sachet water, bottled water and the local water vendors (*Mairuwa)*. Indeed the provision of drinking water that is safe and aesthetically acceptable is a priority as anything less will undermine the confidence of consumers. This, [5] noted could lead to complaints and use of water from sources that are less safe.

Sachet and bottled water are subject to regulations under National Agency for Food and Drug Administration Control (NAFDAC), yet there are more concerns about the purity of sachet water. The ever-increasing demand for readily available water has led to the general perception that bottled water is safer for consumption than sachet water [9]. The integrity of some sachet water brands have been questioned as well as the hygienic level of the environment where some of the water is produced with reports of health problems resulting from their consumption ([8], [10]). [8] investigated some brands of sachet water in Lagos, and concluded that; while some brands are contaminated others are of good quality but assumptions of its purity should be avoided. On the other hand, bottled water includes natural mineral water, water from springs and wells, but could also include purified water which is mostly treated municipal water. Despite the packaging and attractive nature of bottled drinking water, [11] investigated and realized that the consumption of some bottled water has led to the outbreak of typhoid and cholera also [12] reported that some bottled water in Lagos market did not meet the recommended standard by regulatory bodies in Nigeria, and therefore unfit for human consumption.

Unlike sachet and bottled water, *Mairuwa* and borehole water are not subject to regulation, hence its quality may not be tested before consumption. *Mairuwa* water are supplied by the local water vendors in jerry cans from various sources and used for domestic purposes. However most vendors do not take cognizance of its hygiene, but are more concerned about making quick sales. While borehole water is sourced from the ground, during the construction process, drilling fluids, chemical castings and other materials may find their way into the borehole well thereby polluting the water. If the well is disinfected and piped within a short space of time contamination may be avoided [13]. Apparently not every individual has the financial strength and awareness to take such measures. The effect of not carrying out a detailed chemical test on the groundwater may lead to health issues.

The World Health Organization prescribed that water quality tests involve about fifteen parameters, both biologically and chemically derived [5]. These constituents were noted to have direct impacts on public health and include Iron bacteria, algae, fungi, chloride, colour, hardness, manganese, iron, pH, total dissolved solids, amongst others. The global response to the problem of sustainable access to safe drinking water and basic sanitation culminated in the inclusion of specific water-related targets in the Sustainable Development Goals (SDGs) number six (6). The goal is to ensure availability and sustainable management of water and sanitation for all by 2030. In view of these, the study assessed the quality of water used for domestic purposes in the coastal region of Ilaje, Bariga, Lagos state.

The Study Area

The study was conducted in Ilaje-Bariga Community of Shomolu LGA in Lagos Metropolis (South-Western, Nigeria). Lagos State is composed of 27 Local Government Area and Shomolu is one out of the lot. Ilaje is a ward and suburb of Bariga Local Council Development Area. It is 12km from Ikeja, the capital of Lagos, bounded in the north by Seriki-Okuta, to the south by Akoka to the west by Orile Bariga and to the east by the Lagos Lagoon (Fig. 1). Ilaje-Bariga lies between latitude 4°N, 14°N and Longitude 3°E, 15°E of the equator with about 22 hectares of land and a perimeter of about 3km. This community has an estimated population of 43,880 occupying an area of 16km^2 [14].

The area has a low-lying undulating flat landform, but with some very rugged areas having scarp slopes and gorges. The altitude varies from sea level to about 15m above sea level in some parts. The major water body in the area is the Lagos Lagoon in the south eastern part of the area.

Presently Ilaje is an unplanned area with an uncontrolled land use, overcrowded population, unpaved bad road, uncontrolled waste disposal, dirty environment, no sewer

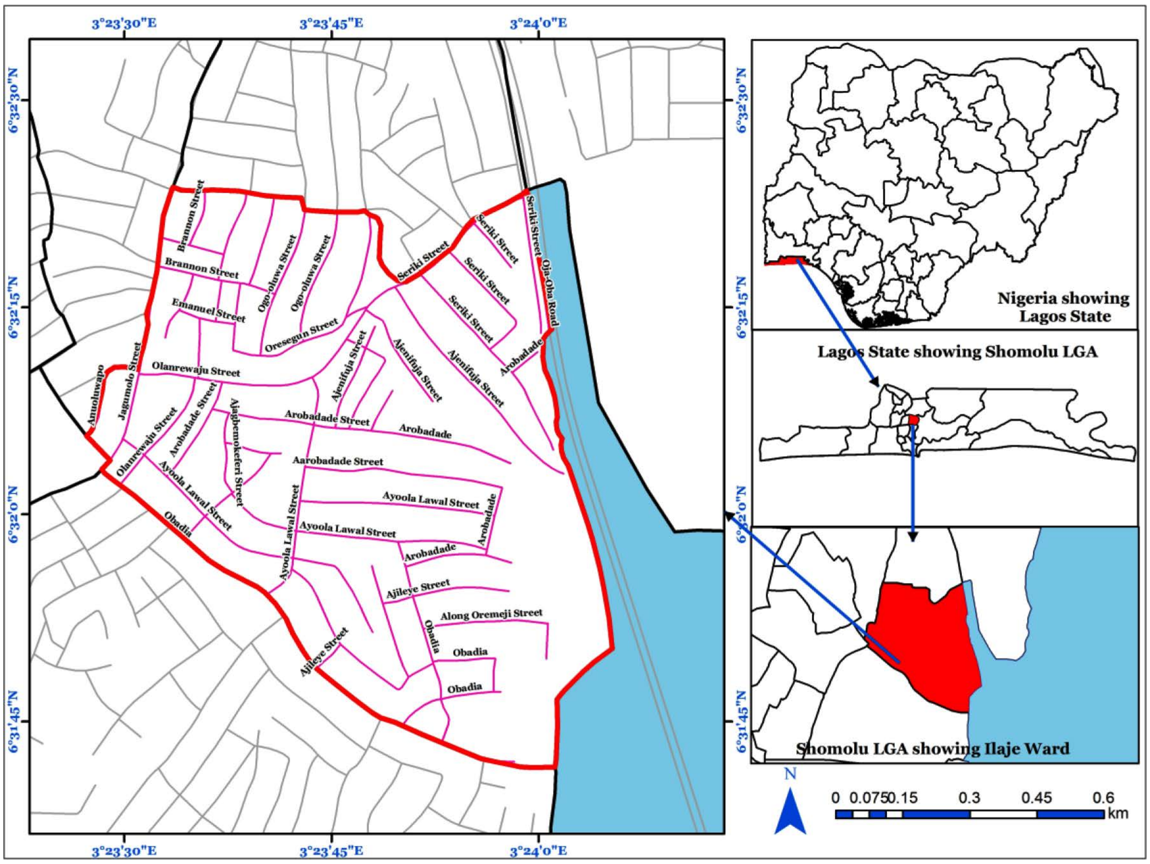

Figure 1. Ilaje coastal area, Lagos state.

or drainage system and mostly flooded during the rainy season. Some of the buildings are badly constructed with inferior building materials and lacks sufficient air space between them [15]. Generally, this area lacks potable water, sanitation and other social amenities.

MATERIALS AND METHODS

A reconnaissance survey was carried out in the study area to identify the various water sources and to identify water quality issues by interviewing residents about same. The interview was semi-structured, conducted with two (2) residents in five (5) streets close to the lagoon as it was aimed at finding out the quality issues they had encountered with available water sources. Samples of water (one each), were afterwards collected from different locations on the same day using sterilized bottles that were marked by each water source. These locations were chosen close to populated areas where residents frequently obtain water. For the water quality analysis, the focal point was mainly on pipe borne water as this is the most frequently used water in the community for domestic purposes. Residents noted the discolouration in the water few days after collection from this source unlike other water sources which appeared colourless. Water samples collected from the study area were analyzed in the laboratory to determine the physico-chemical characteristics of the water, seven parameters were analyzed. These include; appearance, colour, pH, total solids, hardness, iron, and manganese. The World Health Organization prescribed that water quality tests involve about fifteen parameters, both biologically and chemically derived [5]. The study was however was limited to the seven earlier identified because of our primary interest in addressing issues of discolouration in their water. The results of this analysis were compared with Nigeria and WHO recommended standard for drinking water in Nigeria to determine the potability of the water.

Appearance and Colour: Appearance was determined by organoleptic visual observation of the water samples for any suspended particles. The visual presence is indicated as clear or not clear respectively. Water samples were physically observed and the colour as either colourless, yellow, light yellow or rust brown.

pH: The pH of the water samples was determined potentiometrically using a potable hand held/Bench top pH meter (palintast water proof). The pH meter was first standardized/ Calibrated against buffer solutions of known pH values 4, 7 and 9.2

Total Dissolved Solids (Tds): The TDS was determined gravimetrically by taking a liquot of the water sample in a clean, dry beaker, evaporated on a plate and completely dried in an oven maintained at 105°C. TDS was the difference between the mass of the dried empty beaker and that of the beaker containing the residue with the results expressed in mg/l.

Total Hardness: 100cm^3 water sample was measured into a conical flask (250 cm^3) and 2.0ml buffer solution was added and mixed. Eight drops of Erichrome black T indicator was introduced followed by titration with 0.01M EDTA solution. At the end point, solution changed from wine red to pure blue.

Calculation of Total hardness as $CaCO_3$ (mg/l)
= titre value × 20

Iron and Manganese: Sample pre-treatment 100ml of thoroughly well mixed water sample was transferred into a beaker and 5ml concentrated nitric acid was added. The beaker was placed on a hot plate and evaporated to dryness. The beaker was then cooled and another 5ml concentrated nitric acid was added. Heating was continued until a light-coloured residue was observed. Then 1ml concentrated nitric acid was added and the beaker was warmed slightly to dissolve the residue. The walls of the beaker were then washed with distilled water. The volume was adjusted to 50ml. Iron and Manganese were determined in the digested samples using atomic absorption spectrophotometer (analyst 200 Perkin Elmer).

RESULTS AND DISCUSSION

Water from all the selected source were colourless and clear at the time of analysis. The results of other tests carried out indicated varied levels of contamination even though most were within acceptable limits. Results showed that the total dissolved solids (TDS) in water from borehole and wells in the area were at high levels of 1,600 and 826mg/l respectively (fig 2).

TDS is said to comprise inorganic salts and small amounts of organic matter that are dissolved in water (WHO, 2008). They usually originate from industrial wastewater, sewage, natural sources and piping used to convey water. Issues with piping were noted at borehole site hence the high value could be attributed to this. Wells are also rarely constructed with standard materials in the area hence the tendency for material deposition in such water. As expected, TDS values in sachet water were least and within the acceptable limits by both the WHO and the Standard Organization of Nigeria (SON).

At minimal values, TDS has not been associated with any health hazard. At levels greater than 1,200mg/l, it may be objectionable to consumers with such issues such as staining and unpleasant taste which were also alluded to by residents in the area. Very high levels of TDS may however result in gastro-intestinal irritation [16].

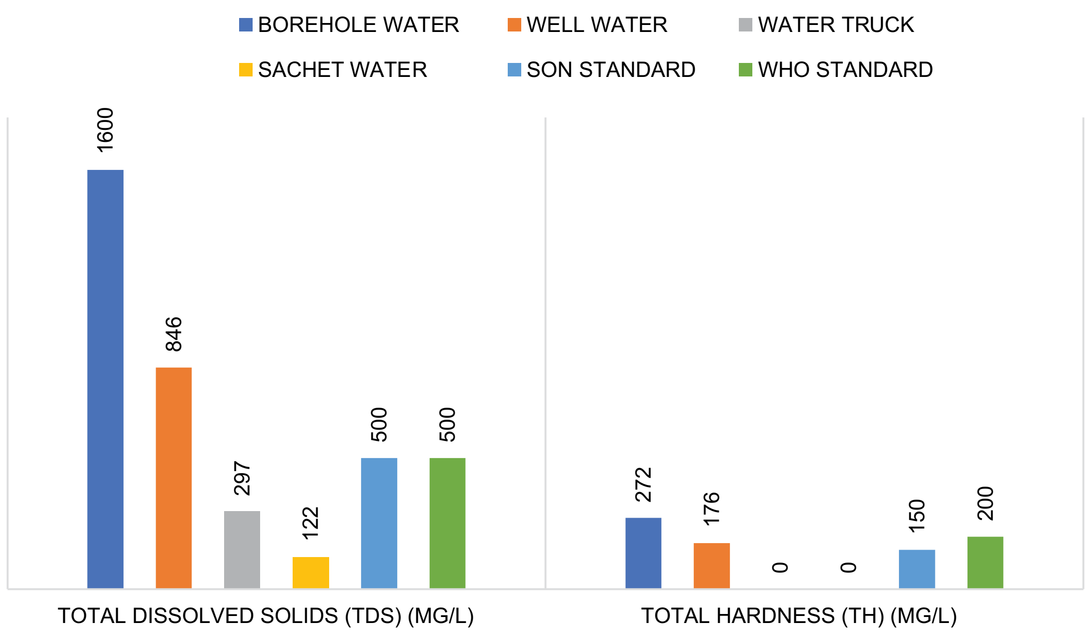

Figure 2. Results of Total Dissolved Solids and Total Hardness from selected water sources.

The acceptable limit for Total Hardness (TH) from the WHO and SON were varied, being 200 and 150mg/l respectively. Water from the borehole returned a value above both standards (272mg/l) while that of the selected well had a value slightly above the SON standard but within the WHO limit (176mg/l). Hardness in water is noted to be caused by dissolved calcium and magnesium with barely any reliable evidence of health implications. Yet hardwater has implications for domestic use as it consumes excess soap and subsequently soap curd deposition. Depending on pH and alkalinity, TH above 200mg/l can also result in scale deposition in heaters, pipework and tanks within buildings. [5]

The pH level across all water sources was less than both the WHO and SON standards with the best being from sachet water at 5.3 and the worst from borehole at 3.6 (Fig. 3). These reflect acidity beyond acceptable limits.

Similar pH values for sachet water was noted by[17]. On the other hand, pH values from the borehole is similar to that reported by [18] of the private borehole in Omoku, Rivers State, a coastal area having a pH value of 4.74 and well water having a mean pH of 6.06. Although pH has no real direct impact on consumers, it is one of the most significant operational water quality parameters. Low pH however is likely to be corrosive, leading to contamination of drinking water and adverse effect on its taste and appearance [5].

The standard values from WHO and SON were varied for Iron constituent in water put at 1 and 0.3mg/l respectively (Fig. 3). Hence while sachet and borehole water were within WHO acceptable limits, only the latter met SON standards. Water from both well and water truck had values above both standards. Iron in the study area occurs most likely through the corrosion of steel and cast-iron pipes during water distribution. Residents complained of water appearance being colourless initially but turned brownish over time when stored. There are no established health implications for iron contamination but water potability may be significantly impaired beyond 1.0mg/l.

Results of test for Manganese indicated levels within WHO standard for all sources except the well but only sachet and borehole were within SON limits (Fig. 3). High concentration of Manganese can result in adverse neurological effects following extended exposure [5] For domestic use, water contaminated by it, may have an unpleasant metallic flavor, form a brownish-black slime in toilet tanks and clog water systems.

CONCLUSION

The study set out to investigate the causes of issues identified in water from various sources by residents of Ilaje coastal area. Some of these issues include taste dissatisfaction, change on water colour over time, material deposits, and slimy texture. The study found various levels of contaminants in water from the selected sources, most of which were within either the WHO or SON acceptable limits. However significant levels of hardness, total dissolved solids, Iron and Manganese in water from some sources would explain the issues raised by residents.

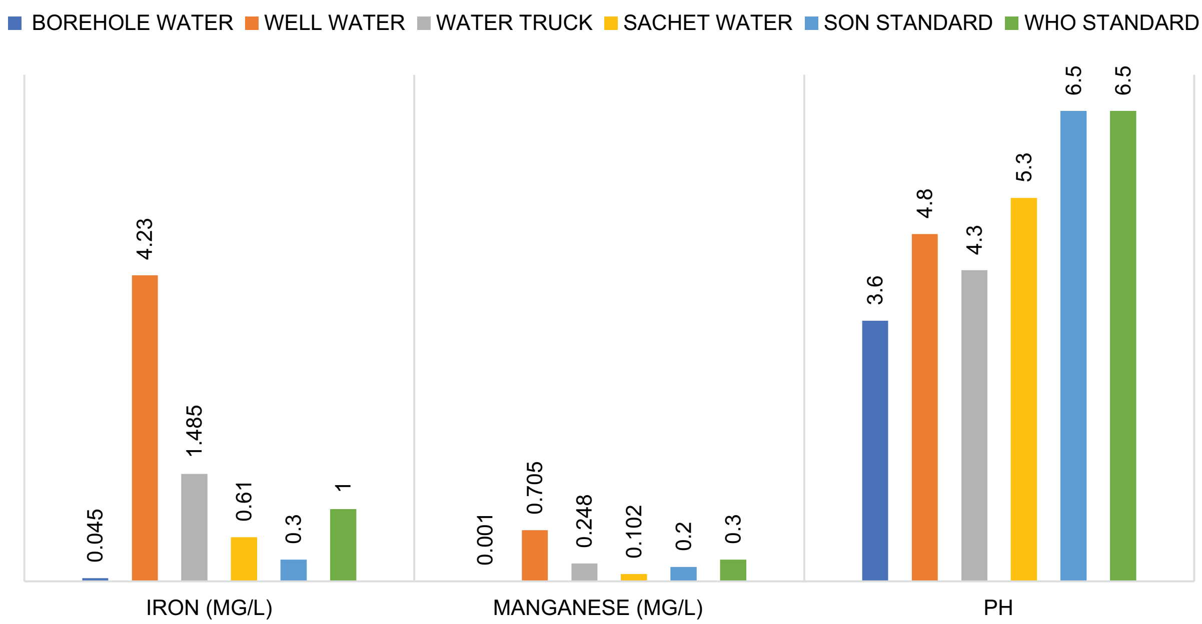

Figure 3. Results of pH, Iron and Manganese constituents from selected water sources.

In view of these, the following recommendations were made:

1. Application of Ion water softeners for hardness reduction and other element-specific softeners to regulate Iron and Manganese levels preferably at household level.
2. Regular replacement or chemical treatment of plumbing and water distribution systems to reduce the buildup of contaminants over time.
3. The use of metal water pipes should be reduced and replaced with standard plastic pipes to reduce deposition of corroded materials.
4. Adoption of more appropriate water storage practices at household level
5. Constant water system monitoring especially in such coastal area
6. Provision of mini-water treatment plants in the area.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

The evaluation of factors in utilizing the potential of solar energy: the case of Turkey

Ayşe TOPAL[1], Buket ÖZOĞLU[2], Dilek EKŞİOĞLU[3]

[1]*Nigde Omer Halisdemir University, Business Department, Nigde, Turkey*
[2]*Nigde Omer Halisdemir University, International Trade and Logistics Department, Nigde, Turkey*
[3]*Nigde Omer Halisdemir University, Graduate School of Social Sciences, Nigde, Turkey*

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ABSTRACT

The importance of energy which has a significant role in socio-economic development of countries is increasing because of a fast-growing population and industrialization. The fact that the fossil resources are insufficient to meet the demand if new reserves cannot be found in the near future and the threat to human and environmental health lead the countries to seek renewable clean energy resources. Turkey, which is dependent on foreign energy due to being poor in terms of fossil fuels as a country, has high solar energy potential but cannot utilize this potential fully. In this paper, the importance and potential of solar energy in Turkey, the problems encountered in utilizing solar energy have been studied. In this study, semi-structured interview was used as qualitative data collection technique. The experts to be interviewed were selected from people with at least five years of academic or sector experience in solar energy. As a result of the research, it was reached by all experts interviewed that Turkey need to increase the benefit from solar energy for Turkey's social and economic development and there are various obstacles in front of utilizing this benefit. However, it is seen that expert opinions vary in terms of solutions.

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INTRODUCTION

The importance of energy in the development of countries is increasing with the growth in population and industrialization all around the world. Fossil energy has been used extensively to meet the energy need of nations for centuries because of the ease and availability of these resources. However, renewable resources gained a significant attention recently as there is a scarcity in fossil energy resources to meet the needs in the near future, and the effects of fossil fuel on the environment and human health such as global warming, acid rain and nuclear radiation wastes threat human life.

Solar energy is one of the most common renewable energy among various types of renewable energy resources currently used. It was used for the first time in the solar water pump made by Belidor in 1725. Later, in 1860, Mohuchok worked on solar radiation steam engines, solar pumps and

*Corresponding author.
*E-mail address: ayse.topal@ohu.edu.tr

solar cookers using parabolic mirrors. With the emergence of oil during the First World War, the importance given to solar energy decreased. Today, solar energy has gained importance again due to the availability of solar power, the depletion of fossil resources and the damage it causes to the environment [1]. The effects of solar energy technologies on the environment were analyzed in the study of [2]. It has been concluded that solar energy technologies have almost no harm to the environment compared to fossil resources. If due importance is given to the land and existing vegetation during the installation of technologies, to the location selection that does not harm the living area, and to keeping the toxic substances to be used in the system under control, the effects of solar energy can be minimized. With these benefits, solar power increased at a rate more than total renewable supply in 2018 [3].

Energy, which is of great importance in terms of growth and social development, is more important in developing countries such as Turkey. Turkey ranks first among developing countries in terms of foreign dependency in energy. It met approximately 72% of its energy consumption from abroad in 2019 [4]. According to the data of 2020 in the TCMB balance of payments, a total of 24211 million dollars in our current account deficit is due to energy imports [5]. Only 17% of energy consumption in Turkey is met by renewable energy [4]. It is known that Turkey has an annual solar energy potential of 2741 hours due to its geographical location [6]. It is seen that Turkey, which has a wide geographical opportunity to benefit from solar energy in factors such as the slope status of the land, transportation status, agricultural status, topographic structure, network connection, geological structure, property status, distance to the sea, cannot obtain the expected benefit from its solar energy potential [7]. Although Germany, the world leader in electricity generation from solar energy, has an annual solar energy potential of 1300–1900 hours and Turkey and Germany use the same solar energy technologies, as of 2019 Germany produces 47517 GWh from solar energy, while Turkey produces 9578 GWh [8–9]. This situation has caused us to draw attention to the problems encountered in electricity production from solar energy in Turkey.Renewable energy projects necessitate significant investment in both research and manufacturing capacity, which frequently surpasses the capabilities of the private sector. Therefore, governments play a significant role in the expansion of this industry, trying to enhance the international competitiveness of domestic manufacturers through their economic policies. Government support and education are of great importance in the evaluation of the current potential in the production of electrical energy from solar energy in Turkey. Yılmaz [10] mentioned in his study that studies in the field of renewable energy gained momentum with the entry into force of the Renewable Energy Law (YEK) in Turkey in 2005. It has been analyzed that general incentive applications, regional incentive applications, incentives for large-scale investments, and incentives for strategic investments are provided in the regulation made in 2012 due to the lack of fixed price guarantee and unlicensed production right in YEK 2005. In the study of İraz and İsa [11], the solar energy policy implemented by the European Union (EU) in 2007 was shown as an example for the government to intervene in the renewable energy market. It has been stated that the role of government support and incentives is among the reasons why EU has developed in solar energy. It has been determined that the tariff guarantee, investment support and quota systems applied in Turkey are the most effective methods applied in sixty-three countries. It has been concluded that the regulations regarding obstacles to the use of solar energy in Turkey have not been used yet and concrete strategies have not been formed. Dinçer [12] conducted a comparative analysis of financial, technological barriers and incentives in electricity generation and use from solar energy between Turkey and EU countries. It was determined that Turkey's thermal solar energy potential is in the fourth place after China, US, and Japan. As a result, although EU countries have less solar energy potential than Turkey, it has been seen that they gain more benefits with the development of financial and technological incentives. It suggested to increase incentives in Turkey, spread the use of solar energy to the base, and improve inter-ministerial coordination and cooperation. It was stated that although they do not have a high solar energy potential compared to Turkey, the point reached by countries such as Germany and France, which have achieved higher values in electricity generation from solar energy, is remarkable.

Considering the solar power situation in Turkey, this study is important for comprehending and finding experts' perspectives on the factors affecting the use of solar energy. The main question of this study is what experts in the energy field think about solar power industry in Turkey and the problems encountered in utilization of solar power. Sub-questions to find the answer to the main question are listed below.

1. What are your thoughts on Turkey's energy mix and what do you think about the low share of solar energy in this mix?
2. What are your thoughts on what should be done or developed to increase the share of solar energy in Turkey?
3. Do you find the studies of universities on solar energy (research and development (R&D), project, plan, program) sufficient? What are your thoughts?
4. Are there departments teaching solar energy in vocational and technical high schools, and universities in Turkey and are the trainings oriented to the needs of the sector?

5. Are there any issues in the energy legislation regarding solar energy that you think should be improved or changed?
6. What do you think about the problems and impacts Turkey faces on solar energy transportation, customs, expertise, technology supply and other issues?
7. What are your thoughts about the impact of solar technology supply on the low share of solar energy?
8. Do you find the current transmission capacity and transformer share for electrical energy produced from solar energy sufficient?
9. Do you think that small-scale YEKA areas should also be determined next to the large-scale YEKA areas for the dissemination of small-scale YEKA projects (solar energy projects)?

THE STATUS OF SOLAR ENERGY

Solar energy is a most available energy in the world. It is reachable from most countries which have days with sunshine. Solar energy is used in two ways, electrical and thermal energy. The earlier use of solar energy was mostly thermal energy for heating water. Technological development in solar energy has led to use it as electrical energy. There are two types of technology to transform solar energy to electrical energy: Concentrating solar power (CSP) and Photovoltaic power (PV).

CSP is a solar energy technology which generates electricity by using first concentrators to transform sunlight to heat and second heat engines to transform heat into electricity with Rankine, Brayton, and Stirling cycles [13]. CSP may be used as a heat storage alone or with fossil fuels which have a back-up role for the times there is no sunshine. There are several types of CSP in use. In the Figure 1, the development of CSP technology was shown according to receiver temperature (~250–450 °C, ~500–565 °C, ~720 °C, and >700 °C), plant type (parabolic trough collector-PTC, solar power tower-SPT, linear Fresnel reflector-LFR, power dish collector-PDC), heat transfer material (oil or steam, steam or salt, gas, salt, particle), thermal energy storage capability, power cycle (Small Rankine cycle, Stirling, and Brayton cycle), cycle peak temperature (~240–440 °C, ~480–550 °C, ~720 °C, and >700 °C), efficiency of design cycle (~28–38%, ~38–44%, ~38%, and >50%), solar electricity generation efficiency per year (~9–16%, ~10–20%, ~25%, and ~25–30%).

Solar photovoltaics (PVs) allow direct transformation of solar energy to electricity. They are formed from semi-conducting material layers. It is a significant electricity source for fulfilling energy demand in developing nations, particularly in rural and isolated areas, without polluting the environment. PV systems' improved efficiency and further cost reductions suggest that solar producing systems will play a key role in the future. Among renewable energy technologies, photovoltaics provides the most flexibility. The lack of moveable components, the extremely gradual deterioration of sealed solar cells, and the great ease of their usage and maintenance are the most appealing aspects of solar

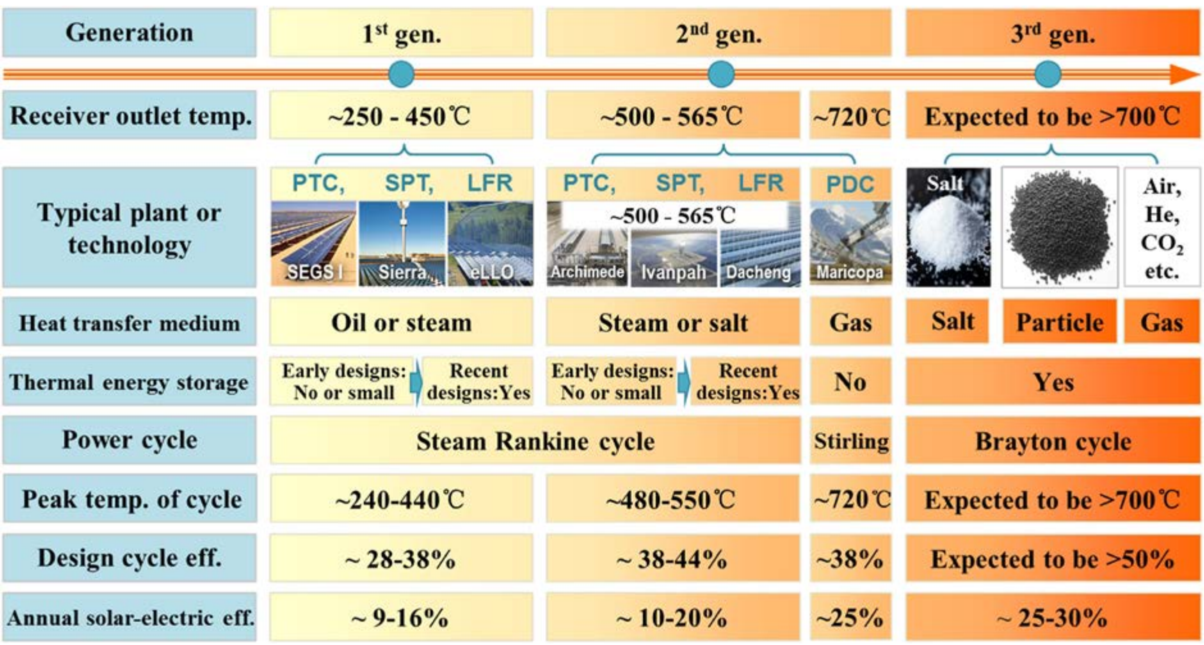


Figure 1. The development of CSP technology [14].

panels. Another benefit is that it is modular. All generating sizes, from milliwatts to megawatts, may be achieved [15]. Main materials used in PV cells are crystalline materials, thin films, organic and polymer cells, hybrid solar cells, dye-sensitized solar cells, and nanotechnology [16]. PV power plants can be categorised into four groups in terms of implementation. These are [17]:

- Domestic solar systems that are not connected to the grid: These plants supply energy to families and villages in distant areas that are not linked to the national grid. Light, cooling, and other low-power demands are often supplied by these plants.
- Non-domestic solar systems that are not connected to the grid: These plants were the first commercial use of solar panels. They are suitable for situations where a little quantity of power has a high value such as telecommunication, pumping for water, and cooling for vaccine.
- Distributed photovoltaic systems that are connected to the grid: These plants provide electricity to a dwelling linked to the grid. Residential, commercial, and industrial buildings may all be served with these plants. These are less expensive than off-grid installations since they do not require battery storage devices because they are directly linked to the grid.
- Centralized photovoltaic systems that are connected to the grid: These are used as a replacement for traditional centralized power generator or to improvement of the utility distribution network.

Solar PV has been a cheaper option compared to new fossil fuel plants in most countries in the last decade therefore it had seen a rapid increase in the recent years around the world. From 2014 to 2019, total PV production increased almost by four time as seen in Figure 2a and the most capacity in PV belongs to China as show in Figure 2b.

China is the world leader in solar PV module production, as seen in Figure 3. Other Far East countries such as South Korea and Malaysia follow China with %6 shares. Then, US comes with %3 and Europe with %2.

The current energy supply in Turkey is mostly dependent on fossil fuels as shown in Figure 4. Even though Turkey is poor in terms of fossil fuels therefore importing mostly from Russia and Iran, it has considerable renewable energy resources, particularly wind and solar.

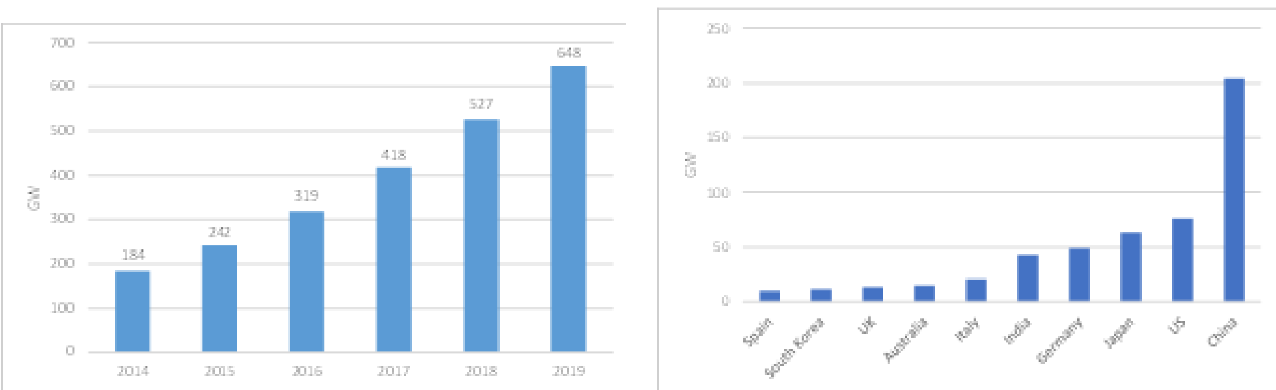
According to the Turkish Solar Energy Potential Atlas (GEPA) as seen in Figure 5, the total sunshine duration is 2741 hours in a year and the total radiation intensity is 1.527 kWh/m^2 in a year [21].

Turkey has begun to assess the potential in this area in recent years, focusing on solar energy and taking efforts to capitalize on its benefits. As a result, the share of solar energy has increased in recent years. As presented in Figure 6a and 6b, 9250 GWh electricity is generated from solar energy and installed capacity reached to approximately 6000 MW in 2019.

DATA AND METHODOLOGY

The case study technique, which is one of the qualitative research methodologies, is utilized in this study. The purposeful sampling approach was used to identify the study's sample group which consists of six experts who have more than five years' experience in energy subject in general and solar energy in particular. The information of the interviewed experts is shown in Table 1. During the data collecting procedure, a semi-structured interview method was used.

In the semi-structured interview method, which is a qualitative research technique, the researcher prepares an



(a) (b)

Figure 2. (a) Worldwide solar PV growth (GW) [18]. (b) Solar PV capacity of countries in 2019 (GW) [19].

interview protocol that includes questions that he/she plans to ask about the subject he/she is researching. In addition to these questions, the researcher can affect the course of the interview with other questions or sub-questions according to the flow of the interview. The researcher may ask the interviewee to elaborate on their answers, and this gives the researcher the opportunity to explore the subject in depth. Semi-structured interview technique provides convenience in research because it offers a certain level of standardization and flexibility in the questions prepared by the researcher in the interview protocol [23] (Türnüklü, 2000). Besides, being able to communicate directly with people while interviewing is an important advantage. It provides instant feedback to the data obtained during the interview process. Since the researcher asks the questions in a conversational manner during the interview process, they are more likely to get answers to their questions. Being able to control the different conditions that arise according to the progress of the interview process allows the researcher to advance the interview as desired. Since it is an oral process, it can be applied to illiterate people and to all small and large groups [24].

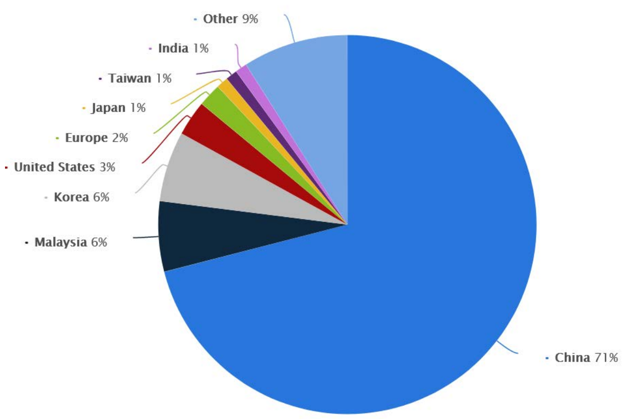


Figure 3. Distribution of solar PV module production worldwide in 2019 [19].

Nine open-ended questions were asked in the semi-structured interview form to the experts selected by purposeful sampling approach. Questions to reveal why Turkey cannot produce electricity from solar energy at the expected level despite being a country with high solar potential were asked questions through face-to-face interviews.

Content validity of the data, as well as detailed profiles of the subject and experts in the study, have been used to assure the validity and reliability of the research. Furthermore, reliability was evaluated according to Miles and Huberman's [25]'s reliability calculation. It was found that it is 91%. As this value is over %70, it meets the reliability.

RESULTS

The findings derived from the answers to the semi-structured interview questions gathered from experts are presented in this part.

Table 2 shows the experts' answers to the first sub-question "What are your thoughts on Turkey's energy mix and what do you think about the low share of solar energy in this mix?".

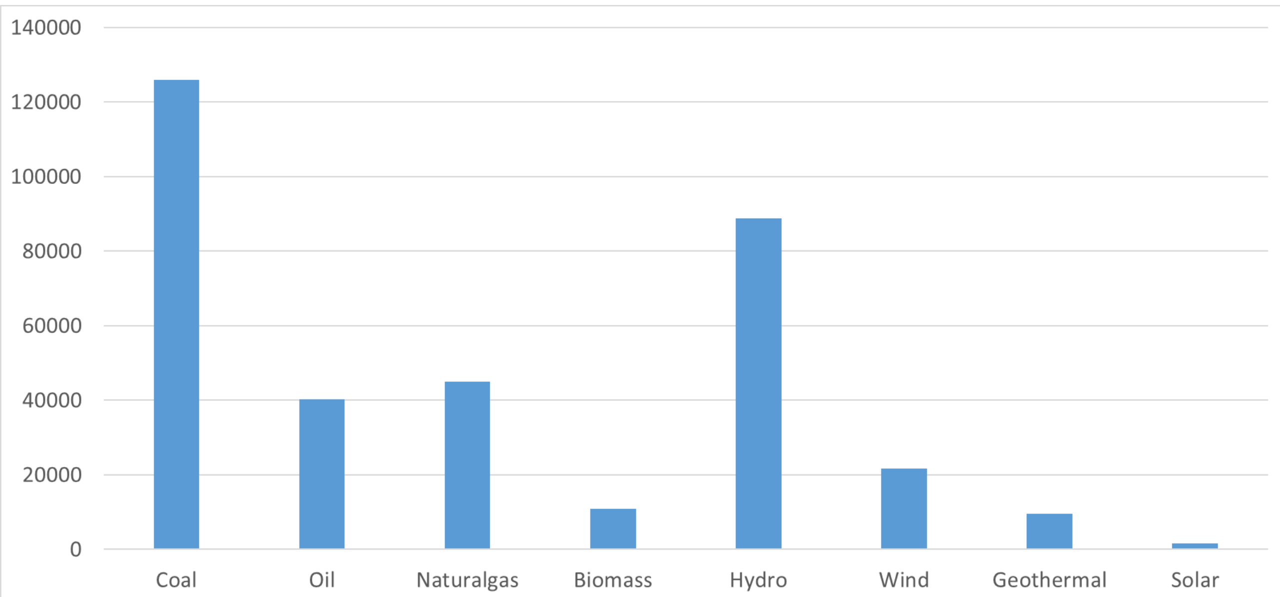


Figure 4. Energy supply of Turkey in 2019 [20].

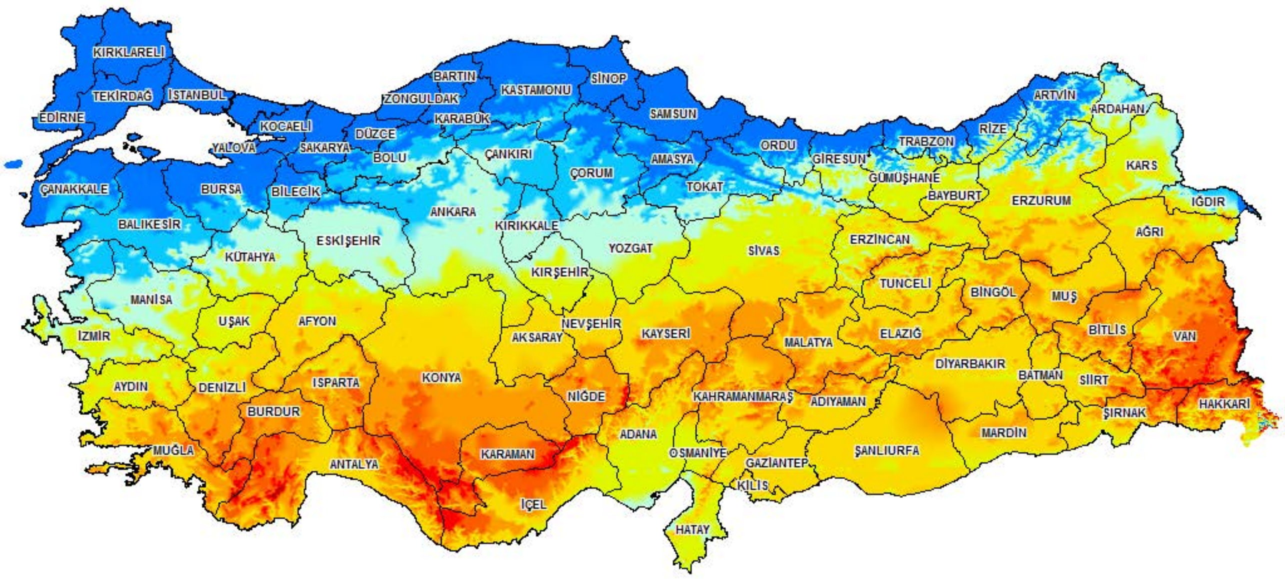


Figure 5. City based solar energy potential atlas [22].

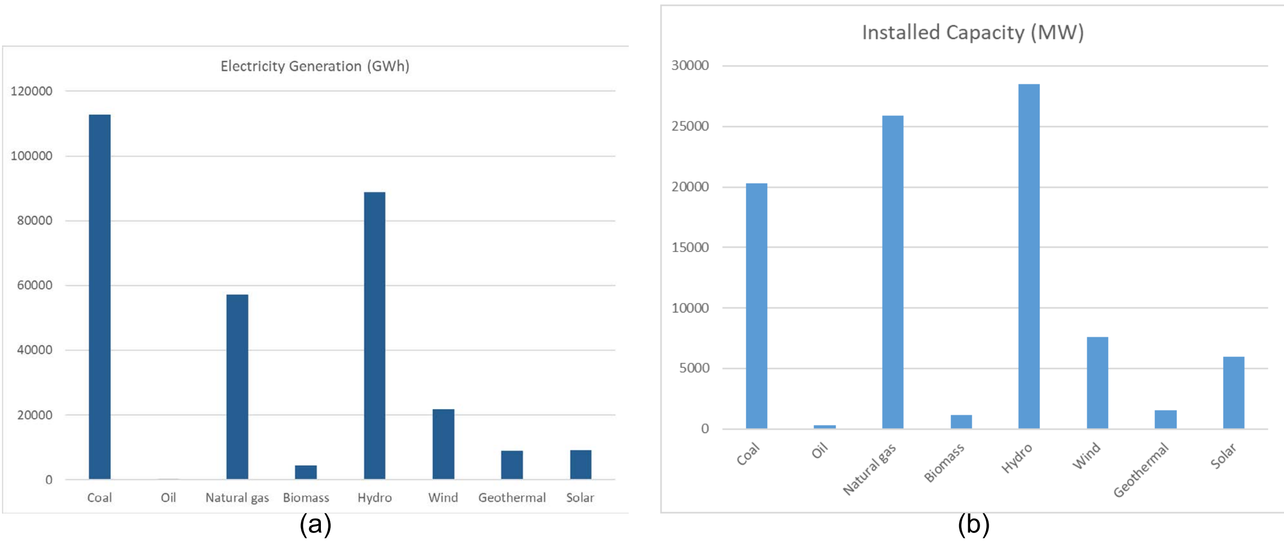


Figure 6. (a) Electricity generation of Turkey in 2019 [20]. (b) Installed capacity of Turkey in 2019 [20].

Table 1. Code and characteristics of experts

Code	Position	Industry
EXP 1	CEO	Energy
EXP 2	General secretary	Media
EXP 3	Academician	Education
EXP 4	Education specialist	Education
EXP 5	Project planning specialist	Government
EXP 6	Engineer	Manufacturing

It can be observed from Table 2 that all experts agree with the low share of solar energy in Turkey energy mix. They all expressed that the share is low compared to high solar potential in Turkey. Also, Expert 1 and Expert 6 stated that there is high fossil fuel use, particularly coal and natural gas. In addition to these statements, Expert 1 also expressed that fossil fuel-based energy imports have accounted for the majority of current account deficit and the lack of public awareness is responsible for low solar energy demand from consumption viewpoint.

Table 2. Experts' views on Turkey energy mix and the share of solar energy

Answers	Experts	f
Low solar share in the mix	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6	6
High coal and gas use	EXP 1, EXP 6	2
Budget deficit due to fossil fuel export	EXP 1	1
Low demand for solar energy due to the lack of public awareness	EXP 1	1

Table 3. Experts' views about increasing the share of solar energy

Answers	Experts	f
Incentives	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6	6
Encouraging distributed systems (on-site generation and on-site consumption)	EXP 1, EXP 2	2
Mandatory roof solar panels for new buildings	EXP 1, EXP 2	2
Large capacity solar power plants	EXP 1	1
Energy storage systems	EXP 1	1

Table 4. Experts' views about university engagement in solar energy

Answers	Experts	f
Insufficient	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6	6
Insufficient solar energy research	EXP1, EXP 2, EXP 3, EXP 5	4
Not innovative	EXP 1	1
Fossil fuel-based studies common	EXP 1	1
Lack of financial support for R&D	EXP 4	1
Lack of human resources at universities	EXP 6	1

Table 3 presents the experts' answers to the second sub-question "What are your thoughts on what should be done or developed to increase the share of solar energy in Turkey?".

Increasing incentives currently given or introducing new ones was the main suggestion given by all experts. Expert 1 stated that it is necessary to encourage the construction of large-capacity solar power plants to rapidly reduce the share of fossil fuels. It is necessary to build solar power plants (SPPs) in all provinces with the capacity to meet their needs. It is also necessary to add energy storage systems to all these SPPs so that energy supply and demand are balanced. Expert 1 and Expert 2 told that encouraging distributed systems and making installation of solar panels mandatory on the roofs of all new buildings are suggested to increase the share of solar energy.

Table 4 shows the experts' answers to the third sub-question "Do you find the studies of universities on solar energy (R&D, project, plan, program) sufficient? What are your thoughts?".

University engagement in solar energy was found to be insufficient by all experts. Reasons for insufficiency vary. Expert 1, Expert 2, Expert 3, and Expert 5 stated that there are very few researchers who have been trained and have done scientific studies on solar energy. Expert 1 claimed that universities are not innovative as they stay behind of recent developments and the studies promoting fossil fuels are still common practice in academic settlings. Expert 4 told that scientific institutions such as TUBITAK have insufficient R&D establishment and support projects. Expert 6 pointed to the insufficient numbers in people working on solar energy at universities therefore less productivity.

Table 5 shows the experts' answers to the fourth sub-question "Are there departments teaching solar energy in vocational and technical high schools, and universities in Turkey and are the trainings oriented to the needs of the sector?".

All experts stated that educational institutions are not capable to meet the human resources needs of the sector. Universities should work on R&D and processes while vocational high schools should train blue-collar intermediate staff. Vocational and technical high schools should open departments for the needs of the sector and provide required training. Expert 1 and Expert 6 claimed that except for few technical high schools, most of the educational institutions are only teaching theoretically and this is leading the lack of

Table 5. Experts' views about solar energy education

Answers	Experts	f
Education sector do not meet the human resources needs of the solar energy sector	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6	5
Too theoretical education	EXP 1, EXP 6	2
Need to train teachers	EXP 2, EXP 5	2
Specialization is needed	EXP 1	1
Lack of training instruments	EXP 2	1
A common platform for vocational and technical high schools regarding solar energy	EXP 2	1
Need for highly educated professionals	EXP 3	1
Lack of foreign language (English)	EXP 6	1

practical skills in students. Expert 2 and Expert 5 presented that there is a need to train teacher and lecturers to increase the efficiency of solar energy courses or programs given in educational institutions as solar energy is a dynamic subject it requires to update study materials periodically. Expert 1 found that it is necessary to open new departments in educational institutions catering to solar energy sector for specialization in profession. Expert 2 expressed that there are 44 vocational high schools which have solar energy programs, but almost none of them have the tools and equipment to provide training in accordance with the sector. Only small materials among necessary training equipment are provided by the school authorities themselves. Expert 2 also stated that constructing a common platform for vocational and technical high schools regarding solar energy will be beneficial. On the other hand, Expert 3 said that the sector needs not only intermediate technical staff, but also manpower at undergraduate and postgraduate level however efforts on this subject are insufficient. Additionally, Expert 6 stated that there is a need for using English at a sufficient level as solar energy sector is operating globally however most of the educational institutions in Turkey is not capable to teach English.

Table 6 shows the experts' answers to the fifth sub-question "Are there any issues in the energy legislation regarding solar energy that you think should be improved or changed?".

Most experts stated that incentives need to be increased. There should be incentives for energy cooperatives and unions. A certain price mechanism should be created for the electricity produced on the roofs such as a feed in tariff or as a purchase guarantee. This should be a price that will facilitate investment increase and overcome the obstacles in front of investment decisions. Also, exemption from certain taxes such as VAT for a certain period will reduce the costs around 21% and consequently will reduce the amortization period approximately 1 year and this will encourage investors for solar energy investments. Three experts (Expert 2, 4 and 5) have suggested to create new regulations for getting more benefits from roofs such as introducing a regulation for roof renting, electricity subscription for roof and energy contracting. Expert 1 also suggested to use mechanisms that restrict fossil fuels in addition to the incentives encouraging renewable energy. Expert 2 added that regulations for encouraging R&D in industry/universities and solar technology production will be beneficial. Expert 6 suggested to establish a special unit in the Energy Ministry to follow all the current developments in solar energy globally.

Table 7 shows the experts' answers to the sixth sub-question "What do you think about the problems and impacts Turkey faces on solar energy transportation, customs, expertise, technology supply and other issues?".

Table 6. Experts' views about solar energy legislation

Answers	Experts	f
More incentives for renewable energy (such as feed-in tariffs, purchase guarantee, VAT exemption)	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5	5
Regulation for roof panels and distributed systems	EXP 2, EXP 4, EXP 5	3
Restrictive measures on fossil fuel imports	EXP 1	1
Regulation for R&D in industry and universities	EXP 2	1
Regulation for encouraging solar technology production	EXP 2	1
Need for a special unit in Energy Ministry for solar energy regulation	EXP 6	1

Table 7. Experts' views about problems encountered in solar energy technology supply

Answers	Experts	f
Problems due to low market potential of Turkey	EXP 3, EXP 4, EXP 5	3
Need to increase the number of customs control centres	EXP 4, EXP 5	2
Vibration problem in transportation	EXP 4, EXP 5	2
Need for competent human resources	EXP 3, EXP 5, EXP 6	2
There is a problem in the implementation of legislation	EXP 1	1
Nothing goes as planned; disruptions on supply of technology	EXP 1	1
A serious decrease in productivity and flow of work	EXP 1	1
Technology import from Far East	EXP 3	1
Long transportation time	EXP 5	1
Lack of coordination between institutions	EXP 6	1

Table 8. Experts' views about the effect of solar energy technology supply on low solar share

Answers	Experts	f
High import cost > low solar energy use	EXP 1, EXP 2, EXP 3, EXP 4, EXP 5, EXP 6	6
Technology production inside the country will decrease the cost	EXP 1, EXP 2	2

Table 9. Experts' views about the effect of solar energy technology supply on low solar share

Answers	Experts	f
Low transmission and distribution capacity for solar energy	EXP 1, EXP 3, EXP 4, EXP 5	4
Enough capacity till 2023	EXP 2, EXP 6	2
Need for microgrids	EXP 1	1
More off-grid systems	EXP 1	1

Experts 3, 4 and 5 claimed that the market share of Turkey in global solar energy technology is low therefore the priority is given to the countries with high shares. This causes the loss of several incentives such as volume and time guarantees or special discounts. Turkey mostly supplies technological parts from Far East countries such as China and Thailand (Expert 3) and this increases lead time (45 days) of orders (Expert 5). Experts 4 and 5 stated that imported solar energy technology orders are checked at the customs control centers in Gebze and Ankara in Turkey and obtain a certificate of origin. Since there are two control centers to control these technologies, reports can be obtained from here in 3 months. For acceleration in customs, there should be an increase in the capacity of legislation, quality control centers, existing quality control centers. These experts also told that imported technologies should arrive without vibration in transportation however this is not taken care of in most cases. This affects the efficiency obtained from technologies. More importance needs to be given to the logistics of solar energy technology. Experts 3, 4 and 5 told that the technologies we purchase should not have contact with hand or air, which can cause faults in the supply, therefore a separate unit should be created at the customs, unit personnel should receive training in solar energy technologies. Expert 1 claimed that legislation is efficient on the paper but there is a problem in implementation therefore disruptions occur in supply of technology and a serious decrease in productivity and workflow happens. These necessitate conducting more inspections. Also, lack of coordination between institutions has been mentioned by Expert 6.

Table 8 shows the experts' answers to the seventh sub-question "What are your thoughts about the impact of solar technology supply on the low share of solar energy?".

All experts have agreed on that high import costs lead to low solar energy use. This is more prevalent in recent years because of decrease in Turkish lira value. Experts 1 and 2 told that increasing local production of technology will lower the cost therefore will increase the use of solar energy use in the long run.

Table 9 shows the experts' answers to the eighth sub-question "Do you find the current transmission capacity and transformer share for electrical energy produced from solar energy sufficient?".

Table 10. Experts' views about the dissemination of solar energy projects

Answers	Experts	f
All scales should be encouraged	EXP 1, EXP 3, EXP 4, EXP 6	4
More importance must be given to small scale projects	EXP 2, EXP 5	2

It is stated by Experts 1, 3, 4, and 5 that transmission and distribution capacities need to be increased to develop solar energy ratio in Turkey energy mix. Experts 2 and 6 claimed that there is enough capacity until 2023. Expert 1 told that there is a need for microgrids and off-grid systems in Turkey to increase the use of solar energy by public.

Table 10 shows the experts' answers to the nineth sub-question "Do you think that small-scale YEKA areas should also be determined next to the large-scale YEKA areas for the dissemination of small-scale YEKA projects (solar energy projects)?".

Experts 1, 3, 4 and 5 told investments for all scales need to be supported and small-scale areas need to be determined in YEKA areas in addition to large-scale areas. This will expand the solar energy sector and therefore increase the share of solar energy. In addition, Experts 2 and 5 stated that more importance must be given to small scale projects to disseminate solar energy use to public.

CONCLUSION

It is seen that Turkey has a high solar energy potential, but the expected benefit in electricity generation cannot be obtained from this potential. Semi-structured face-to-face interviews were conducted with the participants selected according to their fields of expertise, on which factors are effective in not benefiting from Turkey's solar energy potential sufficiently.

It has been found from the interviews that Turkey does not benefit from the solar energy potential at the expected level due to importing technologies because of lack of competent personnel, low market potential in the global technology supply, encountering problems in supply chain (transportation, customs, and expert workforce), insufficient small size solar energy projects, transmission and distribution capacity being an obstacle to the development of the sector in terms of volume, inadequate legislation, lack of training in the field of solar energy to meet the needs of the industry, insufficient R&D studies at universities.

Various suggestions have been made by experts to solve these problems.

- Increasing the support given to R&D in industry and universities,
- Supporting universities to create a workforce that will work on R&D,
- Opening of departments in vocational schools for the needs of the sector,
- Increasing customs control centers and creating a separate unit in customs, providing special training to the employees in this unit,
- Requesting logistics companies to take the necessary care in transportation of solar technology,
- Increasing the current share in the transmission and distribution capacity,
- Make the necessary arrangements in the legislation to facilitate the operations,
- Increasing public awareness about solar energy,
- Encouraging the use of solar energy technologies on roofs and having to transfer the remainder to the transformer,
- Abolition of VAT and OTV in the legislation for domestic use,

Coordination of the Ministry of Energy and Natural Resources with the Ministry of Customs and Trade regarding the problems in customs, with the Ministry of Transport and Infrastructure regarding the problems in transportation, with the Ministry of Education regarding the problems in education, and with the Ministry of Environment and Urbanization regarding the solar energy use in buildings.

In order to accelerate its economic and social development, increase its welfare level, and reduce foreign dependency on energy, which is the primary item in the current account deficit, Turkey needs to increase its electricity production from solar energy. Considering the problems encountered in the use of electricity from solar energy and evaluating the solution proposals will increase the rate of benefiting from the solar energy potential in Turkey.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Investigation of energy costs for sludge management: a case study from dairy industry

Pelin YAPICIOĞLU*, Mehmet İrfan YEŞİLNACAR

Department of Environmental Engineering, Harran University Faculty of Engineering, Şanlıurfa, Turkey

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ABSTRACT

Sludge management has been regarded as an environmental challenge to deal with due to high energy costs for wastewater treatment plants. From this perspective, energy costs of sludge management should be defined and calculated in order to obtain an effective energy management in wastewater treatment plants. Energy consumption of sludge management is the major constituent of the operational costs. Especially, dewatering processes have led to high electricity consumption at industrial wastewater treatment plants. This paper aimed to define the role of design and operational parameters on energy costs of sludge treatment process in terms of total organic carbon (TOC) and sludge volume index (SVI) considering water-energy nexus. Dissolved Air Flotation (DAF) sludge and centrifuge decanter were used for sludge dewatering process in a dairy wastewater treatment plant. Lime is used for sludge stabilization. Energy cost index has been figured out using a new derived numerical method. This study proposed a new developed methodology for energy cost assessment of sludge management. This paper revealed that energy costs would be lower if the wastewater treatment plant was operated under design conditions. If the plant was operated at design conditions, nearly 63% of reduction on energy costs of sludge handling process could be ensured. It has been recommended this plant could be operated under design conditions.

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INTRODUCTION

Dissolved air flotation (DAF) process has been used since early years for industrial wastewater treatment. DAF process has been applied in order to treat the types of wastewater such as dairy wastewater which has high concentrations of organic substances [1, 2]. Dissolved air flotation process is a type of flotation process that separates fats, oils and grease (FOG) and the other organic substances from wastewater [3]. Contaminant substances have been disposed with the use of dissolved air in a wastewater system generated by injecting air under high pressure into a recycle stream of purified DAF effluent by a blower. A coagulant chemical such as ferric chloride or aluminum sulfate should be used in order to agglomerate the colloidal particles, and a flocculant material should be added (polyelectrolyte) in order to conglomerate the particles into heavier flocks [1].

***Corresponding author.**
*E-mail address: pyapicioglu@harran.edu.tr

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Chemical substances accumulate at DAF tank and form the chemical treatment sludge. DAF process leads to the large amount of sludge.

Sludge has originated as a byproduct of wastewater treatment processes, and sludge management is a significant challenge at the operation of wastewater treatment plants (WWTPs) from both economic and environmental perspectives of view [4]. A typical industrial sludge contains approximately 90–98% of water [5]. It should be dewatered before the final disposal. Also, dairy wastewater sludge contains huge amounts of pathogens due to the feedstocks used in the production step such as raw milk. So this chemical sludge has very highly organic content and large concentrations of carbonaceous material. The main sludge treatment techniques have been considered as thickening, aerobic or anaerobic stabilization, conditioning and dewatering [4, 5]. There are many technologies have been carried out as sludge treatment processes. Lime use is a widespread and economical technique for sludge stabilization process [6]. Stabilization process is applied for the removal of organic materials and pathogens from treatment sludge. Filter press, belt filter and centrifuge decanter are majorly used for sludge dewatering process. Dewatering processes have been carried out to separate water from sludge and to reduce sludge volume [5]. Industrial sludge has a high volume and low settleability [5]. Sludge handling and disposal activities can account for 25–65% of the total operational costs of WWTPs [7]. For many authorities and scientists regard that sludge management is a crucial environmental challenge due to the investment and operational costs for WWTPs [6].

Sludge handling units lead to intensely higher operational costs which are estimated to be 50–60% of the total costs of WWTPs [8, 9]. Energy costs of sludge management have the highest ratio on operational costs. Particularly, sludge dewatering processes need large amount of energy. Sludge is occurred in the result of wastewater treatment processes. So, a correspondence could be considered between water and energy in terms of sludge handling process. The water-energy nexus is a recently used type of systematic approach that underlines the linkages between water and energy [10]. It is clear that energy is a necessity in order to treat and distribute water [10]. Furthermore, energy is used directly for water generation, distribution, and treatment, and is depleted by heating, cooling and pumping processes [11]. According to many researchers, wastewater and sludge treatment processes are negligible for the water-energy nexus; they focus more on water consumption in the energy sector. In fact, energy consumption of the wastewater treatment plants (WWTPs) should be a significant consideration of the water-energy nexus. This study determines the energy costs of an industrial wastewater treatment plant in terms of sludge management process using water-energy nexus. High energy consumption leads to the high operational costs of the WWTPs. Energy cost constitutes a higher ratio of total operational costs of a wastewater treatment plant. Energy demand of a sludge handling process is based on the volume of treated sludge (sludge flow), sludge settleability and organic and water content. In order to obtain energy efficiency and to reduce the energy costs, it should be focused on these operational parameters.

Operational parameters of the industrial wastewater treatment plants do not match the design parameters for many factors such as the inaccurate estimation of the employees or production capacity [12]. This mismatch has an unfavorable effect on sludge management and energy costs [12, 13]. This study aimed to reveal the role of design and operating conditions on energy costs of sludge management related to DAF tank using centrifuge decanter. The aim of this paper is also in order to develop a new estimation method for energy costs of sludge management in the wastewater treatment plants. This paper recommended a new estimation method for energy management of sludge handling units. The originality of this study is that a new developed model for energy cost assessment of sludge management was carried out. Also, the novelty of this paper was that effect of design and operating sludge parameters in terms of total organic carbon (TOC) and sludge volume index (SVI) were investigated and benchmarked with each other. The other objectives of this study are to determine the effect of TOC and SVI on operational costs of sludge management. Also, energy costs of electricity consumption of decanter were figured out. From this purpose, a new estimation model was developed. In the literature, several researchers have focused on environmental and economic assessment of waste activated sludge using life cycle assessment (LCA) method. Uggetti et al. (2011) [14] reported the economic costs of sludge treatment wetland using LCA approach. Nielsen (2015) [15] investigated on chemical use, energy, and greenhouse gas emissions of a sludge reed bed. Sid et al. (2017) [16] researched how energy was consumed throughout the whole plant and how operating conditions affected this energy requirement for an activated sludge system. Apart from previous studies, a new estimation model was developed for energy cost assessment of sludge management processes in this paper.

MATERIALS AND METHODS

Description of the Industrial WWTP

The dairy industry has been located in Turkey. In this study, a full-scale dairy wastewater treatment plant was selected as the pilot plant. The main wastewater accumulation points of the dairy industry are the clarification, pasteurization and homogenization processes. The wastewater and sludge analyses were performed using Standard Methods [17]. This industrial plant is a kind of small-scale WWTPs. Figure 1 showed the wastewater treatment and sludge handling flow diagrams. Table 1 demonstrated the influent and sludge characterization.

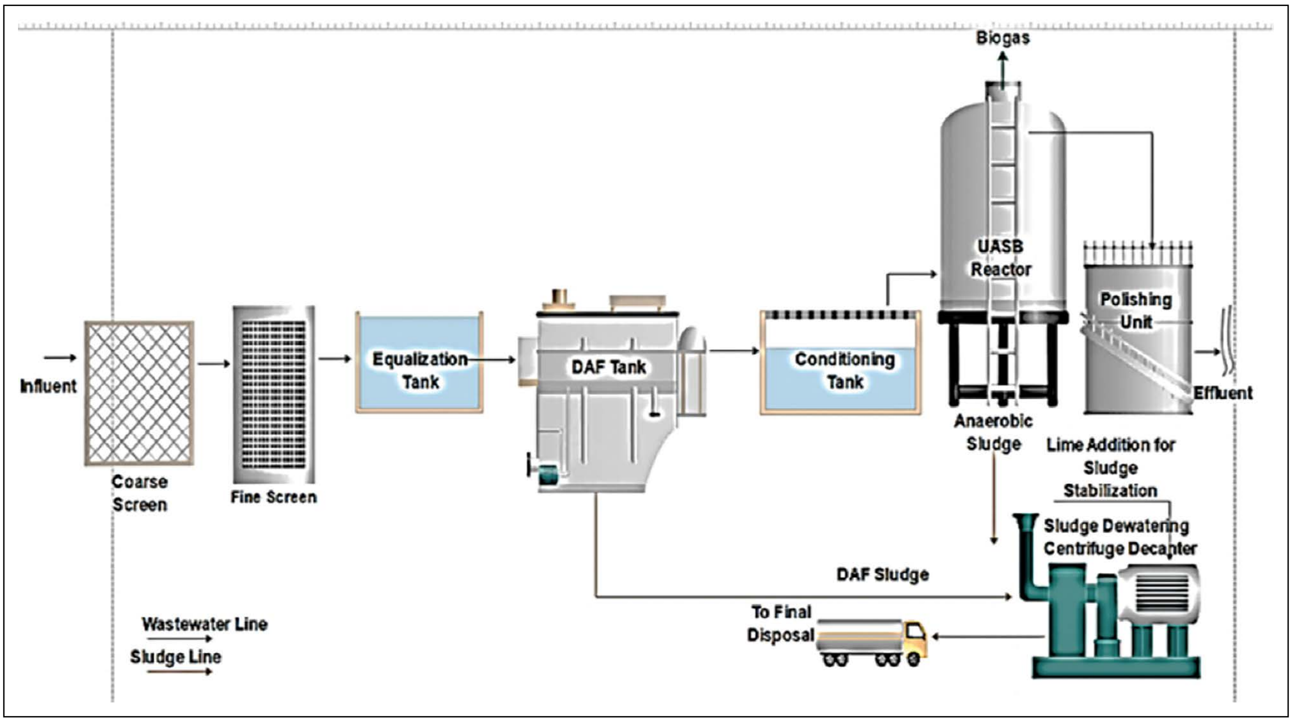

Figure 1. Wastewater treatment and sludge handling flow diagram.

Table 1. Wastewater and sludge characterization

Parameter	Value
COD (mg L^{-1})	12000
FOG (mg L^{-1})	350
TSS (mg L^{-1})	425
pH	6
Flow Rate (Q) (m^3 d^{-1})	2100
Raw Sludge Water Content (%)	95.5
Dewatered Sludge Water Content (%)	13
Raw Sludge Solids Content (%)	4.5
Dewatered Sludge Solids Content (%)	87

* Standard deviations of COD, FOG, TSS, pH and flow rate were 8.21, 7.64, 6,45, 4.21 and 8.13 respectively.

In this paper, a DAF unit was continually operated under specific operational conditions to ensure the highest removal efficiency. DAF tank is a kind of crossflow plate pack tanks. At DAF tank, polyaluminum chloride (PAC) was used as the coagulant substance and polyelectrolyte (PE) was used as the flocculant material. In this study, powder form of PAC was used. AC 100 S particular type of PAC was prepared as the aqueous solution. As seen from Figure 1, sludge is generated from DAF tank and up flow anaerobic sludge bed (UASB) reactor. Anaerobic sludge is stabilized so there is no need to stabilize it with lime. Sludge generated in wastewater treatment processes typically contains very small amounts of solids distributed throughout a large volume of water. Besides, anaerobic sludge has no require to be dewatered due to low water content and stability. DAF sludge has low solid content (4.5%) and high organic content. This sludge could be dewatered in order to reduce its volume and decrease the water content in the sludge. Dewatering aimed to decrease the water content and to reduce the water content to 25%, nearly. In this WWTP, centrifuge decanter was used as sludge dewatering technology. Sludge dewatering technology needs huge amount of electricity. It could be considered that large amount of energy costs in WWTPs is corresponded to sludge dewatering processes. So, energy costs of sludge dewatering processes should be evaluated at WWTPs.

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Table 2. Wastewater and sludge characterization

Parameter	Value
q_s (m^3 d^{-1})	100
Q_s (m^3 d^{-1})	42
V_s(m^3 $year^{-1}$)	15330
TOC_d (mg kg^{-1})	80000
TOC_o (mg kg^{-1})	50600
SVI_d(mL g^{-1})	150
SVIo (mL g^{-1})	100
µ (kWh $m^{-3}$$sludge^{-1}$)	100000
Ω (TL kWh^{-1})	1.05
PD (kW)	200

*At all abbreviations, "d" defines the design parameters and "o" defines the operational parameters.

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Determination of Energy Costs

There are several methods could be defined in the literature depending on the variables used for energy costs assessment of WWTPs. Many investigations demonstrated that it was possible to use operational parameters such as the volume of wastewater treated, the volume of sludge, and the other parameters based on wastewater and sludge characterization [18] in order to estimate the energy costs. In this study, energy cost assessment methodology was modified based on the model developed by Hernandez-Sancho et al. (2011a) [18].

Energy cost indicator (ECI) is the meaning of the energy cost index of a sludge dewatering process based on sludge volume, organic content and settleability of sludge. In this model, energy cost indicator (ECI) which was derived from the performance index (PI) has been figured out for design and operational conditions. The performance index (PI) constitutes of operational flow rate (Q) (m^3 d^{-1}) and the design flow rate (q) (m^3 d^{-1}) of the WWTP.

The performance index (PI) was adapted from a study by Castellet-Viciano et al., (2018) [13] for sludge management in this study. It comprises of operational sludge flow (Q_s) (m^3 d^{-1}) and the design sludge flow (q_s) (m^3 d^{-1}). Eq. 1 demonstrated the estimation of the adapted performance index for sludge management processes.

$$PI= [(q_s-Q_s)/Q_s] \times 100 \quad (1)$$

Energy cost indicator (ECI) was derived from the performance index (PI); the model included the volume of treated wastewater per year (V) (m^3 $year^{-1}$) and biochemical oxygen demand (BOD) (g m^{-3}). The basic equation model for small-scale plants was given in Eq.2 [13].

$$ECI=1983.106\ V^{0.717}\ e^{(-14.327\ BOD+0.660PI)} \quad (2)$$

In this study, energy cost indicator (ECI) was derived from this equation tool (Eq.2.) for sludge management and the model constituents of the volume of sludge per year (Vs) (m^3 $year^{-1}$) and total organic carbon of sludge (TOC) (mg kg^{-1}) or sludge volume index. TOC shows the organic content of sludge and SVI shows the settleability of sludge. The derived estimation model of ECI for small scale WWTPs was shown in Eq.3. The values of ECI were figured out both design and operational parameters.

$$ECI=1983.10^6\ Vs^{0.717}\ e^{(-14.327\ TOC,\ SVI+0.660PI)} \quad (3)$$

A new model was developed for the estimation of energy costs of sludge management in this paper. Energy costs (ε) (€ m^{-3} $sludge^{-1}$) could be estimated with the help of Eq. 4.

$$\varepsilon= ECI \times \mu \times \Omega \times 1000 \quad (4)$$

Where:

ECI: Energy cost index

µ: electricity consumption for dewatering of per 1 m^3 sludge (kWh m^{-3} sludge)

Ω: specific cost per 1 kWh energy of the plant (TL kWh^{-1})

Electricity consumption of the plant was ensured from the electricity counters and bills of the centrifuge decanter. Ω is used as the specific cost related to Turkey [19]. Energy costs corresponded to design and operational conditions were figured out and benchmarked using a new developed estimation model in this paper. The data set used in this study was shown in Table 2.

Energy costs for decanter also calculated using sludge amount (V) m^3 $year^{-1}$, the design power of decanter (PD) (kWh m^{-3} $sludge^{-1}$) and Ω (TL kWh^{-1}). Eq. (5) shows the calculation term.

$$\varepsilon= PD \times V \times \Omega /10000 \quad (5)$$

RESULTS AND DISCUSSION

Benchmarking of Energy Cost Indicators

The results revealed that energy cost indicators of sludge management in terms of TOC and SVI corresponded to design parameter were lower than operational parameter for both two types of sludge parameter. The values of energy cost indicators related to design and operational TOC parameter were 0.657 and 1.08, respectively. Similarly, energy cost indicators corresponded to design and operational SVI parameter were 0.686 and 2.51, respectively. It could

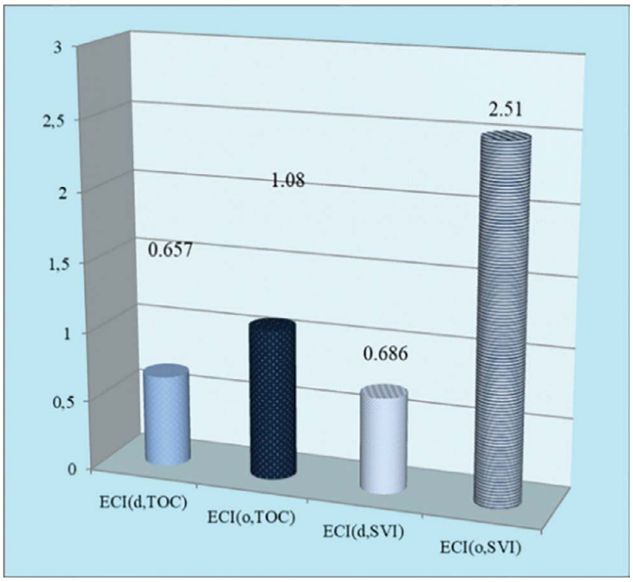

Figure 2. Benchmarking of energy cost indicators.

be considered that energy cost indicators related to SVI parameter were higher than TOC parameter. Figure 2 shows the benchmarking of the energy cost indicators of sludge dewatering process.

PI is very significant variable in the model. When the sludge is dewatered under design conditions, it could be said that the value of PI will be zero. If the gap between the operational and the design sludge volumes increase, the value of PI will be higher. According to the basic model, as PI is low, energy cost index reduces. In this study, PI was calculated out as 1.38. If WWTPs are operated at design sludge flow, energy cost index of the plants could be lower. There are many studies related to this topic. Using of cost functions was carried out, in the previous studies. Most of developed models for WWTPs have been focused on determination of the operational costs and the costs of maintenance activities of the treatment and pumping equipment. Hernandez-Sancho et al. (2011b) [20] applied an energy cost modelling using statistical method for 341 WWTPs in Spain. Castellet-Viciano et al. (2018) [13] investigated the impact of design flow on energy costs for small, middle and large scales of WWTPs. They reported that PI was 0.20, 0.40, 0.60 and 0.80 for the small-scale WWTPs [13]. The value of PI was calculated as 1.38. Apart from the previous studies, the energy costs of sludge management were focused in this paper.

Energy cost Assessment

According to findings, energy costs corresponded to design parameters were lower than operational parameter for both 2 sludge parameters. If the plant is operated under design conditions, energy costs would be lower. Energy costs of design and operational parameters in terms of TOC of sludge dewatering process were 69.0 and 113.4 TL

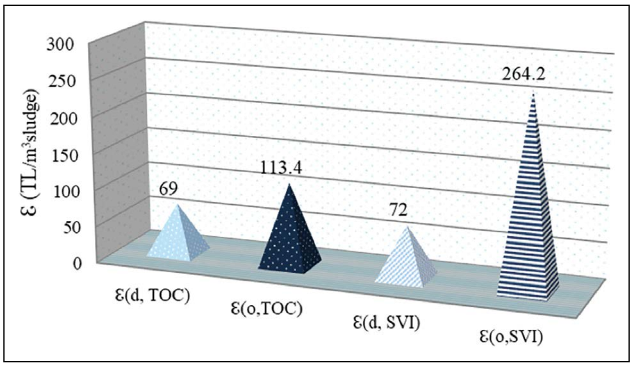

Figure 3. Energy costs of sludge dewatering process.

m^{-3} sludge, respectively. Energy costs of design and operational parameters related to SVI were 72.0 and 264.2 TL m^{-3} sludge. Energy costs of SVI parameter were higher than TOC parameter. It could be said energy consumption was higher for settling of sludge than for sludge stabilization process. TOC defines the organic content of sludge and is used as stabilization indicator. Figure 3 shows the energy costs of sludge dewatering process.

Energy costs of decanter was calculated as 321.93 TL m^{-3} sludge considering only energy consumption. It is obvious that operational costs were lower than energy costs of electricity consumption.

Molinos-Senante et al. (2013) [21] used a cost function model to describe the costs of sludge and waste management for a wastewater treatment plant. In a study by Plumlee et al. (2014) [22] the costs of advanced wastewater treatment processes which were microfiltration, ultrafiltration, nanofiltration, reverse osmosis, ozone, ultraviolet (UV) treatment with H_2O_2 and biological activated carbon were investigated. They found that membrane treatment led to the highest costs and ozone led to the lowest costs. Yumin et al. (2016) [23] determined the operational costs of WWTPs in rural areas using cost functions which membrane bioreactor technology, sequencing batch reactor, purification tank, biological filter and artificial wetland were used at 221 different WWTPs. In the literature, the investigations corresponded to energy costs of sludge management are limited. Many studies focused on technical, economic and environmental evaluation of sludge management using life cycle assessment (LCA) method. In a study by Uggetti et al. (2011) [14] economic performances of sludge treatment wetlands were applied using LCA method. They found that sludge treatment wetlands were the most appropriate technology for decentralized sludge management in small regions. Ushani et al. (2018) [24] performed a similar study. They carried out energy and cost benefit analysis for scalability of a sludge disintegration process to be applied at pilot scale. They observed bacterial disintegration in terms of energy analysis. They reported that sodium thiosulphate induced immobilized protease secreting bacterial disintegration was a feasible process with net profit of 2.6 USD Ton^{-1} of sludge. Yapıcıoğlu and Yeşilnacar (2020) [25] used the similar assessment method to determine the energy costs of a dairy wastewater treatment plant in terms of wastewater treatment process. They found that energy cost indicator of the existing treatment process was lower than optimum operating conditions.

CONCLUSIONS

The results revealed that energy cost indicators of sludge dewatering process related to design parameter were lower than operational parameter in terms of TOC and SVI.

Energy costs of design and operational parameters in terms of TOC were 69.0 and 113.4 TL m^{-3} sludge, respectively. Energy costs of design and operational parameters related to SVI were 72.0 and 264.2 TL m^{-3} sludge. Energy costs of SVI parameter were higher than TOC parameter. It could be said energy consumption was higher for settling of sludge than for sludge stabilization process.

If the plant is operated at design conditions, energy costs of sludge management could be lower. According to this study, if the sludge management is carried out under design conditions, approximately 63% of reduction on energy costs could be ensured.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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Research Article

Insights to improve covered lagoon biodigesters through by-products recovery in pig farms

Larissa A. NASCIMENTO, Raphael R. M. OLIVEIRA, Izabelle de P. SOUSA, Priscila S. MARADINI, André P. ROSA*

Federal University of Viçosa, Department of Agricultural Engineering, Viçosa, MG, Brazil

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ABSTRACT

Pig farming activity has an important role in the Brazilian economy and generates effluents with a high polluting potential. The covered lagoon biodigester is a simple and suitable alternative for the treatment of swine manure. This work aimed to propose improvements to the pig effluent treatment system composed by covered lagoon biodigesters. Therefore, a survey of a typical plant configuration of pig effluent treatment was accomplished and alternatives were suggested in order to get a greater energy sustainability in farms through resource recovery. The proposed interventions were based on studies of scientific papers, technical equipment manuals, technical research and consultation with professionals of the field. The optimization of the systems operation considers some criteria, such as: (i) need for solids removal; (ii) organic loading; (iii) operation temperature; (iv) effluent recirculation; and (v) biogas energy recovery. Firstly, a typical scenario was identified without any improvements, in which the biogas is sent to flares without energy recovery. Subsequently, systems improvement insights were proposed, mainly regarding effluent heating through a solar heating system or by recovering the thermal energy from biogas and biogas recovering. The treatment optimization would increase the efficiency of organic matter removal and biogas production, as well as electric energy production and reduction in greenhouse gases emissions. The use of tools such as Life Cycle Analysis (LCA) can favor decision making and comparing proposed alternatives.

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INTRODUCTION

Pig farming is among the main agribusiness activities in Brazil. In 2019, the country produced approximately four million tons and exported 861 thousand tons of pig meat, being the fourth largest producer and exporter in the world, and the fifth consumer. Brazil's Southern region is responsible for 66.0% of the national production, followed by the Southeastern region, responsible for about 18.0% [1]. The intense swine activity generates large amounts of manure rich in organic matter and nutrients such as nitrogen, phosphorus, and eventually antibiotics and steroid hormones with high polluting potential, thus requiring treatment and

***Corresponding author.**
*E-mail address: andrerosa@ufv.br

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an adequate final disposal in order to minimize impacts to the environment [2, 3]. Anaerobic digesters stand out as a great treatment alternative because of their low costs of implementation and operation, low energy demand, reduced sludge yield and the biogas generation, a by-product with high energy potential [4].

Anaerobic digesters are available in the market in different models and configurations. Their selection must take into account local climate conditions, effluent characteristics, and financial resources available for their construction, operation and maintenance. The covered lagoon biodigester (CLB) is a simple technology, easy to build and operate, being among the main swine manure treatment alternatives in Brazil [5, 6]. Despite the advantages, there are some inherent limitations that can compromise treatment efficiency and biogas recovery. For instance, the absence of automated features to control and optimize the operational temperature and a full understanding of the hydraulic regime, which influences the distribution of microorganisms in the reactor and the accumulation of inhibitory metabolites by the microorganisms [7].

Anaerobic processes are carried out by various Bacteria and Archaea. The biological activity of these microorganisms is strongly affected by operational and environmental factors [4, 8], such as hydraulic retention time, temperature, and pH. Therefore, monitoring those factors is important to guarantee a stable and efficient treatment process and increase the biogas production, which can be used to generate thermal and electric energy.

According to Oliveira et al. [8] and Santos et al. [10], anaerobic digestion of swine manure in Brazil can generate energy in an order of 1,750 TWh.year^{-1}, contributing, for instance, to the generation of electricity from biomass, which in 2019 was 52,111TWh [11]. However, such potential isn't utilized. Regarding the state of Minas Gerais, only 34.8% of its pig farms have a CLB installed. From those with biodigesters, few of them generate decentralized energy from biogas recovery. Besides the energy potential, biogas recovery would avoid an average emission of 0.535 Mt CO_2.year^{-1}, making pig farming more sustainable [10]. In addition, the biogas recovery in Brazil may collaborate to achieve the following goals signed in the Paris Agreement: (i) reduce greenhouse gases by 37.0% below emission levels in 2005 until 2025 and 43.0% below emission levels in 2005 until 2030; (ii) increase the share of sustainable bioenergy in its energy matrix by 18.0% until 2030; and (iii) achieve a 45.0% share of renewable energy in the composition of the energy matrix until 2030 [12].

The low use of the biogas energy potential is associated with the lack of regulation and policies to encourage the development of accessible and appropriate technologies for the Brazilian context [13]. There are some studies regarding the optimization of CLBs treatment efficiency and biogas recovery in order to improve pig farms sustainability [8, 14–20]. Thereby, the implementation of constructive and operational improvements in covered lagoon biodigesters enables increasing the treatment efficiency and biogas recovery. This work aimed to present scenarios and alternatives associated with constructive and operational improvements of covered lagoon biodigesters, as well as integrating their by-products recovery in order to improve pig farms sustainability.

MATERIAL AND METHODS

The base layout scenario of treatment plants in pig farms, as well as the constructive and operational parameters improvements and by-products recovery alternatives were assessed based on technical literature review, manufacturer's manuals, and benchmarking of operational practices, experiences reported by pig farm facilities and technical reports from government agencies related to pig farming and biogas energetic recovery. CLBs optimization strategies contemplated technological alternatives and by-products recovery. The following aspects were considered: (i) solids removal; (ii) organic loading; (iii) operational temperature; (iv) effluent recirculation, and (v) biogas energy recovery. The possible alternatives to improve the system efficiency were described and compared with each other, presenting their advantages and disadvantages.

RESULTS AND DISCUSSION

Base Scenario for Pig Farms Using Covered Lagoon Biodigesters

The effluent treated by biodigesters requires a certain level of post treatment before being discharged into water bodies [6]. A stabilization pond is an interesting choice considering its advantages such as low constructive and management investments, as well as treatment efficiency, however this alternative requires a large construction area [21]. In addition, there are studies regarding the use of a stabilization pond to remove hormones present in swine manure such as progestogen, which poses potential risk to aquatic organisms [22]. Regarding the methane present in the biogas, its global warming potential is 25 times higher than that of CO_2 in a time span of 100 years [23]. Given that, it is environmentally more interesting to transform CH_4 into CO_2 through combustion, which can be done in flares, a mandatory equipment for safety purposes [8].

The flowchart in Figure 1 suggests a base layout scenario of treatment plants in pig farms in Brazil, featuring a covered lagoon biodigester and a post-treatment unit, with final disposal alternatives for the main by-products (Fig. 1). Initially, swine manure passes through a screen in order to retain small rocks, pieces of plastic and other unwanted coarse materials to get stuck inside the biodigester (Fig. 1, 2). The pass-

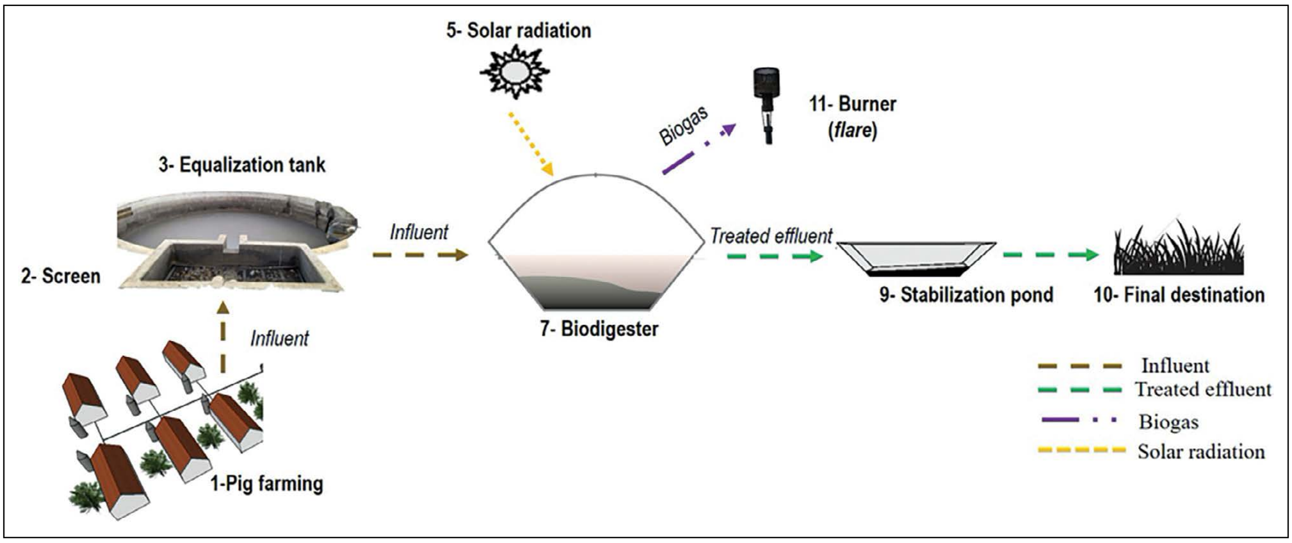

Figure 1. Base scenario for pig farms with covered lagoon biodigester treatment system.

ing liquid effluent is then stored in an equalization tank (Fig. 1–3). Afterwards, the swine manure is pumped to feed the biodigester (Fig. 1–7). The main by-products of anaerobic digestion are the effluent and the biogas. The first goes to a post-treatment, usually a stabilization pond (Fig. 1–9), being subsequently applied in the soil or used for crop fertigation (Fig. 1–10). The biogas generated is burned in flares (Fig. 1–11) [24]. Finally, the CLB's main source of heat is the incident solar radiation on the top of the biodigester (Fig. 1–5).

Improved Pig Farm Base Scenario Flowcharts

Two different layouts containing constructive and operational improvements and biogas destinations are shown in Figure 2 and Figure 3. In Figure 2 the heating system is based on solar energy, while in Figure 3 it is based on the thermal energy released from biogas combustion.

Figure 2 presents the treatment system indicated in the base scenario (Fig. 1), with a proposal of a pre-treatment by a solid-liquid separator, in order to reduce the total solids content to a range suitable for CLB operation (Fig. 2–4); a swine effluent heater ran by solar panels (Fig. 2–6); and a biogas purification system that will be designed according to the quality required for its use (Fig. 2–12). Finally, the biogas energy recovery in three ways: (i) burning in boilers to generate thermal energy (Fig. 2–13); (ii) burning in a motor generator to produce electricity (Fig. 2–14); and (iii) fuel generation (Fig. 2–15).

Figure 3 presents the treatment system indicated in the base scenario of Figure 1 with the proposal of a pre-treatment by a solid-liquid separator, in order to reduce the total solids content to a range suitable to the CLB operation (Fig. 3, 4); a swine effluent heater run by thermal energy released by biogas burning (Fig. 3–6); and a biogas purification system that will be designed according to the quality required for its use (Fig. 3–12). Finally, the biogas energy recovery in three ways: (i) burning in boilers to generate thermal energy (Fig. 3–13); (ii) burning in a motor generator to generate electricity (Fig. 3–14); and (iii) fuel generation (Fig. 3–15).

Improvement Alternatives

The aspects related to some treatment stages and their operational conditions, as well as improvement alternatives for these, are detailed below.

Solids Removal

Solids removal objectives the removal of coarse solids, in order to avoid abrasion and obstructions in equipment and pipes [21]. Pre-treatment alternatives are a function of pig farm management, biodigester set up, and effluent characteristics in terms of solids content, which is considered a limiting factor. In general, CLB's operate with low levels of total solids, up to 3.0%, and the pre-treatment is recommended for higher levels [8]. The phase separation reduces the swine effluent solids contribution, reducing the entry of recalcitrant material in the biodigester, allowing it to be more conducive to microbial action and, consequently, improving biogas production. There are several pre-treatment methods, such as decanting, centrifugation, sieving and/or pressing, dehydration by wind, forced air or heated air. The most used are decanting and sieving [17, 18, 25]. Decanting pros are the low costs of implementation and maintenance. However, it requires greater manpower. The sieves are classified as static, vibrating and rotating. Regarding the static sieve, maintenance and cleaning are major issues, as the formation of a thin layer of solids on the sieve surface can cause operational problems. The rotating and vibrating sieves allows continuous operation with little or no obstruction of the screens, enabling it to remove coarse and fine particles. However, they have a high initial investment cost and rely on power to operate [25].

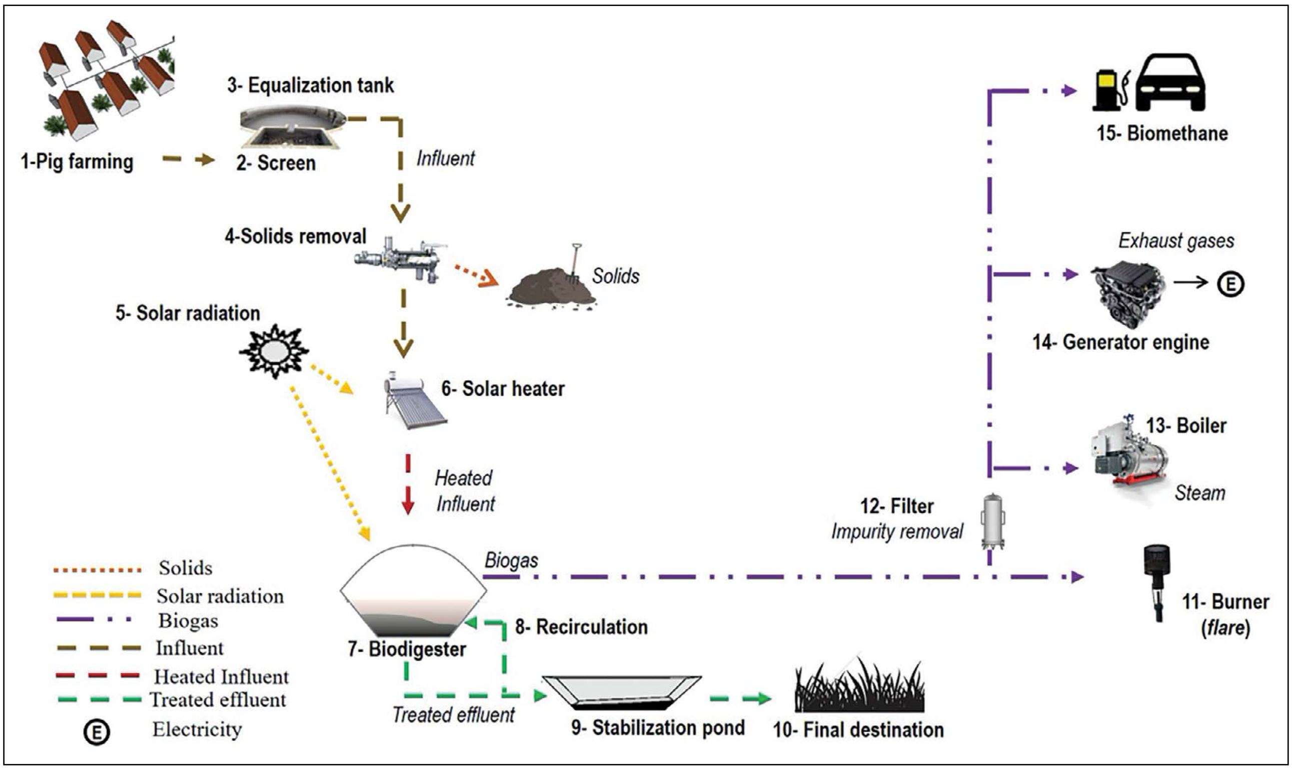

Figure 2. Improvements for the anaerobic process considering pre-treatment, swine effluent heating via solar energy and alternatives for the use of biogas.

The best pre-treatment alternative depends on the effluent characteristics, number of animals, land area and economic resources availability. Considering that rotating sieves are available in the market in different sizes and capacities, that way attending pig farms from different sizes, this alternative was selected and presented in Figure 2–4 and Figure 3, 4. The solid fraction retained by the sieve can be composted and used as a solid biofertilizer [25].

Biodigester Feeding - Organic Load in Terms of Volatile Solids

The volumetric organic load (VOL) influences anaerobic process dynamics, since it directly impacts the optimal conditions for microbial growth. CLBs usually treat effluents with a volumetric organic load of 0.3 to 0.5 $kgSV.m^{-3}$ $reactor.d^{-1}$ [8]. Feeding the biodigester with VOLs above the designed capacity can lead to system failure; while feeding it below the VOLs designed capacity leads to a low food/microorganism ratio, resulting in low biological activity, thus reducing the treatment efficiency [6].

Many studies have shown an increase in the methane yield for the co-digestion (AcoD) of swine manure with other substrates such as microalgae, agricultural and food residues. Astals et al. [24] reported an increase in the methane yield of microalgae from 0.163 to 0.245 m^3_{CH4} kg^{-1VS} (volatile solids) by applying the co-digestion with swine manure [27] reached 0.187 m^3_{CH4} kg^{-1}_{VS} in pig manure digestion, compared to 0.388m^3_{CH4} kg^{-1}_{VS} in pig manure and food waste co-digestion, in the ratio 17:83, respectively. This increase is due to overcoming ammonia inhibition which is sometimes a feature in digestion of pure manure and optimizing the carbon to nitrogen (C/N) ratio in the feedstock for the AD [28]. Although the C/N ratio is widely used to explain the synergies that occur during anaerobic co-digestion, specific microbes from pig manure, macro and micronutrients, and alkalinity can be also linked [29]. However, the co-digestion of lipid rich co-substrates may present operating problems, which are usually associated with foaming, clogging, and biomass flotation inside the reactor; and inhibition of the microorganisms due to the accumulation of long chain fatty acids [30].

Operational Temperature

Temperature is a parameter of great importance in anaerobic treatment, impacting microorganism's metabolism and biochemical reactions rates [8, 25]. Anaerobic reactors work under thermophilic (50.0 to 65.0°C) or mesophilic (20.0 to 45.0°C) conditions, being the optimal temperature for microorganism development the range between 35.0°C and 37.0°C [7, 26, 33]. Considering that Brazil is a tropical country, most anaerobic reactors operate at temperatures close to the lower limit of the mesophilic range. According to Sousa [18], the internal temperature of a covered lagoon biodigester without temperature control, in the city of Teixeiras, Minas Gerais (20º34'07,2" W, 42º52'01,6" S), varied

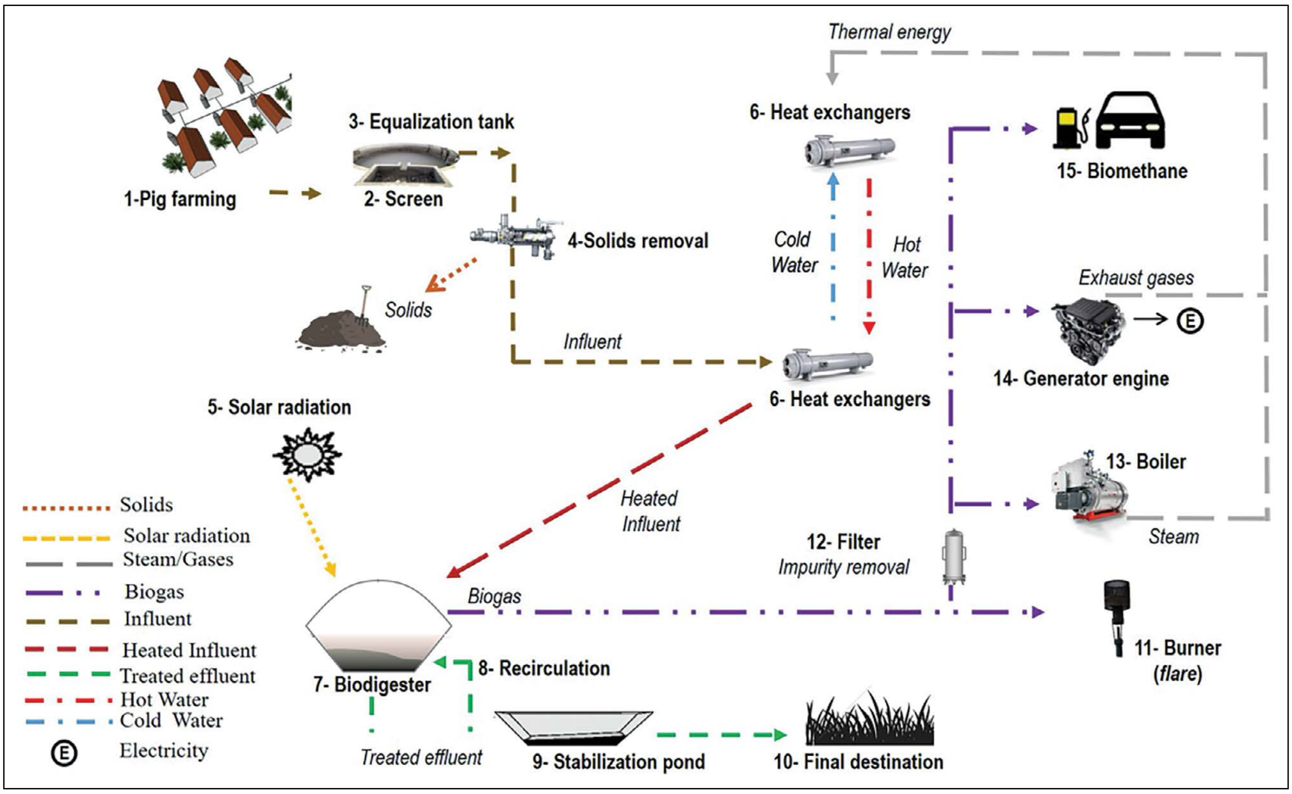

Figure 3. Improvements for the anaerobic process considering pre-treatment, heating the swine effluent via thermal energy from burning biogas and alternatives for the use of biogas.

from 20.5 to 26.8 °C, well below the optimum temperature, which may have contributed to decrease the system efficiency in terms of organic matter removal and biogas yield. Furthermore, anaerobic microorganisms are particularly sensitive to temperature variation; even small changes up to 2°C may cause inhibition [8]. Thus, a temperature control system will ensure proper conditions for microbial activity, increasing treatment efficiency and biogas yield. Some alternatives are shown in Figure 2–5, Figure 2–6, Figure 3–5 and Figure 3–6 and described below.

The heat required for anaerobic reactions in the CLB comes from the effluent itself, from the heat released by microbial activity and, mainly, from the solar radiation on the top of the biodigester. The heat released by microbial metabolism does not affect the effluent temperature substantially, whereas solar incidence is responsible for up to 84.0% of the heat transfer rate to the interior of the biodigesters in the summer [17, 34].

Solar radiation plays an important role in CLB temperature control. It varies seasonally and along longitude and latitudes. The rate of solar radiation absorption by biodigesters varies according to local landscape aspects such as trees, buildings and other objects that may block the sunlight, as well as the reactor's layout, and the gasometer dome color and material properties. According to a study by [33], solar reflectance of a digester dome, external ambient temperature and solar irradiance are the factors that mostly influence the biodigester internal temperature. The same study showed that a black color dome with a reflectance of 4.8% lead the biodigester internal temperature close to 46.0 °C in periods of intense solar radiation like summer, while a white color dome with a reflectance of 77.6% lead to an internal temperature of 38.0°C during the same time of the year. The study clarifies that the heat provided by the solar incidence on the gasometer dome is inconveniently affected by different factors, making it difficult to control the temperature inside the biodigester. Given that, choosing a gasometer dome with a low reflectance is helpful to avoid the system overheating during periods of higher solar incidence, as well as adopting other mechanisms of temperature control are necessary to ensure the system operational stability throughout the year.

Han et al. [35] proposes a heating system by installing an external tank containing a heat exchanger with continuous flow of hot water (Fig. 3–6), which heats the swine effluent before it enters the biodigester. The exhaust gases from the internal combustion engine (Fig. 3–14) or the steam emitted by a boiler (Fig. 3–13) could also be used as a heating source in the heat exchangers. In addition, the heat exchanger could be installed inside the biodigester [32, 34].

Solar heaters are also an alternative to increase the swine effluent temperature (Fig. 2–6). Dong and Lu [15] developed and integrated a large-scale solar-powered water-heating system (SPWHS) to a biogas plant installed in a pig farm in China, which increased the biogas yield. Results showed an increase of 11.2% in biogas yields generated by the integrated system compared to the biogas plant without the SPWHS, as well as an increase of 14.3% in the swine manure biomass energy transformation ratio of SPWHS [15]. Duan et al. [36] compared, via modeling, three different heating systems alternatives for an anaerobic reactor in China powered by pig slurry at different organic rates: solar energy, biogas boiler and cogeneration system. The solar energy heating system obtained a better result when the treatment system was fed with higher organic loads, reducing solar panel area and, consequently, the cost [36]. Zhang et al. [37], in turn, simulated a hybrid heating system for an anaerobic reactor in China combining solar energy and a biogas boiler in order to provide thermal energy for buildings. The proposed system features advantages in energy savings (94.9%) and reduction of carbon emissions (2,961.85-ton year^{-1}) compared to the traditional fuel sources in the country (coal) [37]. However, the results also showed that the energy contributions are very small during the winter, due to the lower incidence of solar radiation and higher volumes of rain and snow, making this kind of system a good fit for tropical countries [15, 36, 37].

Internal Effluent Recirculation

The absence of a mixing system may lead to an accumulation of sludge in the bottom of the reactor and less contact is provided between microorganisms and substrate. Moreover, the sedimentation reduces the reactor useful volume and, consequently, the hydraulic retention time, leading to a loss of solids in the effluent [8]. Effluent recirculation (Fig. 2–8 and 3–8) is an insight that has been shown to be advantageous in anaerobic digestion, favoring substrate degradation, once it reintroduces methanogenic bacteria in the reactor. This process increases cell residence time by allowing a better contact between substrate and microorganisms, contributing to keep the effluent in an even temperature inside the biodigester [38].

In addition, this feature is theoretically simpler than a mixing structure with a certain number of agitators to maintain the effluent suspended, not to mention the energy costs associated and the complicated maintenance. Furthermore, the effluent can be recirculated back into the biodigester in different points, helping to keep the system homogene in terms of microorganisms and ensure a better contact between them and the substrate. In a study developed by PROSAB [39], regarding the treatment of landfill leachate in anaerobic reactors, the recirculation attenuated the effluent organic load and promoted an endogenous inoculation of biomass, since it reintroduces microorganisms more adapted to the substrate [39]. However, despite the advantages of the recirculation process, the studies still do not focus on covered lagoon biodigesters. Thereby, this is a promising research field as an alternative to improve the CLB configuration.

Biogas Energy Recovery

There are several alternatives for biogas energy recovery, such as: (i) thermal energy generation through biogas burn in boilers and ovens (Fig. 2–13 and 3–13); (ii) electricity generation in motor generators (Fig. 2–14 and 3–14); (iii) biogas processing for use as vehicular fuel (biomethane) (Fig. 2–15 and 3–15); (iv) and injection into the natural gas line. Each biogas recovery alternative requires a level of purity, which means a higher concentration of methane and lower concentration of other components, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2) and humidity. In some cases, it is necessary to remove these components to prevent damage in equipment and structures such as engines and pipes [40].

Moreover, the economic viability of biogas energy recovery depends on local factors, such as the property's energy consumption and the concessionaire's electricity tariff. In this way, it is necessary to carry out specific economic studies for each location involving, for example, the net present value and the payback time [41]. The machinery needed for energy production can be very expensive for small producers [42]. In addition, the biogas flow may be insufficient for some generator engines available on the market. For instance, the smallest commercial motor generator of the ER-BR brand requires a minimum biogas flow with 65% methane concentration equal to 14 Nm^3 h^{-1}. However, this issue may be solved by storing the biogas in a reservoir to be fed to the generator when the flow rate is convenient. Furthermore, for the engine to function efficiently, biogas must have a minimum content of 55% methane [43].

The use of tools such as Life Cycle Analysis (LCA) supports decision making on sustainability aspects at environmental levels. The LCA allows to evaluate and compare the environmental performance of the effluent treatment system, quantifying the impacts by categories, such as carbon footprint, eutrophication, acidification, among others, in addition to enabling proportions of improvements to the system in order to reduce the impacts [44, 45].

CONCLUSIONS

Covered lagoon biodigester is a simple and suitable alternative for pig waste treatment. The optimization of this system requires evaluations of some constructive and operational aspects, such as: (i) analyzing the need to implement a phase separation step to retain solids; (ii) developing strategies to increase the reactor operational temperature for mesophilic or thermophilic ranges, as well as maintaining it stable; and (iii) promoting the recirculation of the treated effluent in the system in order to promote a better contact between substrate and microorganisms and ensuring an even temperature of the effluent under treatment.

The use of strategies to improve the anaerobic digestion process in biodigesters promotes an increase in the treatment efficiency and in the biogas production. The biogas energy recovery depends on some factors such as local and economic issues and the amount and composition of biogas produced. The main possible biogas uses from the typical scenario correspond to: (i) thermal energy generation through burning in boilers and ovens; (ii) electricity generation in motor generators; (iii) processing for use as vehicular fuel (biomethane); and (iv) injection into the natural gas line.

However, the biogas energy recovery is still not very widespread, which highlights the need to disseminate techniques and studies in order to improve the economic viability of biogas energy processes. Furthermore, new regulations and policies may encourage the development of accessible and appropriate technologies for the Brazilian context. The use of tools such as the Life Cycle Analysis (LCA) can favor decision making and comparing proposed alternatives.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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