



Research Article

THE INVESTIGATION OF FLOW RATE EFFECT ON LEACHATE TREATMENT BY ELECTROOXIDATION PROCESS

Alper Erdem YILMAZ¹, Yeşim DEDE SAĞSÖZ*², Merve SAKARYA³,
İbrahim CENGİZ⁴

¹Atatürk University, Environmental Engineering Department, ERZURUM; ORCID:0000-0002-0666-7653

²Atatürk University, Environmental Engineering Department, ERZURUM; ORCID:0000-0001-6709-2737

³Atatürk University, Environmental Engineering Department, ERZURUM; ORCID:0000-0002-0844-1498

⁴Bayburt University, Emergency Aid and Disaster Management Department, BAYBURT;
ORCID:0000-0003-3171-6629

Received: 15.11.2019 Revised: 25.04.2020 Accepted: 11.05.2020

ABSTRACT

In the study, the leachate of the Erzurum Municipality Solid Waste Regular Storage Facility was used. Leaching waters formed in solid waste storage areas and the contents depend on rainfall and the characteristics of the stored waste. The leachate includes a high amount of organic matter it contains, nitrogenous substances, heavy metals, high salinity; it causes pollution of underground and surface receiving environments. Therefore leachate must be treated before being discharged. For this purpose, an electrooxidation process was used for the treatment of leachate. The effect of the flow rate change on the treatment efficiency in the continuous electrooxidation process is investigated. The flow rate was selected as 5, 7.5, and 10 ml/min. The constant current of 20 A was applied with a direct current intensity supply (40 V-250 A) in 600 ml. In the reactor (600 ml) at a constant current of 20 A, the effluent water temperature increased from 15 °C to 31 °C while the pH value was reduced to a value of 8.2 to 4.8. At the constant current of 20 A, approximately 90% chemical oxygen demand (COD) removal was obtained at a flow rate of 5 ml/min, which is the best removal efficiency obtained from flow rate experiments. It is seen from the same study results that the energy consumption value is 55 kWh/m³ at 20 A current and 5 ml/min flow rate. As a result, the electrooxidation process can be used for the treatment of leachate, especially for organic matter removal.

Keywords: Leachate, electrooxidation, titanium electrode.

1. INTRODUCTION

Rising waste generation, health problem, social conflicts, environmental degradation, and climate change have a major influence on waste management. Fast population and economic growth are responsible factors for the increase in municipal solid waste generation in developing countries [1]. According to an estimate, the amount of waste generated around the world stands at 12.7 billion tonnes in 2000 which will be increased to 19 billion tonnes in 2025 and 27 billion tonnes in 2050 [2]. Landfill leachate is a rather complex and dirty wastewater. Character of

* Corresponding Author: e-mail: yeşim.dede25@gmail.com, tel: (537) 555 92 32

leachate is the result of biological, chemical and physical processes and specific wastes in landfills [3]. Most organic matter in solid waste is biodegradable and can be broken down into simpler compounds by anaerobic and aerobic microorganisms. Leachate in landfills where solid wastes are stored is composed of surface drainage and the degradation of wastes, and rain, groundwater, and water from underground sources.

Leachate components are grouped under 3 main headings.

- Leachate consisting of aqueous parts of solid wastes poured and pressed into storage area,
- Leakage from decomposition in anaerobic environment,
- If the rainfall in the storage area is not controlled, it is defined as the leakage water generated by the storage area [4].

Characteristics of leachate varies according to solid waste storage height, heat, storage age, solid waste components, physical chemical and biological activities in the storage, water content in solid waste, hydro geological status of storage area, pH, operation of storage area, degree of stabilization, redox potential and climate conditions. But the most important one is the waste component. Biological, chemical and physical processes of organic and inorganic components determine the character of leachate [5].

The solid waste content affects the leachate composition and hence its treatability. The leachate contains the compounds and elements occurring in the solid waste facility. Factors such as the solution between leachate and waste, pH of the medium, dissolution, retention, precipitation and redox reactions affect the chemical processes. Redox potential affects the solubility of nutrients and nutrients in leachate. There are 5 different stabilization stages according to the age of the waste. Biogas content and content of all these stages vary in leachate parameter. Observation of biogas and leachate parameters during this process is important in terms of responding to problems that may occur in waste stabilization.

The first stage after burying in the solid waste landfill is the 'acclimation phase' or the environmental adaptation process. The solid waste stored in this process starts to accumulate moisture through the bacteria in the aerobic environment and the amount of oxygen decreases and consequently deterioration begins. The second phase is the transition phase and anaerobic conditions occur in the environment by increasing the moisture content of the waste and consuming the amount of oxygen.

The increase in chemical oxygen demand and total volatile acid accelerates the microbiological effects in the airless environment. In the third phase (acid formation phase), the wastes are converted to volatile acids by acidogenic bacteria, where the pH values of the leachate are reduced. COD, BOD and high volatile acid values are measured for leachate characterization. The fourth stage is the methane formation stage. The acid compounds produced in the preceding stages are converted by the methane bacteria into carbon dioxide and methane gas. At this stage, the concentration of volatile organic acid is reduced by methane and the acidic leachate is converted to pH conditions. During this phase, the gas production in the storage area reaches the highest level. The last stage, the maturation stage, is the stage where perishable substances and nutrients become limiting and stable concentrations of leachate content occur due to reduced gas production [6].

Leachate waters are generally classified into three main groups such as old (> 10 years), young (< 5 years), intermediate (5–10 years) depending on the residence time at the landfill site [3]. Young leachate is associated with low nitrogen concentration, volatile fatty acids and COD content greater than 5 g/L, which are the intermediates of aerobic disintegration at the landfill site [7]. The leachate in aged depots is rich in ammonia nitrogen due to hydrolysis and fermentation of the nitrogenous parts of biodegradable substrates. Organic carbon is mainly based on high molecular weight persistent substances in leaking waters of aged landfill sites. Leakage water is affected by methane fermentation, where permanent fulvic and humic compounds are formed in

anaerobic degradation in older deponias. Humic and fulvic acid, which are depicted as humic substances in elderly deponias, are quite high and occur naturally [8].

As a result of all this, leachates are a mixture of high concentration organic and inorganic contaminants including ammonia nitrogen, humic acids, xenobiotics, heavy metals and inorganic salts, and must be removed due to their toxicity or unfavourable effect on the environment [9]. Conventional treatment methods are not sufficient to remove due to complex features of leachate. Advanced treatment methods are more suitable for leachate treatment.

Among the advanced treatment methods, electrochemical wastewater treatment is now of increasingly interest because it has many advantages such as high capacity for medium and small scale use, simple equipment, low initial investment, reduced chemical reagent, easily automated electrical speed control, high removal efficiency for complex wastewaters and is an environmentally friendly "green" technology due to low generation of secondary chemicals, high selectivity [10]. Due to these advantages, electrochemical treatment is suitable for leachate treatment. Electrooxidation is one of the types of electrochemical treatment. Electrooxidation has very efficiency for the complex wastewater treatment under the activity of direct and indirect oxidants as $\cdot\text{OH}$ radical, H_2O_2 , O_3 [11]. Electrooxidation is based on direct or indirect oxidation of organic matter using an insoluble anode material such as boron coated diamond [12], coated titanium [13,14], platinum [15,16], and graphite [17,18].

The aim of this study is to investigate the use of leachate treatment of electrooxidation process under various parameters with titanium anode electrode. The effects of flow rate were investigated. Initial pH, current and reaction time on the COD removal efficiency were investigated as well.

2. STUDIES

All chemicals used in the study were commercially available (Merck and Sigma). The leachate used in the study was taken from Erzurum Solid Waste Landfill Site and subjected to biological treatment in membrane bioreactor. Membrane bioreactor (MBR) effluent water properties are given in Table 1.

Table 1. MBR output leachate characteristics

| Parameters | Units | Change Interval |
|-------------------------|--------------------|-----------------|
| COD | mg/L | 2000-2200 |
| pH | pH | 9.5 |
| Electrical conductivity | mS/cm | 40-42 |
| Temperature | $^{\circ}\text{C}$ | 16-21 |

In this study, the effects of flow rate parameter were investigated to determine COD removal in leachate by electrooxidation process. The electrolytic cell used for the treatment of leachate by electrooxidation process is made of glass with 10 cm inner diameter and 22 cm depth heat jacketed reactor. Ti/Pt sieve plates were used as anode material and Ti sieve plates were used as cathode material. The total surface area of the plates was calculated to be approximately 2600 cm^2 . In order to prevent ohmic losses, the distance between the plates is 3 mm. A total of 5 anodes and 5 cathodes were studied with 10 plates. The volume of the actual wastewater used in all experiments was determined as 1000 ml. The anodes and cathodes used in the experimental studies are positioned parallel to each other. Direct current intensity supply (Quasar 500 Switch Mode) is supplied to the system using electricity. The effect of flow rate was studied in the range of 5, 7.5 and 10 ml/min, and the effect of current intensity in the range of 5, 10, 15 and 20 A. Schematic representation of the system is given in Figure 1.

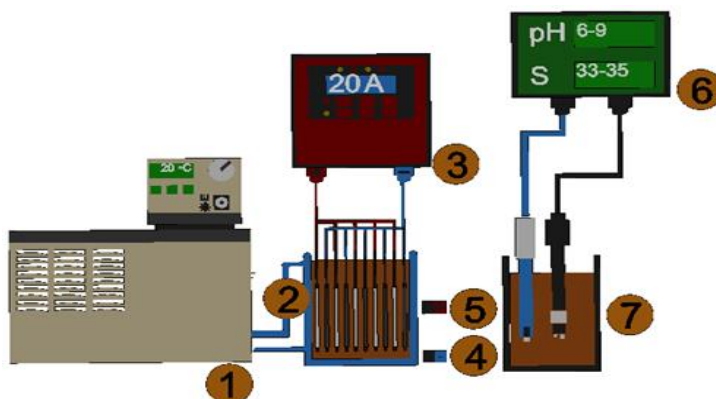


Figure 1. Experimental setup * 1-Constant temperature liquid circulator, 2-Heat jacketed reactor, 3-DC power supply, 4-Cathode (Ti), 5-Anode (Ti/Pt), 6-Multiparameter meter (pH and Conductivity)), 7-Sample container

2.1. Equations for the calculation of experimental data

2.1.1. Calculation of removal efficiency

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

Here, C_o (mg/L) initially shows the concentration of contaminants in the wastewater, and C_e (mg/L).indicates the concentration of contaminants remaining in the wastewater at a certain time.

2.1.2. Calculation of current density

$$J = \frac{I}{A} \quad (2)$$

Here, J indicates the current density (mA/cm²), 'I' shows the applied current intensity (A), and A shows the active electrode surface area (cm²).

2.1.3. Calculation of energy consumption

$$W = \frac{I * V * t}{\rho} \quad (3)$$

Here, W represents the energy consumption value (kWh/m³), I is the current intensity applied (A), V is the applied potential (V) in the system, t is the time (h) and V is the total solution volume (m³) in the reactor.

3. CONCLUSION

3.1. Effect of flow rate on pH variation

The flow rate of the wastewater to the electrochemical reactor is an important parameter that influences the removal of pollutants as it determines the hydraulic residence time in the reactor and the duration of the exposure of the wastewater to the electrochemical reactions [19]. The results should be clear and concise. In the studies where the treatment of leachate treatment was examined, in the experiments where the effects of flow rate of 5, 7.5 and 10 ml/min for

electrooxidation process were examined, without using supporting electrolyte, at the natural pH value of the wastewater and at current intensity values of 5, 10, 15, 20 A, at different flow rates was studied. In the experiments where the flow rate is 5, 7.5 and 10 ml/min, the time-dependent change of the initial pH value of the leachate is shown in Figure 2.

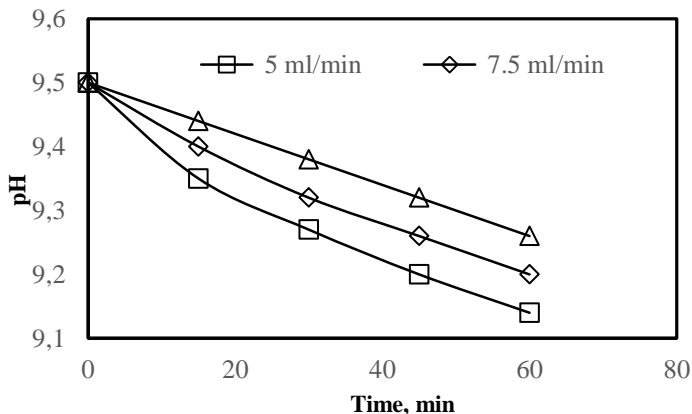


Figure 2. Variation of the initial leachate pH value during the reaction at 5 A constant current intensity, Flow rate: 5, 7.5 and 10 ml / min, Reaction time 60 minutes

Figure 2 shows the pH change at 5 A at flow rates of 5, 7.5 and 10 ml/min of MBR effluent. At 5 A constant current, the initial pH decreased from 9.49 to 9.13 at 5 ml/min after a 60 minute reaction time. At 7.5 ml/min, the pH value decreased to 9.24 at the end of the reaction time. At 10 ml/min the pH decreased to 9.32. According to the information obtained from the data, there is no rapid decrease in pH values.

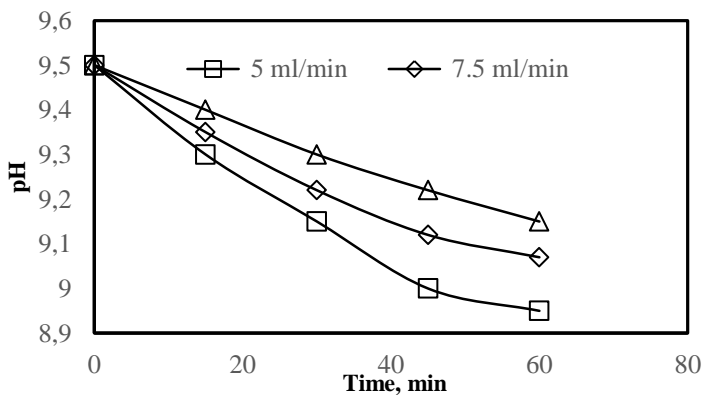


Figure 3. Variation of the initial leachate pH during the reaction at a constant current strength of 10 A, Flow rate: 5, 7.5 and 10 ml/min, Reaction time 60 min

Figure 3 shows the pH change at 10 A at flow rates of 5, 7.5 and 10 ml/min of MBR effluent. At 10 A constant current, the initial pH decreased from 9.50 to 8.95 at 5 ml/min after a 60 minute reaction time. At 7.5 ml/min, the pH value decreased to 9.07 at the end of the reaction time. At 10 ml/min the pH decreased to 9.20.

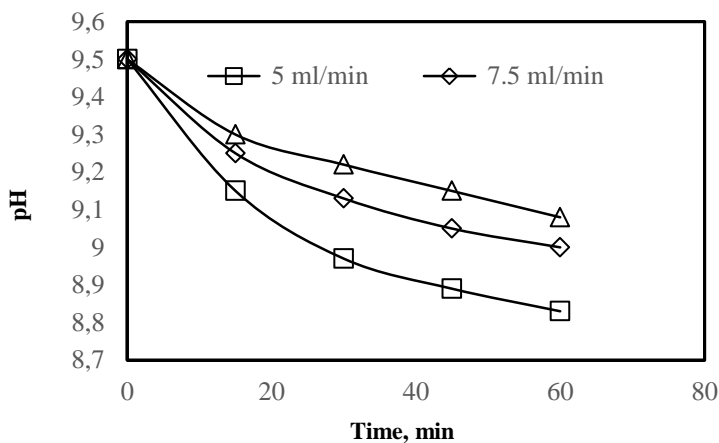


Figure 4. Variation of the initial leachate pH during the reaction at a constant current intensity of 15 A, Flow rate: 5, 7.5 and 10 ml/min, Reaction time 60 min

Figure 4 shows the pH change at 15 A at flow rates of 5, 7.5 and 10 ml/min of MBR effluent. At 15 A constant current, the initial pH decreased from 9.50 to 8.83 at 5 ml/min after a 60 minute reaction time. At 7.5 ml/min, the pH value decreased to 9.04 at the end of the reaction time. At 10 ml/min the pH decreased to 9.16.

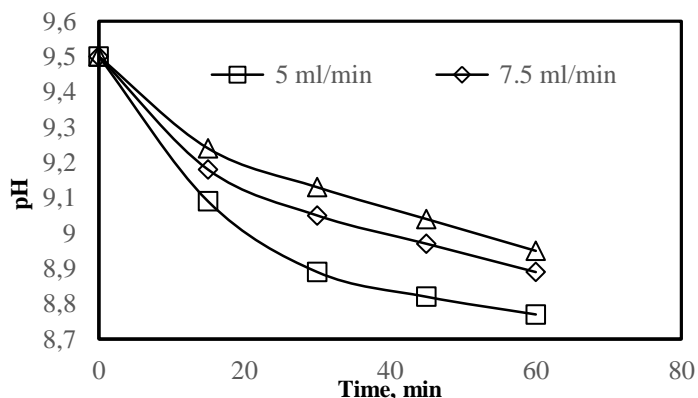


Figure 5. Variation of the initial leachate pH during the reaction at a constant current intensity of 20 A, Flow rate: 5, 7.5 and 10 ml/min, Reaction time 60 min

Figure 5 shows the pH change at 20 A at flow rates of 5, 7.5 and 10 ml/min of MBR effluent. At 20 A constant current, the initial pH decreased from 9.50 to 8.76 at 5 ml/min after a 60 minute reaction time. At 7.5 ml/min, the pH value decreased to 8.93 at the end of the reaction time. At 10 ml/min the pH decreased to 9.01.

3.2. Effect of flow rate on COD removal

In the experiments where the effects of flow rate on the increase of MBR effluent by electrooxidation process were investigated, COD data were examined during the reaction

depending on the flow rate of 5, 7.5 and 10 ml/min. With the help of the obtained data, the graphical results shown in Figure 6; 5, 10, 15 and 20 A current intensity were prepared.

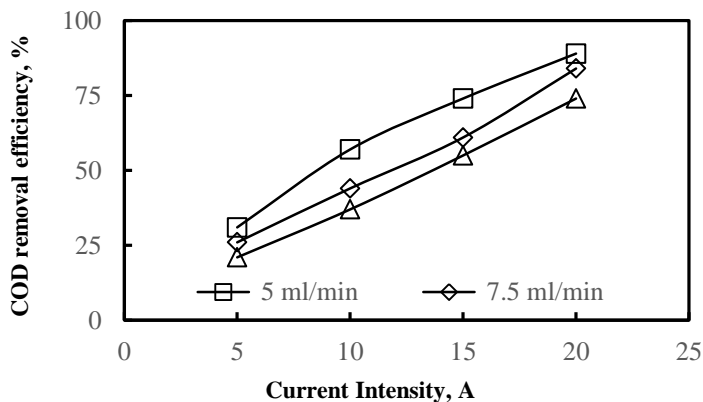


Figure 6. Change of initial leachate COD removal value during the reaction at different flow rates, Flow rate: 5, 7.5 and 10 ml / min

Figure 6 shows that the MBR effluent COD removal efficiencies are in all flow rates and current intensities investigated. In experiments where the flow rate is 5 ml/min at 5 A at 60 minutes, COD removal efficiency is 31%, 26% at flow rate is 7.5 ml/min and 21% at flow rate is 10 ml/min. The highest removal efficiency at 10 A is seen in the experiments where the flow rate is 5 ml/min. In experiments where the flow rate is 5 ml/min at 10 A at 60 minutes, COD removal efficiency is 57%, 44% at flow rate is 7.5 ml/min and 37% at flow rate is 10 ml/min. The same trend is observed in the experiments carried out 15 and 20 A constant current intensity. As can be seen from the numerical data, both the decrease of the flow rate value and the increase of the current intensity from 5 A to 20 A significantly increased the COD removal efficiency.

3.3. Effect of energy consumption

One of the important parameters to be considered in the experiments where the effects of flow rate on COD removal efficiency is the energy consumption values resulting from the applied potential to the system. The mathematical equation given in equation 3 is used in the calculation. The energy consumption values for each flow rate and the current are shown graphically in Figure 7.

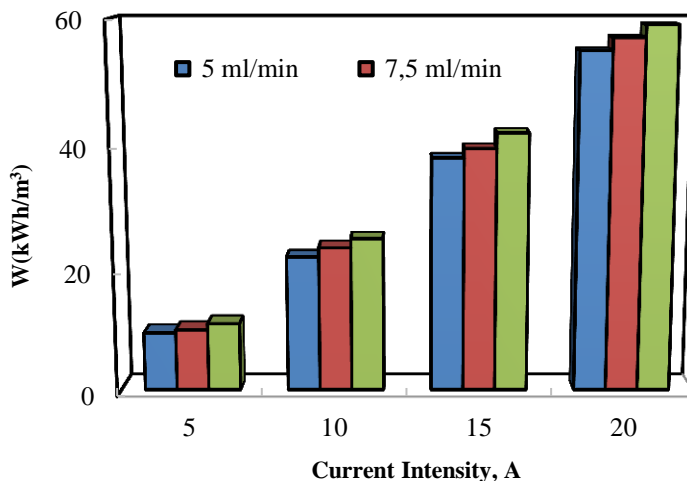


Figure 7. Change of initial leachate energy consumption value at different flow rates during the reaction, Flow rate: 5, 7.5 and 10 ml / min

As can be seen from Figure 7, the increased flow rate has led to an increase in the energy consumption value for each current intensity. The data shown in Figure 7 were calculated for a reaction time of 60 minutes. At 5 ml/min flow rate, energy consumption values for 5, 10, 15 and 20 A were measured as 9.5, 22, 38 and 55 kWh/m³, respectively. At a flow rate of 7.5 ml/min, energy consumption values for 5, 10, 15 and 20 A were measured as 10, 23.5, 39.5 and 57 kWh/m³, respectively. At a flow rate of 10 ml/min, the energy consumption values for 5, 10, 15 and 20 A were measured as 11, 25, 42 and 59 kWh/m³, respectively. The energy consumption values vary slightly, depending on the difference in shear forces that will emerge in the system at different flow rates. It is seen that energy consumption values increase at constant electrical conductivity values due to higher shear forces at higher flow rate values. When the equation 3 is examined, it is seen that the applied potential values formed in the system have a linear relationship with energy consumption. Increasing the applied potential value and reaction time leads to an increase in the energy consumption values generated in the system. The change in flow rate changes the hydraulic residence time in the reactor. As the energy consumption changes in direct proportion with the hydraulic residence time, the decrease in the flow rate has led to an increase in the energy consumption values. This was ignored for the 60 minute reaction time given in Figure 7. When the removal efficiencies and energy consumption values are examined together, it is seen that the low flow rate causes both COD removal efficiency and decreases energy consumption values.

4. CONCLUSION

The feed rate of the waste water to the electrochemical reactor is an important parameter that affects the expense of the pollutants as it determines the residence time of the reactor and therefore the duration of the exposure of the waste water to the electrochemical reactions. Increased wastewater flow rate resulted in a decrease in COD efficiency, provided that the value of each current intensity examined was the same. The increase in wastewater flow rate resulted in a decrease in COD removal efficiencies, since it prevented the full realization of oxidation reactions occurring on the insoluble anode electrode surface in the electrooxidation process.

Increased wastewater flow rate has led to an increase in shear forces in the system, leading to an increase in energy consumption values. However, a suitable flow rate for optimum values of both parameters should be determined by considering the pollutant removal efficiency and energy consumption values together.

REFERENCES

- [1] Mishra, S., Tiwary, D. and Ohri, A., (2018). Leachate Characterisation and Evaluation of Leachate Pollution Potential of Urban Municipal Landfill Sites. *International Journal of Environment and Waste Management*, 21, 217–230.
- [2] MoE, (2006) Population Decline and the Environment and Fifty Years of Minamata Disease, Origin of Japan's Environmental Problems, Japan: Annual Report, Ministry of Environment, Government of Japan.
- [3] Stegmann, R., Heyer, K., and Cossu, R., (2005). Leachate Treatment. Tenth International Waste Management and Landfill Symposium, October 2005, Sardinia, Italy
- [4] Varank, G., (2010). Katı Atık Depo Sahalarının Geçirimsiz Taban Sistemlerinden Kirlenici Geçişinin İncelenmesi ve Taban Sistemlerinin Rehabilitasyonu (Doctoral Dissertation, YTÜ Fen Bilimleri Enstitüsü).
- [5] Duran, E. B, Cuci. Y., (2016). Katı Atık Düzenli Depolama Sahası Kimyasal ve Elektrokimyasal Arıtım Yöntemlerle Arıtılabilirliğinin Araştırılması. *Kahramanmaraş Sütçü İmam Üniversitesi Mühendislik Bilimleri Dergisi*, 19 (2), 104-110.
- [6] Öztürk, F. (2012)., Katı Atık Sızıntı Suyu Miktarını Azaltıcı Yönetim Stratejileri, Doctoral Dissertation, Fen Bilimleri Enstitüsü.
- [7] Akkaya, E., Demir, A., Varank, G., (2011). Characterisation of Odayeri Sanitary Landfill Leachate. *Sigma*, 3, 238-251.
- [8] Topal, M., Karagözoğlu, B., Erdal, K., (2011). Sızıntı Sularının Doğal Arıtımı. *Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi*, 11(2) 1-16.
- [9] Robert, D., & Miksch, K., (2006). Landfill Leachate Treatment Methods : A Review. *Environmental Chemistry Letters*, 4(April), 51–61.
- [10] Tien, T. T., & Luu, T. Le., (2019). Electrooxidation of Tannery Wastewater with Continuous Flow System: Role of Electrode Materials. *Environmental Engineering Research*.
- [11] Peralta-Hernandez JM, Martinez-Huitile CA, Guzman-Mar JL, Ramirez AH., (2009). Recent advances in the application of Electro-Fenton and Photoelectro-Fenton process for removal of Synthetic Dyes in Wastewater Treatment. *J. Environ. Eng. Manage*, 19,257-265.
- [12] Domínguez, J.R., González, T., Palo, P., Sánchez-Martín, J., (2010). Anodic Oxidation of Ketoprofen on Boron-Doped Diamond (BDD) Electrodes. Role of Operative Parameters. *Chemical Engineering Journal*, 162(3), 1012-1018.
- [13] Kong, W., Wang, B., Ma, H., Gu, L., (2006). Electrochemical Treatment of Anionic Surfactants in Synthetic Wastewater with Three-Dimensional Electrodes. *Journal of Hazardous Materials*, 137(3), 1532-1537.
- [14] Santos, I., Afonso, J., Dutra, A., (2010). Behavior of a Ti/RuO₂ Anode in Concentrated Chloride Medium for Phenol and Their Chlorinated Intermediates Electrooxidation. *Separation and Purification Technology*, 76(2), 151-157.
- [15] Fino, D., Jara, C.C., Saracco, G., Specchia, V., Spinelli, P. (2005). Deactivation and Regeneration of Pt Anodes for the Electro-Oxidation of Phenol. *Journal of Applied Electrochemistry*, 35(4), 405-411.
- [16] Carbonio, E.A., Nagao, R., Gonzalez, E.R., Varela, H., (2009). Temperature Effects on the Oscillatory Electro-Oxidation of Methanol on Platinum. *Physical Chemistry Chemical Physics*, 11(4), 665-670.

- [17] Sathish, M., Viswanath, R.P., (2005). Electrochemical Degradation of Aqueous Phenols Using Graphite Electrode in a Divided Electrolytic Cell. *Korean Journal of Chemical Engineering*, 22(3), 358-363.
- [18] Sundarapandiyam, S., Chandrasekar, R., Ramanaiah, B., Krishnan, S., Saravanan, P., (2010). Electrochemical Oxidation and Reuse of Tannery Saline Wastewater. *Journal of Hazardous Materials*, 180(1-3), 197-203.
- [19] Zodi, S., Merzouk, B., Potier, O., Lapique F. and Leclerc, J. P., (2013). Direct Red 81 Dye Removal by a Continuous Flow Electrocoagulation/Flotation Reactor, *Sep. Purif. Technol.*, 108-215.