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Removal of Landfill Leachate's Organic load by modified Electro-Fenton process

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The leachate of landfill is a potential pollutant source containing a high rate of non- biodegradable pollutants and organic resistant material. The aim of this study was to evaluate the effects of the various operating parameters such as treatment time, current voltage (potential difference), distance between the electrodes, electrode material, initial pH value of the solution, initial concentration of hydrogen peroxide ($H_2\,O_2$), and the determination of optimal range by the Electro-Fenton (E-Fenton) process to remove refractory organic material from the landfill leachate. The treatment process was evaluated in a discontinuous reactor made up of a Plexiglas tank with the dimensions 20 cm × 16 cm × 10 cm, and an effective volume of 1 l. he highest removal efficiencies of the Chemical Oxygen Demand (COD), ammonia nitrogen (NH_3-N), phosphate, and turbidity were 85%, 30.9%, 78.2%, and 56.2%, respectively, under optimal operating conditions; these efficiencies were achieved in a duration of 30 minutes, a current voltage of 30 V, a distance of 3 cm between the electrodes, an initial pH value of 3.5 by the iron electrode, and the addition of hydrogen peroxide in a single step with a concentration of 15 mg/l. The results showed that the E-Fenton process, as a flexible technology, could be used for the treatment and the mineralization of landfill leachate with a high concentration of the pollutant.

Keywords: Current voltage, Electro-Fenton, Electrode, Turbidity

1. INTRODUCTION

The sanitary landfilling as the common and the main method, is used for removing municipal solid waste in many countries [1]. The generated leachate from these places contains a high rate of organic and inorganic pollutants, and heavy metals that depend on the age and the type of solid waste in the landfill; the treatment of this leachate is difficult. If the collection and the depletion of this leachate are not performed carefully and safely, it is likely that the potential pollution sources will become a threat to the soil, the surface water, and the groundwater [2]. Therefore, the leachate should be refined to reach the standard limit of depletion before it is released into the environment. The leachate treatment, owing to the presence of pollutants, is often the main concern in the management of municipal waste [3]. During the past two decades, among the physiochemical process, Advanced Oxidation Processes (*AOPs*) have been of great interest in the reduction of the organic load of landfill leachate. The AOP_S are able to transform non-biodegradable pollutants into non-toxic biodegradable materials [4]. This process is used when common techniques of treatment are ineffective, the kinetic energy of the process is very low, the pollutants are resistant to chemical oxidation and/or they are partially oxidizing in the liquid medium, or if the pollutants are more sustainable, and even more toxic by-products are produced from the primary compounds [5].

The most popular Advanced Oxidation Process (AOP_S) is the Fenton process, which uses Fe^{+2} and H_2O_2 (the Fenton reagent) to decompose refractory organic components [5]. In the Fenton reaction, the electron exchange between the ions of ferrous iron (Fe^{+2}) and H_2O_2 in the acidic condition lead to the production of the hydroxyl radical (OH°). (Eq. (1)) [6].

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^0 \qquad \text{Eq. (1)}$$

Owing to the high quantity of produced sludge during the Fenton treatment, the conventional Fenton process can be adjusted to E-Fenton by the combined application of electricity [1,4]. The E-Fenton process based on Fenton's chemical reactions is a suitable technology that is used in wastewater treatment. This process is one of the proposed options employed in the Electrochemical Advanced Oxidation Process ($EAOP_S$) [7]. The E-Fenton process is one of the electrochemical indirect methods. In this process, by the use of electricity power in an acidic medium and at the experiment's site, the production of the free hydroxyl radical (which has an unpaired electron and a short lifetime) and the oxidation of organic materials to CO_2 can be increased at the same time, and the iron sludge production will be reduced greatly; and there will not be other problems related to the transportation and the storage of H_2O_2. In addition, the costs of chemical consuming will be decreased significantly [8,9].

The main reactions of the E-Fenton process, which occur in the refined solution, include the following [8,10]:

$$Fe \rightarrow Fe^{+2} + 2e^- \qquad \text{Eq. (2)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{Eq. (3)}$$

$$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ + OH_2^0 \qquad \text{Eq. (4)} \quad \text{(in bulk of solution)}$$

$$Fe^{+3} + e^- \rightarrow Fe^{+2} \qquad \text{Eq. (5)}$$

$$Fe^{+2} + OH^0 \rightarrow Fe^{+3} + OH^- \qquad \text{Eq. (6)}$$

$$OH^0 + H_2O_2 \rightarrow OH_2^0 + H_2O \qquad \text{Eq. (7)}$$

The E- Fenton process is based on the employment of a sacrificial iron anode in the solution (Eq. (2)); the water molecules are simultaneously reduced at the cathode electrode surface (Eq. (3)). In the meantime, by entering H_2O_2 into the reactor in accordance with $(Eq_s.(1) and (4))$, the hydroxyl free radical is produced and Fenton's reaction is started. Furthermore, the continuous reduction of ferric ions leads to the regeneration of ferrous ions (Eq. (5)) [8]. Although Reactions 6 and 7 consume the amount of the produced hydroxyl radical as a result of the combination with ferrous ion and hydrogen peroxide, the produced hydroxyl radical, owing to its high oxidation potential, leads to the non-selective degradation and the destruction of organic pollutants and organic-based metals [7].

Recent studies have shown that the E-Fenton technique has been used in the treatment of various types of industrial wastewater such as olive oil extraction, distilling alcohol, in the tannery industry, in the treatment of wastewater as well as on a wide range of industrial pollutants. This technique is very effective and eco-friendly, and does not produce secondary pollutants [8]. Usually, the E-Fenton process is used less frequently than the common Fenton process for the treatment of landfill leachate [4,9,11]. In a study that was conducted by Mohajeri et al. (2010), the E-Fenton process was used to remove the COD and colour from the landfill leachate. By using this system and the tested operating condition, the maximum COD and colour removals achieved were 94% and 95.8%, respectively [4]. Lin and Chang (2000) examined the E-Fenton process in combination with the assistance of the chemical coagulation method as a form of pre-treatment before the biological treatment of landfill leachate. The authors used two pairs of anodic and cathodic electrodes (cast iron plates). The obtained removal efficiency of colour was 100% while they added H_2O_2 to the electrolytic cell before the start of electric current [11].

Furthermore, Zhang et al (2006), by using the Ti/RuO_2 and IrO_2 electrodes as anode materials and the addition of Fenton's reagent from the outside of the electrolytic cell, treated the resistant landfill leachate. In this study, the COD removal efficiency reached 83.4% after 75 minutes [9].

In the present work, we proposed a novel, E-Fenton process, in which Fenton's reagent was applied to generate hydroxyl radical in the electrochemical reactor and ferrous ion is regenerated by the reduction of ferric ion on the cathode. This process would be used for the treatment of high organic resistant material in landfill leachate. The effect of operational parameters such as reaction time, the intensity of electric current (voltage), the distance between the electrodes, the electrode material, the initial pH value, and the initial H_2O_2 concentration on the process efficiency of removing COD, ammonia nitrogen (NH_3-N), phosphate, and turbidity from the leachate were explored and discussed in order to determine the optimum conditions.

2. EXPERIMENTAL

2.1. Description of landfill and leachate features

The studied leachate sample was collected from the Kahrizak landfill site located in the Kahrizak area. The site lies between the latitudes of 35°18′ to 35° 35′ N and the longitudes of 51° 14′ to 51° 39′ E in the Rey township of Tehran, Iran. The leachate used in this study was collected from landfill drainage channels using 20-litre plastic pots, transferred to the laboratory under the standard method condition and stored at a temperature of 4℃ [12]. The amounts of NH_3-N, COD, phosphate, and turbidity in the leachate sample were immediately analysed. The characteristics of the leachate sample collected from Kahrizak landfill are presented in Table 1. All chemicals were prepared from purchased from Merck; all the tests were conducted at ambient temperatures (25 ± 2℃) and analysed based on the standard methods for the examination of water and wastewater (APHA) [12]. For pH value measurement, a pH meter (*HQ-USA-Hach*) was used before the measurement of the pH meter was calibrated at room temperature by a standard buffer (possessing pH values of 4.0, 7.0, and 10.0). The turbidity was analysed by a turbidity meter (*WTW-TURB355IR)*. The amount of NH_3-N was analysed by using Nessler's reagent in a colorimetric method. The COD was determined using the closed reflux titrimetric method. The phosphates of the samples were measured by a spectrophotometer (*DR/5000, Hach USA*). The Whatman filter paper (Grade 40) was used for the filtration of the samples and a digital multimeter (Rogle) was used to determine the electric current. To investigate, after the E-Fenton process, the efficiency of COD, $NH_3 - N$, phosphate, and turbidity were calculated via the fallowing formula (Eq.(8)):

$$CR\% \;=\; (\,C_0 - C_i/C_0 \times \,100) \qquad \text{Eq. (8)}$$

, where C_0 and C_i were the amount of COD, $NH_3 - N$, phosphate and turbidity before and after the E-Fenton process respectively[13].

Table 1. Qualitative characteristics of Kahrizak landfill leachate before treatment

Parameter		Value
Chemical Oxygen Demand (COD)	(mg/L)	70000-90000
Ammonia Nitrogen (NH_3_N)	(mg/L)	200-270
Phosphate	(mg/L)	70-90
Turbidity	(NTU)	1771
pH		7.2-7.7

2.2. Characteristics of reactor

All the tests were carried out in a discontinuous reactor with the dimensions 20 cm ×16 cm ×10 cm, and an effective volume of 1 l. The reactor was made of Plexiglas and had one cathode and one anode of iron or aluminium with a dimension of 20 cm × 12 cm × 1 cm. The electrodes of the monopolar array were connected to a digital DC power supply (*Matrix Ltd., MPS-30051 ,40 V, 3 A*) in a parallel configuration. In each phase, 1 l of the leachate sample was poured into the electrolytic cell; the initial leachate pH value was adjusted to the desired values with concentrated H_2SO_4 and $NaOH$ before adding Fenton reagents. Furthermore, a pre-decided amount of hydrogen peroxide solution (30%) was used to activate E-Fenton reactions in manually and in a single step before the electric current was turned on. During the experiment, in order to facilitate a better mixing of the reactor content, the reactor was equipped with a magnetic stirrer (200 rpm). During the E-Fenton process, certain parameters, including reaction time, current voltage (potential difference), distance between the electrodes, electrode material, the initial pH value of the solution, and the initial H_2O_2 concentration, were modified in order to obtain the optimal conditions for the removal efficiency of $NH_3 - N$, COD, phosphate, and turbidity (Table 2).

At the beginning of each phase, the electrodes were placed in hydrochloric acid (35% HCl V/V) for 5 minutes and then washed with water. After the E-Fenton process, the floc-containing solution was left for 60 minutes to settle, and then, it was filtered to prepare for chemical analysis. Finally, the analysis and the comparison of the results were performed by using the SPSS software (*version 23, SPSS Inc., Chicago, IL*) and the ANOVA test. All statistical analyses were considered to be significant when $p < 0.05$.

Table 2. Parameters evaluated and their ranges

Parameters	Conditions
Time of operation (min)	5,15,30,45,60,90,180
Inter –electrode distance(cm)	1,3,5,7.5,10
Applied voltage(V)	5,10,15,20,30,40
Electrode material	Al/Al- Fe/Fe
pH	3.5 ,5, 7.5 , 9 , 10.5
Initial H2O2 concentrations (mg/L)	7.5,15,100,200

3. RESULTS AND DISCUSSION

In this section, the results obtained from the study are provided and discussed.

3.1. Effect of reaction time on the efficiency of E-Fenton process

Reaction time is one of the effective factors in the advanced oxidation process that has a positive effect on the mineralization of leachate [14]. In order to determine the optimal time and its impacts on the E-Fenton process, the experiment was evaluated in durations ranging between 5 and 180 minutes with the injection of H_2O_2 (15 mg/l) at start of the process. Fig. 1 shows the impact of the reaction time on the profile of each pollutant. The results show that the maximum removal efficiency of COD (85%), phosphate (78.6%), $NH_3 - N$ (30.9%), and turbidity (56.2%) occurred in the first 30 minutes of reaction time, and later it gradually slowed down. It can be justified that the initial rapid degradation is mainly due to the prevalent degradation of some complex compounds of wastewater to simpler species. Over time, owing to the consumption of the H_2O_2 that was added to the system, the removal efficiency of the process is decreased after 30 minutes. Another reason behind the reduction of efficiency by increasing the residence time is due to the increase of the solution temperature that is being treated. The interesting point is that the kinetic reaction is accelerated by increasing the temperature of the electrochemical cell. As previously stated, therefore, On the other hand, by increasing the temperature over 25°C, the degradation of the parasitic reaction of H_2O_2 to oxygen and water is accelerated according to $(Eq_s\ (9) and (10))$, [15].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2\ H_2O \qquad \text{Eq. (9)}$$

$$2H_2O_2 \rightarrow O_2\,(\mathrm{g}) + 2\ H_2O \qquad \text{Eq. (10)}$$

The effect of increased reaction time on the reduction of organic load is consistent with the reported research of Zhang et al. (2006), which was conducted on landfill leachate such that the organic matter was degraded quickly during the first 15–30 min of reaction time, and then, it was slowly until it was completed in 75 minutes [9]. In another similar study by Mohajeri et al. (2010), which was conducted on the landfill leachate of Pulau Burung (in Malaysia), the maximum COD removal (94.07%) was achieved during the first 43 minutes of reaction time [4].

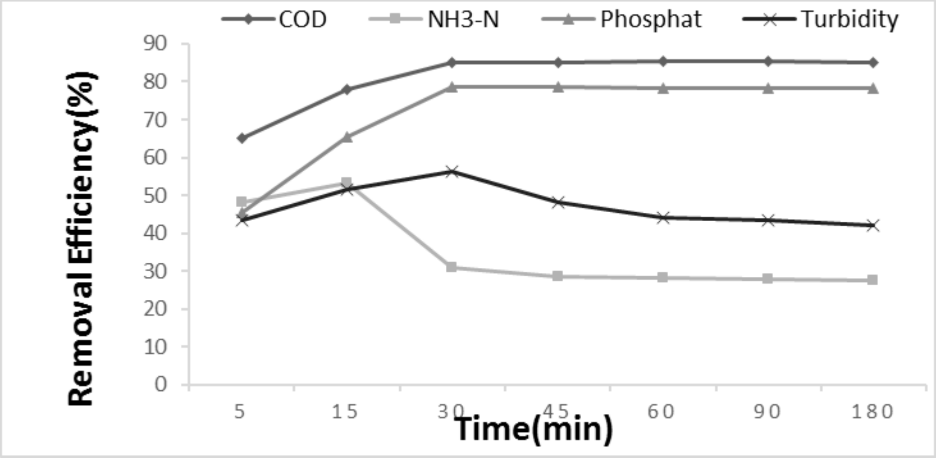

Figure 1. Effect of reaction time on COD, $NH_{3\_}N$ and phosphate and turbidity removal efficiency in the E-Fenton process. (Voltage: 30 V, distance between the electrodes: 5 cm, initial pH: 3.5, Electrode material: Fe – Fe, initial H_2O_2 concentration: 15mg/l)

Table 3. ANOVA of the parameters of leachate measured by E-Fenton process

Parameters	ANOVA	Degree of freedom	F test Statistic
COD (mg/L)	Reaction time	7	6295.1*
	Applied Voltage	6	6376.30*
	Initial pH	5	390474.01*
	Electrode material	2	25.3*
	Electrode distance	5	218133.6*
	Initial H_2O_2 concentration	4	255534.4*
NH_3- N (mg/L)	Reaction time	7	0.91^{ns}
	Applied Voltage	6	53.1*
	Initial pH	5	2654.9*
	Electrode material	2	62415.8*
	Electrode distance	5	36.05*
	Initial H_2O_2 concentration	4	38.21*
$PO_4 - P$ (mg/L)	Reaction time	7	175.13*
	Applied Voltage	6	2485.26*
	Initial pH	5	140.15*
	Electrode material	2	140.15*
	Electrode distance	5	1433.10*
	Initial H_2O_2 concentration	4	483.01*
Turbidity (NTU)	Reaction time	7	1.04^{ns}
	Applied Voltage	6	1.04^{ns}
	Initial pH	5	8953.3*
	Electrode material	2	3390671.9*
	Electrode distance	5	2593.07*
	Initial H_2O_2 concentration		2498.9*

The ANOVA results in the E-Fenton process express that the reaction time highly affects the reduction of COD and the phosphate of leachate, although it has no considerable affect on the reduction of $NH_3 - N$ and the turbidity of leachate (Table 3). Based on these results, the optimal reaction time was determined as 30 minutes for future experiments.

3.2. Effect of current voltage (potential difference) on the process efficiency

Another performance parameter in the E-Fenton process is the applied voltage to the electrodes. The production of the required Fe (II) for the chemical oxidation of Fenton is increased when the used current to electrodes is increased. However, it is possible that the obtained efficiency does not change significantly under the application of high DC current while the consumed energy is increased in this technique [10]. The applied voltage to the system must thus be determined carefully. Therefore, the next experiment was conducted to optimize the voltage of leachate in voltages ranging from 10–40 V under an optimum time of 30 minutes and the sudden injection of hydrogen peroxide (15 mg/l) at the start time of the process. As observable in Fig. 2, the organic load removal of leachate has an increasing trend. By increasing the voltage from 10 V to 30 V, the removal efficiencies of COD, $NH_3 - N$, phosphate, and turbidity were obtained as 85.3%, 30.9%, 78.2%, and 56.2%, respectively. By increasing the voltage from 30 V to 40 V, significant changes were not observed in the removal of the organic material. The results of this study suggest that the only source of Fe^{2+} ions for reaction are the iron electrodes in the system. The change of the applied voltage on the sacrificial cast iron anode electrode surface was a primary factor in electro-generation of Fe^{2+}in the E-Fenton process (Eq. (2)).

Determine the amount and concentration of released iron ions (Eq. (2)), regeneration of Fe^{2+} through continuous reduction of Fe^{3+} at the cathode (Eq. (5)) and finally the produced concentration of OH° related to voltage (that is applied to electrical cell) are controlled [3,17]. Fe^{2+} is so important that in its absence, H_2O_2 cannot oxidize big molecules. Of course, the incidence of parasitic adverse reactions is to be expected by increasing the voltage from 30 to 40 V. These reactions decrease the oxidation of organic compounds that will result in the reduction of process efficiency [18]. In other words, competitive reactions due to further increasing oxygen discharge at the anode (Eq. (11)) and hydrogen evolution at the cathode (Eq. (12)), experience a decrease in efficiency. Furthermore, H_2O_2 is reduced to water under high voltage, which, in turn, further decreases the efficiency (Eq. (9)) [9].

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad \text{Eq. (11)}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Eq. (12)}$$

In contrast, as observable in Fig. 2, due to the low concentration of the oxidant produced factor in the low voltage applied (0 V–10 V), the degradation rate is low. Therefore, the lower concentration of the hydroxyl radical is obtained in reaction Eq. (1). According to the results shown in Fig 2, a slight increase was seen in removal of $NH_3 - N$ in the E-Fenton process that may be ascribed; the oxidation of $NH_3 - N$ through the hydroxyl radical is quite low. The statistical analysis results from the E-Fenton process show that the applied voltage highly affects the reduction rate of COD, $NH_3 - N$, phosphate ($P < 0.05$), although it has no affect on the leachate turbidity reduction (Table 3). This behaviour, which demonstrates that the electrical current loading greatly affects the treatment efficiency, has been proved by several authors. The obtained results show that despite the increase of organic load removal of COD and TOC with the increase of the application current, when the applied current intensity was increased from the optimum amount, the amount did not experience significant changes or decreased slowly [10]. So, the best voltage to remove the organic materials obtained was 30 V.

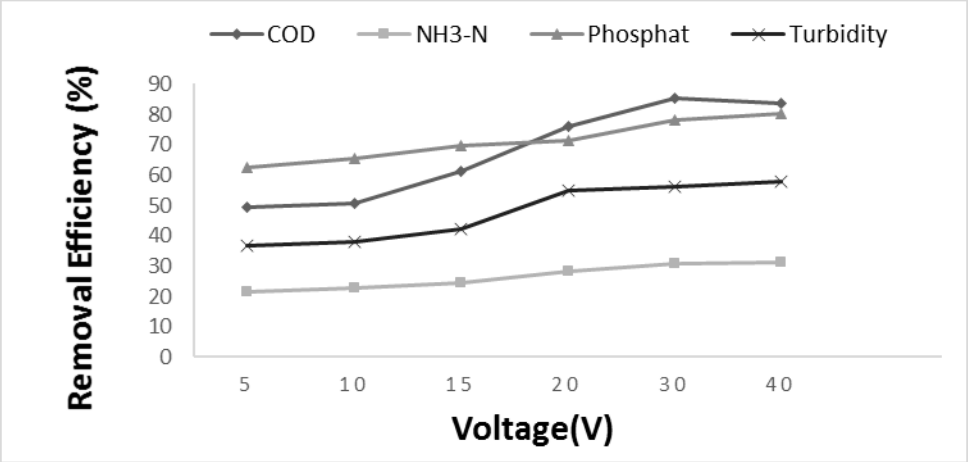

Figure 2. Effect of voltage changes on COD, NH 3-N, phosphate and turbidity removal efficiency in the E-Fenton process. (Time: 30 minutes, distance between the electrodes: 5 cm, initial pH: 3.5, Electrode material: Fe – Fe, initial H_2O_2 concentration: 15mg/l)

3.3 The effect of distance between the electrodes on the process efficiency

Another important parameter is the distance between the electrodes; this parameter also affects the removal of pollutants from the E-Fenton process. To find the optimum distance between the electrodes for the landfill leachate, the iron electrodes were placed at distances ranging from 1 cm to 10 cm under similar optimum voltage and time of the earlier steps. The effect of distance between the electrodes on the removal efficiency of pollutants has been shown in Fig. 3. by increasing the electrode distance from 1 cm to 3 cm, which changed the removal efficiency in COD, from 82.6% to 85%; in $NH_3 - N$, from 25.6% to 30.9%; in phosphate, from 75.6% to 78.6%; and in turbidity, from 48.2% to 56.2%. In this case, therefore, the maximum removal efficiency of COD, $NH_3 - N$, phosphate, and turbidity were 85%, 30.9%, 78.6%, and 56.2% at a distance of 3 cm between the electrodes. The lower removal efficiency of the pollutants will be obtained in shorter or higher distances than within this range.

In the E-Fenton process, Fe^{2+}will be regenerated by the reduction of the ferric ion at the cathode with the chain reactions of Fenton. If the electrodes are located at too short a distance from each other, the electro-regenerated Fe^{2+}can be easily oxidized to form a ferric ion at the anode, which, in turn, will prevent the efficiency of the Fenton chain reactions [10]. In other words, a decrease in the distance between the electrodes leads to the reduction of ohmic drop through the electrolyte and the reduction of the energy consumption. Furthermore, the higher distance between the electrodes limits the amount of transport volume of ferric ions to the cathode surface, which has the task of ferrous ion regeneration [9].

Therefore, the produced (OH°) from Reaction (1) could not increase the ferrous ion regeneration effectively. The statistical results express the affect of electrode distance on the reduction efficiency of COD, $NH_3 - N$, phosphate, and turbidity (Table 3). These results are consistent with the results obtained by Mohajeri et al. (2010) [4]. These authors kept the distance between the electrodes at a distance of 3 cm while Atmaca (2009) changed the distance between the electrodes and found the suitable distance to remove pollutants in range from 1.8 cm – 2.8 cm [2]. According to these researchers, increasing the distance between the electrodes increased the cost of the E-Fenton process consuming energy; therefore, the minimum distance between the electrodes must be selected. In general, the best results are obtained for minimum distance (3 cm) of the removal efficiency of organic pollutants in the E- Fenton method.

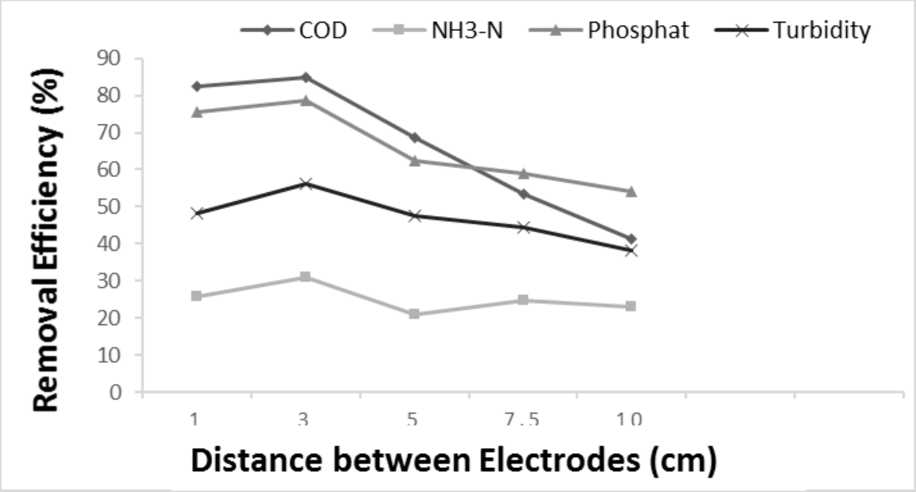

Figure 3. Effect of distance between the electrodes on COD, NH_3-N, phosphate and turbidity removal efficiency in the E-Fenton process. (Voltage: 30V, Time: 30 minutes, initial pH: 3.5, Electrode material: Fe – Fe, initial H_2O_2 concentration: 15mg/l)

3.4. Effect of electrode material on the efficiency of E-Fenton process

One of the key steps in the E-Fenton process is the selection of anode and cathode electrode material. For example, the selection of the unstable electrodes lead to the decomposition of the electrode in the electrolytic cells; on the other hand, a high-oxygen overvoltage anode can generate (OH°) in the E-Fenton process [18]. The commonly used electrodes for the anode are iron, aluminium, and platinum; the commonly used electrodes for the cathode are iron, aluminium, carbon; these materials are chosen because they are cheap, available, and effective [10]. In this research, to compare the electrode's material, the E-Fenton process was conducted by two different electrode materials, Al and Fe, under similar laboratory conditions; the reaction time, voltage, and optimum distance between the electrodes were obtained from the earlier steps with a pH value of 3.5, with the sudden injection of hydrogen peroxide (15 mg/l) during the beginning of the process. The results of two materials were compared. The results from the removal efficiency of COD, $NH_3 - N$, phosphate, and turbidity have been shown in Fig. 4. As observable in the figure, while the reaction time reaches 30 minutes, the results from a pair of iron electrodes for COD and $NH_3 - N$ were 85% and 30.9%, respectively, which was more effective than the use of Al electrodes; with the removal efficiencies for COD and $NH_3 - N$ as 72.6% and 24.2% by Al electrodes while the maximum removal efficiencies of phosphate and turbidity were 82.1% and 59.4%, respectively, which were obtained by a pair of Al electrodes.

The regeneration of the iron ions on the surface of the cathode (Eq. (5)) was one of the important reactions in the E-Fenton process. When the pair of the iron electrodes were used in the reactor, iron ions (with corrosion at the anode surface) were produced (Eq. (2)). It seems that the regeneration and generation of iron ions (Fe^{2+}) is increased when the iron electrodes have been used. Therefore, the consumption of the added hydrogen peroxide is increased through Fenton's reaction with the iron catalyst [19].

On the other hand, the increase of reaction time in the aluminium electrode's pair arrangement leads to Eq. (13) on the anode surface.

$$Al \rightarrow Al^{3+} + 3e^- \qquad \text{Eq. (13)}$$

The aluminium electrodes produced metallic ions. The increase of hydrogen peroxide (owing to the lack of Fe^{2+} ions solution as Fenton' reagent from the sacrificial iron anode) leads to the reduction of the organic compounds removal; therefore, the removal efficiency of the pollutants reduces [20]. So, the efficiency is higher because of a greater production of the oxidation reagent (OH°) in the arrangement of the iron electrode's pair [21]. In the studies conducted by Davarnejad et al. (2014) on the treatment of petrochemical plant wastewater, the use of the iron electrode pair had more acceptable efficiency than the aluminium electrode that was consistent with the results of the present study [19].

It is noteworthy that Al is more expensive than Fe (Al is about thrice the price of the latter). In addition, Al electrodes are consumed much faster than Fe; furthermore, its ability to release less toxic substances on agricultural land is one of the reasons for its selection in the following experiments [21].

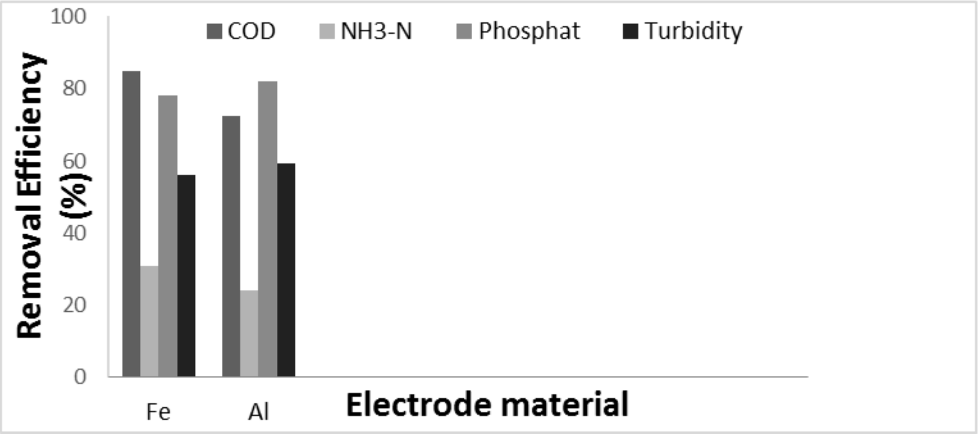

Figure 4. Effect of electrode material on COD, NH_3_N, phosphate and turbidity removal efficiency in the E-Fenton process. (Time: 30 minutes, distance between the electrodes: 3 cm, initial pH: 3.5, Voltage: 30 V, initial H_2O_2 concentration: 15mg/l)

According to the statistical analysis expression, the electrode material, in the E-Fenton process, significantly affects the reduction of COD, NH_{3}_N, phosphate, and the turbidity of leachate ($P < 0.05$) (Table 3). As a result, the pair arrangement of iron electrodes, as the optimum combination in removal efficiency, was performed in the following experiments.

3.5. Effect of initial pH of the solution on the process efficiency

The most effective and important parameter in the E-Fenton process is the pH value. The pH performance controls the production of hydroxyl radicals and concentration of ferrous ions in the solution. Therefore, this parameter affects the performance of oxidation. Depending on the nature of the treated compound and the type of the advanced electrochemical oxidation process, an acidic or alkaline solution is determined [6]. To test the effect of the initial pH value on the removal efficiency of the pollutants, its value has been set by adding diluted H_2SO_4 and $NaOH$ to the solution in the range between 3.5–10.5. Furthermore, the other parameters under optimum condition from the previous levels were conducted using the iron electrodes. The result of the pH effects on the removal amount of pollutants has been shown in Fig. 5; as specified, the maximum removal efficiency of the COD, $NH_3 - N$, phosphate, and turbidity were obtained at a pH value of 3.5. At this pH value, after 30 minutes of the start of the reaction, the removal efficiency of COD, $NH_3 - N$, and phosphate were obtained as 85%, 30.9%, and 78.2%, respectively. The removal efficiency decreased significantly by increasing the initial pH values of the samples so that the maximum removal efficiency of COD, $NH_3 - N$, and phosphate were 29.8%, 13.1%, and 45.3%, respectively at a pH value of 10.5. At the end of the 30 minutes of reaction time, the pH value has a direct impact on the stability of H_2O_2 and the determination of the type and the state of iron in solution [10]. The Fenton and the processes derived from it, such as E-Fenton, are conducted in an acidic solution with a pH value from 2–4 [18]. The process at a high pH value, especially higher than 5, is reduced intensively because the H_2O_2 is unstable in a basic solution and may decompose to give oxygen and water, and lose its oxidation ability in the alkaline condition [1]. Furthermore, the regeneration of Fe^{2+}(as a required factor in the process) is performed within a pH value ranging from 2–4 only via Eq. (5). By increasing the pH value to 9, the E-Fenton process is stopped and the coagulation process is replaced such that the efficiency will be further decreased [3]. On the other hand, a pH value below the optimal amount can impede continuous oxidation through the three following ways: (I) The $[Fe\,(H_2O)^{2+}]$ formed reacts steadily and slowly with H_2O_2 in order to produce fewer hydroxyl radicals at extremely low pH values [1].

(II) The scavenging effect of H^+ on OH° becomes more important at a lower pH [1]. The electro- generated H_2O_2 will react with H^+as $[H_3O_2^+]$, which leads to the reduction of the reaction rate between H_2O_2 and Fe^{2+} (Eq. (1)). Therefore, a lower amount of hydroxyl radical will be produced [10]. (III) The low pH can exceptionally inhibit the reaction between $Fe^{3+}$and H_2O_2 [10]. The removal efficiency reduction of turbidity with an increasing of the initial pH is another result that can be observed in Fig. 5. The removal efficiency of turbidity was 56.2% at the end of the treatment period (30 minutes). According to the results, the Fe^{3+} ions are precipitated as ferric hydroxide complexes ($Fe\,(OH_3)$) and ferric oxy-hydroxides ($FeOOH^{+2}$) at pH values above 4; therefore, the sludge production increases [22]. As iron has the ability of participation in Fenton's reaction in the solution state only, by increasing the pH, iron transforms to colloid, and then exits from the catalytic cycle after precipitation.

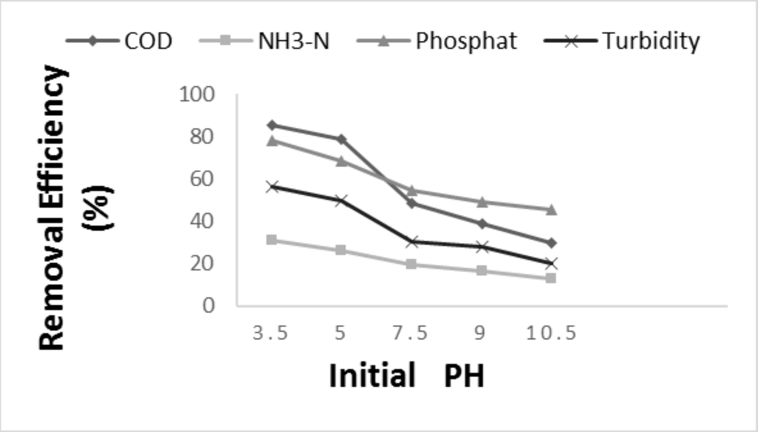

Figure 5. Effect of initial pH of the solution on COD, $NH_{3\_}N$, phosphate and turbidity removal efficiency in the E-Fenton process. (Time: 30 minutes, distance between the electrodes: 3cm, Electrode material: Fe – Fe, Voltage: 30 V, initial H_2O_2 concentration: 15mg/l)

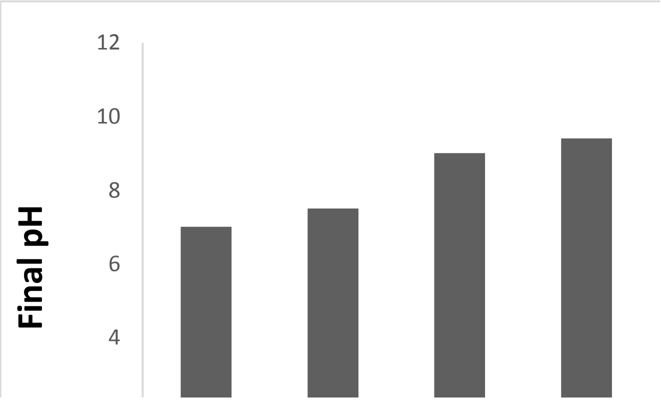

Figure 6. The pH change after E-Fenton process. (Time: 30 minutes, distance between the electrodes: 3 cm, Electrode material: Fe – Fe, Voltage: 30 V, initial H_2O_2 concentration: 15mg/l)

As a result, the sufficient catalyser will not remain in experimental environment that leads to the degradation of H_2O_2, the reduction of the organic load removal efficiency, and the increasing turbidity in the solution [23]. In addition to viewing the results, it can be concluded that $NH_3 - N$ failed to be oxidized effectively via the hydroxyl radicals. In this condition, a low removal efficiency is observed. This can occur probably owing to the slow absorption of the $NH_3 - N$ through the $Fe(OH)_n$ flocs that form in the reactor by increasing of the pH value. Another reason is the $NH_3 - N$ stripping through bubbles of gasses that are obtained from the electrolysis of produced water [2]. In addition, the pH is increased due to the reduction of water at the cathode electrode surface (Eq. (3)) and the formation of (OH°) in (Eq. (1)) during the E-Fenton process, which also has been reported in several studies [24]. In this research, the final pH value was about 7 when the initial pH was less than 3.5. However, final pH value has the small drop in alkaline solutions (pH > 8) as shown in Fig. 6. In this research, the optimal initial pH value to conduct the experiments was selected as 3.5. According to the studies that were conducted by Atmaca (2009) and Mohajeri et al. (2010), the effects of initial pH value on COD or TOC removal of landfill leachate were evaluated [2,4]. The optimal value of pH = 3.5 was determined by these authors, while Lin and Chang (2000) and Zhang et al. (2006) found the maximum removal at a pH value of 4 [9,11].

The result of the ANOVA test ($P < 0.05$) in the E-Fenton process shows that the initial pH is highly effective on the reduction efficiency of COD, $NH_3 - N$, phosphate, and turbidity (Table 3).

3.6. Effect of initial H_2O_2 concentrations on the removal efficiency

The determination of the optimal concentration of H_2O_2 in the E-Fenton process, especially due to the economic performance in relation to the cost of H_2O_2 and adverse effects that may effect on the performance of the process, is very essential [8]. In order to determine the effect of the initial concentration of H_2O_2, the removal efficiency of pollutants has been studied for H_2O_2 concentrations in the range of 7.5, 15, 100, and 200 mg/l at the optimum conditions (time = 30 min, voltage = 30 V, pH = 3.5, the distance between electrodes = 3 cm) and a combination of Fe–Fe electrodes. In Fig. 7, the effect of H_2O_2 concentration on the profile of each pollutant has been recorded. According to this graph, the removal efficiency of pollutants often had increased linearly for the removal efficiency ranging from 53.6% to 85% for COD, 24.6% to 30.9% for $NH_3 - N$, and 57.5% to 78.2% for phosphate by increasing the concentration of H_2O_2 from 7.5 mg/l to 15 mg/l. While by increasing the concentration of H_2O_2 to more than 15 mg/l, the removal efficiency of organic load decreased, in a concentration of 200 mg/l the removal efficiency reached below than 64.3% for COD, 26.4% for $NH_3 - N$, 58.1% for phosphate, and 35.4% for turbidity.

The results express the fact that the dosage of H_2O_2 is an important factor in the E-Fenton process [9]. In this method iron is used as andic electrode to produce Fe^{2+}, and H_2O_2 is used as oxidizing agent to produce hydroxyl radical [2]. Therefore, Fenton's reagents (Fe^{2+}+H_2O_2) are produced electrochemically and led to the formation of hydroxyl radical, which, because of high oxidizing properties, is able to completely oxidize organic materials or partially oxidize organic resistant materials and is able to convert them from landfill leachate into simpler organic compounds as well [25]. On the other hand, the residues formed in these processes, during settling, act as a coagulant and dissolve organic compounds and deposit them .Therefore, in this process organic matter removal is due to either the oxidation of particles or trapping particles in the formed clots [26]. It is necessary to determine the optimal concentration of hydrogen peroxide in the E-Fenton process due to the cost of its preparation and the adverse effects that may has on the process [27].

In fact, hydrogen peroxide is the main source of hydroxyl radicals (Fenton' reagent) in the Fenton and the E-Fenton processes. Increasing a certain amount of H_2O_2 leads to an increase in the concentration of OH°; therefore, the efficiency of organic load will increase. The excess or lack of a certain amount (optimum) will change the mechanism of Fenton's reaction and certain excessive reactions will occur [28]. The excessive addition of this material decreases the removal efficiency of pollutants because H_2O_2 has a scavenging effect on hydroxyl radicals [4]. This feature leads to the consumption of more hydroxyl radicals. This phenomenon has been shown in context of (Eq_s. (7) and (14)). The Eq. (7) is a direct effect of H_2O_2 increasing. Its product leads to production of the hydroperoxyl radical of [$OH°_2$] (a species with a much weaker oxidizing power compared to the hydroxyl radical) in solution. This radical will consume the OH° in Reaction 14; so, the efficiency of organic load will further decrease [24].

$$HO_2^0 + HO_2^0 \rightarrow H_2O + O_2 \qquad \text{Eq. (14)}$$

$$OH^0 + OH^0 \rightarrow H_2O_2 \qquad \text{Eq. (15)}$$

Furthermore, increasing the amount of hydrogen peroxide leads to the degradation of H_2O_2 to oxygen and water spontaneously, and the recombination of hydroxyl radicals. Therefore, decreasing the concentration of hydroxyl radicals and reducing the compound elimination efficiency (Eq_s. (10) and (15)).

Furthermore, this phenomenon was reported by (Mohajeri et al. 2010) [4]. On the other hand, in a low concentration of H_2O_2, the hydroxyl radicals will not be produced sufficiently to remove the organic compounds. According to the result of the ANOVA test ($P < 0.05$), the affect of oxidant concentration on the reduction COD, $NH_3 - N$, phosphate, and turbidity are observed. As the result, the optimal concentration of H_2O_2 was considered as 15 mg/l in order to conduct the experiments.

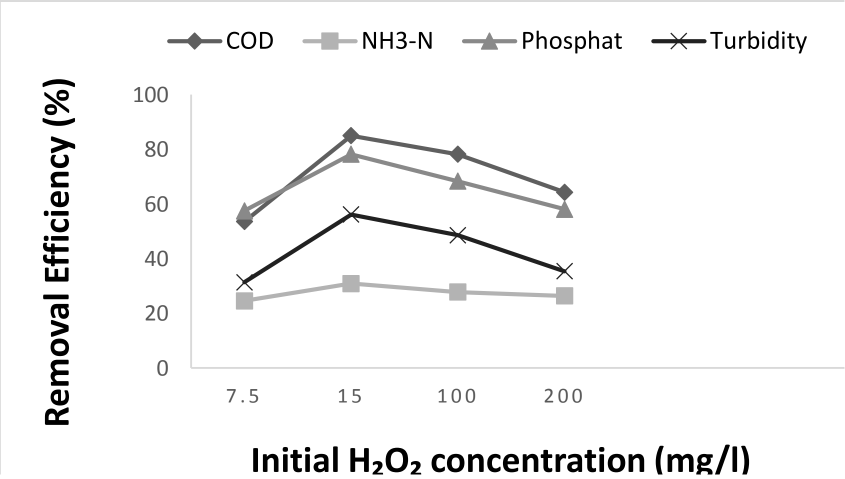

Figure 7. Effect of Initial H_2O_2 concentration on COD, NH_3_N, phosphate and turbidity removal efficiency in the E-Fenton process. (Time: 30 minutes, distance between the electrodes: 3 cm, initial pH: 3.5, Voltage: 30 V, Electrode material: Fe – Fe)

4. CONCLUSION

The results of this experiment showed that Fenton reagent was successfully produced in landfill leachate by an electrochemical process and the E-Fenton process is considered as possible process to reduce COD, $NH_3 - N$, phosphate, and turbidity of the leachate.

The maximum reduction efficiencies of COD, $NH_3 - N$, phosphate, and turbidity were experimentally deduced under the optimum condition (reaction time = 30 minutes, voltage = 30 V, distance between the electrodes = 5 cm, initial pH value = 3.5, initial concentration of $H_2 O_2$ = 15 mg/l) by the Fe electrodes as 85%, 30.9%, 78.2%, and 56.2%, respectively.

The statistical analysis expressed that the applied voltage, the distance between the electrodes, the material electrode, the initial pH value of the solution, and the initial concentration of $H_2 O_2$ were highly effective on the reduction of COD and the phosphate of leachate in the E-Fenton method. In addition, the results show that there is no interaction between reaction time and turbidity reduction as well as applied voltage and the reduction of $NH_3 - N$ and turbidity leachate. In general, it can be said that the E-Fenton process is an economical and eco-friendly process. This process is used to remove resistant and toxic compounds. The efficiency of this process can be improved by UV radiation or biological treatment.

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