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Application of electro-Fenton process for medical waste sterilization plant wastewater

Ömür Gökkuş*, Yalçın Şevki Yıldız

Faculty of Engineering, Department of Environmental Engineering, Erciyes University, TR-38039 Kayseri, Turkey, Tel. +90 3522076666; emails: omurgokkus@erciyes.edu.tr (Ö. Gökkuş), yyildiz@erciyes.edu.tr (Y.Ş. Yıldız)

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ABSTRACT

Sterilization at high-temperature water vapor is the most common method to make medical waste harmless before storage. Although it is microbiologically a very effective method, the effluent quality parameters of the wastewater from sterilization process do not meet the local or national standards. In this paper, we studied removal of total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP) of medical waste sterilization plant wastewater by electro-Fenton (EF) method. In addition, before the treatment studies, some experiments were also carried out to determine cathodically H_2O_2 production, which has vital importance to EF process. In the treatability study, anode and cathode configuration of the electrochemical cell were selected as platinum and graphite for Fenton's oxidation. Optimum parametric conditions for EF process were determined as initial pH (pH_i) 2, 700 mA current, 75 mg/L Fe^{2+}, and 0.2 L/min air flow rate, and at these optimum conditions 46.3% TOC, 27.7% TN, and 63.1% TP removals were achieved.

Keywords: Electro-Fenton; Medical wastewater; TOC removal; Phosphate removal; Nitrogen removal

1. Introduction

Effective sterilization has become a matter of increasing importance in medical solid waste management because of the concerns for hygiene and environmental pollution [1]. Most of the present medical waste sterilization methods are expensive or environmentally hazardous and cannot remove medical wastes safely. The mismanagement of medical waste can cause catastrophic effects not only to the people involved in clinical facilities, but also to those in the surrounding areas [2]. The most common method used to make medical wastes harmless before storage is sterilization at high-temperature water vapor both in Turkey and throughout the world [3]. High-temperature water vapor sterilization involves the use of steam under pressure, delivered at a particular temperature for an appropriate time in order to achieve the required lethality. This is normally achieved using autoclaves [4]. Medical wastewater contains chlorinated molecules in high concentrations, and heavy metals such as mercury and silver. But major contaminants for medical wastewater can be given as chemical oxygen demand (COD), phosphorus, and biological oxygen demand (BOD) at high concentrations [5]. It should be noted that removal of the wastewater from autoclave sterilization should meet the standards. Conventional treatment methods are insufficient to

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*Corresponding author.

treat wastewater because of its high contaminant properties. Therefore, different and more effective treatment options should be explored and evaluated [3]. In addition, this type of wastewater cannot be discharged to sewerage system untreated. At present, so many types of advanced oxidation processes (AOP's) have been developed and used to remove non-biodegradable organic pollutants from wastewater [6–8]. Nowadays, there has been an increasing interest in the use of *in situ* electrogenerated hydrogen peroxide by means of oxygen reduction (Eq. (1)) in Fe^{2+} containing acidic solutions in order to develop electro-Fenton (EF) processes to treat wastewater [9]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

One of the most popular electro-oxidation (EO) processes is the EF process which proceeds by the following chain reactions (Eq. (2)) [10]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \qquad (2)$$

Many authors have reported that different carbonaceous materials such as graphite [11–14], graphite felt [15–17], reticulated vitreous carbon (RVC) [18,19], activated carbon fiber (ACF) [20–23], carbon nanotube [24–26], BDD [27–32], and gas diffusion electrode (GDE) [18,33–36] could be used as cathode materials. According to Yahya et al., ciprofloxacin was completely degraded by EF and reached 94% of mineralization at optimum conditions using a carbon felt cathode and Platinum (Pt) anode [7]. Similar results were presented by Ganzenko et al. and the authors reported that complete mineralization of caffeine solution (>93%) would almost be achieved after 2 h treatment with 1,500 mA current value [37].

According to the Reaction (2), in Fe^{2+}-catalyzed Fenton reactions, ferrous iron continuously regenerated at the cathode (reaction (3)) thus avoiding Fe^{3+} accumulation in the medium and consequently eliminating the production of iron sludge [15]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ (at carbon based cathode)} \qquad (3)$$

Additionally, as is known, iron ions may be removed from the wastewater after the treatment of EF oxidation by adding alkaline chemicals, resulting in the generation of chemical sludge. This disadvantage resulting from the sludge treatment is important for EF process. It is evident that the decrease in the Fe^{2+} dosage will reduce the amount of chemical sludge and save chemicals.

Graphite is one of the most widely used electrode material for electrochemical production of hydrogen peroxide because it has low cost, high oxygen reduction activities, high hydrogen evolution over potential, and low hydrogen peroxide decomposition activity [8,21]. Wang et al. investigated the removal of the color from the real dyeing wastewater by the EF technology using graphite cathode, and they achieved 70.6% color removal under the specified operation conditions in 150 min. On the other hand, Pozzo et al. indicated that the graphite cathodes would be affected by the working potential due to the simultaneous occurrence of several side reactions, and they suggest that the optimal value must be determined between current efficiency and reaction time [38].

EF technology for treating synthetic wastewater with relatively less constituents and low dye concentrations has been used by so many researchers. However, the studies which focused on the treatment of real wastewater using EF technology are quite limited. This work investigates the feasibility and efficiency of total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP) removals from a real wastewater using the EF technology. In this study, the performance of the graphite electrodes was evaluated by the H_2O_2 production and also, the removal efficiency of EF system was investigated for medical waste sterilization plant wastewater.

2. Experimental

2.1. Effluent

The wastewater used in this work was collected from a Medical Waste Sterilization Plant Wastewater (MWSP) with 5,000 kg per day capacity, located in the city of Kayseri (Turkey), producing approximately 50 m^3 of wastewater daily. The wastewater resulting from various operations such as shredding compacting and vapor sterilization at high temperature (121–148°C) of the medical waste were kept in refrigerator at 4°C without any pre-treatment. The chemical analysis result of MWSP is given in Table 1.

According to Table 1, COD_{total} and $COD_{soluble}$ values are close to each other. Likewise, TP and TN values of MWSP are 102 and 109 mg/L, respectively, a figure much higher than what is specified in the regulation value. Therefore, this type of wastewater cannot be easily treated by traditional methods such as biological treatment to meet the local wastewater discharge requirement.

Table 1
The characteristics of the wastewater sample taken from MWSP

Parameters	Values	Permissible level[a]
pH	8.8	6.5–10
Conductivity (μs/cm)	1,163	–
TOC (mg/L)	648	–
COD_{total} (mg/L)	1,891.9	1,000
$COD_{soluble}$ (mg/L)	1,360.5	–
TP (mg/L)	102.1	10
TN (mg/L)	109.4	60
SS (mg/L)	467.5	400
TSS (mg/L)	1,930	–
Turbidity (NTU)	675	–
BOD_5 (mg/L)	906	600
SO_4 (mg/L)	31	1,000

[a] Kayseri Water and Sewerage Administration (KASKI) recommendations for effluent discharge in sewer (KASKI 2013).

2.2. Chemicals and electrodes

All chemicals were analytical grade reagents and used as received. All solutions were prepared with ultrapure water obtained from Elga Option Q7 system with resistivity 18.2 MΩ cm^{-1} at room temperature. Sodium sulfate, sodium nitrate, and sodium chloride (Merck, 99.5%) solutions were used as supporting electrolytes. SEM images of the graphite used in the EF experimental studies are depicted in Fig. 1.

The graphite sheets, each with the area of 53.9 cm^2 were purchased from SKC Carbon Co. (Istanbul, Turkey). After each treatment period the cathode was immersed in sulfuric acid solution for one night, then washed with distilled water and dried in air. Iron(II) sulfate heptahydrate (Merck, 99.5%) and iron(III) chloride (Merck, 99%) were used as catalyst in EF experiments. On the other hand, Pt anode was successfully used to degrade various toxic and recalcitrant compounds such as herbicides and pesticides, and also Pt anode is environmentally preferred since it releases much lower amounts of toxic metallic ions [39,40]. The Fe^{2+} concentration was determined using the 1,10-phenanthroline (Aldrich 97%), and also ammonium acetate (Merck 96%) (pH Buffer) and HCl (Merck, 37%) were used for iron(II) analysis.

Phosphate standards were prepared from KH_2PO_4 (Merck, 98%). Potassium titanium (IV) oxalate (Alfa Aesar) was used to determine electrogenerated H_2O_2 concentration. H_2O_2 (Merck, 35%) was used as standard for hydrogen peroxide analysis. The mixture of ammonium molybdate (Carlo Erba, 83%) and ammonium metavanadate (Alfa Aesar, 99%) were used as color developer in phosphorus analysis. Potassium dichromate (Merck 99.5%), mercury chloride and silver sulfate (Merck, 95–97%) were used as COD reagents. Potassium hydrogen phthalate (Carlo Erba, 99.5%) was used for preparation of standard calibration curves for COD and NPOC analyses.

2.3. Electrolytic system

The experiments were performed in a rectangular open and undivided cell with the volume of 500 ml (110 × 75 × 85 mm), supplied with a magnetic stirrer (800 rpm) (Fig. 2). A platinum wire (length = 150 mm) was used as the anode. Two graphite cathodes were used in the electrolytic cell and anode was placed horizontally between the cathodes. Initial pH of the solution was adjusted to the desired value with 1 N H_2SO_4 and 1 N NaOH. The potential of work

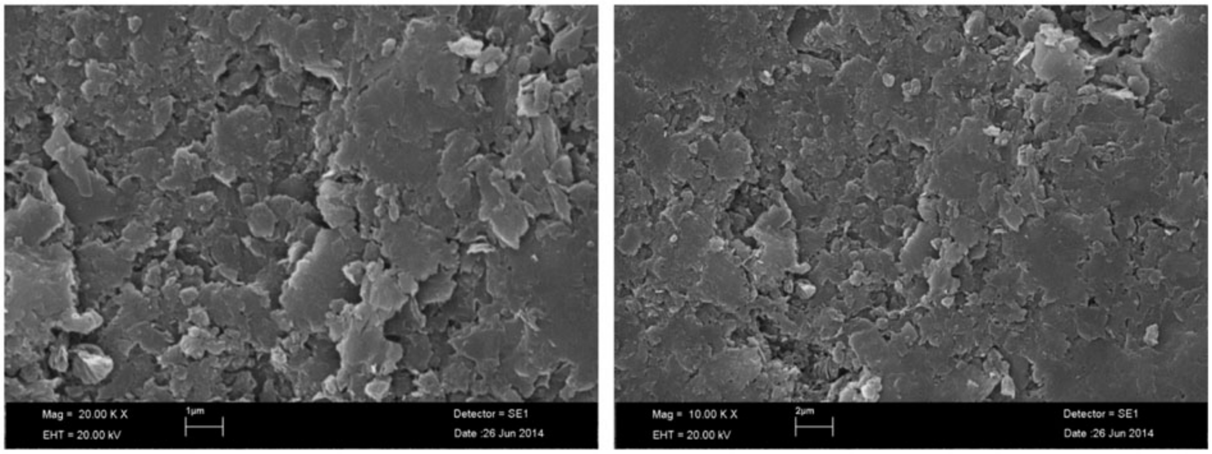

Fig. 1. SEM images of the graphite sheets used in the EF studies.

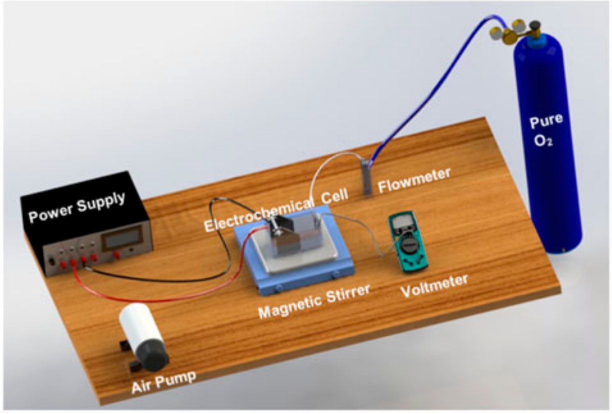

Fig. 2. Schematic diagram of experimental setup.

electrodes was controlled by a DC (GWinstek SDP 3,606, 30 V, 6A). The graphite cathodes were fed with variable pure O_2 gas (96% purity) flow rates (0.1–1.5 L/min) to continuously generate H_2O_2 from O_2 reduction. The distance between anode and cathodes was kept constant as 4 cm.

The reactor was also equipped with an air-supplying system that consisted of an air pump and a stone diffuser for mixing the contents of the reactor. Electrolysis time was 450 min for each run. Samples were withdrawn from the reactor at 50 min time intervals. Aliquots of 2 mL were withdrawn from electrolyzed solutions and centrifuged at 4,000 rpm before analysis. All the experiments were performed at room temperature.

2.4. Analytical procedures

The solution pH was monitored with a WTW inolab 7110 pH-meter. The mineralization of medical waste sterilization plant wastewater was monitored from their TOC decay, determined with a Shimadzu TOC-L analyzer. TN was obtained with a Shimadzu TNM-1 unit coupled to the TOC analyzer. Ferrous ion concentration was measured by spectrophotometric method (λ = 510 nm) using 1,10-phenanthroline a spectrophotometric reagent for iron [41]. The analysis of phosphorus was carried out using the yellow vanadomolybdophosphoric acid method by a spectrophotometer (Hach-Lange DR 2500) according to the Standard Methods for Examination of Water and Wastewater [41]. Hydrogen peroxide concentration was measured by absorbance measurement (λ = 410 nm) of a colored complex formed by reaction with potassium titanium oxalate [34,42–44]. The titanium(IV)-peroxide complex is yellow-orange in color and absorbs at a wavelength of 410 nm. All experiments were repeated twice, and averages were reported.

2.5. Experimental procedures

2.5.1. Electrogeneration of H_2O_2 at graphite cathode

The experiments were performed under galvanostatic conditions using 500-ml distilled water in electrolytic system described in Section 2.3. In these experiments graphite electrode was used in order to investigate the generation of H_2O_2 and except where otherwise specified 50-mM Na_2SO_4 was added to provide ionic strength. In H_2O_2 generation tests iron was not added in order to prevent hydrogen peroxide from being consumed in the Fenton reaction. In the electrolytic system, pure O_2 were bubbled near the cathode to produce H_2O_2 by reduction of dissolved oxygen in acidic solutions containing dilute supporting electrolyte. All H_2O_2 production trials were carried out at room temperature for 100 min. At 10 min intervals, 2-mL samples were taken for analyzing the concentration of the H_2O_2, and the cell potential values were recorded.

2.5.2. EF experiments

The experiments were performed under galvanostatic conditions using 500-ml distilled water in electrolytic system described in Section 2.3. The cell was operated in constant current mode (I) between 300 and 1,000 mA using power from a DC supply during the EF experiments. Electrolyses were carried out on MWSP which was continuously saturated with pure oxygen by bubbling the gas inside the cell at different flow rates of 0.1–1.0 L min^{-1}. Unlike the experiments of H_2O_2 electrogeneration, iron(II) or (III) as catalyst at different concentrations was added to the electrolytic system to initiate the Fenton reactions in EF experiments.

3. Result and discussion

3.1. Electrogeneration of hydrogen peroxide using graphite cathode

Carbon is widely used as a cathode material for hydrogen peroxide generation because it exhibits a range of electrochemical activities towards oxygen reduction, high over potential for hydrogen evolution and low catalytic activity for hydrogen peroxide decomposition [45]:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (4)$$

The achievement of the EF process in the degradation of organic pollutants depend strongly on amount of hydroxyl radical produced at the medium. Hydroxyl radical production is affected from H_2O_2 production performance of the cathode [46]. Therefore, it is important to investigate the effect of cathode materials in the production of H_2O_2 in absence of iron ions. To this end, we investigated the optimum conditions of system variables at different levels in order to reach optimum H_2O_2 production.

Several experiments were carried out to determine the effect of the operational parameters including the pH_i, current, concentration of supporting electrolyte and pure O_2 flow rates on the generation of H_2O_2 using the graphite cathode.

3.1.1. Effect of pH on H_2O_2 production

It is a well-known fact that optimum value of the pH is 2–4 for Fenton reactions. Likewise, electrochemically H_2O_2 generation needs acidic pH values due to instability of H_2O_2 in basic solution, especially $pH > 5$ [47]. Fig. 3 shows the variation in the amount of electrogenerated hydrogen peroxide dependent upon pH_i of the solution.

As is seen in Fig. 3, a low pH is favorable for the electrogeneration of H_2O_2 since its synthesis consumes protons. On the other hand, a high proton concentration may promote H_2 evolution and reduce the current efficiency [48]. Fig. 3 also indicates that when pH is 2, 3, 4, 5, and 6, the concentration of H_2O_2 are 28.97, 210.71, 118.22, 192.92, and 183.74 mg/L, respectively. H_2O_2 is electrogenerated at cathode surface by reduction of dissolved oxygen in acidic medium, so the lower pH is beneficial to the higher H_2O_2 production [49]. Contrary to the expectations, a remarkable decline was observed when pH decreased under pH 3. This result could be explained by the fact that H_2O_2 remains steady at low pH values below 3 because of the formation of oxonium ion ($H_3O_2^+$) [20,47]. In addition to this, the higher level of hydrogen ion also promoted the decomposition of H_2O_2 [49]. As a result, in this study, pH 3 is the optimal pH value for the electrogeneration of hydrogen peroxide.

3.1.2. Effect of current on H_2O_2 production

To determine the influence of the current on hydrogen peroxide production, a further series of electrolyses was carried out at the selected current values between 30 and 80 mA. It can be seen in Fig. 4 that during the 100 min of electrolysis, the H_2O_2 concentration exhibits a gradual rise in all of the applied current values, and it then continues to increase even if it is slight.

Fig. 4 shows the time course of H_2O_2 electrogeneration depending on different current values. The curves indicate that H_2O_2 generation increase with increasing current value, but after the current of 70 mA, there is a reduction in the production of H_2O_2 because of side reactions such as the 4-electron reduction of oxygen to water and the decomposition of hydrogen peroxide according to the related Eq. (5) and reaction as follows [38]:

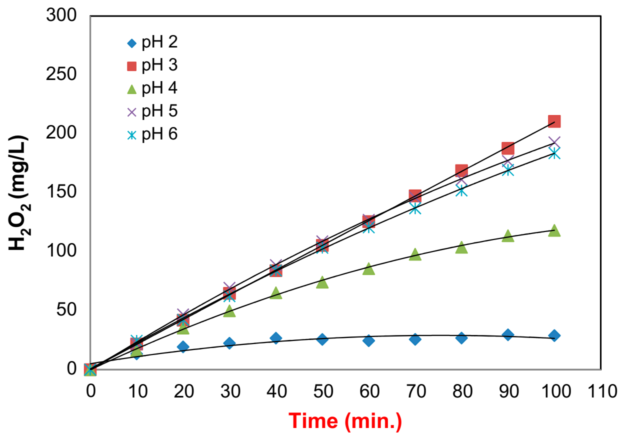

Fig. 3. Influence of pH_i on H_2O_2 production. [Conditions: $I = 60$ mA, pure O_2 flow rate at 0.3 L min^{-1}, 50 mM Na_2SO_4].

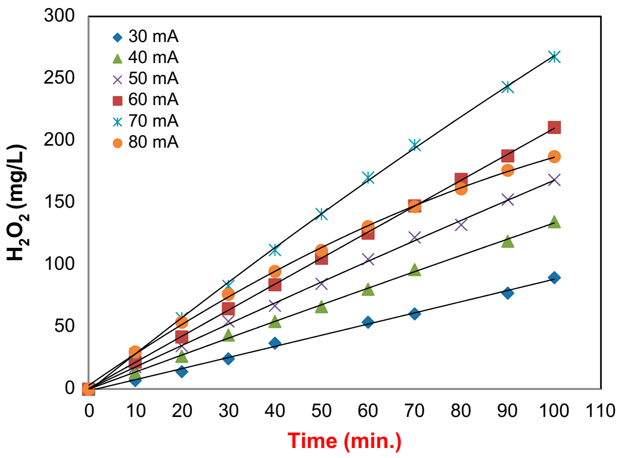

Fig. 4. Influence of current on H_2O_2 production. [Conditions: pH 3, pure O_2 flow rate at 0.3 L min^{-1}, 50 mM Na_2SO_4].

$$O_2 + 4H^+ + 4e^- \rightarrow 6H_2O \quad (5)$$

Moreover, the competitive electrode reactions, such as the discharge of O_2 and H_2, also inhabit the reactions for H_2O_2 generation [20]. The data obtained from the experiments showed that 70 mA current value provided the best H_2O_2 production result. At this optimum current value, 267.58 mg/L H_2O_2 was produced electrochemically.

3.1.3. Effect of supporting electrolyte concentration on H_2O_2 production

Electrolyte improves the solution conductivity, and accelerates the electron transfer, thus benefiting the electrochemical reactions. Therefore, supporting electrode is necessary, especially in the solution without enough conductivity [47]. In this study, sodium sulfate was used as supporting electrolyte with different concentrations between 20 and 80 mM. The obtained results were given in Fig. 5.

According to Fig. 5, 50-mM supporting electrolyte concentration provided the best H_2O_2 production result. This could be explained by the fact that higher Na_2SO_4 concentrations led to higher current, which resulted in faster and larger production of hydrogen peroxide [47]. However, as mentioned before too much increase in current may lead to side reactions.

3.1.4. Effect of pure O_2 gas flow rate on H_2O_2 production

When the oxygen flow rate is increased, the amount and mass transfer of dissolved oxygen increases as well [50]. In the EF process, H_2O_2 is generated from oxygen reduction. The efficiency of oxygen is not only important for the generation of H_2O_2, but for the running cost [39,47]. Fig. 6 shows the seven different scenarios for the determination of optimum O_2 flow rate, and one of them was carried out under oxygen-free medium (0.3 L/min N_2) in order to exhibit the importance of O_2 for H_2O_2 production.

In this part of the study, a series of tests were carried out to evaluate the influence of supplied gas on the hydrogen peroxide production. For this purpose, pure oxygen gas flow rate was changed in the range of 0.1–1.5 L/min and also, hydrogen peroxide production potential was evaluated in the case of oxygen-free medium by passing through nitrogen gas at 0.3 L/min constant rate in the solution. The Fig. 6 shows that inflow gas rate notably affects the concentration of hydrogen peroxide. In oxygen-free electrolysis study, only 7.4 mg/L hydrogen peroxide was achieved in 100 min. On the other hand, maximum hydrogen peroxide production was determined as approximately 268 mg/L at 0.3 L/min pure oxygen flow rate. When oxygen flow rate was increased more than 0.3 L/min, a decrease in hydrogen peroxide production was observed due to the resistance of the medium that increased with the excessive mass of bubble in the constant potential system [49].

3.2. Treatability studies of MWSP using EF process

After determining the optimum conditions for graphite electrode concerning electrochemical H_2O_2

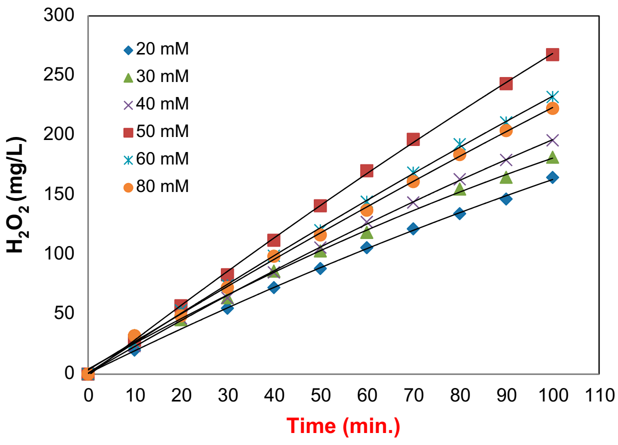

Fig. 5. Influence of supporting electrolyte concentration on H_2O_2 production. [Conditions: pH 3, $I = 70$ mA, pure O_2 flow rate at 0.3 L min^{-1}].

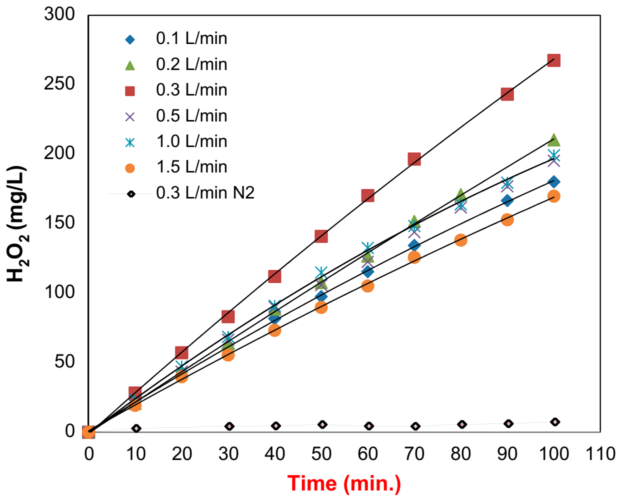

Fig. 6. Influence of O_2 flow rate on H_2O_2 production. [Conditions: pH 3, $I = 70$ mA, 50 mM Na_2SO_4].

production, the second step of the study investigated its effectiveness in EF process. For this purpose, MWSP was used as a pollutant to examine the oxidation performance of EF process. Fenton reaction could be catalyzed by several metal ions such as Fe^{2+}, Co^{2+}, Ag^{+}, Cu^{2+}, Mn^{2+} [51]. In this study, Fe^{2+} was used as catalyzed for Fenton reactions. Initially, the optimum conditions for H_2O_2 production were used to treat MWSP by EF process.

Contrary to expectations, only 8.2% TOC removal was achieved by using EF treatment at optimized condition for the production of H_2O_2, and this result is not sufficient to reach the permissible levels to discharge. The obtained results indicate that optimized condition for electrochemical H_2O_2 production is not feasible for EF treatment application. According to the preliminary test, it is clear that higher current and longer electrolysis time are required to achieve more treatment efficiency.

Findings urge us to conduct a different optimization study for treatment of MWSP by EF method. In this part of the study, optimum conditions were investigated for the EF treatment of a real wastewater.

3.2.1. Effect of pH on EF treatment

Fenton processes are efficient in the acidic range and the oxidation ability of hydroxyl radical was fairly strong at acidic conditions [52]. It has been confirmed that the optimal value of pH is 2–4 [39]. Only strong acid media was investigated in order to maintain increase in the mineralization of MWSP. Fig. 7 shows the TOC removal along the time for all pH conditions studied.

According to Fig. 7, the highest mineralization was found when pH was maintained at a value around 2. The main reason for this may be explained by the increase in ionic strength at excessive low pH. Despite the fact that many researchers report pH 3 as the most convenient pH value for Fenton reaction; our results were similar to those of Rosales et. al. [53]. In fact, Fenton process becomes less effective under pH 3 because the regeneration of Fe(II), through reaction between Fe(III) and H_2O_2, is inhibited, but we didn't encounter such a situation since the Fe(II) is continuously regenerated from the reduction of Fe(III) on the cathode surface [53].

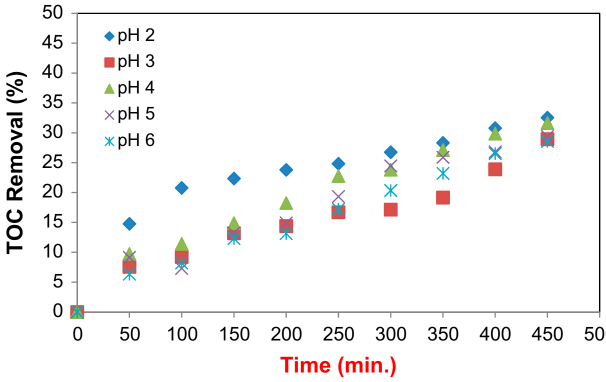

Fig. 7. Investigation of optimum pH value for TOC removal of MWSP during EF treatment. [Conditions: I = 500 mA, Fe^{2+} = 25 mg/L (0.45 mM), pure oxygen flow rate = 0.3 L/min].

3.2.2. Effect of Fe^{2+} on EF treatment

It is known that hydroxyl radicals could be generated from Fenton's reagent, i.e. hydrogen peroxide and ferrous ions with proportionate ratios (Eq. (2)). There exists an optimal concentration of ferrous ions for the oxidative degradation of TOC [44]. On the other hand, the addition of too much Fe^{2+} ions lead to scavenging effect as a result of ferrous ions reacting with the hydroxyl radicals second time [54].

As seen in Fig. 8, TOC removal does not show a continuous rise with increasing Fe^{2+} concentration. These results can be explained by *in situ* H_2O_2 production into the reactor medium. There is a suitable molar rate between H_2O_2 and Fe^{2+} ions for $OH^{\cdot}$ production. If Fe^{2+} ions, which are added externally, exceed the molar ratio, EF system may tend to result in chemical coagulation instead of producing hydroxyl radical production [51]. For this study, optimum Fe^{2+} concentration was achieved as 75 mg/L and TOC removal was 37% at this optimum concentration. When the Fe^{2+} concentrations exceeded the optimum value, EF treatment system began to lose its stability.

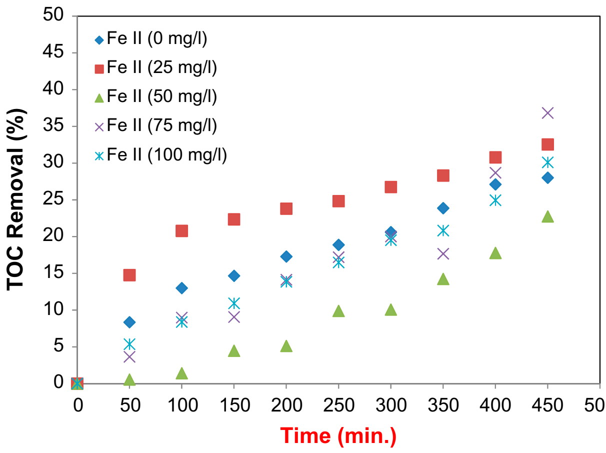

Fig. 8. Investigation of optimum Fe^{2+} concentration for TOC removal of MWSP during EF treatment. [Conditions: pH 2, I = 500 mA, pure oxygen flow rate = 0.3 L/min].

3.2.3. Effect of applied current on EF treatment

Cathodic potential is a highly effective parameter for electrochemical H_2O_2 production, and also undoubtedly, it is one of the most important factors that determine treatment performance [55]. Although increase in current values cause an increase in removal efficiency in such processes as electrocoagulation process, this fact is not valid for EF processes. With the increase in the voltage or current applied, the degradation of substrate increases at the beginning, and then trends to be stable and even worse because of the side reactions and polarization [39].

The influence of applied current on TOC removal has been investigated in the range of 300–1,000 mA and the results are depicted in Fig. 9.

These data show a gradual increase in TOC removal rate with raising current. This enhancement of the oxidation power can only be explained by the greater production of H_2O_2 from Eq. (1) leading to generation of higher amount of hydroxyl radicals from Fenton's reaction Eq. (2). Fig. 9 also shows a decrease in TOC removal percentages after 700 mA. Özcan et al. report that at higher current values, the $4e^-$ reduction of O_2 leading to the formation of H_2O (Eq. (5)) begins to compete with the formation of H_2O_2 (Eq. (1)) [56]. As a result of this, the mineralization decreased after 700 mA.

3.2.4. Effect of oxygen flow rate on EF treatment

Oxygen is one of the most important parameters for EF system because increasing the oxygen distribution rate can increase the dissolved oxygen concentration into the solution and the mass transfer rate of dissolved oxygen and finally increase the production of H_2O_2 production [47]. Using of pure oxygen is not only important for the generation of H_2O_2, but for the running cost. There are generally two approaches to improve the production of H_2O_2. One is to select a cathode with large surface area, and the other is to enhance the oxygen flow rate [39]. The effects of the O_2 flow rate on EF treatment are shown in Fig. 10.

In order to investigate the effect of oxygen flow rate on EF treatment, gas flow rate has been changed in the range of 0.1–1 L/min. As expected, TOC removal percentages increased with increasing oxygen flow rate. According to the results, the best TOC removal was achieved at 1.0 L/min oxygen flow rate. As shown in Fig. 10, it is clear that O_2 flow rate has a significant effect on removal of TOC. Degradation is faster at 1.0 L/min, and better results are attained (44%). On the other hand, TOC removal is 33% at 0.1 L/min oxygen flow rate in 450 min electrolysis time. Consequently, it is clear that EF treatment performance is seriously affected by oxygen flow rate.

3.2.5. TP and TN removal of MWSP by EF treatment at optimum conditions

Since organic nitrogen and inorganic nitrogen are included in TN, the significant decrease in TN concentration indicates that a major nitrogen removal by gaseous nitrogen (N_2 or NO_x) is achieved along with the mineralization of organic carbon. The decrease in TN concentration and the continuous increase in NH_4^+ concentration indicates the reduction of NO_3^-. The reduction function of graphite cathode might be used to explain the nitrogen removal [34]. Pozzo et al. reported that hypophosphites are intermediates of

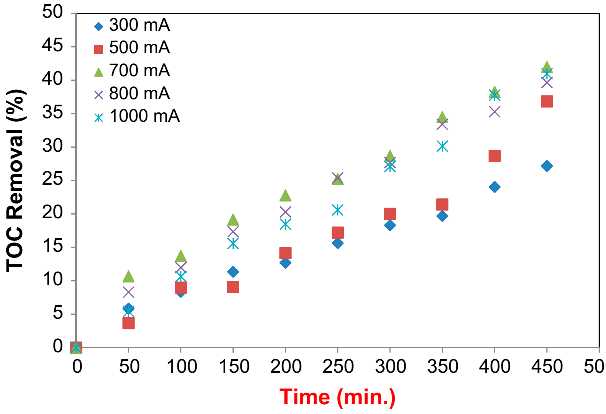

Fig. 9. Investigation of optimum current for TOC removal of MWSP during EF treatment. [Conditions: pH 2, Fe^{2+} = 75 mg/L, pure oxygen flow rate = 0.3 L/min].

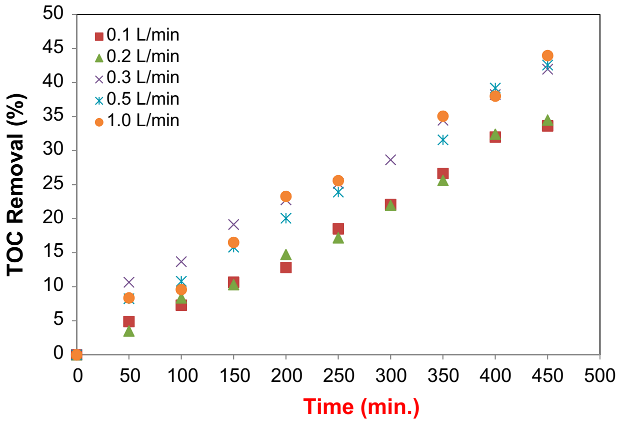

Fig. 10. Investigation of optimum O_2 flow rate for TOC removal of MWSP during EF treatment. [Conditions: pH 2, I = 700 mA, Fe^{2+} = 75 mg/L].

phosphorus and excessive amounts of Fenton's reagents may cause negative effects on phosphorus removal results. Imbalance in the amounts of reagents may lead to formation of side reactions, and this negatively affects the process performance. Hypophosphites that occur as intermediates in the phosphorus removal studies can develop competitive reactions between iron and hydrogen peroxide. Overdosage of hydrogen peroxide leads to a definite hindrance of the oxidation especially when this reagent is continuously produced [57].

In this part of the study, TN and TP removal efficiency of EF process were investigated for MWSP. For this purpose, TN and TP values of MWSP were evaluated during the EF process at the optimum conditions obtained for TOC. Fig. 11 shows the TN and TP removal results by EF treatment at optimum conditions. It was observed that no notable removal of TN was attained in comparison with TOC removal. During the electrolysis, the maximum TN removal was 18% in 450 min. EF cannot be considered to be an effective process in nitrogen removal because TN removal occurs when oxygen is supplied to the system during EF process. Thus, nitrogen present in the wastewater is oxidized up to NO_3-N. In this study, higher nitrogen removal efficiency was not achieved in terms of TN results.

There are two basic removal methods for the phosphate removal, which are adsorption and chemical precipitation. The essential mechanism to remove phosphate is separation of insoluble form of phosphate from the solution. If ferric ions are used as coagulant, it is needed to have neutral or close to neutral pH values (pH 7–10) to constitute insoluble $FePO_4$ compounds [58]. However, phosphate sedimentation cannot be mentioned in the study because the pH does not obey this rule since EF process needed excessive acidic pH value. At optimum conditions obtained for TOC, 55% TP removal was obtained. The reason for the TP removal is iron ions added as catalytic amount into the system to initiate the Fenton reactions.

3.2.6. Energy consumption for EF treatment

At the end of the study, system energy consumption was determined depending on applied current. Energy consumption was assessed by electrical power definition (Eq. (6)):

$$\text{Energy} = \text{Current} \times \text{Voltage} \times \text{Time} \tag{6}$$

According to the results, variation of system energy consumption vs. time for EF treatment at optimum conditions is depicted as follows.

Fig. 12 shows the energy consumption of EF process and the total of 47.6 kW-h/m^3 is needed during 450 min of EF process (pH 2, I = 700 mA, Fe^{2+} = 75 mg/L, pure oxygen flow rate = 1.0 L/min).

On the other hand, system energy requirement was also evaluated for electrochemical H_2O_2 production. In-situ H_2O_2 generation requires less time and current than the EF treatment, and thus it requires less energy than the EF treatment. Energy consumption results of H_2O_2 production is as follows.

According to Fig. 13, total energy requirement of the system during 100 min is approximately 4.83 kW-h/m^3 (pH 3, I = 70 mA, pure oxygen flow rate = 0.3 L/min, 50 mM Na_2SO_4) and this value is nearly equal to one-tenth of EF treatment.

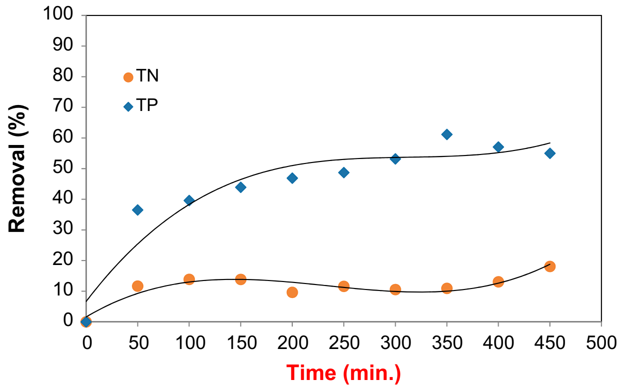

Fig. 11. TP and TN removal of MWSP by EF Treatment at Optimum Conditions. [Conditions: pH 2, I = 700 mA, Fe^{2+} = 75 mg/L, pure oxygen flow rate = 1.0 L/min].

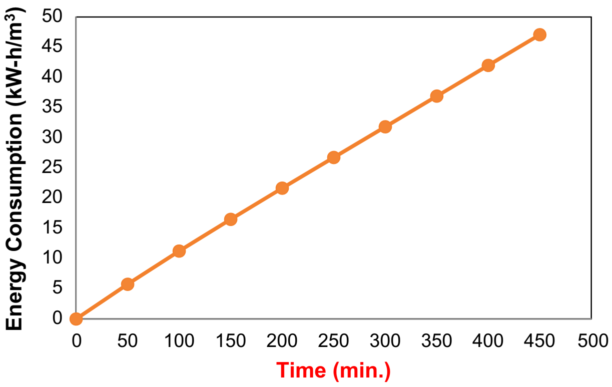

Fig. 12. Energy consumption of EF process at optimum conditions.

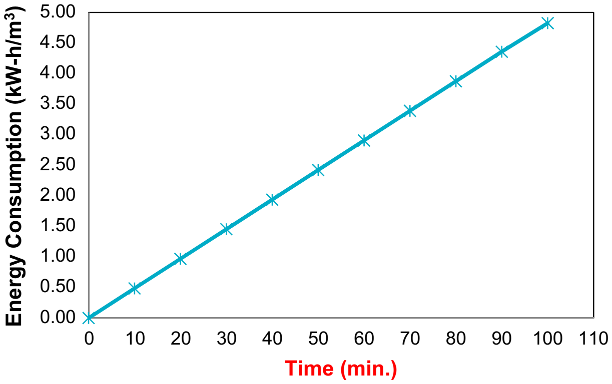

Fig. 13. Energy consumption of *in situ* H_2O_2 generation at optimum conditions.

4. Conclusions

In this work, treatment of MWSP by EF method was investigated using carbon-based graphite cathode and Pt wire anode. In the scope of the study *in situ* H_2O_2 production potential of graphite electrode was evaluated in detail. The maximum accumulation of H_2O_2 obtained at 70 mA in 0.05 M Na_2SO_4 aqueous solution with oxygen mass flow rate 0.3 L/min was 268 mg/L after 100 min. The results obtained in EF studies demonstrate that MWSP wastewater can be treated by EF process. Batch experiments in EF experiments determined that the best operative conditions for the mineralization of MWSP are pH 2, I = 700 mA, Fe^{2+} = 75 mg/L, pure oxygen flow rate = 1.0 L/min in terms of TOC mineralization. At these optimum conditions, TOC, TN, and TP removals are 44, 18, 55%, respectively. The energy requirements using the EF process and H_2O_2 production were 47.6 and 4.83 kW-h/m^3 at the optimized conditions.

Although EF treatment is not so effective for TP and TN content of the wastewater since it is an oxidative process, TOC standard can be almost provided by using EF treatment of MWSP. EF process can be used as a pre-treatment process before biological treatment or it could be combined or modified with other technologies (e.g. using UV irradiation or different carbon cathode materials) for better treatment of other types of wastewater.

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