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RESEARCH ARTICLE

THE EFFECTS of PH and HYDROGEN PEROXIDE CONCENTRATION on CHEMICAL OXYGEN DEMAND (COD) and COLOR REMOVAL FROM LEACHATE by ELECTRO-FENTON METHOD

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ABSTRACT

This study investigated how COD and color removal efficiencies from leachate changed with pH (2.5-4) and H_2O_2 (1000-3000 mg/L) by electro-Fenton method. Maximum COD and color removals were 68% and 69%, respectively, with electrical energy consumptions of 0.79 and 0.108 kWh/m^3. Since the removal efficiencies obtained could not meet the discharge limits in Turkey, it would be more appropriate to apply electro-Fenton together with other treatment methods to achieve higher COD and color removal efficiencies.

Keywords: *COD, Color, Electro-Fenton, Leachate, pH, Hydrogen peroxide*

1. INTRODUCTION

The leachate contains various toxic organic pollutants, ammonia nitrogen compounds, heavy metals due to the decomposition of solid wastes during their disposal in landfills and the effect of rainwater. Therefore, landfill leachate can cause severe hazards to the environment and public health in surface and groundwater. Although the characterization of leachate varies according to the amount of solid waste, its composition, humidity, age and climate of the landfill, seasonal weather changes, they are mostly characterized by high concentrations of dissolved organic carbon, chloride, conductivity and low heavy metal contents [1,2]. Because it contains high levels of pollutant components, leachate must be treated with economical and efficient methods before it is released into the environment.

Physical-chemical treatment processes such as chemical oxidation, membrane treatment, adsorption, coagulation-flocculation and adsorption are used individually or together with biological treatment processes [1]. Depending on treatment objectives, combinations of these methods can also be used. Most easily degradable organic substances in leachate can be efficiently removed by conventional biological treatment processes. Advanced oxidation processes (AOPs) such as Fenton (Fe^{2+}/H_2O_2), hydrogen peroxide with UV radiation (UV/H_2O_2), photo-Fenton (Fe^{2+}/H_2O_2/UV), ultraviolet (UV) are more efficient treatment technologies for removing degradation-resistant pollutants and colours [3]. Fenton technology is preferred because of its advantages, such as applicability and high efficiency [2]. Fenton processes, which are defined as the reactions of hydrogen peroxide (H_2O_2) with iron ions, can

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effectively oxide organic or inorganic compounds [4]. Classical Fenton reactions occur as follows. In Fenton processes, $OH^{\bullet}$ radicals are generated by Equation 1 and serve as the first step for other Fenton reactions (Equations 1-6).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{2+} + OH^{\bullet} + OH^{-} \quad (1)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (2)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (3)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad (4)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad (5)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (6)$$

Equations (1-3) form the cycle in which O_2 oscillates and Equations. Equations (4) and (5) serve as termination reactions. $OH^{\bullet}$ radicals, which have a standard potential of 2.80 V, can effectively take electrons from other materials and oxidize them. The pH range in which the Fenton process is effective is 2.8-3. Compared to $OH^{\bullet}$, $HO_2^{\bullet}$ radicals produced by the Fenton-like reaction are less effective at breaking down organic compounds [5]. Some disadvantages of Fenton processes are as follows: (i) Relatively high costs and risks associated with the storage, transportation, and transportation of H_2O_2 (ii) High amount of chemical to acidify effects to pH 2-4 and neutralize processed solutions before disposal (iii) Iron sludge accumulation the end of treatment, and (iv) General mineralization does not occur due to the formation of Fe (III) complexes via produced carboxylic acids, which $OH^{\bullet}$ radicals can not destroy [6].

The electro-Fenton method extends the Fenton process and is developing the traditional Fenton method [7,8]. Four types of Fenton processes can be performed. In Type 1, ferrous ions and hydrogen peroxide are generated by sacrificial electrodes. In Type 2, while ferrous ion is produced from the sacrificial anode, hydrogen peroxide is added externally (Eq. (7)).

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (7)$$

In Type 3, hydrogen peroxide is produced using oxygen scattering cathodes, and ferrous ions are added externally. In Type 4, the hydroxyl radical is generated in an electrolytic cell using Fenton's reagent, and the ferrous ion is regenerated by reducing ferric ions on the cathode. Even if Type 4 seems attractive, H_2O_2 production is relatively slow because the solubility of oxygen in water is low, and the process efficiency is low at low pH (pH <3) values in the H_2O_2 production process dominated by acidic conditions [9].

Literature data indicate that advanced oxidation processes are effective methods for removing pollutants from leachate. For example, Altin [10] removed 94% of COD and 97% of color removal from leachate using the photo-electro-Fenton method. (COD: 2350 mg/L; pH: 3; H_2O_2: 3000 mg/L; current: 2.5 A; UV source: 4 watts time: 20 min). Sruthi et al. [11] obtained 88.6% COD removal from leachate with heterogeneous Fenton process (COD: 6160 mg/L; pH:3; H_2O_2: 0.03 molar and catalyst (Fe^{2+}/Fe^{3+}): 700 mg/L, leading a molar ratio $[H_2O_2]/[Fe^{2+}]$ of 2.64; pH: 3; time: 90 min), a

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COD removal of 87.5% was achieved by heterogeneous EF process in the same study (pH: 3, Catalyst: 25 mg/L, Voltage: 4 V). Also, these research results showed that catalyst dosage, input pH and voltage values significantly affect the heterogeneous EF process efficiency. Also, the BOD_5/COD ratio of the leachate increased from 0.03 to 0.52 after the Fenton treatment, indicating biodegradability increases [11]. In another study, 70% COD removal from the leachate was obtained by the Fenton process (COD: 2500 mg/L, pH: 2, H_2O_2: 0.187 mol/L and catalyst: 1745 mg/L, leading a molar ratio $[H_2O_2]/[Fe^{2+}]$ of 6; current density: 206 A/m^2 and inter-electrode gap: 1.8 cm, time: 150 min) [12]. Using the same method as Altin [10], Asaithambi et al. [2] achieved 100% color and 97% COD from leachate.

The present study constitutes the second stage of two-stage research conducted by us before [13]. Under optimum experimental conditions determined in the first stage, the effects of initial pH and H_2O_2 concentration on COD and color removal were revealed.

2. MATERIALS AND METHODS

2.1. Characteristics of Leachate

The leachate samples were taken from the landfill in Samsun. An average of 300 m^3 of leachate is produced daily at the site, and a waste of about 800-900 tons collected every day is discharged to the landfill. A representative analysis of the leachate used in the experiments was as follows: pH: 7.50-7.90, COD: 7150-9000 mg/L, conductivity: 20-40 mS/cm, and color: 2102-3596 Pt-Co.

2.2. Experimental Set-Up

EF experiments were done in a volume Plexiglass reactor of 860 cm^3 for EF times of 0-45 minutes. The experiments used two anodes (iron) and two cathodes (steel) (4.5 cm x 5.5 cm in dimension). The total activated anode surface area of the anodes was 94.64 cm^2. The anode and cathode materials were mounted with a monopolar connection before connecting to the power supply (30V, 6A). The electrochemical set-up is shown in Figure 1.

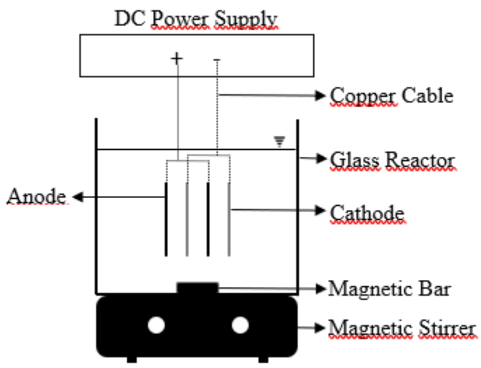

Figure 1. Schematic of the electrochemical set-up.

Experiments were carried out with 750 ml of wastewater at 250 rpm mixing speed. For Fenton reactions, hydrogen peroxide (35%) was added externally, while iron ions were obtained by dissolving the iron used as the anode in wastewater with the effect of current. Before each experiment, the oxide layers formed on the electrode surfaces were kept in concentrated hydrochloric acid (37% HCl) and

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then rinsed with distilled water as required. NaOH and H_2SO_4 were used to adjust the wastewater pH to the desired values, and pH values were measured by an Orion 4 Star pH meter. Samples needed for COD and color measurements were taken at periodic intervals of 2.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40, and 45 minutes and centrifuged before necessary measurements were made. COD and color analyses were carried out with a Merck Spectroquant Nova 60A photometer.

2.3. Analytical System

The closed reflux colorimetric method was used to measure the chemical oxygen demand with a Merck Spectroquant Nova 60A model photometer. The Pt-Co method was used for color analysis [14]. COD removal efficiencies (Eq. 8) were calculated using:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (8)$$

Where C_0 represents the initial COD concentration (mg/L), C_t represents the concentration of COD corresponding time (mg/L).

2.4. Calculations

Electrical energy consumptions were calculated by Eq. 9 [15].

$$E = \frac{UxIxt}{V} \qquad (9)$$

Where E represents energy consumption (kWh/m^3), U denotes the voltage (V), I denotes current (A), t represents time (second), V represents wastewater volume (litre).

3. RESULTS AND DISCUSSION

3.1. Influence of pH

The initial pH is one of the main factors affecting the performance of electro-Fenton systems [4]. It is known that the optimum pH value is around 3 for these processes [16,17,18]. The effects of pH values ranging from 2.5 to 4 were investigated on COD and color removal efficiencies. COD removal was not obtained during the first 7.5 minutes (Figure 2a). At the end of the 10th minute, the COD removals were 19.7%, 27.7%, 18%, and 16% for pH values ranging from 2.5 to 4. Relatively high removal efficiencies were achieved for all pH values between the 10th and 30th minutes, indicating that hydroxyl radicals increased in the reactor with time. For pH: 3, a maximum COD removal efficiency of 68% was reached at the end of the 25th minute. At this minute, electrical energy consumption was 0.79 kWh/m^3. After the 30th minute, the removal efficiencies for all pHs decreased to zero. This case is an indication of the depletion of hydroxyl radicals in the reactor. The maximum removal efficiency was obtained at pH: 3, which was considered as optimum pH. Asaithambi et al. [2] reached a maximum COD removal efficiency of 97% with pH: 3, which was on the leachate treatment by the electro-Fenton. In another study by Atmaca [19], the maximum COD removal efficiency in the treatment of leachate by the electro-Fenton method was reached at pH: 3 and 30 minutes treatment time. Figure 2b shows the effect of different pH on color removal. As shown in Figure 2b, color removal at the end of the 5th minute reached a maximum for all pH. At the end of the 5th minute, the colour removals were 52%, 61%, 60%, 57% for pH ranging from 2.5 to 4. At this minute, energy consumptions were 0.120, 0.126, 0.116 and 0.126 kWh/m^3 for pH values ranging from 2.5 to 4. Color removal efficiencies decreased rapidly between the 5th and 10th minutes, indicating that hydroxyl radicals in the reactor rapidly decreased. Figure 2a and Figure 2b show that the maximum COD and color removal efficiencies were acheved at pH 3, which was considered optimum.

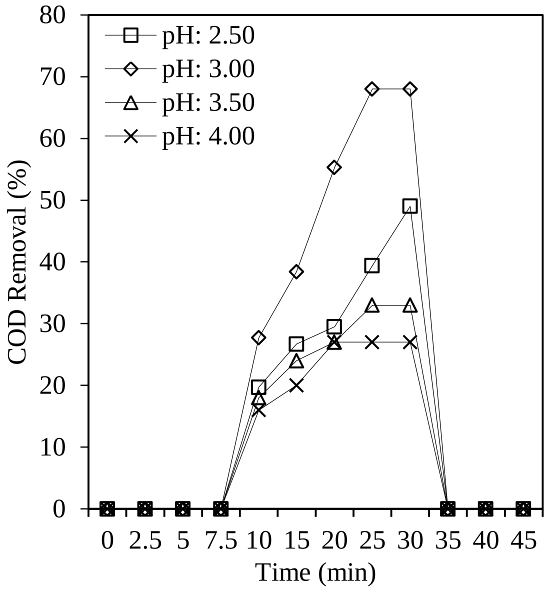

Figure 2a. The effect of pH on COD removal (Conditions: current density: 100 A/m^2, H_2O_2: 2000 mg/L, stirring rate: 250 rpm, inter-electrode gap: 1.5 cm).

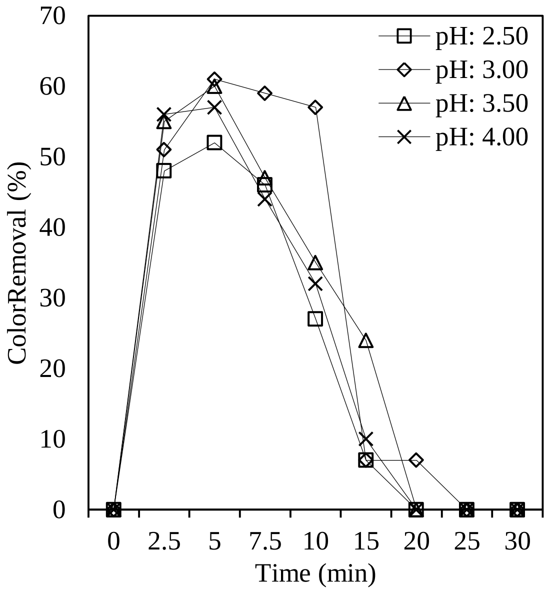

Figure 2b. The effect of pH on color removal (Conditions: current density: 100 A/m^2, H_2O_2: 2000 mg/L, stirring rate: 250 rpm, inter-electrode gap: 1.5 cm).

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3.2. Influence of H_2O_2

The primary source for the generation of $OH^{\bullet}$ radicals is H_2O_2, and this chemical is critical in Fenton processes [5]. The effects of H_2O_2 concentrations ranging from 1000 to 3000 mg/L on COD and color removal were investigated. Figure 3a shows that a maximum COD removal efficiency of 68% was reached at the end of the 25th minute. At this minute, electricity consumption was 0.79 kWh/m^3. Figure 3a also shows a rapid increase in COD removals between the 10th and 25th minutes at optimum H_2O_2 concentration (2000 mg/L). At other concentrations, a slight increase or decrease in removal efficiencies was observed between these minutes. The reason for this is the increasing hydroxyl radicals over time. At H_2O_2 concentrations above 2000 mg/L, the removal efficiencies decreased. This case can be explained by the fact that the excess H_2O_2 chemical converts the hydroxyl radicals to the less reactive $HO_2^{\bullet}$ radicals (Eq. (2)). After the 25th minute, removal efficiencies decreased for all concentrations of hydrogen peroxide. As shown in Figure 3b, color removals increased for all concentrations during the first 5 minutes. At the end of the 7.5th minute, color removal efficiency reached a maximum of 69% for 2000 mg/L H_2O_2 with an energy consumption of 0.108 kWh/m^3. After 7.5th minutes, removal efficiencies decreased for all H_2O_2 concentrations.

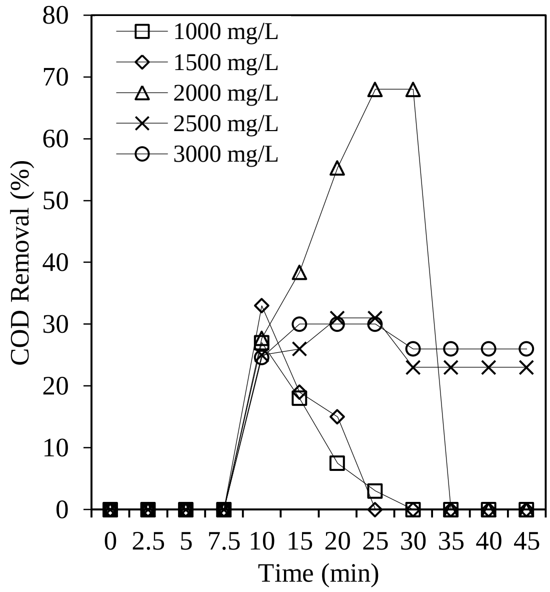

Figure 3a. The effect of H_2O_2 concentration on COD removal (Conditions: pH: 3, current density: 100 A/m^2, stirring rate: 250 rpm, inter-electrode gap: 1.5 cm).

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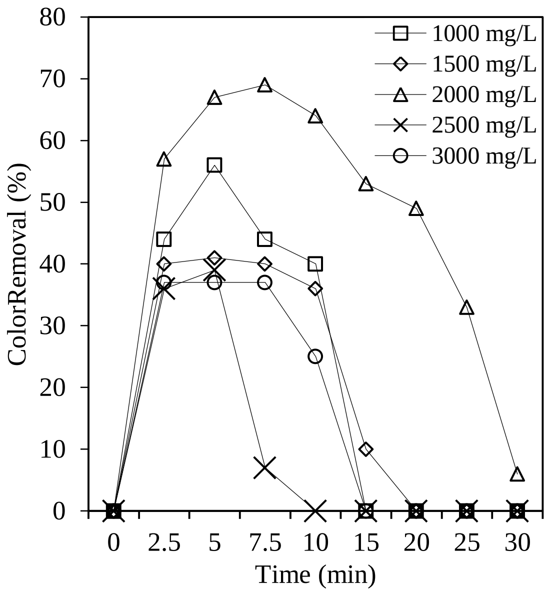

Figure 3b. The effect of H_2O_2 concentration on color removal (Conditions: pH: 3, current density: 75 A/m^2, stirring rate: 250 rpm, inter-electrode gap: 1.5 cm).

4. CONCLUSIONS

The results achieved can be summarized as follows:

$[H_2O_2]/[Fe^{2+}]$ molar ratios were 5.97 and 26.27 for maximum COD (68%) and color (69%) removal, respectively. These values show that relatively more H_2O_2 was consumed for color removal, and a total treatment cost of 71 USD/m^3 was calculated.

It is expected that COD will be removed with lower efficiency than color removal due to the breakdown of intermediate and by-products generated in wastewater treatment processes. However, this difference was not observed in this study, indicating that the color components in the leachate used in this study are resistant to removal such as COD. Physical removal of possible colloidal elements in the leachate before the electro-Fenton process should be considered a fundamental approach.

Higher color removal efficiencies were obtained in the first minutes, as the increase in the dissolved iron ions from the anode over time caused the wastewater to become colored.

The relatively high H_2O_2 concentrations consumed may limit the use of this method for the treatment of leachate consisting of high levels of organic compounds. Therefore, evaluating the electro-Fenton method as a pre-treatment process, especially before the biological treatment of large volume leachate, would be more beneficial and economical than using it alone.

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REFERENCES

[1] Oulego, P., Collado, S., Laca, A. and Diaz, M. (2016), Impact of leachate composition on the advanced oxidation treatment, Water Research, 88, 389-402.

[2] Asaithambi, P., Govindarajan, R., Yesuf, M.B. and Alemayehu, E. (2020), Removal of color, COD and determination of power consumption from landfill leachate wastewater using an electrochemical advanced oxidation processes, Separation and Purification Technology, 233, 115935.

[3] Solmaz, S.K.A., Birgul, A., Ustun, G.E and Yonar, T. (2006), Color and COD removal from textile effluent by coagulation and advanced oxidation process, Coloration Technology, 122, 102-109.

[4] Nidheesh, P.V and Gandhimathi, R. (2012), Trends in electro-Fenton process for water and wastewater treatment: An overview, Desalination, 299, 1-15

[5] He, H and Zhou, Z. (2017), Electro-Fenton process for water and wastewater treatment, Critical Reviews in Environmental Science and Technology, 47(21), 2100-2131.

[6] Sires, I and Brillas, E. (2018), Laboratori d'Electroquı´mica dels Materials i del Medi Ambient, Departament de Quı´mica Fı´sica, Facultat de Quı´mica, Universitat de Barcelona, Martı´ i Franque`s. Barcelona, Spain, 1-11.

[7] Liu, X., Zhou, Y., Zhang, J., Luo, L., Yang, Y., Huang, H., Peng, H., Tang, L. and Mu, Y. (2018), Insight into electro-Fenton and photo-Fenton for the degradation of antibiotics: Mechanism study and research gaps, Chemical Engineering Journal, 347, 379-397.

[8] Martinez-Huitle, C.A. and Brillas, E. (2009), Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Applied Catalysis B: Environmental, 87(3-4), 105-145.

[9] Babuponnusami, A. and Muthukumar, K. (2014), A review on Fenton and improvements to the Fenton process for wastewater treatment, Journal of Environmental Chemical Engineering, 2(1), 557-572.

[10] Altin, A. (2008), An alternative type of photo-electro-Fenton process for the treatment of landfill leachate, Separation and Purification Technology, 61(3), 391-397.

[11] Sruthi, T., Gandhimathi, R., Ramesh, S.T. and Nidheesh, P.V. (2018), Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes, Chemosphere, 210, 38-43.

[12] Wang, Z., Li, J., Tan, W., Wu, X., Lin, H. and Zhang, H. (2019), Removal of COD from landfill leachate by advanced Fenton process combined with electrolysis, Separation and Purification Technology, 208, 3-11.

[13] Atmaca, K. and Beyazit, N. (2020), The effect of cathode material, current density and anode-cathode gap on the COD and color removal from leachate by electro-Fenton method, Desalination and Water Treatment, 201, 431-437.

[14] APHA, AWWA, WEF. (2017), Standard Methods for the examination of water and wastewater, 23rd ed., American Public Health Association, American Water Works Association and Water Environment Federation, Washington DC.

[15] Alaton, I., Kabdaslı, I., Hanbaba, D. and Kuybu, E. (2008), Electrocoagulation of a real reactive dyebath effluent using aluminum and stainless steel electrodes, Journal of Hazardous Materials, 150(1), 166-173.

[16] Hammami, S., Oturan, N., Bellakhal, N., Dachraoui, M. and Oturan, M.A. (2007), Oxidative degradation of direct orange 61 by electro-Fenton process using a carbon felt electrode: Application of the experimental design methodology, Journal of Electroanalytical Chemistry, 610(1), 75-84.

[17] Ma, L., Zhou, M., Ren, G., Yang, W. and Liang, L. (2016), A highly energy-efficient flow-through electro-Fenton process for organic pollutants degradation, Electrochimica Acta, 200, 222-230.

[18] Hsueh, C.L., Huang, Y.H., Wang, C.C. and Chen, C.Y. (2005), Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system, Chemosphere, 58(10), 1409-1414.

[19] Atmaca, E. (2009), Treatment of landfill leachate by using electro-Fenton method, Journal of Hazardous Materials, 163(1), 109-114.