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Advantages and Disadvantages of Nuclear Energy in Turkey: Public Perception

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ABSTRACT

Turkey intends to build three nuclear power stations in the Akkuyu, Sinop and Igneada regions to meet its increasing energy demands. This policy, however, is still a highly controversial topic in Turkey as nuclear energy has both advantages and disadvantages. The related literature on this topic is divided into two groups; supporters claim that nuclear energy may decrease Turkey's energy dependency on other countries, as it already imports approximately 70% of its total energy demand. In contrast, opponents argue that nuclear energy poses serious risks to the environment, which in turn can affect human health and lives. This discussion is, however, held mainly by decision makers, NGOs, the media and scholars. The related literature shows that we know little about how the civil populace perceive the pros and cons of NPPs. In order to fill in this gap, this research aims to explore citizens' perceptions of the advantages and disadvantages of NPPs through semi-structured interviews with people local to the Akkuyu, Sinop and Igneada regions. It concludes that people are well informed about pros and cons of NPPs. They raise three main advantages including cheap electricity, low carbon dioxide and reliability, and two disadvantages, including issues of nuclear waste and the risk of accident.

Keywords: Energy policy, nuclear energy, renewable energy, the environment and Turkey.

INTRODUCTION

Nuclear energy is one of the most important energy sources worldwide, providing about 11% of the world's electricity, and 21% of electricity in OECD countries with over 380,000 megawatt thermal (MWe) total capacity (Kaplan et al., 2017). There are about 440 commercial nuclear power reactors operating in 31 countries, with approximately 65 more reactors under construction (Ozcan et al., 2016; Akyuz, 2016). Turkey is one of these countries, constructing nuclear power plants (NPPs) in order to meet its increasing energy demand due to its rapidly growing economy and population. The country intends to build two NPPs in Sinop and Mersin, and has plans to build one more NPP in Igneada (Coskun and Tanriover, 2016), though the latter is still under discussion.

Turkey's nuclear energy policy, however, is still a controversial topic as NPPs have both advantages and disadvantages that are perceived in diverse ways due to the different values which shapes people's understandings of NPPs. While supporters claim that NPPs are cheap, reliable and environmental friendly energy sources, opponents argue NPPs are costly, non-renewable and eco-unfriendly. The literature shows that this discussion is mainly held by only politicians, NGOs, scholars and the media, and although there are many studies considering the pros and cons of NPPs we, however, still have little information about the true public perception of NPPs. As citizen are at the centre of the risks and benefits related to NPPs, the question becomes one of what the public opinion about the advantages and disadvantages of NPPs actually is, an issue which is still not clear in the literature to date.

In order to fill this gap in the literature, this research aims to explore how the public perceives of pros and cons of NPPs in the Akkuyu, Sinop and Igneada regions by investigating the following research questions: (1) what are the advantages of NPPs that residents living near planned NPPs know/support?; and (2), what are the disadvantages of NPPs that residents living near NPPs know/support? By doing so, this research aims to explain public perception of the pros and cons of the NPPs planned in the Akkuyu, Sinop and Igneada regions, which in turn may help decision makers to develop a nuclear energy policy that properly reflects people's concerns and priorities.

This paper consists of two main sections. The main purpose of first of these is to introduce the related literature on nuclear energy policy of Turkey, and the advantages and disadvantages of NPPs. The second part aims to explore how the public perceives the pros and cons of NPPs through semi-structured interviews with people local to the Akkuyu, Sinop and Igneada regions. This study concludes that people indicated three main advantages, including cheap electricity, low carbon dioxide and reliability, and two disadvantages, including issues of nuclear waste and risk of accident; these viewpoints indicate that public is, in fact, very well informed about NPPs.

Development of Nuclear Energy Policy of Turkey

As of August 2017, there were 31 countries with a total of 447 nuclear reactors worldwide, which between them produce about 17% of the world's electricity with an installed net capacity of approximately 392 gigawatt (GW) (Elliott, 2016). Nuclear power capacity worldwide is increasing steadily, with 59 nuclear reactors currently under construction in 16 countries (Ozcan et al., 2016). Turkey is one of these countries, currently constructing two NPPs in the Akkuyu and Sinop regions and with plans to build a third in Igneada (Coskun and Tanriover, 2016). The previous Turkish Energy Minister, Taner Yildiz, claims that the commissioning of the Akkuyu and Sinop nuclear power plants will reduce the natural gas bill by $7.2 billion per year (Jewell and Ates, 2015). It is estimated that the share of nuclear energy, in terms of total energy consumption, is intended to be 8–10% in 2020, and 20% by 2030 (Aras, 2013). The Akkuyu and Sinop reactors would replace a little under 10% of the total electrical generation capacity (Jewell and Ates, 2015).

Although Turkey has only begun to construct NPPs over the last decade, its nuclear energy policy goes back to the 1950s (Jewell and Ates, 2015); Turkey has no NPPs, but it has had a nuclear energy program for more than 60 years. The country's interest in nuclear energy started in the 1950s when the Turkish Atomic Energy Commission (TAEC) was established in 1956 in Ankara to oversee the peaceful use of atomic energy (Jewell and Ates, 2015). First construction begun on a 1 MW research reactor at the Çekmece Nuclear Research and Training Centre (ÇNAEM) in 1959, and which started operation in 1962 (Oner, 2011). The country established its second nuclear research centre at the Ankara Nuclear Research and Training Centre (ANRTC) in 1969 (Ozcan et al., 2016). It issued a new nuclear tender for the construction of a nuclear reactor at the Akkuyu and Sinop sites but cancelled it in 1988 due to financial difficulties (Erdogdu, 2007). Similarly, Turkey announced another tender for the construction of a nuclear power plant at Akkuyu in 1996. The post-modern coup IN 1997 and a massive earthquake in 1999 slowed the country's tender process, which ended in 2001 because of a further financial crisis (Akcay, 2009; Ozacan et al., 2016).

Turkey announced a new nuclear tender in 2008, and made an agreement with Russia for the construction of four nuclear power plants in 2010 with VVER-1200 reactors with a total capacity of 4.800 MW in the Mersin province, located on the southern coast of Turkey. It is expected that construction for the first plant will start at Akkuyu in 2018 and that this plant will come online in 2020. The Akkuyu NPP will be built, owned and operated by a Russian subsidiary of Rosatom, which is a state-owned nuclear company. It is estimated that the project will ultimately cost $20 billion and will employ about 10,000 people. The life cycle of the nuclear plant is rated as being approximately 60 years (Aras, 2013; Aghayev and Aktas, 2017; Heffron and Hatinoglu, 2014; Melikoglu, 2016).

Figure 1. Planned Nuclear Power Reactors at Akkuyu (World Nuclear Association, 2017)

	Type	**MWe gross**	**Start construction**	**Start operation**
Akkuyu 1	VVER-1200	1200	2018	2023
Akkuyu 2	VVER-1200	1200	2019	2023
Akkuyu 3	VVER-1200	1200	2020	2024
Akkuyu 4	VVER-1200	1200	2021	2025

An intergovernmental agreement on nuclear power plant construction and cooperation for the Sinop Nuclear Power Plant on the Black Sea coast, which is the second Turkish nuclear power plant project, was signed with Japan in 2013. The consortium for the Sinop NPPs includes Japan's Mitsubishi and Itochu, France's GDF Suez and Areva, and EUAS from Turkey, the latter of which owned only 49% of the share. It is estimated that this 5000-5600 MWe water nuclear reactor with a combined capacity of about 4.5 GW will cost approximately $22-25 billion, of which 70% will be debt financed. The project still remains on of a feasibility study, though site preparation is already underway. The construction of the second NPP, however, will start in 2017 once an environmental impact assessment (EIA) has been conducted and approved. It is expected that the first unit at the Sinop plant will be active by 2023, and the fourth unit will enter service by 2028 (Gunay and Iseri, 2017; Kok and Benli, 2017; Melikoglu, 2016).

Figure 2. Planned Nuclear Power Reactors at Sinop (World Nuclear Association, 2017)

	Type	**MWe gross**	**Start construction**	**Start operation**
Sinop 1	Atmea1	1150	2017	2023
Sinop 2	Atmea1	1150	2018	2024
Sinop 3	Atmea1	1150	-	By 2030
Sinop 4	Atmea1	1150	-	By 2030

Turkey plans to build a third nuclear power plant. The Turkish Energy Atomic Authority (TAEK) has identified Igneada, which is 12 km from the Bulgarian border in the Eastern Thrace region, virtually on the Black Sea coast, as a third NPP site (Kurt, 2014). The project was confirmed in October 2015, but is still under negotiation with several companies, including Chinese companies and the U.S.-based Westinghouse to develop and construct a four-unit nuclear power plant. It is estimated that the NPP at Igneada will be active by 2030 (Gunay and Iseri, 2017).

Figure 3. Planned Nuclear Power Reactors at Igneada (World Nuclear Association, 2017)

	Type	**MWe gross**	**Start construction**	**Start operation**
Igneada 1	AP1000	1250	-	By 2030
Igneada 2	AP1000	1250	-	By 2030
Igneada 3	CAP1400	1400	-	By 2030
igneada 4	CAP1400	1400	-	By 2030

Advantages and Disadvantages of NPPS In Turkey

As summarized above, Turkey's nuclear energy policy is not new but rather is a very heated ongoing debate by politicians, decision makers, NGOs, activists and, particularly, the academic world, as it has both advantages and disadvantages which can be perceived in diverse ways depending on people's values. It is not interesting that the related literature is divided into two main groups; while supporters claim that NPPs are carbon free, cheap and reliable energy sources, opponents disagree, claiming that nuclear energy is costly, risky and eco-unfriendly energy in comparison with renewable energy sources such as solar and wind power.

Supporters raise some of the advantages of NPPs. The first of these is that it is argued NPPs will reduce Turkey's heavy dependence on oil and natural gas imports (Kurt, 2014; Aras, 2013; Kok and Benli, 2017), which in turn will enhance the security of energy supplies and ultimately the security of the nation (Erdogdu, 2007). Since 1960, electricity consumption in Turkey has grown on average by 9% per year, as compared to 7% for the world as a whole (Jewell and Ates, 2015). Turkey had a total installed electricity-generating capacity of 41.8 GW in 2008, a 78% increase on the same for 1998 (Kurt, 2014). Turkey, however, meets nearly 70% of its energy demands through imports (Akyuz, 2015). For this reason, Oner (2011) states that Turkey needs NPPs to meet the increasing energy demand of its own domestic sources. Secondly, fossil fuels are significant sources of the greenhouse gas emissions which cause climate change and global warming (Talinli et al., 2010). There are, however, no such gases released in the nuclear power-generated electricity (Sirin, 2010). NPPs are one of the few energy production methods that emit virtually no air-polluting or greenhouse gases (Erdogdu, 2007). As Turkey is facing environmental problems due to increasing CO2 emissions, NPPs could indeed represent a serious option by which to combat environmental issues such as climate change (Aras, 2013). Thirdly, supporters note that NPPs are a sustainable energy source. This is particularly true when compared with renewable energy, which is directly affected by meteorological conditions. Renewable sources are, as a nature of their design, dependent on meteorological conditions, such as the absence of sufficient sun, wind, and water sources, which affect their effectiveness (Coskun and Tanriover, 2016). It seems true that nuclear energy is a sustainable energy source in that it provides energy 7 days a week, 24 hours a day. Fourthly, NPPs are relatively cheap to run. They have low operation costs. Aras (2013) states that NPPs are particularly cost-competitive compared with fossil fuel for electricity generation, which means electricity could well become cheaper in Turkey thanks to NPPs. Fifthly, NPPs have long operational lifespans. While reactors were made to last only 40 years in the 1960s, as a result of the technological development in the nuclear industry over the time, the lifespans of NPPs have been reliably extended to 80 years (Ozcan et al., 2016).

NPPs are, however, not without controversy. Opponents note a number of their significant disadvantages. Firstly, Jewell and Ates (2015) raises the human resource challenge that Turkey does not have sufficient operators and regulators to properly oversee implementation and safe operation. Turkey lacks the human resources to effectively regulate nuclear safety and manage large-scale NPPs (Gunay and Iseri, 2017). Indeed, NPP projects require competent and well-trained human resources (Sirin, 2010) as they represent a highly sophisticated technology. Secondly, opponents claim that nuclear energy is a costly energy source. It requires large investment costs. NPPs are much more expensive than conventional electric generation technologies; it is not incidental that Turkey's previous NPPs have been cancelled due to economic reasons. Thirdly, NPPs have an associated potential risk of accident which pose threat to people and the environment (Ertor-akyazi et al., 2015). The world has witnessed 33 nuclear accidents and incidents to date (Akyuz, 2015). Security concerns have been raised in particular since the disastrous accident at Chernobyl in 1986, which still today poses risks to the environment and human health (Kok and Benli, 2017). It is known that NPPs are particularly vulnerable to natural events such as tsunami and earthquake; for instance, the Akkuyu site is near an active Mediterranean earthquake zone, which increases people's concern in this regard (Akcay, 2009). Fourthly, as Sirin (2010) states, the main issue in relation to NPPs is waste management. NPPs create toxic, long-lived radioactive waste but the nuclear industry still has no effective solution to the treatment and disposal of such waste. Nuclear waste can remain hazardous for hundreds of thousands of years. In other words, it poses an unacceptable risk to people and the environment. Additionally, disposal of waste in these plants is a costly process. Nuclear waste issues cost around £2.5 billion a year (Ozcan et al., 2016). Another criticism is that NPPs are considered the first step to developing nuclear bombs, which threaten worldwide peace. It is a fact that civil nuclear power plants can produce plutonium for military uses but Turkey has signed and approved the Non-Proliferation Treaty (Akcay, 2009).

MATERIALS AND METHODS

The empirical research involved a qualitative case study approach. This method is used extensively in various disciplines within the social sciences such as sociology, administrative science, political sciences and environmental studies (Gomm, 2009). The qualitative case study methodology provides tools for researchers to study complex phenomena within a real-life context, especially when the boundaries between the phenomenon and the context are not immediately evident (Eckstein, 2000). Three cases have been chosen for the collection of data. They include the Akkuyu, Sinop and Igneada regions, which are places where Turkey plans to build NPPs. There are, however, many ways to collect data for case study research which include interview, observation, surveys, questionnaires, and so on. Primary data has been collected through individual interviews. This research has applied the semi-structured interview method to achieve its research objectives.

Interviews were chosen as the primary method of data collection because they allow the researcher to collect more detail than is possible through surveys or questionnaires (Pfefferbaum et al., 2013:311). As McNamara (1999) states, interviews are particularly useful in elucidating the 'story' behind a participant's experiences, opinions, thoughts, and feelings. The interview method is an ideal way of discovering the public's experiences of, and thoughts about, NPPs in the area in which they live. The sampling universe for interview included all people living in the Akkuyu, Sinop and Igneada regions where the NPPs will be built. There is no 'ideal' number by which to ensure reliable interview data in the literature, but 90 people participated in interviews which were undertaken between 2014-2017. The sampling size relied on the concept of 'saturation', or the point at which no new information or themes are observed in the data. The random sampling (RS) method was used to select participants in interviews as it is one of the most common and straightforward probability samples by which one can guarantee a representative sample in quantitative social science research in particular, and in scientific research generally (Marshall, 1996). Lastly, all data has been analysed through the thematic analysis method.

Figure 4. Characteristics of Participants in the Interview

Characteristics		**%**	Characteristics		**%**
Gender	Male	53	**Age**	18-25	15
	Female	47		25-35	20
				35-45	26
				45-55	15
				55-65	10
				65 and older	14
Employment Status	Full time	20	**Level of Education**	Postgraduate	10
	Part-time	10		Bachelor Degree	53
	Unemployed	08		High School	16
	House wives	20		Elementary and Secondary School	11
	Student	14			
	Retired	10			
	Student	12		Others	10
	Retired	06			

RESULTS AND DISCUSSION

The thematic analysis of the interview data gave rise to two main themes. Accounts of the corresponding five sub-themes, each of which is illustrated by direct quotes from the transcripts, are given below. A thematic map, consisting of the two main themes and five sub-themes, is presented in Figure 5.

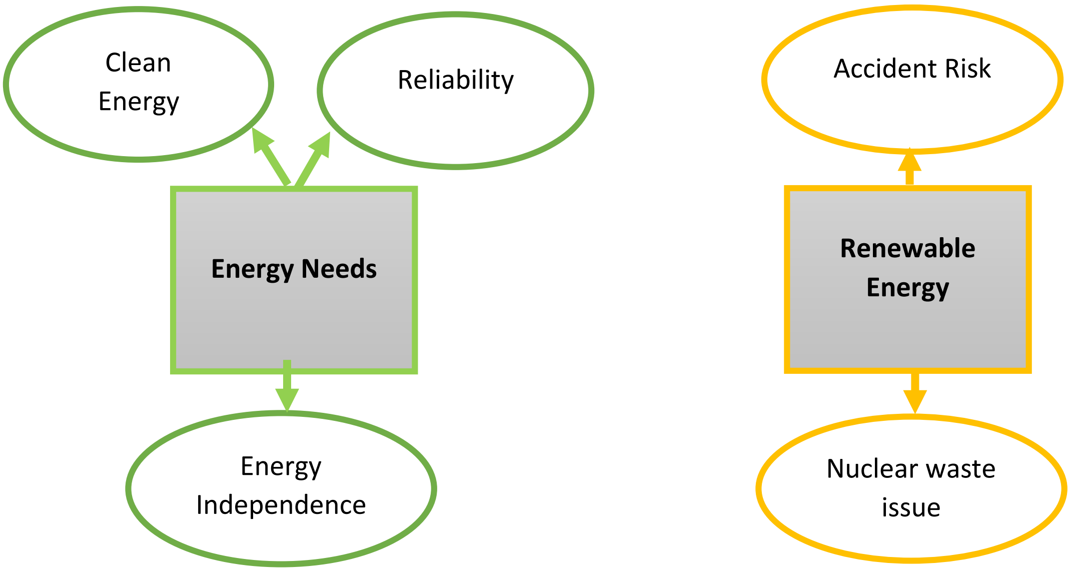
Energy Needs

Energy Independence *(N= 75 quotations assigned to this theme)*

It is well known that Turkey has a heavily dependence on fossil fuels imports. The country meets only about 30% of its total energy demand through its national resources. This is the main concern of the survey participants that consider NPPs to be a solution to Turkish energy dependency. They commonly raise the point that nuclear power plants will mitigate Turkey's energy dependence on oil and natural gas, which will also make a considerable contribution to the Turkish economy through reduced import costs. Accordingly, supporters connect NPPs to energy independence and an improved economy. One of the citizens living near the Akkuyu power station states:

"I pay a lot of money for oil and natural gases because we import them from Russia, Iran and Iraq. Turkey does not have oil and natural gases. In other words, we are dependent on these countries to meet our energy demand. If we build NPPs in our country we will import less oil and natural gases which will improve our economy. Then Turkey will be an independent country as it will meet its energy with its own resources."

Figure 5. Themes Map.



Clean Energy *(N= 64 quotations assigned to this theme)*

This refers to 'carbon-free' energy. Turkey mainly uses fossil fuels to meet its energy demands, which in turn causes serious environmental issues, such as air pollution, due to high emissions of carbon dioxide. It is also stated that the burning of fossil fuels causes climate change and global warming, which also affect Turkey. For this reason, NPPs are regarded as a solution to these environmental problems as they do not emit pollutants or greenhouse gases. Participants, therefore, categorise NPPs as a clean energy source. One stated:

"*I live in Igneada during summer but go to Istanbul to visit my parents in the winter. I know that people use coal and oil a lot and this leads to air pollution in the city. Fossil fuels are very dangerous to our environment and health. I believe that NPPs will mitigate this issue as they do not produce* carbon dioxide"

***Reliability** (N= 45 quotations assigned to this theme)*

Most participants compared nuclear energy to renewable energy. Many use solar power in their homes, and their concern is that solar power would not work effectively during winter. In other words, they are concerned that renewable energy is not reliable as it is dependent on the weather. In contrast, they claim that NPPs can work consistently, even in the winter, and for this reason, participants mainly define NPPs as being reliable energy sources compared with solar or wind power. One participant living in Igneada stated that:

"Turkey has four seasons in a year. In the winter and spring, solar power does not meet our energy needs. We need an alternative energy source to meet our energy demand in the town, which cannot be a renewable energy source. In contrast to solar and wind power, the weather conditions do not affect nuclear energy. We can have energy from NPPs at any time and season."

Renewable Energy

***Accident Risk** (N= 82 quotations assigned to this theme)*

Chernobyl is the most well-known nuclear accident, which 90% of participants mentioned when we asked about the disadvantage of NPPs. Particularly, those who live near the Akkuyu NPP are worried about a potential nuclear accident due to the Akkuyu being an earthquake region. It is known that nuclear accidents can cause serious human health problems such as cancer. Security is one of the main concerns citizens have about NPPs. One of participants living near Sinop stated that:

"I find nuclear power plants very risky because if an accident happens we can all die. We have been living in the Black Sea region for more than 50 years. Over the last decade, we have witnessed an increase of cancer rates due to the Chernobyl nuclear accident. We can have similar nuclear accident and I know that if it happens we will die. We should find alternative energy sources to NPPs because of security reasons."

***Nuclear Waste** (N= 65 quotations assigned to this theme)*

Participants are greatly concerned about nuclear waste. They have no idea as to how nuclear waste will be safely disposed of, which is one of the main reasons why they are worried about NPPs. They think that nuclear waste will pose a serious risk to both the environment and their health. One participant from the Sinop region stated that:

"The Black Sea has an amazing green region with famous valleys, lakes and forests. Nuclear waste, however, will kill this beauty because of radioactive materials. Why do we contaminate nature with radioactive waste? We can take advantage of what nature gives us such as wind and solar to generate electricity."

CONCLUCIONS

This paper has presented an analysis that aimed to explore public perception of the pros and cons of NPPs in the Akkuyu, Sinop and Igneada regions, concluding that the people who live near potential NPPs raise three main advantages and two disadvantages. The former includes energy independence, a clean environment and continuous reliability; the latter include waste management and potential accident risk due to natural events. This perception clearly shows that citizens are well informed/educated as to the pros and cons of NPPs in Turkey which are also commonly discussed by scholars, NGOs, politicians and decision makers in a similar way.

What is not clear, however, is how people actually weigh the advantages and disadvantages of NPPs. In other words, it is important to understand the public's acceptance of NPPs. Social acceptance of nuclear energy can be measured using two criteria: risk perception (cons) and benefit perception (pros). How the risks and benefits of NPPs is perceived in the public mind answers the question of how acceptable NPPs are considered by society generally. However, the risk and benefit perception of individuals is directly associated with values. The judgement of NPPs is essentially a value judgement as influenced by social, political and economic factors, rather than an objective determination. The perception of the risks and benefits by people who have different values can vary significantly.

As citizens perceive the pros and cons of NPPs in different ways due to their different values, it is important that governments should establish appropriate mechanisms to include the public's concerns and priorities in any associated decision-making process. Participation in environmental decisions is recognised as an environmental human right by various sets of international legislation such as the Rio Declaration and the Aarhus Convention. Principle 10 of the Rio Declaration, for example, states that: "Environmental issues are best handled with the participation of all concerned citizens, at the relevant level."

Public participation in the decision-making process regarding nuclear management is the key to reducing a distorted public perception of risk regarding nuclear energy, and increasing public support. *As* Slovic et al. (2011) states, public participation in nuclear energy issues may make the decision process more democratic, improve the relevance and quality of technical analysis, and increase legitimacy through greater public acceptance of the resulting decisions. For these reasons, Turkey's nuclear energy policy, therefore, should guarantee the mechanisms that encourage public participation in any decision-making process in relation to NPPs.

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Removal of Dyes from Wastewater by Adsorption Using Modified Boron Enrichment Waste: Thermodynamic Criteria

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ABSTRACT

In this study, Methylene Blue (MB) and Malachite Green (MG) removal from synthetic wastewaters using modified boron enrichment waste by adsorption process were aimed. Boron enrichment waste was modified with acid and ultrasound together. The boron enrichment process waste could be used as an effective adsorbent due to its constituents including ulexite, calcite, dolomite, zeolite and some clays. About 84% MB and 80% MG removal were obtained by modified boron enrichment waste (MBEW) at optimum equilibrium conditions (Contact time: 20-10 min., adsorbent dose: 625-375 mg/L, pH: 11-10, shaking speed: 200 rpm and temperature: 25^{0}C) respectively. Besides, the thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were also calculated. Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. Thermodynamic study demonstrates the spontaneous and endothermic nature of sorption process due to negative values of free energy change and positive value of enthalpy change, respectively. All the studied results showed that the modified enrichment waste could be used as effective adsorption material for the removal of methylene blue and malachite green from aqueous solutions.

Keywords: Dyes, boron ore, boron enrichment waste, adsorption, colour removal.

INTRODUCTION

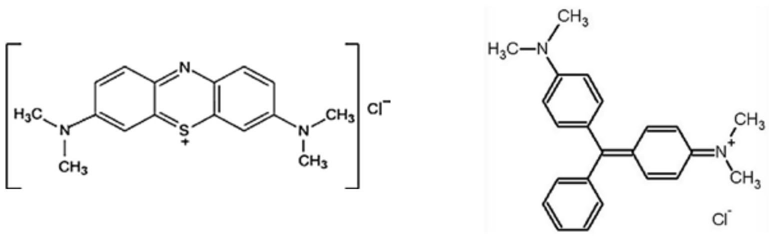
Many kinds of synthetic dyestuffs appear in the effluents of wastewater in A great number of industry such as dyestuff, pharmaceutics, food, coke, petroleum, pesticide, textiles, leather, paper, plastics, etc. Since a very small amount of dye in water is highly visible and can be toxic to creatures in water, the removal of color from process becomes environmentally important [1, 2]. Dyes may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life in them [2-4]. There are many different types of dyeing auxiliary. Such auxiliaries are extensively utilised in dyeing for all dye systems (eg disperse dyes/polyester, reactive dyes/cotton, acid dyes/wool, etc.) [5]. There are commonly used some paint types, for example, methylene blue (MB) and malachite green (MG) have wide applications which includes dyeing [6]. For the treatment of wastewater several investigations have been carried out to assess the potential of waste materials like fly ash, sawdust, bagasse ash and rice husk ash for their use as an effective alternative to activated carbon which is quite expensive. The properties of adsorbates and adsorbents are quite specific and depend upon their components. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater [7, 8]. Adsorption is between many methods (coagulation, flocculation, ion exchange, membrane separation, fenton, electrochemical oxidation etc.) is the most widely used In terms of efficiency, because of technical feasibility and easy [9, 10].

In this study, Modified Boron Enrichment Waste (MBEW or AUBEW) was used as adsorbent for removal of Methylene Blue (MB) and Malachite Green (MG) in synthetic color wastewater. The present study deals with the adsorption efficiency of modified leach waste for the removal of MB and MG from aqueous systems.

MATERIAL AND METHODS

Adsorption experiments and Adsorbates

Methylene blue (MB, Basic blue 9, C.I. 52015) is a basic dye, with the molecular formula $C_{16}H_{18}ClN_3S{\cdot}3H_2O$ (molecular weight 373.90 g mol^{-1}) with CAS No. 61-73-4, was chosen as adsorbate [11] and Malachite Green (MG) is a cationic dye, with the molecular formula $C_{23}H_{25}N_2Cl$ (molecular weight 364.911g mol^{-1}) with λ_{max} (nm) 618, was chosen as adsorbate [12]. The chemical structure of the dye is shown in Fig. 1. A stock solution of methylene blue and malachite green were prepared (1000 mg/L) by dissolving required amount of dyes in distilled water. The stock solution was diluted with distilled water to obtain desired concentration.



(a) (b)

Figure 1. Chemical structure of methylene blue (a) [11] and malachite green (b) [13]

Batch adsorption experiments were performed in 250 mL flasks with 100 mL of dye solutions containing adsorbents. The flasks were agitated on a shaker. Investigation the effect of different parameters on MB and MG adsorption was followed according to adsorbent dose, contact time, shaking speed and pH.

The dye concentrations in the solutions were determined at the beginning (C_0) and end (C_e) of the shaking period. The removal percentage (R (%)) of MG as well as the adsorbed quantity at the surface of waste materials (qe(mg/g)) were determined using Eqs. (1) and (2) respectively [6, 14].

$$\text{R, sorption (\%)} = \left[\frac{(Co - Ce)}{Co}\right] x\ 100 \qquad (1)$$

The equilibrium amount of dye adsorbed from aqueous solution was determined by the following equation:

$$qe = \left[\frac{(Co - Ce)}{W} \text{ x V}\right] \quad (2)$$

where q_e is the amount of dye adsorbed at time t (mg $g^{-1}_{adsorbent}$); W is the adsorbent mass (g); C_0 and C_e are the initial and equilibrium solution concentrations of dye in aqueous solution (mg L^{-1}), respectively, and V is the volume of the solution (L)[1, 14].

Characterization Of Enrichment Waste

Modified Boron Enrichment Waste (MBEW or AUBEW) was used as adsorbents for dye removal from water in this study. MBEW formed during boron enrichment process was supplied from Etibor Colemanite and Ulexite Production Plant (Eti Mine Works General Directorate Bigadiç Boron Works Management Offices¸ Balıkesir, Turkey). Acid-ultrasound modified boron enrichment waste (MBEW) was treated with HCl and ultrasound for to increase the activated surface of adsorbent. The sono-modified process was performed by indirect sonication in an ultrasonic water bath, which was operated at a fixed 35-kHz frequency approximately 60 minutes.

The research was conducted with pH meter (Hach Multi-HQ40d Instruments) and a thermal stirrer (ZHWY-200B, Zhicheng Analytical Co., Ltd) was used for the batch adsorption experiments. The color solutions were filtered through 0.45-µm membrane filters (Millipore Corp., Bedford, Mass.) after settling. The exact concentration of basic dye was determined using a UV–Vis spectrometer (Hach Lange DR 2800) at a wavelength of maximum.

Optimizations and thermodynamics of adsorption

Methylene blue and malachite green removal efficiency from synthetic wastewater containing 100 mg/L and 50 mg/L stock dye solution, respectively, using MBEW as adsorbent was investigated. The results of experimental studies for to determine the optimum adsorption conditions at different initial contact time, adsorbent dose, pH, shaking speed and temperature were given in Fig.2 and 3.

Adsorption studies have focused on the adsorption thermodynamics to describe the adsorbent's adsorbate dependence. Thethermodynamic parameters reflect the feasibility and spontaneousnature of the process. These parameters include Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) and were calculated using Eqs. (3) and (4), as previously reported.

$$Ln\, K_D = \Delta S/R - \Delta H/(R * T) \quad (3)$$

$$\Delta G = \Delta H - \Delta S \text{ *T)} \quad (4)$$

where $K_D = {q_e}/{C_e}$ is the MB/MG concentration at equilibrium adsorbed at the surface of waste materials (mg/L), R is the universal constant of gas (8.314 J/mol K), and C_e is the MB/MG concentration at equilibrium (mg/L) [14-16].

RESULTS AND DISCUSSION

Optimizationof adsorption

Dyes removal was studied using MBEW as adsorbents from synthetic wastewaters at initial adsorbent dose between 125-2000 mg/L, temperature 25^0 C, original pH value 5-6.5 range for MB and pH value 9 for MG, shaking speed 200 rpm and contact time 0-150 minutes at two dyes.

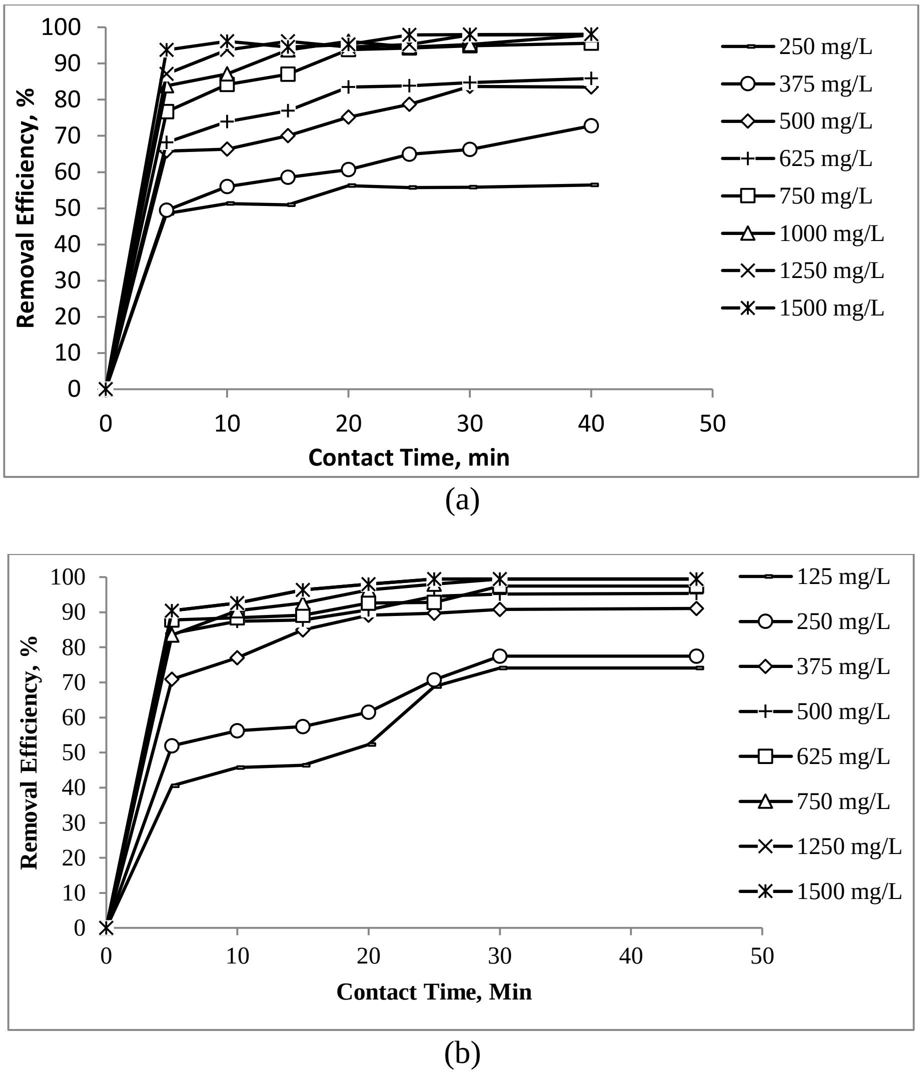


Figure 2. Effects of contact time on color removal efficiency with MBEW a) Methylene blue b) Malachite green (Initial Conditions = pH:5-6, 9 Temperature: 298 Kelvin, Dye Concentration: 100 and 50 mg/L, shaking speed: 200 rpm).

The dye removal percent increased with the increase in dose of adsorbents. The optimum removal efficiencies were obtained at adsorbent dosages 83%, and 77% for methylene blue and malachite green, respectively. The optimum adsorption dosage was 625 mg/L and 375 mg/L for MB and MG, respectively

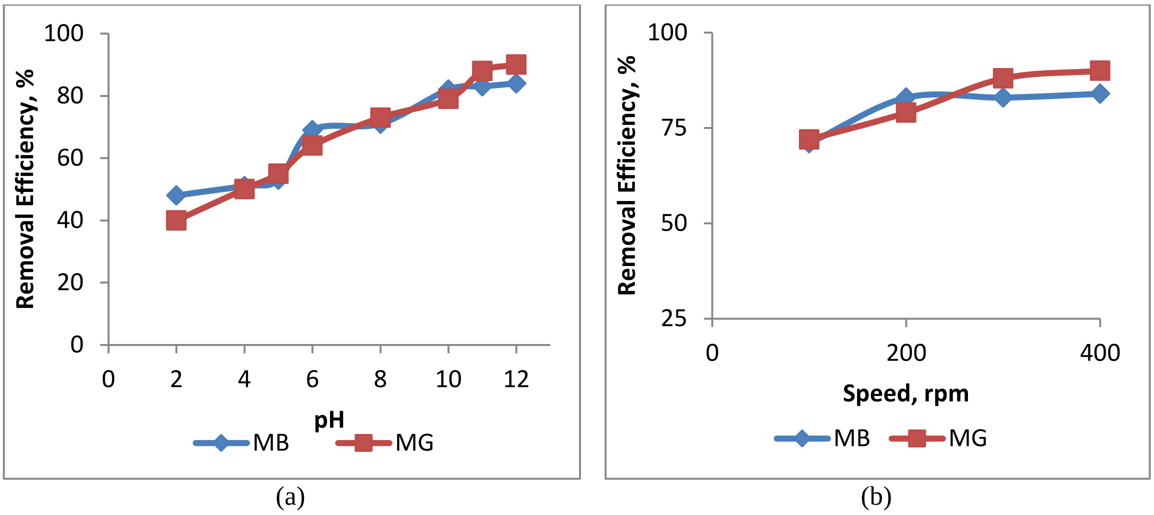


Figure 3. Effects of pH and stirrer speed on color removal efficiency with MBEW a) pH b) Speed (Initial Conditions = Temperature: 298 Kelvin, Dye Concentration: 100 and 50 mg/L, contact time: 20 (MB) and 10 (MG) minutes, dosage: 625 (MB) and 375 (MG) mg/L).

Thermodynamics of adsorption

For to determine the adsorption thermodynamic; ln K_c and 1/T relations of equilibrium data at different temperature (25 ^{0}C, 35 ^{0}C and 45 ^{0}C) were investigated. The results of the experiments were given in Fig.4 and Table 2.

The thermodynamic parameters of the adsorption system are Gibb's energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°), and the equilibrium constant (K). The adsorption process can occur spontaneously at the normal and high temperatures, because of $\Delta H^{\circ} > 0$ and $\Delta S^{\circ} > 0$.

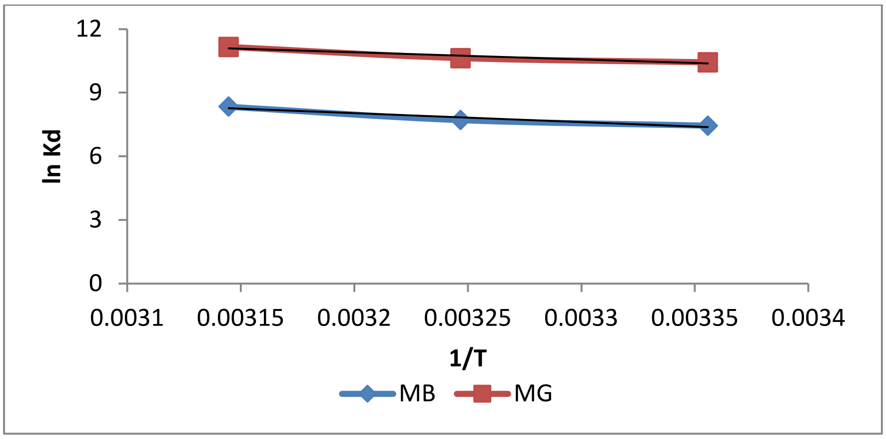


Figure 4. Thermodynamic parameters for the adsorption of dyes onto MBEW for MB and MG

Table 2. Thermodynamic parameters for the adsorption of MB and MG onto MBEW.

Dyes	Adsorbent	T (K)	lnb	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
Methylene Blue	MBEW	298	1,536	-18,271	35,217	0,179
		308	1,571	-20,065		
		318	1,650	-21,860		
Malachite Green	MBEW	298	1,363	-25,704	28,187	0,180
		308	1,382	-27,512		
		318	1,430	-29,321		

Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. The results indicated that the boron enrichment process waste could be a promising adsorbent for removal of MB from aqueous solution. Thermodynamic study demonstrates the spontaneous and endothermic nature of sorption process due to negative values of free energy change and positive value of enthalpy change, respectively.

CONCLUSION

In this study, different adsorbents show promising adsorption capacity for methylene blue removal and malachite green. The ability of modified of boron enrichment waste as an adsorbent to remove MB and MG from aqueous solutions was investigated. The operating criterions for the maximum color removal were dye solution concentration (0.1 and 0.05g/L), MBEW sorbent dosage (0.125 g/200 mL and 0.075 g/200 mL), contact time (20 min and 10 min) for MB and MG respectively, speed (200 rpm) and temperature (298 K). Removal of methylene blue and malachite green dyes are pH dependent and the maximum removal was attained at pH 11 and 10, respectively. Thermodynamic (negative ΔG values) study indicates that the adsorption of dye is feasible, and spontaneous in nature. It was found that MBEW developed can effectively remove dyes, in their competition also behaves as a good adsorbent. It is believed that the results of this study will contribute to use of boron enrichment waste released from boron mineral processing plant in different disciplines.

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Adsorption of Azo Dyes from Textile Wastewater by *Spirulina Platensis*

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ABSTRACT

Due to the mushrooming of industrial activities nowadays, the released contaminants have posed risks to the stability of ecological system. In particular, the mixture consisting of colourants used in the textile industry and water resources is detrimental to human health. In order to circumvent this problem, strategies such as precipitation, membrane filtering, adsorption and electrochemical procedures have been applied. It is commonly known that adsorption is economical, eco-friendly and easy to operate. In this study, microalg, which is a kind of cyanobacteria (i.e. *Spirulina plantensis*), was used to eliminate azo-dyes from the aqueous solution via adsorption. Microalg was tested at various conditions (i.e. pH, dye concentration, temperature, biomass amount and contact time). The removal percentages of Acid Black 210 and Acid Blue 7 dyes by using microalg biomass at pH=2 were 95.35 % and 92.56 %, respectively. Meanwhile, conditions such as 100 mg/L dye concentration and 0.5 g/L biomass would lead to removal percentages of 98.55 % and 97.05 % for Acid Black 210 (60 minutes contact time) and Acid Blue 7 (75 minutes contact time), respectively. The spectrofotometric measurements show that adsorption method has a great potential for removing colourants in aqueous solutions. It could serve as an alternative method for.

Keywords: *Spirulina platensis*, waste water, azo-dyes, textile industry, adsorption

INTRODUCTION

Nowadays, many synthetic dyes have been extensively applied in many industries such as textiles, rubber, paper, plastics, leather, food, pharmaceuticals, petrochemicals, dyestuffs and cosmetics. The release of significant amounts of synthetic dyes to the environment has been causing many serious environmental and health problems. It has been reported that more than 100,000 types of dyes and pigments (total mass 7x105 tons) are produced annually (Crini, 2006).

Synthetic dyes can be categorized as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes) (Mohan & Karthikeyan, 2004). Reactive dyes are highly water-soluble polyaromatic molecules. The reactive dyes are commonly used in textile dyeing processes. Meanwhile, about 20% - 40 % of these dyes remain in the effluents because the dye molecule might react with hydroxyl ions in the solution (Axelsson *et al.*, 2006). These dyes are hardly removed under aerobic conditions. Consequently, they might be decomposed into carcinogenic aromatic amines under anaerobic conditions (Kaner *et al*., 2010). Obviously, the release of these dyes into the ecological system is highly undesirable. The three common groups of reactive dyes are azo, anthraquinone and phthalocyanine dyes (Greluk & Hubicki, 2013). Among these dyes, azo dyes are organic compounds prepared by coupling a diazonium compound with a phenol or an aromatic amine (Kamboh *et al*., 2011). Azo dyes is the largest and most versatile class of dyes; therefore, they are widely used in industries (Chen *et al*., 2009). In general, during the dyeing processes, approximately 30 % -70 % of azo dyes used are hydrolyzed and mixed with the wastewater (Ambrosio & Campos-Takaki, 2004), which is detrimental to public health (Heiss *et al*., 1992). Hence, effective removal of azo dyes from wastewater is crucial (Liu *et al*., 2013).

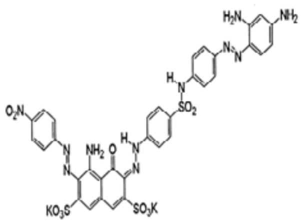
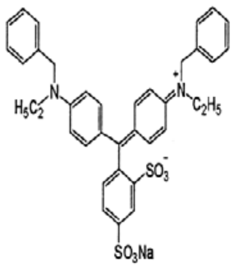
Usually, dye wastewater is treated by flocculation combined with treatment methods such as flotation, electroflocculation, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion-exchange, irradiation, precipitation, ozonation, and katox. This combined technique employs activated carbon and air mixtures, which is generally expensive and ineffective in dye removal (Gupta & Suhas, 2009). A more economical and eco-friendly technique such as adsorption has been proposed (Aksu & Tezer, 2005)by using non-growing or dead microbial mass. It involves a number of metabolism-independent processes (e.g. physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation, and microprecipitation) that occur essentially in the cell wall (Aksu, 2005). Many biosorbents such as fungi, bacteria, chitosan, algae and peat have been used to remove pollutants from aqueous solutions (Aksu, 2005). It is worth to mention here that biosorbents such as Chlorella vulgaris (Aksu & Tezer, 2005), Ulothrix sp. (Dogar *et al*., 2010)and Scolymus hispanicus(Barka *et al*., 2011) have been successfully employed to remove dyes from aqueous solutions. On the other hand, the *Spirulina platensi*s biomass has been commonly used to remove metals such as cadmium, cooper, lead and nickel(Fang *et al*., 2011). Its application in dye removal, however, is very limited. *Spirulina platensis*, which is a member of blue-green algae, is an alternative source of protein, polysaccharide, lipid and vitamin for human(Costa *et al*., 2004). Also, it contains functional groups such as carboxyl, hydroxyl, sulfate, phosphate and other charged groups (Fang *et al*., 2011)which are usuful for dye-binding. This microalgae is abundant and relatively cheap for adsorption process (Celekli *et al*., 2010). In this study, the removal of dyes found in the textile industries will be performed by using *Spirulina platensis*.

MATERIAL AND METHODS

Dyes

Anionic textile dyes, i.e., C.I. Acid Black 210, C.I. Acid Blue 7 were generously supplied by Burboya Bursa for Dyes Manufacturing and Trading Company. The chemical structures of the dyes are shown in Table 1. The stock solutions of the dyes were prepared using distilled water with a concentration of 10,000 mg/L (1 g / 100 mL). The maximum a bsorbans (λmax) of the individual dyes was determined by UV-Visible spectrophotometer. The cyanobacteria (*Spirulina. platensis*) was obtained from Istanbul Spice and Food Industry and Trade Company in the form of powder.

Table 1. The chemical properties of Acid Black 210 and Acid Blue 7 dayes .

C. I. name	Acid Black 210	**C. I. name**	Acid Black 7
Ionization	Acid	**Ionization**	Acid
λmax (nm)	500	**λmax (nm)**	600
Molecular weight	938.02 g/mol	**Molecular weight**	690.81 g/mol
CAS Number	99576-15-5	**CAS Number**	3486-30-4
C. I. number	30027	**C. I. number**	42045
chemical formula	$C_{34}H_{25}K_2N_{11}O_{11}S_3$	**chemical formula**	C37H35N2NaO6S2
Chemical Structure		**Chemical Structure**	

Batch Adsorption Studies

Experiments were conducted with 250 mL Erlenmeyer flasks containing 100 mL of aqueous solution mixed with dyes. Flasks were agitated on a rotary shaker operating at 100 rpm and 25 ºC. The influences of physicochemical variables such as pH (2, 4, 6, 8 and 9, adjusted by the addition of 1 M HCl or 1 M NaOH solutions), initial dye concentration (25, 50, 75, 100 and 125 mg/L) and biomass dosage (0.5, 0.7, 1, 1.4 and 2 g/L) on adsorption were examined after the equilibrium was reached. Finally, specimens were centrifuged for 15 min at a speed of 10000 rpm in order to estimate the dye concentration. The concentrations of the two dyes in the aqueous solution were measured from UV−vis spectra (UV-1201 V, Shimadzu) in order to calculate the maximum absorption. The maximum absorption values of AB 210 and AB 7 dyes are listed in Table 1.

The dye removal can be calculated using Eq.1:

$$\% \text{ Removal} = \frac{(Co-Cf)}{Co} \times 100 \qquad (1)$$

Co: the initial concentration (mg/L) of dyes in solution

Cf: the equilibrium concentration (mg/L) of dyes in solution

RESULTS AND DISCUSSION

Considering the environmental and health risks caused by pollutants in wastewater, a proper treatment method must be devised. Recent studies show that techniques combining microorganisms such as bacteria, fungi and algae with some physical and chemical techniques are efficient in dye adsorption (Vandevivere *et al*., 1998). In this study, *S. platensis* was used as biosorbent. The effects of pH, temperature, dye concentration and contact time on the adsorptions of Acid Black 210 and Acid Blue 7 textile dyes were examined.

Effect of Solution pH

The effect of pH on the adsorption capacity of dyes were studied by preparing samples of dye solution in 100 mL flasks with different pH values of 2, 4, 6, 8 and 9 while keeping other variables constants. The obtained results illustrated in Fig. 1, shows that as pH value increases, the percentage of adsorption activity decreases. The highest dye adsorption for AB 210 and AB 7 was recorded as 95.55 % and 92.56 %, respectively, at pH 2.0. And the lowest dye adsorption activity was observed as 5.07 % and 0 %, respectively, at pH 9. As a result, the optimal pH value for adsorption of dye solutions of AB 210 and AB 7 was found at 2. Under acidic conditions, the surface of *S. platensis* is positively charged as well as the dyes detach in the anionic form (D-SO_3^-). Therefore, electrostatic interactions amid the dyes sulfonated groups and *S. platensis* surface (positively charged) happened (Dotto *et al*., 2012). The number of sites that are positively charged decreases while the number of sites that are negatively charged increases. This happens when the pH of the system increase. The adsorption of dye anions is not supported or liked by the surface site that is negatively charged. This is due to electrostatic repulsion power. In the same vein, the lower adsorption of acid dyes at alkaline pH takes place owing to the extra hydroxyl ions(Namasivayam & Kavitha, 2002).

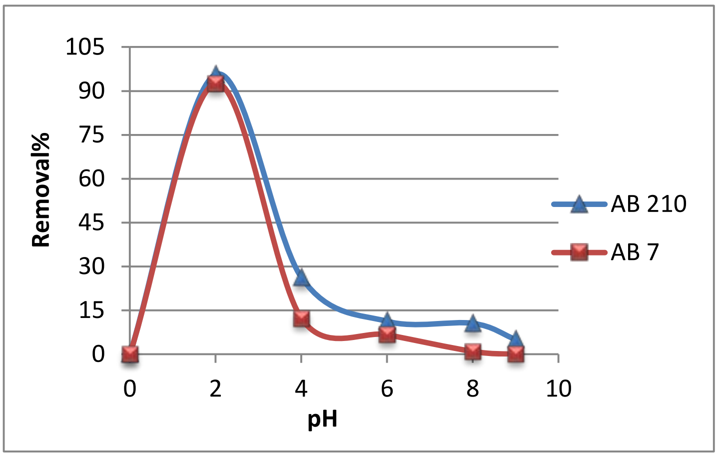


Figure 1. Effect of pH on acidic dyes removal efficiency of *S. platensis* biomass (dye consentration: 100 mg/L; Biomass level: 0,5 g/L; Contact time: 30 min; T = 25 °C)

Effect of Biosorbent Dosage

Biosorbent mass ranging from 0.5 to 2.0 g/L was considered. Here, the pH is 2, the concentrtaions of AB 210 and AB 7 solutions are 100 mg/L, the contact time is 30 min and the operating temperature is 25 °C. The results are shown in Fig. 2. As seen, the adsorption efficiencies of AB 210 and AB 7 dyes decrease from 97.56 % and 88.53 % to 0 %, respectively, as the biosorbent dosage increases from 0.5 to 2 g/L. The decrease in adsorption efficiency at higher biosorbent dosage can be attributed to the adsorption sites that remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption is increased by increasing the biosorbent dosage (Ratnamala *et al*., 2012). Also, aggregation may occur which would reduce the total biosorbent surface area. This would reduce the amount of dye biosorbed per unit of weight of biomass (Crini & Badot, 2008). Due to the fact that the greatest adsorption capacity observed was 0.5 g/L, this biosorbent dosage was used in subsequent studies.

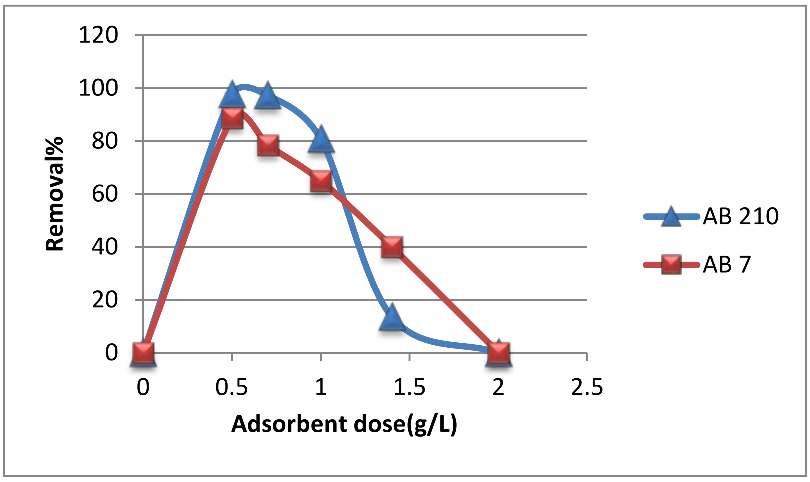


Figure 2. Effect of adsorbent dose on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Contact time: 30 min; T = 25 °C)

Effect of İnitial Dye Concentration

The influence of dye concentration on the adsorption capacity was studied by experiments carried out with different concentrations of AB 210 and AB 7 from 25 to 200 mg/L. As shown in Fig. 3, the adsorption capacity was increased from % 94,37 to % 97.7 and from % 87,5 to % 91,6 respectively, by increasing the initial dye concentration from 25 to 125 mg/L. This took place due to the concentration gradient, which is the driving force(Crini & Badot, 2008). In addition, the contact of dye and biosorbent can go up in high concentrations of dye(Chen *et al*., 2008).

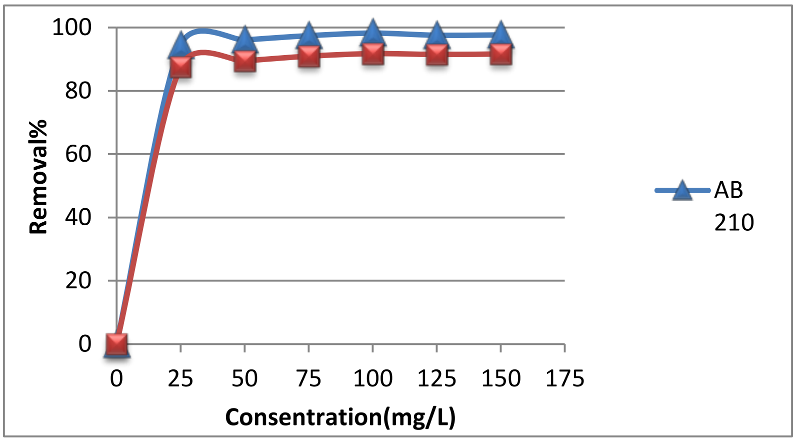


Figure 3. Effect of initial dye consentration on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; Biomass level: 0,5 g/L; Contact time: 30 min; T = 25 °C)

Effect of Contact Time

In this experiment, the contact time was varied from 15 to 135 minutes. An adsorption rate is typically high within the first 30 minutes and reaches a plateau thereafter. Fig. 3, shows that the dye removal is rapid within the first 15 minutes and it reaches equilibrium after 60 minutes. In a physical adsorption process, most adsorbates are usually adsorbed within a short contact time(Mall *et al*., 2006). At the beginning of adsorption, the dye molecules are adsorbed externally in a rapid manner. When the external surface becomes saturated, the dye molecules are then absorbed into the pores of biomass (Colak *et al*., 2009).

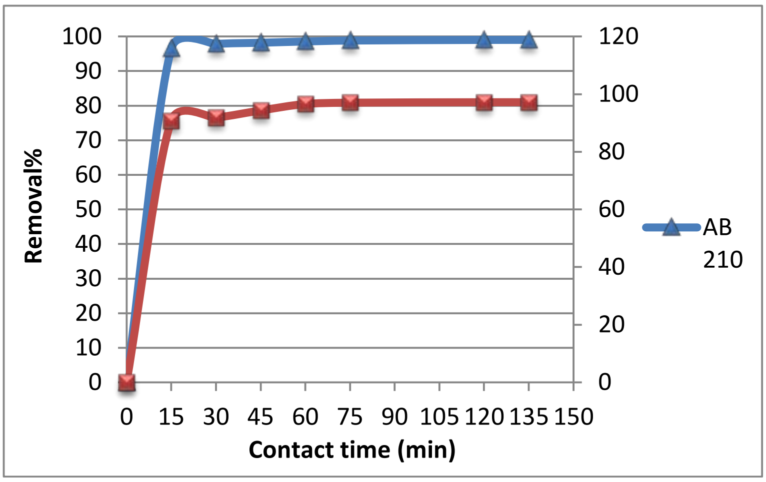


Figure 4. Effect contact time on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Biomass level : 0,5 g/L; T = 25 °C)

Effect of Temperature

Here, the operating temperatures were fixed at 30°C, 45°C and 60°C. Meanwhile, the experiments were performed at optimum conditions determined earlier. Fig. 5, shows the effect of temperature on the removals of AB 210 and AB 7. From Fig. 5, as the temperature increases from 30°C to 60°C, the removal efficiencies of AB 210 and AB 7 increase from 97.62% to 98.17% and from 92.61% to 95.01%, respectively. This favourable effect may be due to the increasing mobility of adsorbate molecules and the existence of pores on the surface of adsorbent particles. Similar observations have been reported by(Hussain *et al*., 2009)and the researchers argued that the increase in temperature could enhance the rate of diffusion of the adsorbate molecules.

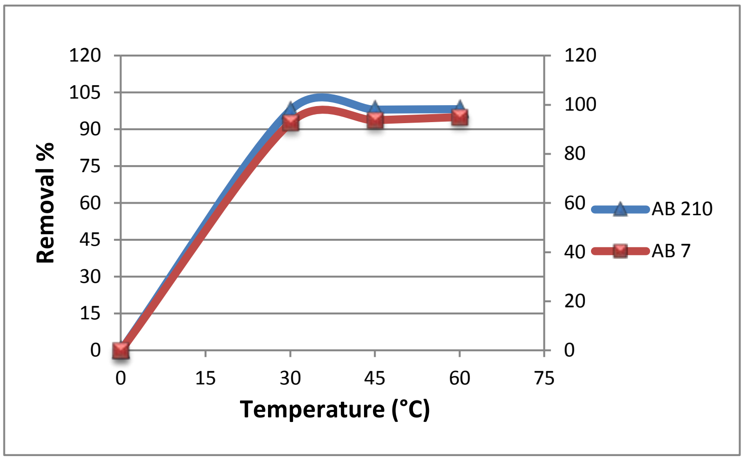


Figure 5. Effect temperatures on acidic dyes removal efficiency of *S. platensis* biomass (pH: 2; dye consentration: 100 mg/L; Biomass level: 0,5 g/L; Contact time: 30 min)

CONCLUSIONS

In this study, the dead *S. platensis* biomass has been used as biosorbent to remove AB 210 and AB7 dyes from aqueous solutions. The effectiveness of the adsorption process has been found to be dependent on conditions such as temperature, contact time, adsorbent dose, solution pH and initial dye concentration. The optimum adsorption conditions have been determined, i.e. pH of 2.0, temperature of 60°C, initial dye concentration of 125 mg/L and biosorbent concentration of 0.5 g/L. *S. platensis* is a suitable adsorbent used for anionic dye removal, as it is abundant and cheap. This study has formulated an effective plan for waste water treatment. However, further work should be performed in order to have a better understanding of dried *S. Platensis* biomass in terms of its binding mechanism. It is concluded that this adsorbent has a great potential for removing dyes from aqueous solutions as it is eco-friendly.

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Improvement of water quality in over-polluted Niğde Creek in Turkey

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ABSTRACT

Kızılca creek, which is one of the main sources of irrigation water in Niğde (Turkey), was extensively polluted due to high amount of organic matters in the point and non-point pollutant sources. This study aims to remove organic matters and improve water quality of the creek by using a pilot-scale hybrid natural wastewater treatment (NWT) system. The system consists of a combination of settling basin, free water surface constructed wetland, and overland flow (OF) system. The system was installed near the edge of the creek in 2014.
Wastewater samples from the inlet and outlet of all stages of the system were collected and analyzed for temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), and the suspended solid (SS) parameters. The obtained results indicated that the high organic matter loads caused the deterioration of the water quality in the creek. The system could remove up to 80%. The results showed water quality of the creek and the treatment performance of the system were affected by temperature, the DO, and seasonal changes. Consequently, the NWT system can be usefully used useful to decrease solid matters in highly polluted streams and thus improve water quality.

Keywords: Constructed wetland system, land treatment, natural wastewater treatment, overland flow system.

INTRODUCTION

Streams or creeks that discharge surface water resources passing through the city's center are polluted and made unusable for useful water use purposes due to agricultural activities, hydrological changes, habitat changes, floods, storm water channels, urban point pollution sources, and biological oxidizable matters that come from other unknown pollution sources (USEPA, 2002). Natural wastewater treatment (NWT) systems such as constructed wetland (CW) and overland flow (OF) have been used successfully as an alternative in the purification of polluted creeks or streams and treatment of wastewater containing different types of pollutants in many case studies worldwide (Reed et al., 1995; Crites et al., 2006; Kadlec & Wallace, 2009; Kim et al., 2014; Li et al., 2014; Morató et al., 2014).

For the prevention of the creek pollutions like these in Turkey, as the creeks were converted into reinforced concrete channels in terms of the work, done in most cases for rehabilitation, ecological structure and biodiversity have been destroyed and the dimensions of the pollution have been increased over time (Tuncsiper, 2017a). High amounts of suspended solid (SS) matter contained in the creek was made the lake eutrophic, by negatively affecting the trophic level of the lake (Tuncsiper, 2016). The high amount of organic matter contained in the over-polluted waters of the creek made the creek anaerobic over time, and thus toxic gasses released by the anaerobic microbial degradation of the SS matters in the stream which becomes anaerobic posed a risk to the environment and human health (Kadlec & Wallace, 2009).

Therefore, in this study, it was aimed to reduce the SS matters in the creek with natural wastewater treatment (NWT) system to be constructed at the edge of the creek and thus improve the water quality of the creek and lake. Pilot-scale NWT system was constructed near the creek in September 2014. In general, the system consisted of a combination of sedimentation basin (SB)-free water surface constructed wetland (FWS-CW)-overland flow (OF) systems was fed with the over-polluted water of the creek (Tuncsiper, 2017b).

In study, with aim to determine the existing organic pollution in the creek/lake and the organic matter or TSS removal efficiency of the pilot system, flowrate-water temperature-pH-dissolved oxygen (DO)-TSS parameters on the sampling points in between the city exit and the lake and the inlet/outlet of the lake and the pilot system are measured monthly.

MATERIALS AND METHODS

Study site and selection of sampling points

Important point sources (see features denoted 1, 2, 3 and 4 on Fig. 1) threatening lake are water discharged from Organized Industrial Zone Wastewater Treatment Facility (OIZWTF), Nigde University Wastewater Treatment Facility (NUWTF), Nigde Municipality Wastewater Treatment Facility (NMWTF), and Kızılca creek. The Kızılca creek is one of the most important feeding (with an average flow rate of 0.43 m^3 s^{-1}) and polluting sources of the lake (Nigde, Turkey). The creek is about 27 km long within the borders of Nigde city, and it flows into the lake. Effluents of the OIWTF and NUWTF are discharged to the lake from the campus area of the Nigde University.

The creek waters are bypassed to the NMWTF on the Channel Street at the out of the city and then the creek waters are discharged to the creek again after being treated together with the domestic wastewater. Therefore, the flowrate of the creek is an average of approximately 0.05 m^3 s^{-1} before the NMWTF entrance and 0.43 m^3 s^{-1} after the NMWTF.

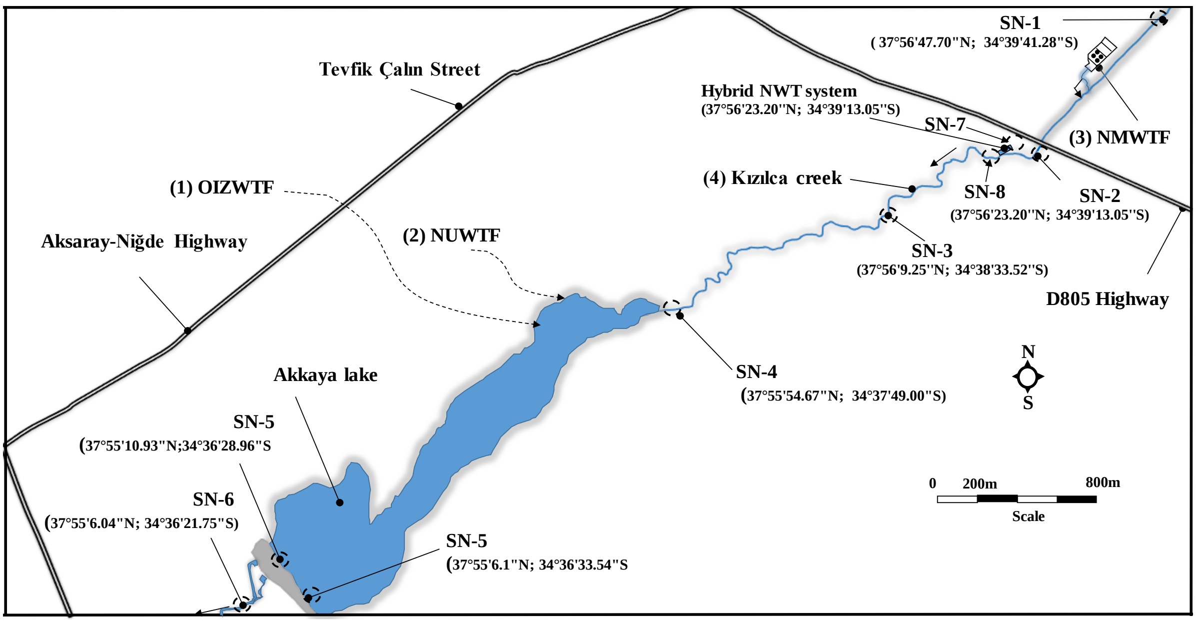

Figure 1. View of layout plan of the study area and sampling points.

Sampling points were selected in accordance with the item C of the article 10th article of the sampling and analysis methods notice in Water Pollution Control Regulations (TWPCR, 2009) and the coordinates of these points were determined by GPS and processed on the map. The samples were taken from 4 different points (SN-1, SN-2, SN-3, and SN-4) before the entrance of the creek into the lake, 2 different points (SN-5) in the lake, the out (SN-6) of the lake, and the inlet (SN-7) and outlet (SN-8) of the NWT system. Samples taken from about 30-40 cm below of water's surface of the creek and lake were homogenized by mixing and analyzed monthly for about 1 year between October 2014 and September 2015.

Configuration of pilot-scale NWT

To reduce organic matter load in Nigde creek, pilot-scale NWT system in a manner that will represent the natural structure of a certain part of the creek was constructed at the edge of the creek in 2014 and operated for about 7 months. The pilot system was combined with the SB, the FWS-CW with filter material, and the OF system. The system generally consists of four stages. The first stage comprises a feeding basin (FB), the second one comprises the SB system, the third one comprises the FWS-CW system, and the fourth one comprises OF system, respectively. The simplified flow diagram of the NWT system is shown in Fig. 2.

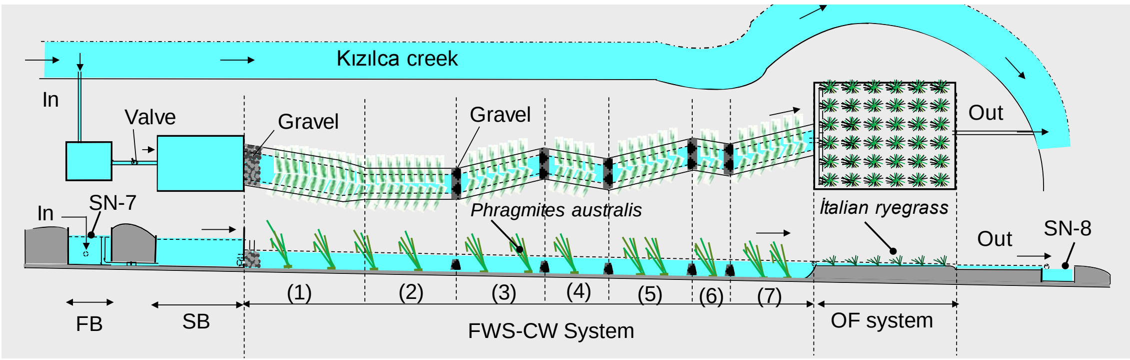

Figure 2. Schematic diagram of the hybrid NWT (SN-7 and SN-8 are sampling locations) system.

The FWS-CW system was designed S-shaped in a manner to represent the convoluted structure of the creek. It was divided into 7 regions based on its twist points. In order to further improve removal efficiency of organic matters, in April 2015, twist places of the system were equipped with filtration layer that serves as a biofilter. The system was planted with the young shoots of *Phragmites communis* (macrophytes) growing in the creek edge. The OF system, which was consisted of washed sand in a depth of about 5 cm, was designed to be able to provide an extra organic matter removal in outflows of the FWS-CW system. It was planted with *İtalian ryegrass*.

Physicochemical analysis of samples

Water temperature, electrical conductivity (EC), dissolved oxygen (DO), and pH were measured at each sampling point by using in-situ multiple water quality gauge (WTW inolab-IDS multi 9430). Total suspended solids (TSS) was analyzed using gravimetric method (SM-2540-B) according to standard methods (Standard Methods for the Examination of Water and Wastewater, 1998).

RESULTS AND DISCUSSION

Variations in the TSS concentrations of the creek and lake water

The average annual values of the flow, the EC, the DO, and the TSS parameters in the creek and lake was in Table 1. As shown in Table 1, because the effluents of the NMWTF were discharged to the creek at the SN-2, its flow-rate at the SN-1 increased from 0.25 m^3 s^{-1} to 0.83 m^3 s^{-1}. In addition, the flow-rate of the SN-6 was higher than other sampling points, because it was taken just ahead (about 200 m) of the point where the lake was discharged to the creek. While the pH and water temperatures did not change much, the EC-the DO-the TSS values showed significant differences over the length of the creek.

Table 1. The average annual values of the flow, the EC, the DO, and the TSS parameters in the creek and lake.

	Sampling Pints	Parameters			
		Flow-rate (m^3 s^{-1})	EC (μS cm^{-1})	DO (mg L^{-1})	TSS (mg L^{-1})
The creek	SN-1	0.25	784±89	2,28±0,69	10±4.3
	SN-2	0.83	1102±55	0,33±0,15	422±248
	SN-3	0.80	1190±80	0,23±0,10	473±269
	SN-4	0.79	909±88	0,91±0,16	348±213
	SN-6	1.17	803±85	1,16±0,17	5±1.2
The lake	SN-5		666±99	4,55±1,12	246±95

± implies standard deviation values.

The pH values, which ranged from 7.0 to 8.1, was very close to neutral at all sampling points. The DO was found at the highest value (2.28 mg L^{-1}) in the first sampling point (the SN-1) where that the creek was least polluted. The values of the DO in the SN-2 sampling point where the outlet waters of the NMWTF are discharged and in the SN-3 sampling point where which the agricultural activities are carried out decreased considerably. The DO values of the SN-1 and 3 were found to be very low because there were agricultural activities at the SN-2 and the effluents of the NMWTF was discharged to the creek in the SN-2. These results indicated that the creek was over-polluted in terms of the TSS at the SN-2 and 3 sampling point, and thus wastewater of the NMWTF and agricultural activities was an important factor in the pollution of the creek.

The pH values, which ranged from 7.0 to 8.1, was very close to neutral at all sampling points. The DO was found at the highest value (2.28 mg L^{-1}) in the first sampling point (the SN-1) where that the creek was least polluted. The values of DO in the SN-2 sampling point where the outlet waters of the NMWTF are discharged and the SN-3 sampling point in which the agricultural activities are located have decreased considerably. The DO values of the SN-1 and 3 were found to be very low because there were agricultural activities at the SN-2 and the effluents of the NMWTF was discharged to the creek in the SN-2. These results indicated that the creek was over-polluted in terms of the TSS at the SN-2 and 3 sampling point, and thus wastewater of the NMWTF and agricultural activities was an important factor in the pollution of the creek.

The annual average DO in the lake was 4.6 mg L^{-1} and the lake water was at the second and third class water quality level in terms of the DO (TWPCR, 2004). Because this value is below the limit value (<5 mg L^{-1}) for eutrophication control (TWPCR, 2004), the use for various purposes the lake water seems to be risky

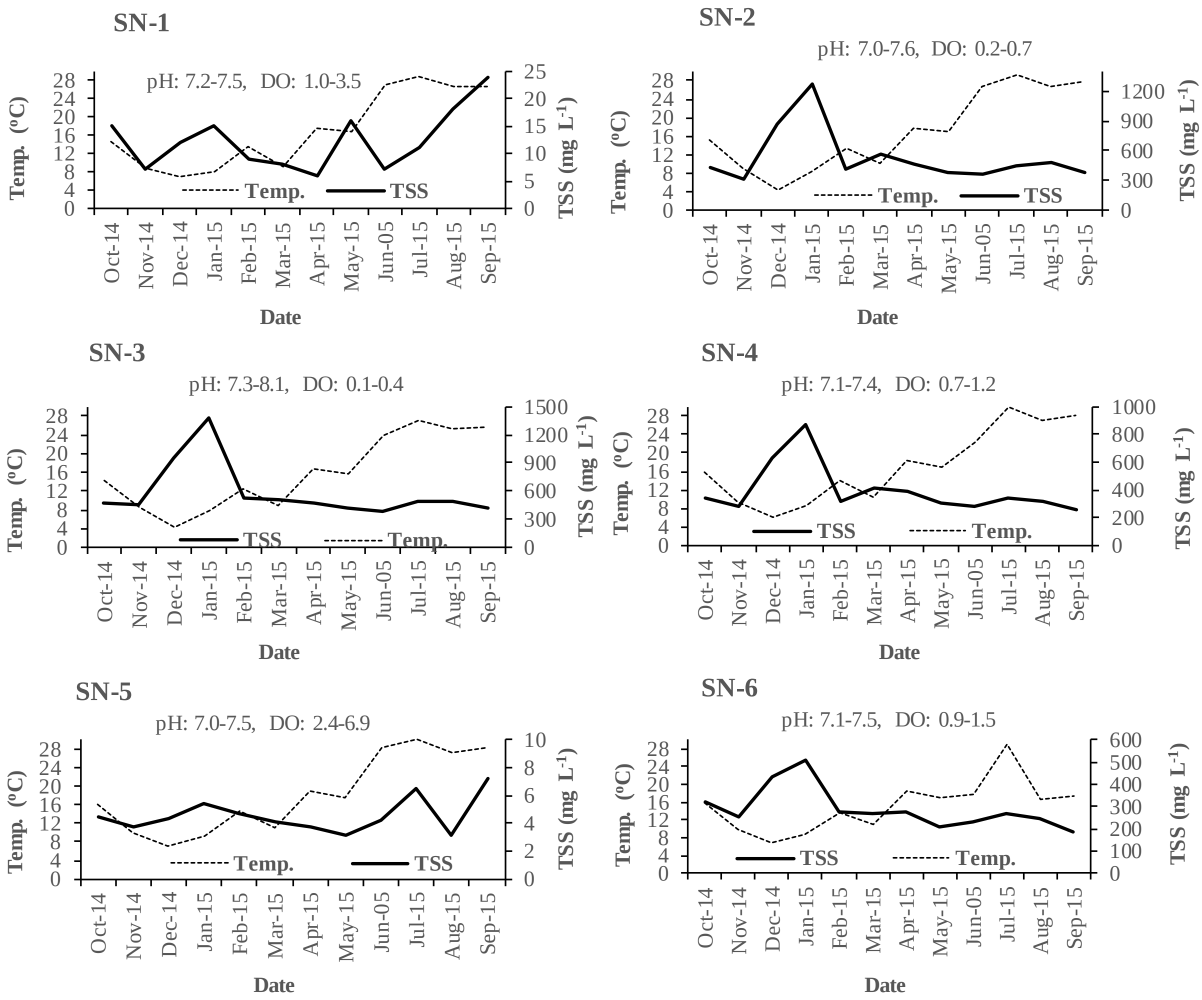

Figure 3. The variation of the BOD concentrations depending on the pH, the DO, and the water temperature in the creek and lake.

The DO values in the final sampling point (the SN-6) was slightly higher than the other sampled points as it was taken just ahead (about 200 m) of the point where the clean waters of the lake were discharged. While the annual average value of SN-1 was 784 µS cm^{-1}, this value increased up to approximately 1102 µS cm^{-1} at SN-2, probably due to the high amount of dissolved substances in the discharge waters of the NMWTF (Özpınar, 2007). The EC values in the SN-3 was high, probably due to the entry of drainage waters containing high organic matter to the creek from agricultural areas after rainy days. The EC values from the SN-3 sampling point toward the downstream part of the creek reduced, probably due to the dilution that occurred along the length of the creek. Because the SN-5 sampling point was taken from the lake, the EC values were found lower compared to the values at the creek, due to probably the high dilution of organic pollutants in the lake. The annual average EC value in the lake water is approximately 666 µS cm^{-1}, and the lake water was at the second class water quality level in terms of the EC (TWPCR, 13). While the EC value increases with the evaporation of the creek and lake waters during the summer and the inflow of polluted water to the creek and lake waters, it decreases with the precipitation, snow and ice melting, and the inflow of the fresh water containing very low dissolved organic matter (Göksu, 2003). As shown in Table 1, the EC values are higher, while the DO values are lower in the regions where the creek is over-polluted. This is presumably due to the biodegradation of high amounts of dissolved organic matter contained in polluted-creek (Tepe & Mutlu, 2004).

As shown in Fig. 3, the TSS in the warmer seasons were found to be higher when compared to the colder seasons. This is probably due to the higher evaporation and the high SS matter to the creek and lake input during the summer period. The variation of the TSS concentrations along the creek was shown in Figure 4. As shown in Fig. 4, the average TSS concentrations were found at the lowest value of 10 mg L^{-1} in the first sampling point (the SN-1) where that the creek was least polluted. The average TSS concentrations in the SN-2 where the outlet waters of the NMWTF are discharged and in the SN-3 that the agricultural activities were carried out increased considerably.

These results indicated that the creek was over-polluted in terms of the TSS at the SN-2 and 3 sampling point, and thus wastewater of the NMWTF and agricultural activities was an important factor in the pollution of the creek. In addition, the average TSS concentrations from the SN-3 sampling point toward the downstream part of the creek declined steadily, probably due to the dilution of the organic matters.

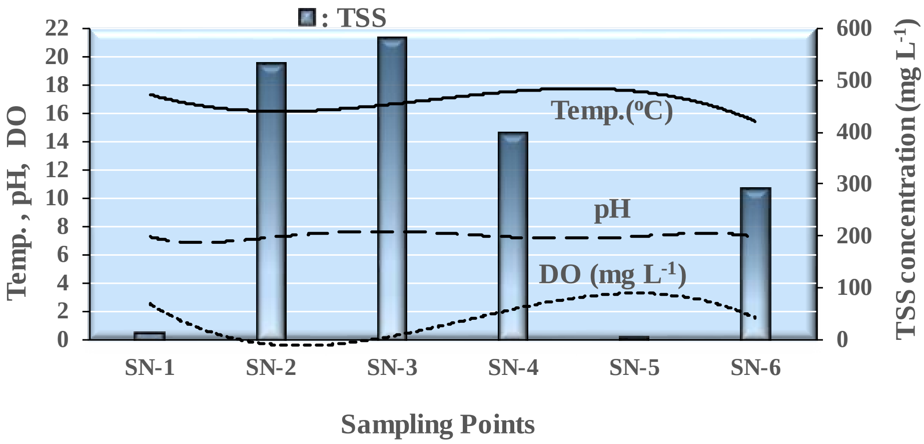

Figure 4. Change of the TSS concentrations along the creek.

Variations in the TSS concentrations of the NWT system

A pilot-scale NWT system was built at the edge of the creek to prevent the existing organic matter pollution in the Kızılca creek in 2014. The variation of average influent and effluent TSS concentrations (mg L^{-1}) in the system operated for about 7 months is shown in Figure 5. The DO concentrations at the entry and the exit of the system was average 0.3 mg L^{-1} and 1.4 mg L^{-1}, respectively. The pH range of the system is between 7.3-7.6 and close to neutral.

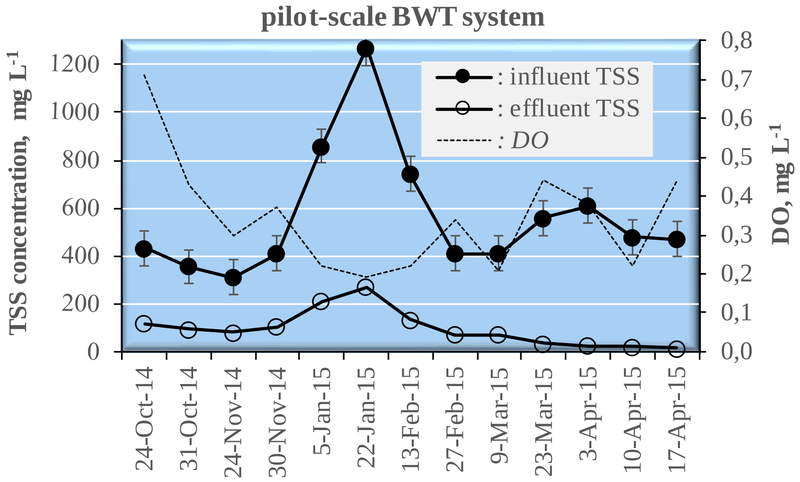

Figure 5. The variation of the average influent and effluent DO and TSS concentrations of the NWT system during the operation period.

The average influent and effluent TSS concentrations of the NWT system at an average water temperature of 11 °C were 563 mg L^{-1} and 96 mg L^{-1}, respectively. So, the system was able to remove the TSS up to approximately 83%. In previous studies (Reed et al., 1995; Crites et al., 2006; Kadlec & Wallace, 2009; Kim et al., 2014; Li et al., 2014; Morató et al., 2014), the TSS removal efficiencies in combined NWT systems consisting of the CW and OF systems ranged from 80 to 95%. In this study, despite higher TSS load (about 563 mg L^{-1}) compared to the other studies (below about 150 mg L^{-1}), the TSS removal of the NWT system was within the range of values in the literature. The results, it is seen that the NWT system produces the TSS below the discharge criteria to the receiving waters (TWPCR, 2004).

CONCLUSIONS

In this study, the existing SS pollution potential in the Kızılca creek and the Akkaya lake was investigated. As a result of the study, it was seen that the creek was extremely polluted in terms of SS matter. Since the creek was discharged to the lake at a high flow-rate of 0.80 m^3 s^{-1}, the high TSS load on the lake was seen as an important threat source in the pollution of the lake. Therefore, a plot-scale NWT system was installed at the edge of the creek to reduce the existing organic matter load.

The NWT system reduced the existing pollution in terms of the TSS. The system reduced the amount of TSS in the creek from an average 563 mg L^{-1} up to 96 mg L^{-1}. The results showed that the combined NWT systems to be installed at the edge of the creek might significantly reduce the existing organic matter load on the creek, and thus the water pollution of the creek and lake might be improved.

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The Effect of Leachate on the Compacted and Consolidated Clay Soils

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ABSTRACT

Solid waste landfills constitute a potential major threat to groundwater quality. Water present in the waste, rainwater infiltration during and/or after the landfilling process and groundwater penetration can result in the generation of leachate. Leachate is a kind of waste liquid consisting of waste contaminants. Clay soils are natural matters to minimize the permeability of natural soil liners in landfill areas. Some contaminants in the leachate can alter compacted clay soils and cause increasing or decreasing permeability.
This study investigates effects of leachate on the permeability of the compacted and consolidated clay soils, thereby evaluating the effectiveness of these clay soils as liners in preventing groundwater contamination. To determine removal capability of compacted and consolidated clay soils, some metal ions (Fe(II), Mn(II)) are also measured in influent and effluent of the lab-scale reactor.
According to results of this study, Fe(II) and Mn(II) removal efficiency increases with time. $Fe(OH)_3$ and MnO_2 precipitations on the clay soil particles increase oxidation rate depending on the autocatalytic effect. Also, in the beginning, some decrease has been observed in the compacted and consolidated clay soils permeability associated with the contamination. However, as time goes by, these results show that leachates may cause an increase in the permeability.

Keywords: Clay soil, leachate, metal ions, permeability.

INTRODUCTION

The landfill is an economical method which has been preferred more than 30- 40 years for the waste disposal of domestic and industrial wastes of developed and developing countries. Regular disposal of these wastes produced every day has a major importance. Every year 450-500 million tonnes solid wastes are produced due to the population of the world and 70% of these wastes are embedded in a solid waste landfill. It is estimated that 70 thousand tonnes wastes are formed in Turkey. 14000 tonnes of wastes are collected in Istanbul (9000 tonnes from European part and 5000 tonnes from the Anatolian part are carried to landfills and eliminated.

Planning and design of solid waste storage area have been developed using a quite complex technology (Shashikumar, 1992; Sertdemir, 2010). One of the most important aims of the solid waste storage area design is to minimize the risks in terms of environmental and human health. Properly constructed landfill should prevent the pollution of underground and surface waters and remove the environmental and social apprehensions. There are some factors need to be considered for the design of the landfill. The most important one is the bottom layer of the landfill and this layer having between 1m and 2 m thickness is a clay layer which is laid with geomembrane. Some researchers indicated that organic chemicals harm compacted clay and the quality of being impermeable of the material. Thus this issue should be considered attentively during the planning of the plant (Shashikumar, 1992).

Leachate occurs from MSW during the landfill process cause of several effects, such as precipitation, rainfall, surface runoff, biological degradation in the waste, etc. (Bou-Zeid et al. 2004; Xue et al.2013). Landfill leachate possesses a dark color and a strong smell, which contains high organic and inorganic contaminants. Leachate has some pollutants in aqueous solution. They are classified as four groups: dissolved organic matter (volatile fatty acid and more refractory organic matter such as humic substances), macro inorganic compounds (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Fe^{2+}, Mn^{2+}, HCO_3), heavy metals (Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}), and xenobiotic organic compounds originating from chemical and domestic residue present at low concentrations (aromatic hydrocarbons, phenols, pesticides, etc.) (Christensen et al. 1991) and microorganisms that indicate, predominantly total and thermotolerant coliform (Moravia et al. 2013; Yao, 2017).

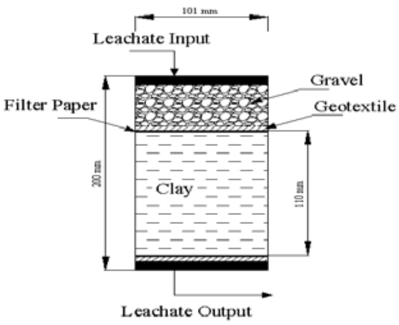
Clays are natural matters to minimize the hydraulic conductivity of natural soil liners in landfill areas. Intrinsically, aplenty clay soils and re-compacted clay liners can represent a key component of landfills (Hamdi et al. 2013).

In this study, the change in clay soil permeability and the removal efficiency of Fe(II) and Mn(II) ions in the leachate in clay soil. For this purpose, leachate sample obtained from Şile – Kömürcüoda landfill in Anatolian Part, is filtered in disturbed clay soil which is subjected to compaction using the standard methods and consolidated reactors, so the permeability of the sample was found as experimentally. The change of Fe(II) and Mn(II) ions in influent and effluent of the reactor were investigated for determination of treatment capacity of clay soil.

MATERIALS AND METHODS

Experimental Setup

In this study permeability with constant head experiment method was used (Janardanan et al. 1989). 6 reactors were used and height of the clay in the reactors was 11 cm. Reactors were equipped with geotextile and porous material. In 3 reactors upper of the clay was compressed with pebble stones and in other 3 reactors piston system was used. Reactors compressed with pebble stones contain clay soil compressed with standard compaction, other 3 reactors contain both compressed with standard compaction soil and consolidated soil. Firstly, reactors were saturated by tap water with 0.3 bar pressure and then fed with leachate Fe(II) and Mn(II) parameters were analyzed in the leachates taken from the effluent of the reactors. Figure and the photo of the experimental setup were shown in Figure 1.



(a) **(b)**

Figure 1. Schematism (a) and photo (b) of the experimental setup.

Permeability Calculation Method

Water comes from the reservoir with constant water level is collected in the tank passing through the soil and the filter. After obtaining a stable stream, water amount collected in the tank is determined at a certain time. "k" is calculated using Darcy's law.

Water load on the sample.

$$H = H_1 - H_2$$

Cross-sectional area of the sample

$$A = \pi * D^2 / 4$$

Permeability coefficient

$$K_t = Q * L / (H * A * t)$$

Analysis Methods

Compaction Experiment

Compaction experiment was performed according to ASTM D 698 methods.

Consolidation Experiment

Measurement watch having 0.01 mm sensitive was installed on the piston system to find compression amount and speed. Then weight amounts were assigned as 19 kg, 38 kg and 76 kg for 0.25 kg/cm^2, 0.5 kg/cm^2 and 1 kg/cm^2 pressure levels, respectively. Consolidation experiment pages were prepared for each reactor and hanging weight, total weight, applied pressure, date, hour were saved. The changes in measurement hours were recorded in pages 4 min, 8 min, 15 min, 30 min, 1 h, 2 h ve 4 h after hanging the weights. This process was repeated during the loading and removing the weights. Then consolidation was completed following the results and graphs of time-compression.

Waste Analysis

For determination of treatment capacity of clay soil, Fe(II) and Mn(II) analysis in effluent of the reactor were performed according to the standard methods (Greenberg, 2005).

RESULTS AND DISCUSSION

Propertıes of Leachate And Clay Soil Used in The Study

Properties of Leachate

Results of Fe(II) and Mn(II) analysis in the leachate from Şile-Kömürcüoda landfill were given in Table 1.

Table 1. Fe(II) and Mn concentrations of leachate (Cansız, 2011).

Date	**Fe(II) (mg/L)**	**Mn(II) (mg/L)**
	65.3	1.33

Properties of clayey soil

Silty clay was used in this study. The colour of the clay varies from yellowish gray to brownish gray. Clay samples of Şile Kömürcüoda Landfill consist of clay (Gürpınar Formation) and sand (Çukurçeşme Formation) from bottom to the top.

Table 2. Properties of clay used in Kömürcüoda Landfill (Sertdemir, 2010; Baştürk et al. 2013).

Chemical Analysis (%)		**Mineral Content (%)**		**Sieve Analysis (%)**	
SiO_2	51-54	Kaolinite	68-71	63 µm	100
Al_2O_3	27-29			40 µm	99
Fe_2O_3	2.5-2.7	Free Quartz	6-9	20 µm	98
TiO_2	1.1-1.2			6 µm	91
CaO	0.1-0.2			2 µm	69
MgO	0.7-0.8	Illit	15-18	1 µm	47
Na_2O	0.0-0.1				
K_3O	2.7-2.9	Others	2-5		
SO_3	----				

Leaking loss 8.5 – 9% water absorption 0.2 – 0.4%

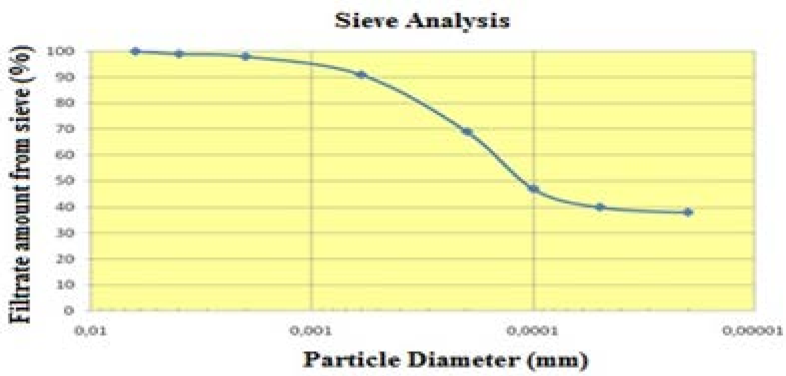


Figure 2. Sieve analysis.

Clay sample of Şile-Kömürcüoda Landfill consists of 68-71% kaolinite, 6-9% free quartz, 15-18% illite, 2-5% other minerals. The permeability of the clay, leaking loss and water absorption capacity were determined as $k=1x10^{-8}$ cm/h, 8.5 – 9% and 0.2 – 0.4%, respectively.

Results of Compaction, Permeability and Consolidation Tests

Compaction Test Results

The change of compaction experiment results was determined for the soil used for filling due to water content of pacing degree obtained with a compaction energy. There are two kinds of Proctor tests. These are Standard Proctor Test and Modified Proctor Test. The connection between the water content of the soil and compressed dry density was determined and results were shown in Table 3 and Fig. 3.

Table 3. Compaction experiment results**.**

Sample coming from	Kömürcüoda
Volume of pot	1000 cm^3
Diameter	10.47 cm
Height	11.56 cm
Number of layers	3
Weight of rammer	2.5
Downfall height	30.5
Number of Strikes	25 strike for each layer

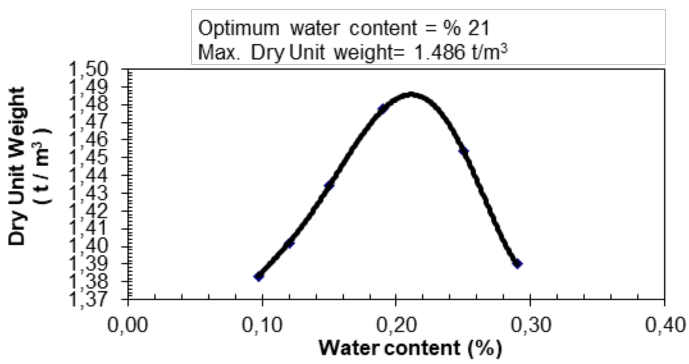


Figure 3. Compaction test results.

Results of Permeability and Consolidation Tests

Results of permeability tests performed using various energy applications on compressed clay sample are given in Figure 4. Permeability tests were done on clay samples compressed with standard compaction. Samples were prepared as 3% more and 3% less than optimum water content. Permeability measurements were performed on prepared 3 samples and permeabilities were determined to pass of the leachates. Same processes were repeated other samples consolidated with standard compaction. Strain and deformation curves of consolidated samples are shown in Figure 4. Permeability values obtained after these processes are given in Figure 5.

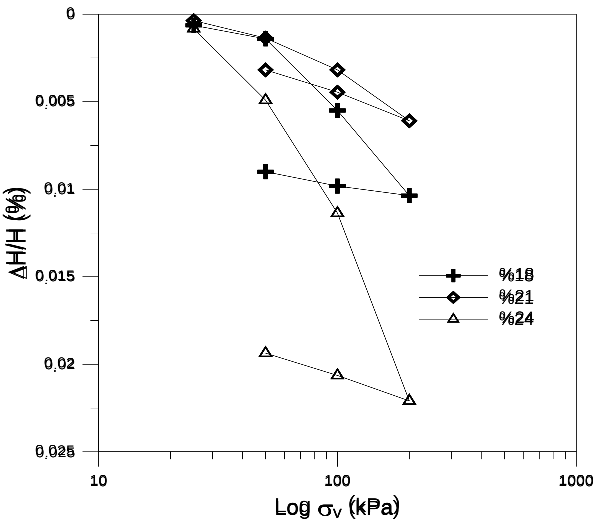


Figure 4. Odometer strain – deformation curve.

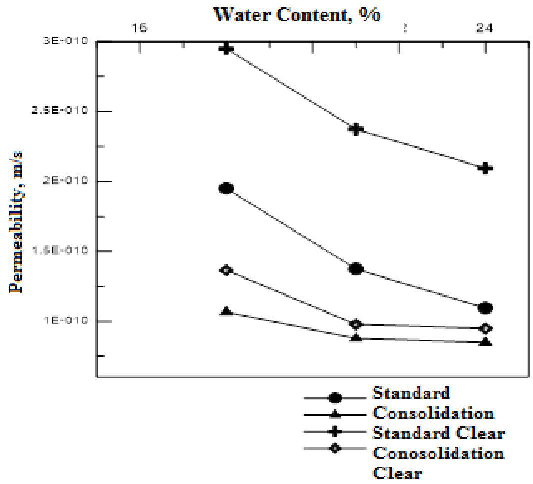


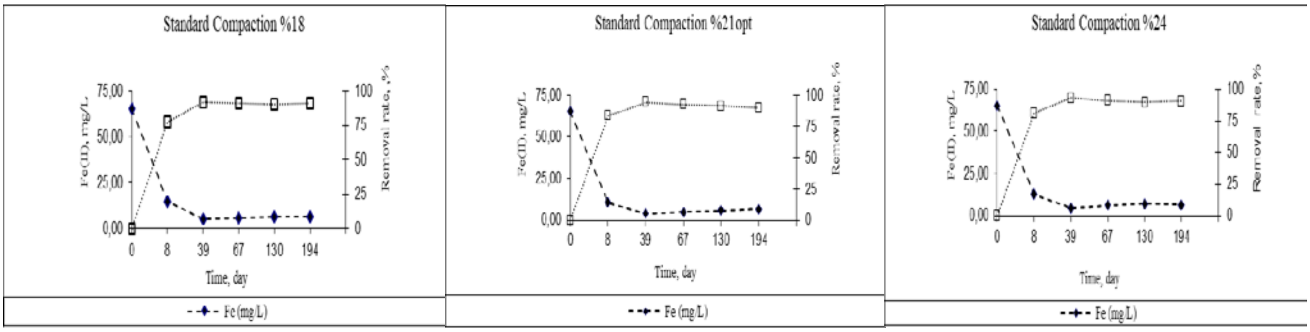
Figure 5. Permeability test results of samples compressed standard compaction and samples applied consolidation with standard compaction.

As can be seen from the figure, changes in permeability of clay sample were observed due to pollution and consolidation application. It has been also observed that suspended materials and microorganisms in the leachate cause a decrease in permeability due to the filling of the gaps in clay soil particules. Besides, water passes quickly in the samples compressed with standard compaction and passes hardly in the samples compressed with standard compaction under consolidation load. Permeabilities of samples compressed with standard compaction and compressed with standard compaction and consolidation are 10^{-10} m/s and 10^{-11} m/s, respectively. The reason of this case is considered as gaps in the samples under loads decrease and cause a difficulty for the passing of the water.

Treatment Experiment Results of Leachate in Clay Soil

In this study removal efficiencies were investigated for Fe(II), Mn(II) in Şile-Kömürcüoda Landfill leachate using destroyed clay soil compressed with standard compaction and standard compaction and consolidation. Found data are given below.

Iron Analysis Results

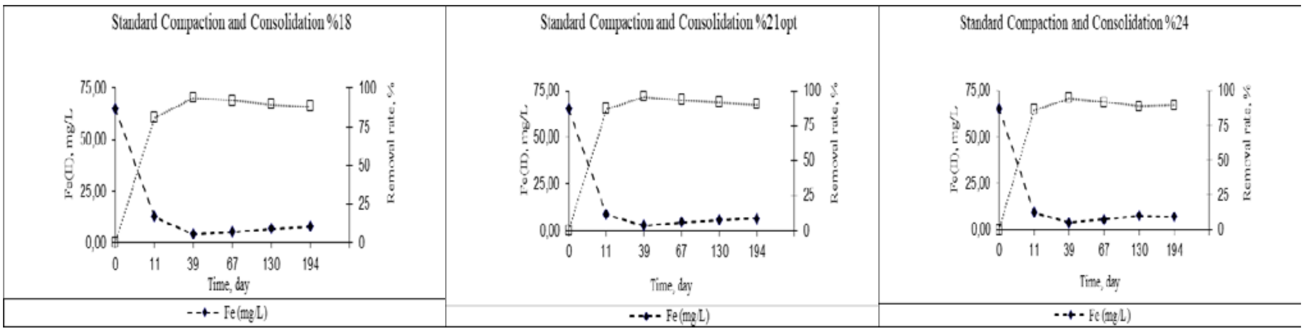


(a) **(b)** **(c)**

Figure 6. Change and removal efficiency of Fe(II) (a) Standard compaction, water content %18(opt.-3), (b) Standard compaction, water content %21(opt.), (c) Standard compaction, water content %24(opt.+3).

The input value of Fe(II) in leachate was found as 65.30 mg/L and first passing of leachate from clay soil took 8 days. As can be seen from the figures, a decrease was observed in Fe(II) value of the effluent leachate from the reactor, so an increase was observed in efficiency. At 39. day, in the reactor containing the sample compressed using standard compaction methods with 21% humidity (optimum), effluent Fe(II) value and removal efficiency were found as 3.84 mg/L and 94%, respectively.

At 39. Day, in the samples having the optimum water contents %21, %18 and %24, Fe(II) effluent values and removal efficiencies were found as 3.84 mg/L, 5.41 mg/L, 4.42 mg/L and %94, %92, %93, respectively (Figure 6). The removal efficiency of the sample compressed with standard method was found as 93 % and removal was monitored during 194 days. However as seen from the figures, it has been observed that removal efficiency increased until 39. day and then it started to decrease. This change can be explained as adsorption until 39. day and desorption afterwords. The removal efficiency of Fe(II) was found to be quite high.



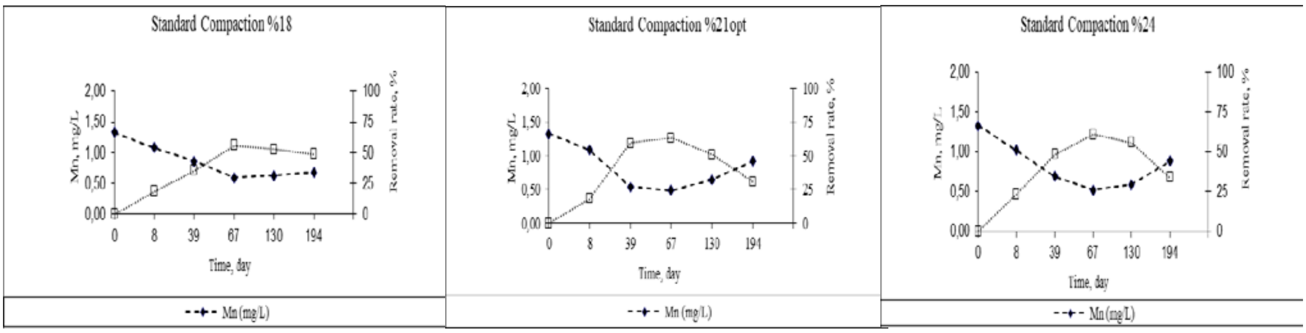
(a) **(b)** **(c)**

Figure 7. Change and removal efficiency of Mn(II) (a) Standard compaction and consolidation, water content %18(opt.-3), (b) Standard compaction and consolidation, water content %21(opt.), (c) Standard compaction and consolidation, water content %24(opt.+3).

The input value of Fe(II) in leachate was found as 65.30 mg/L. The first passing of leachate from compaction and consolidated clay soil took 11 days. On day 11, in the reactor containing compressed and consolidated sample having 21% humidity (optimum), it was found that Fe(II) effluent value was 8.4 mg/L and removal efficiency was 87%; on day 39 it was found that Fe(II) effluent value was 2.79 mg/L and removal efficiency was 96%. On day 11, in the reactor containing compressed with standard method sample having 18% humidity (optimum), it was found that Fe(II) effluent value was 12.5 mg/L and removal efficiency was %80.8; on day 39 it was found that Fe(II) effluent value was 4.19 mg/L and removal efficiency was 93.5%. On day 11, in the reactor containing compressed with standard method sample having 24% humidity (optimum), it was found that Fe(II) effluent value was 9.1 mg/L and removal efficiency was %86; on day 39 it was found that Fe(II) effluent value was 3.83 mg/L and removal efficiency was 94% (Figure 7). Optimum removal efficiency was found high at optimum humidity.

It has been found that removal efficiencies of Fe(II) were 94% for the samples compressed with standard compaction and consolidation and 93% for the samples compressed with standard compaction at 21% humidity (opt).

Manganese Analysis Results

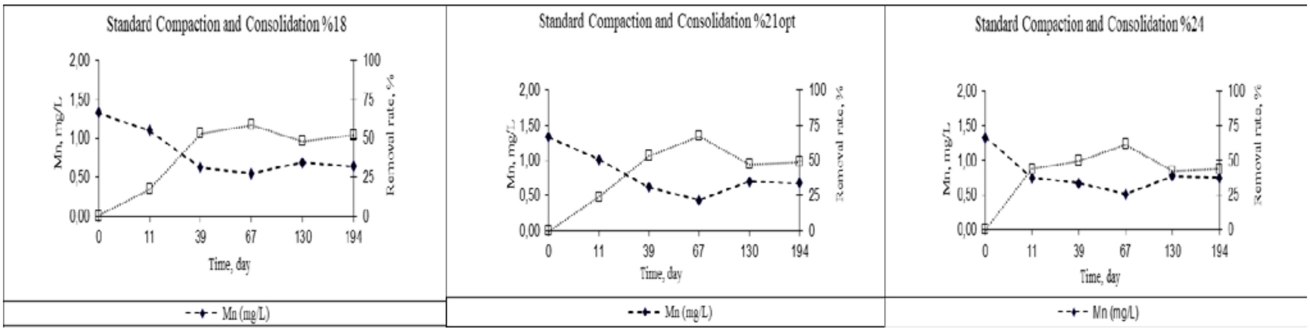


(a) **(b)** **(c)**

Figure 8. Change and removal efficiency of Mn(II) (a) Standard compaction, water content %18(opt.-3), (b) Standard compaction, water content %21(opt.), (c) Standard compaction, water content %24(opt.+3).

Passing of the leachate having 1.33 mg/L Mn(II) input value took 8 days from standard clay soil. As can be seen from the figures, a decrease in Mn(II) of the leachate coming out from the reactor was come true at 8. Day. Mn(II) effluent value decreased to 1.09 mg/L in the reactor containing compressed sample having 21% humidity with standard compaction method. In this reactor removal efficiency of Mn(II) was found to be 18%.

On day 67, in the samples having 21%, 18% and 24% water content, Mn(II) effluent value were found as 0.49 mg/L, 0.59 mg/L, 0.52 mg/L and removal efficiencies were found as 63%, 56%, 61%, respectively. (Figure 8). As seen from the figures, it was observed that average removal efficiency of the samples compressed with standard method was 60% and generally Mn(II) removal efficiency increased until the day 67 then it decreased on other days. This change indicates that desorption has started between the days 67 and 130. At the end of the 194 days monitoring adsorption study, Mn(II) removal efficiency was high in the samples compressed with standard compaction method.



(a) **(b)** **(c)**

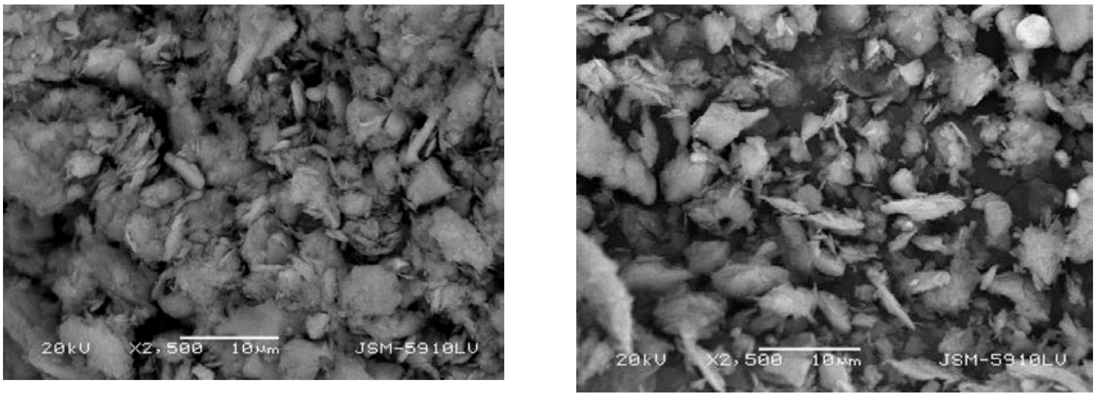
Figure 9. Change and removal efficiency of Mn(II) (a) Standard compaction and consolidation, water content %18(opt.-3), (b)Standard compaction and consolidation, water content %21(opt.), (c) Standard compaction and consolidation, water content %24(opt.+3).

On day 11, Initial Mn(II) value was measured as 1.33 mg/L and first passing of the leachate from standard and consolidated clay soil took 11 days. On day 11, decreases were observed in Mn(II) values in effluent leachate from the reactor. In the reactor containing compressed sample with standard method and consolidation having 21% humidity (optimum), it was found that Mn(II) effluent value was 1.01 mg/L and removal efficiency was 24%; on day 39 it was found that Mn(II) effluent value was 0.62 mg/L and removal efficiency was 53%. On day 11, in the reactor containing compressed sample with standard method and consolidation having 18% humidity (optimum), it was found that Mn(II) effluent value was 1.10 mg/L and removal efficiency was 17%; on day 39 it was found that Mn(II) effluent value was 0.63 mg/L and removal efficiency was 53%. On day 11, in the reactor containing compressed sample with standard method and consolidation having 24% humidity (optimum), it was found that Mn(II) effluent value was 0.75 mg/L and removal efficiency was 44%; on day 39 it was found that Mn(II) effluent value was 0.67 mg/L and removal efficiency was 50%. Similarly, on day 67, removal efficiencies were found as 67% at 21% (optimum) humidity, 59% at 18% humidity and 62% at 24% humidity (Figure 9). As seen from the results, at optimum humidity removal efficiency was found higher than other results.

Removal efficiencies of Mn(II) were found as 67% of consolidated soils compressed with standard compaction method and 63% as of soils compressed with standard compaction method at 21% (opt) humidity.

SEM Analysis Results

Displays of 2500 times enlarged images of clean and contaminated soils taken from Şile-Kömürcüoda Landfill using scanning electron microscopy (SEM) were given in Figure 10.



(a) **(b)**

Figure 10. SEM images of (a) Clean Soil, (b) Contaminated Soil.

Images of clean soil were shown in Figure 10 (a) and contaminated soil in Figure 10 (b). As can be seen from the images, structure of clay particules is amorphous (shapeless). It can be obviously seen from the images that leachate is accumulated between clay balls and surfaces (black parts in balls) in contaminated samples.

Various mechanisms affect the soil permeability as well as removal of pollution in leachate during the passing od leachate in clay soil. These effects are mechanical filtration, sedimentation, adsorption, chemical reaction and biological activities.

Mechanically, filtration is the process by which some pollutants are trapped by the filter material during the polluted water passing through the filter bed. The solids being as suspension form are kept here because their dimensions are larger than the bed material pores. However, contaction of the particles with each other during the filtration large balls are formed, so contamination of pollutants to the effluent water is prevented. Sedimentated materials during the filtration reduce the pore volume and water speed increases due to the narrowing of the section where the water passes. Adsorption is one of the most important process for disposal of colloids and small suspended particules from the water. Adsorption forces are effective for short distances such as 0.01 – 1 µm. However, thickness of the layer covering clay particules is wider than the distance. When this case is considered, adsorption does not affect fastening the particles. However, this situation is different. Particles in water are brought closer clay grains with the transport mechanisms assisting adsorbtion. So, particles are held due to the decrease in the distance. Transport mechanisms are classified as intersection, inertia, gravity, diffusion and hydrodynamic effects. During the filtration, some reactions are occurred. So, dissolved pollutants are separated and turned into less hazardous materials or turned into undissolvable materials and removed from water by sedimentation and adsorption.

CONCLUSIONS

In this study including investigations of clay soil permeabilities and treatment capacities of Fe(II) and Mn(II), yellowish brown-gray silty clay provided from Şile Kömürcüoda Landfill Area was used. For the results of permeability tests with the leachate, permeability changes were observed separately of the samples compressed with standard compaction and consolidation with standard compaction. It was found that permeability of clay soil was low.

The removal efficiency of Fe(II) was 95% of the samples compressed with standard compaction and consolidation at 21% (opt) humidity and removal efficiency of Fe(II) was 94% of the samples compressed with standard compaction at 21% (opt) humidity.

The removal efficiency of Mn(II) was 67% of the samples compressed with standard compaction and consolidation at 21% (opt) humidity and removal efficiency of Mn(II) was 63% of the samples compressed with standard compaction at 21% (opt) humidity.

When the test results of Fe (II) and Mn (II) parameters are examined in general removal efficiencies of the samples compressed with standard compaction and consolidation are higher than removal efficiencies of the samples compressed with standard compaction methods.

In this study removal efficiencies of Fe(II) and Mn(II) were provided after filtering the leachate in clay soil and it was observed that clay is a natural treatment mechanism.

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