

Biodegradability enhancement and pre-treatment of industrial estate wastewater by electro-Fenton process

Esrafil Asgari^a, Mohammad Aghanaghad^{a,*}, Heshmatollah Nourmoradi^{b,c},
Bayram Hashemzadeh^a, Rahim Aali^d

^aDepartment of Environmental Health Engineering, Khoy University of Medical Sciences, Postal number: 85167-53646, Khoy, Iran, Tel. +98 04436252777; Fax: +98 04436257668; emails: aqanaghad.eh@gmail.com (M. Aghanaghad), sasgary@gmail.com (E. Asgari), bayramh53@gmail.com (B. Hashemzadeh)

^bBiotechnology and Medicinal Research Center, Ilam University of Medical Sciences, Ilam, Iran, email: h.nourmoradi2004@gmail.com (H. Nourmoradi)

^cDepartment of Environmental Health Engineering, School of Health, Ilam University of Medical Sciences, Ilam, Iran

^dDepartment of Environmental Health Engineering, Qom University of Medical Sciences, Qom, Iran, email: aali1400@gmail.com (R. Aali)

Received 8 October 2019; Accepted 21 May 2020

ABSTRACT

Advanced oxidation processes have been applied as one of the main commonly treatment methods to improve the biodegradability of persistent organic materials, especially in industrial wastewaters. In this study, the chemical oxygen demand (COD) and total oxygen carbon (TOC) removal efficiency and biodegradability improvement of the industrial estate wastewater were investigated by electro-Fenton process (EFP). The influences of various parameters including pH, H₂O₂ concentration, electrical current density, and reaction time were evaluated on the EFP. The maximum removal efficiency of COD (88%) and TOC (80.8%) was achieved at optimum pH 4, H₂O₂ concentration 13.5 mM, current density 5 mA cm⁻², and reaction time 20 min. The optimum H₂O₂/Fe²⁺ molar ratio was found to be 2. The biodegradability of the wastewater was increased from 0.23 to 0.39 after treatment by EFP under optimum conditions. The results showed that H₂O₂/Fe²⁺ molar ratio was the most important factor in the EFP system. The findings showed that the EFP can be considered as a suitable technique for pre-treatment and biodegradability enhancement of the industrial estate wastewater. So, this wastewater can be easily post-treated by biological treatment methods.

Keywords: Advanced oxidation processes; Biodegradability; Electro-Fenton Process; Industrial estate wastewater

1. Introduction

Nowadays, biological treatment processes are applied as one of the most important procedures for the removal of biodegradable pollutants in industrial wastewaters. The physicochemical properties of industrial estates wastewater (IEW) depend on the type of industries. However, a low ratio of biochemical oxygen demand (BOD₅) to chemical oxygen demand (COD, usually less than 0.3) in

these wastewaters is due to the presence of toxic and non-biodegradable organic compounds. The COD value of IEWs is usually more than 1,000 mg L⁻¹. Therefore, the wastewater pre-treatment should be carried out in order to enhance the biodegradability of organic contaminants in biological treatment processes. Various physical, chemical, and biological procedures are commonly used for the treatment of IEWs. But, in most cases, these treatment processes do not meet the effluent discharge standards. So, advanced

* Corresponding author.

oxidation processes (AOPs) can play an important role in achieving this purpose [1]. AOPs can break down complex organic compounds into simpler and biodegradable ones. Consequently, biological treatment procedures followed by AOPs can easily remove these simpler materials into the wastewaters. AOPs have been extensively applied to oxidize various persistent organic materials into water and wastewater [2]. The electro-Fenton process (EFP) is an attractive AOPs option that has been widely used for the removal of high concentrations of toxic and persistent pollutants into industrial wastewaters [3]. The main advantages of EFP compared to other purification procedures include eco-friendly, flexibility, higher organics removal efficiency, lower reaction time, design simplicity, low cost in reagents, and energy [4]. Many studies have been performed by EFP for the oxidation of toxic pollutants such as formaldehyde, pesticides, textile dyes, drugs, and other recalcitrant chemicals in wastewater [5]. EFP is chemically categorized into two main classes of direct and indirect techniques. In direct technique, H_2O_2 is electrochemically produced by a graphite cathode electrode, but in indirect way, H_2O_2 is manually poured into the reactor. In both these methods, the reactive hydroxyl radicals ($\cdot\text{OH}$) are produced, because of the reaction between *in-situ* generated Fe^{2+} and H_2O_2 . The indirect EFP is more capable of oxidizing pollutants than the direct method [6]. Casado [7] study on the electrocoagulation of an IEW by iron electrodes reported that the value of COD removal $\sim 92\%$ was obtained at the electrical density and wastewater pH 30 m A cm^{-2} and ~ 6 , respectively.

To the best of our knowledge, there is no research on the pre-treatment and biodegradability enhancement of IEW by EFP. The purpose of this study was to investigate the pre-treatment and biodegradability improvement of IEW using EFP for biological post-treatment. The influences of various operational factors including solution pH, electrical current density, H_2O_2 concentration, average oxidation state (AOS), and reaction time were explored in the process.

2. Material and methods

All chemicals including H_2O_2 (17% w/w), HCl, NaOH, K_2MnO_4 , H_2SO_4 , Ag_2SO_4 , HgSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Na}_2\text{S}_2\text{O}_3$ were purchased from Merck Co., (Germany). The chemicals applied were of analytical grade and were used as received without any further purification.

2.1. Wastewater characteristics and sampling

Khoy industrial estate is located in the northwest of Iran. There are many industries including dairy products, carpet weaving, paper napkins, chemicals, food, plastics and lattices, paper recycling, and bitumen processing in the estate. The average daily wastewater flow rate from the estate was nearly $500 \text{ m}^3 \text{ d}^{-1}$ which imperfectly treated by a centralized wastewater treatment plant. Table 1 shows the main properties of Khoy raw IEW. A 24 h flow-proportional composite wastewater sampling (1.5 L) was carried out from the inlet of the treatment plant. The wastewater samples were then transferred to the laboratory and kept at 4°C for the experiments.

Table 1

Average value of main parameters of the industrial estate wastewater

Parameter	Value
Conductivity, $\mu\text{S cm}^{-1}$	2,958
pH	6.5
TSS, mg L^{-1}	385
COD, mg L^{-1}	4,574
TOC, mg L^{-1}	2,290
BOD_5 , mg L^{-1}	1,060
BOD_5/COD	0.23
Cl^- , mg L^{-1}	308

2.2. Experimental setup and procedure

In this research, the pretreatment of the IEW by EFP were conducted in order to enhance biodegradability of organic compounds. The batch experiments were performed into a Pyrex cylindrical vessel with an internal diameter and height of 5.2 and 30 cm, respectively. Two rectangular iron sheets with dimensions of $1 \text{ mm} \times 20 \text{ cm} \times 2.5 \text{ cm}$ (thickness \times length \times width), total surface of 100 cm^2 , were inserted into the reactor at a distance of 2.5 cm from each other. The electrodes were connected to an electrical direct current (DC) power supply with adjustable output voltage. The electrodes were cleaned, dried, and weighed at the end of the experimental runs. The value of Fe consumed was calculated by the eroded weight of the electrodes for all experimental runs. The amount of H_2O_2 added to the reactor was calculated based on $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and also the diminished weight of the electrodes after the reaction. An air pump with a flow rate of 1 L min^{-1} was used to enhance the reaction efficiency and also wastewater mixing. HCl and NaOH solutions (1 N) were used for pH adjustment. Fig. 1 shows the schematic of the reactor in this study. All the experiments

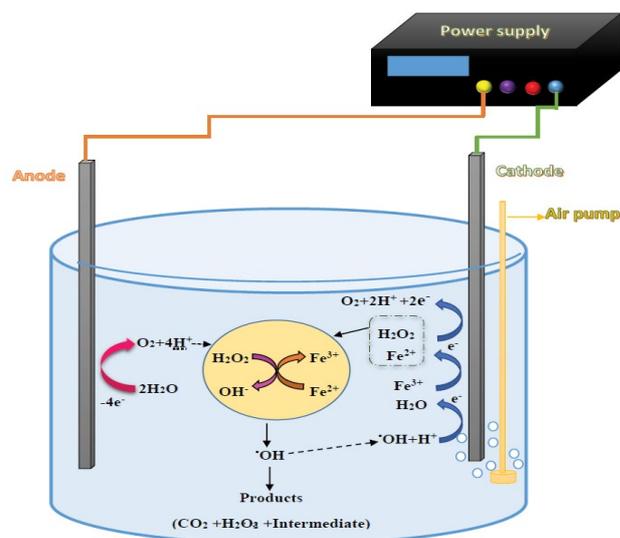


Fig. 1. Schematic of the reactor in this study.

were conducted in duplicate by 300 mL of the wastewater at room temperature (25°C). The experimental runs were listed in Table 2. Biodegradability (BOD₅/COD) experiments were carried out at the optimum situations achieved in the first steps of the study. The increment value of BOD₅/COD was considered as the quantity of biodegradability improvement. The remaining amount of H₂O₂ in the solutions was neutralized by the addition of the desired amount of sodium thiosulphate (Na₂S₂O₃) solution (1 N) after the reaction. The sludge was separated by sedimentation (30 min) in a circular container and the supernatant was then taken from the above zone of the vessel.

2.3. Analysis

The COD of the samples was determined according to the closed reflex method (5220), by spectrophotometer (DR6000, Hatch, USA). The concentration of H₂O₂ and BOD₅ were calculated by the permanganate titration method and OxiDirect BOD meter (Aqua lytic, Germany), respectively. The microbial seeding of BOD tests was taken from the bio sludge of Khoy IEW treatment plant. A total oxygen carbon (TOC) meter (Hach QbD1200 model, Germany) was used to determine the total organic carbons of the samples. The amount of Fe²⁺ in the treated samples was measured by the phenanthroline procedure [8]. Because the remaining H₂O₂ and Fe²⁺ can increase the COD value, the net COD of the samples was calculated by subtracting the total COD and the equivalent COD of H₂O₂ and Fe²⁺.

3. Results and discussion

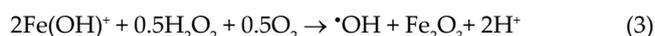
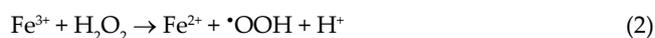
3.1. Effect of wastewater pH on the COD removal efficiency

The COD removal efficiency of the treated wastewater by EFP was determined at various pHs of 3–9, an electrical current of 10 mA cm⁻², H₂O₂ concentration of 10 mM, and reaction time of 30 min. The COD removal efficiency was obtained with and without pH control during the reaction. The wastewater pH control was regulated to the initial value during the reaction. The findings are presented in Fig. 2. As it can be seen, the COD removal was improved from 32.4% to 73.1% at pH 3 and 4, respectively. The COD removal was also reached to 54.5% and 52.8% at pH 5 and 9, respectively. At pH ≤ 6, the wastewater pH was increased by 2 units after the reaction time that it may be associated with OH⁻ formation. A further increment in wastewater pH particularly at pH ≥ 6 can strongly result in the reduction of COD removal. So, the optimum pH of 4 was considered for the subsequent experiments in this study.

The classic Fenton reaction is shown in Eq. (1). At lower wastewater pH, Fe²⁺ ions are the predominant forms of Fe. The Fenton reaction occurs between Fe²⁺ ions and H₂O₂ which produces the hydroxyl radicals with high oxidation potential ($E = 2.8$ eV). As seen in Fig. 2, the lowest COD removal was obtained at pH 3. It may be due to the production of Fe(OH)⁺ which has a lower reaction potential than Fe²⁺ with H₂O₂. Thus, at pH ≤ 3, •OH production was diminished and consequently led to a decline in the degradation rate [4]. Totally, the COD removal efficiency without pH control was higher than the COD removal with pH control.



At pH of 6–9, Fe³⁺ ions are the notable form of Fe in the solution, thus the ratio of Fe²⁺/Fe³⁺ is decreased. According to Eq. (2), Fe³⁺ ions react with H₂O₂ and produce hydroperoxyl radicals (•OOH) with an oxidation potential of 1.25 eV, which have lower oxidation potential than •OH [9]. As seen in Eq. (3), the Fe(OH)⁺ ions are the dominant form of iron at pH of 7–9 which produces the •OH radicals [10]. Though the hydroxyl radicals are spontaneously produced at lower and upper pH values, but it seems that large amounts of •OH radicals were possibly produced at pH 4 under the given experimental situations. Furthermore, the lower COD removal efficiency at higher pH can be due to this fact that •OH has a lower oxidation potential at alkaline pH values than an acidic one. So, the reduction of COD removal efficiency at pH > 4 can be due to the lower oxidation potential of •OH [4].



The EFP had the maximum degradation efficiency of organic matter at acidic pH values, because H₂O₂ is completely converted to •OH in the presence of Fe²⁺ catalyst. According to Gillard and Delaat study, the catalytic behavior of Fe is affected by solution pH. They reported that the highest concentration of Fe²⁺ ions is produced in acidic conditions and subsequently the •OH radicals content was enhanced. Besides, H₂O₂ was so unstable at higher solution pH values and it is decomposed to water and oxygen [11]. When the solution pH is increased, the iron ions form unstable Fe³⁺ complexes, precipitate on the surface of electrodes and finally, the amount of catalyst is decreased. The optimum pH achieved in the present

Table 2
Experimental runs for pre-treatment of the IEW by EFP

No.	Experimental run	pH	H ₂ O ₂ content (mM)	Current density (mA cm ⁻²)	Reaction time (min)
1	Effect of wastewater pH	3–9	10	10	30
2	Effect of H ₂ O ₂ content	a*	0–18	10	30
3	Effect of current density	a*	b*	0–20	30
4	Effect of reaction time	a*	b*	c*	5–40

a*, b*, and c* are the optimum values achieved at the earlier stage of the experimental runs.

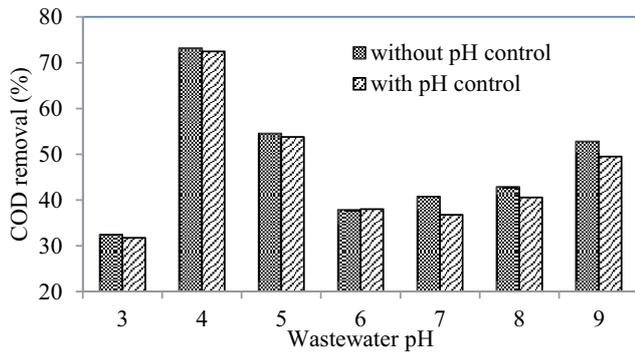


Fig. 2. Influence of wastewater pH on COD removal by EFP (current density = 10 mA cm⁻², H₂O₂ concentration = 10 mM, and reaction time = 30 min).

research is consistent with other studies [12]. All the reactions of the EFP cannot be estimated because of the complexity of the industrial wastewater in this study. The effluent pH was increased to 6.2 after treatment by EFP at the initial wastewater pH 4. This is a benefit factor in this study, because less alkaline chemicals are needed to regulate the effluent pH for post-biological treatment. Also, according to the results, it can be concluded that Eq. (1) was the prevailing reaction in this study. However, other reactions were involved in COD removal [13].

3.2. Effect of H₂O₂ concentration

The effect of H₂O₂ concentrations of 0 mM (electro-coagulation process: ECP) to 18 mM was determined on the COD removal at electrical current, optimum pH, and operation time of 10 mA cm⁻², 4 and 30 min, respectively. As seen in Fig. 3, about 32% of the COD was removed by ECP (in the absence of H₂O₂).

It is noticeable that electro-coagulation can occur during EFP [14]. When H₂O₂ was added at a concentration of 4.5 mM, the COD removal was enhanced to 65.6%. The COD removal increment can be associated with the Fenton reaction and subsequently the production of $\cdot\text{OH}$ radicals which oxidize the organic compounds. An increment in H₂O₂ content to 9 and 13.4 mM improved the COD removal efficiency to 72.4% and 93%, respectively, while the value of consumed H₂O₂ at optimum condition was 85.5%. The higher COD removal efficiency can be due to the higher content of $\cdot\text{OH}$ radicals in the presence of increased levels of H₂O₂ [9]. Based on Fe²⁺ and H₂O₂ concentrations into the wastewater and reduced weight of the electrodes, the best H₂O₂/Fe²⁺ molar ratio was found to be 2 at the optimum COD removal efficiency. Further increase in H₂O₂ concentration to 18 mM led to a decrease in COD removal efficiency to 77.4%. This depletion can be due to the fact that only a small portion of H₂O₂ was effectively used and its residual was degraded or consumed in various useless parallel reactions. Higher amounts of H₂O₂ may disturb the optimum H₂O₂/Fe²⁺ ratio which leads to competitive useless reactions (Eqs. (4)–(6)). The hydrogen peroxide at the higher concentrations can act as a radical sweeper and can compete with organic compounds to react with $\cdot\text{OH}$ [10].

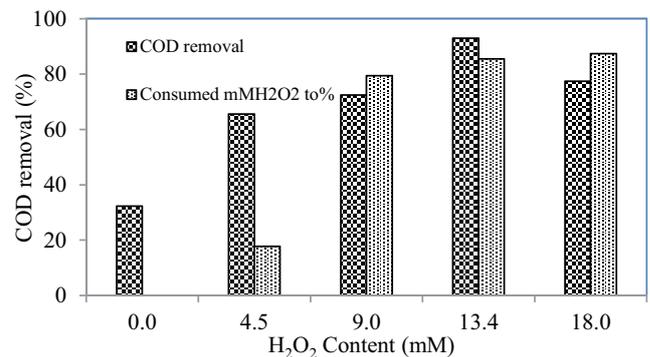


Fig. 3. Influence of H₂O₂ concentrations on the COD removal by EFP (current density = 10 mA cm⁻², pH = 4, and reaction time = 30 min).



3.3. Effect of electrical current density

The effect of electrical currents (0–20 mA cm⁻²) on the COD removal by EFP is presented in Fig. 4. As it can be seen, the COD removal efficiency was enhanced by increasing the current density from 0 to 5 mA cm⁻². This result can be attributed to the production of Fe²⁺ ions and the progress of Fenton reaction in the reactor [3]. The decrease in net weight of the electrodes (0.35 and 0.04 g for anode and cathode, respectively) at the maximum COD removal condition and the consumption of added H₂O₂ into the reactor confirmed this assumption. Fig. 4 shows the effect of various electrical current densities on the COD removal by EFP. The results indicated that the maximum COD removal (86.9%) was obtained at a current density of 5 mA cm⁻². The increment in electrical current led to enhance the anodic corrosion and subsequently the production of Fe²⁺ ions as the major catalyst of Fenton reaction. According to Box–Behnken design, the effect of various factors on the removal of COD by EFP was Fe²⁺ > H₂O₂ > pH [15]. In this study, the COD removal efficiency at the electrical density of 5 mA cm⁻² (86.9%) compared to 0 mA cm⁻² (42.5%) confirmed the vital role of Fe²⁺ in the process. Fig. 4 also shows that by increasing the electrical current from 5 to 20 mA cm⁻², the COD removal was gradually decreased from 86.9% to 73%, respectively. The higher values of the electrical currents (more than 5 mA cm⁻²) led to an increase in ferrous ions concentration in the solution, disturb the balance of H₂O₂/Fe²⁺, and consequently diminished the COD removal efficiency. Moreover, H₂O₂ molecules are degraded by hydroxyl radicals according to Eq. (4) [16]. The optimum H₂O₂/Fe²⁺ molar ratio was found to be 2 under the optimal situation. In comparison with another similar study, the higher COD removal efficiency was also obtained at lower current density [17]. Zhuang et al. [18] reported that the lower electrical current density was more effective in EFP, because the higher levels

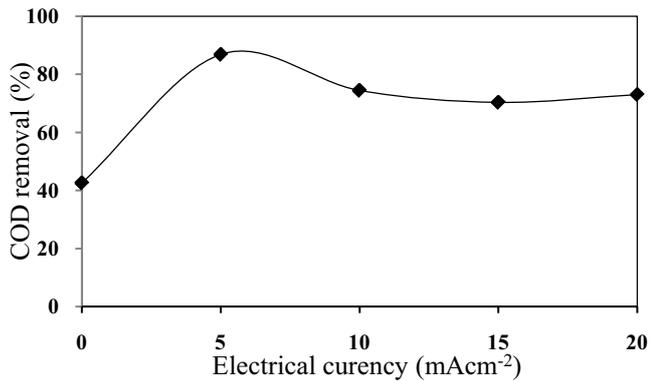


Fig. 4. Effect of electrical current densities on the reduction of COD at optimum pH and H₂O₂ concentration of 13.4 mM and the reaction time of 30 min.

of Fe²⁺ ions participated in pointless reactions (Eq. (5)) and finally decreased COD removal efficiency.

3.4. Effect of reaction time on COD removal and biodegradability improvement

The influence of reaction time (5–40 min) on the removal of COD, TOC, and the remaining amount of H₂O₂ was determined at optimum pH, H₂O₂ dose, and electrical current density conditions. As seen in Fig. 5, by increasing reaction time from 5 to 20 min, the COD removal was enhanced from 54% to 88%, respectively. The COD removal was then diminished to 62.7% at a reaction time of 30 min. Therefore, the maximum COD and TOC removal were obtained at 20 min. The minimum residual H₂O₂ at the optimum COD and TOC removal condition, was achieved at H₂O₂/Fe²⁺ molar ratio of 2. The highest COD and TOC removal at a contact time of 20 min can be associated to H₂O₂/Fe²⁺ ratio at the optimum condition. On the other hand, the lowest level of residual H₂O₂ (9.74 mM) occurred at reaction time 20 min. The increase in residual H₂O₂ can be related to the electrochemical production of H₂O₂ and also the reversible reaction of Eq. 2 [7]. The decrease in COD and TOC removal efficiency after 20 min can be attributed to decomposition and inactivation of H₂O₂. Also, it can be associated with the formation of various by-products and end products such as iron complexes, carboxylic, and oxalic acid that are hardly or non-degradable by EFP. These chemicals can decrease COD and TOC removal efficiency and also the biodegradability of organic compounds [19].

The extent of wastewater oxidation expressed as the AOS was calculated from the experimental data using Eq. (7) [20]. Fig. 6 shows the effect of reaction time on the AOS value. By increasing the reaction time from 0 to 20 min, the AOS value was enhanced from 0.25 to 0.49, respectively. The amount of AOS was slightly decreased after the reaction time of 20 min. The lower values of AOS showed insufficient oxidation and mineralization of organic compounds in the wastewater. This study expressed that the reaction time needed for the mineralization of industrial effluents by EFP was lower than the most AOPs [21]. As seen in Fig. 5, it is noteworthy that the organic materials degradation was

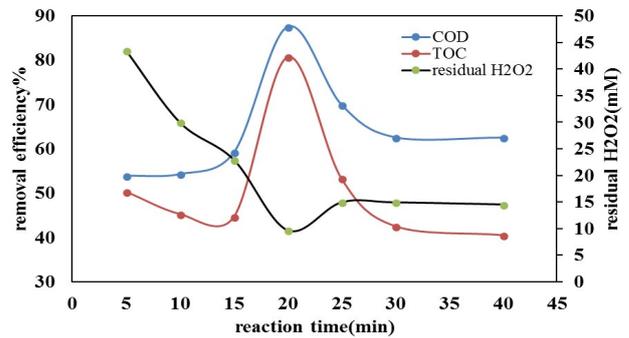


Fig. 5. Effect of reaction times on the COD removal and residual H₂O₂ under optimum conditions (pH = 4, H₂O₂ concentration = 13.4 mM, and current density = 5 mA cm⁻²).

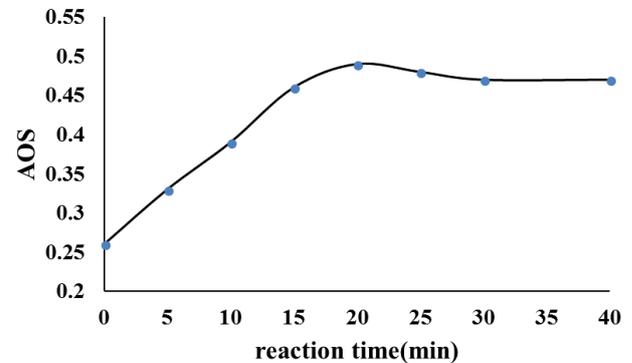


Fig. 6. Average oxidation state under optimum conditions (pH = 4, H₂O₂ concentration = 13.4 mM, current density = 5 mA cm⁻², and reaction time = 20 min) (TOC and COD concentrations are mol L⁻¹unit).

rapidly happened within 10 min but more time was required for the mineralization of some by-products. Consequently, the COD was meaningfully decreased by EFP from 4,574 to 566 mg L⁻¹ over a reasonable running time of 20 min.

$$\text{AOS} = \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \quad (7)$$

Fig. 7 displays the biodegradability (BOD₅/COD) rate of the wastewater at a various reaction time of EFP. Based on the figure, by increasing the reaction time from 0 to 20 min, the BOD₅/COD was enhanced from 0.23 (for the raw wastewater) to 0.39 (for the treated ones). But, the BOD₅/COD was then diminished as time went forward up to 40 min. The low BOD₅/COD value of the raw wastewater can be due to the presence of persistent and non-biodegrade organic pollutants into the wastewater [22]. So, it can be concluded that biological treatment is not a suitable procedure for the removal of the COD into the wastewater. However, the wastewater pre-treatment by EFP can enhance the BOD₅/COD value to 0.39 over the reaction time of 20 min. These findings obviously demonstrated that the degradation of organic compounds into the simpler types can enhance the

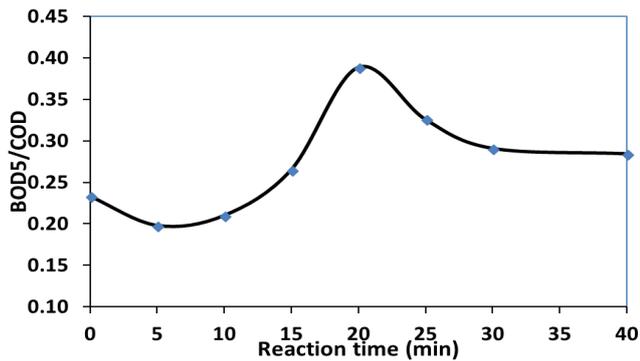


Fig. 7. Biodegradability (BOD₅/COD ratio) as a function of reaction time in the EFP.

biodegradability rate of the wastewater [23,24]. Therefore, the effluent produced by EFP can be powerfully treated by a biological treatment method. Unit energy demand (UED) of the EFP is obtained by Eq. (8):

$$\text{UED}(t) = \frac{A \times V \times t}{10 \times C_i \eta(t)} \quad (8)$$

where, UED is the unit energy demand for each m³ of wastewater (kWh kg⁻¹ COD removed). C_i and η are the initial COD concentration (kgm⁻³) and COD removal efficiency (%), respectively. The parameter of t indicates the reaction time (h), A is the total applied electrical current (Ampere); V is the overall cell voltage (Volt). In this study, the value of UED at the maximum COD removal condition was 2.1. The results showed that the UED value in this study was lower than other studies [25]. The lower UED value can be resulted from less reaction time and electrical current required to the EFP.

3.5. Effect of scavengers on the COD removal efficiency

The COD removal efficiency was assessed in the presence of various scavengers including *tert*-butanol, NaSO₄,

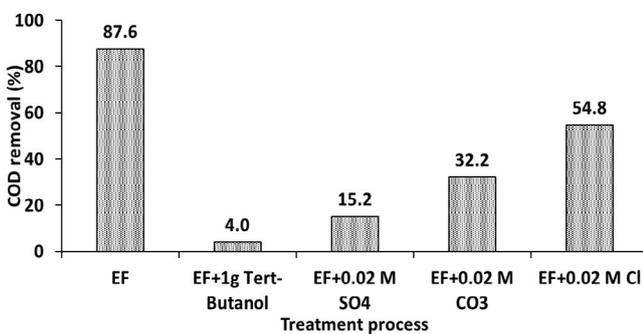


Fig. 8. COD removal efficiency in (pH = 4, H₂O₂ concentration = 13.4 mM, current density = 5 mA cm⁻², reaction time = 20 min) and presence of the radical scavenger materials (*tert*-butanol = 0.045 mol L⁻¹, SO₄²⁻, CO₃²⁻, and Cl⁻ which one = 0.02 mol L⁻¹).

CaCO₃, and NaCl. The results are presented in Fig. 8. As seen, the COD removal percentage was reduced in the existence of various scavengers. The COD removal efficiency by EFP in the absence of scavenger was 87.6%. But, *tert*-butanol, NaSO₄, CaCO₃, and NaCl scavengers diminished the COD removal efficiency to 4%, 15.2%, 32.2%, and 54.8%, respectively. The *tert*-butanol is a strong radical scavenger which has a higher reaction rate constant with $\cdot\text{OH}$. The decrease in COD removal along with these scavengers especially *tert*-butanol clearly confirmed that the electro-Fenton reaction was happened [26]. Long et al. [27] reported that the removal efficiency of diclofenac by electro-Fenton-persulfate was decreased in the presence of *tert*-butanol in the solution. But in this study, the higher COD removal percentage may be also due to the more formation of $\cdot\text{OH}$ and O₂⁻.

4. Conclusion

The maximum removal of COD (88%) and TOC (80.8%) was achieved at electrical current 5 mA cm⁻², pH 4, H₂O₂ 13.4 mM, and reaction time 20 min. The EFP increased the BOD₅ to COD ratio of the wastewater to 0.39. With regard to the COD removal efficiency (4%), in the presence of *tert*-butanol, the Fenton reaction was the most probable effective process in this study. So, the EFP can be considered as a suitable technique for pre-treatment and biodegradability improvement of the industrial estate wastewater.

Acknowledgments

We appreciate the chief manager of Khoy industrial estate wastewater treatment plant for technical supporting and also Khoy Faculty of Medical Science, Urmia, Iran for financial supporting this study.

References

- [1] J.P. Wang, Y.Z. Chen, Y. Wang, S.J. Yuan, H.-Q. Yu, Optimization of the coagulation-flocculation process for pulp mill wastewater treatment using a combination of uniform design and response surface methodology, *Water Res.*, 45 (2011) 5633–5640.
- [2] B. Pendyala, S.R. Chaganti, J.A. Lalman, D.D. Heath, S.R. Shanmugam, S.S. Veeravalli, Using a food and paper-cardboard waste blend as a novel feedstock for hydrogen production: influence of key process parameters on microbial diversity, *Int. J. Hydrogen Energy*, 38 (2013) 6357–6367.
- [3] G. Moussavi, A. Bagheri, A. Khavanin, The investigation of degradation and mineralization of high concentrations of formaldehyde in an electro-Fenton process combined with the biodegradation, *J. Hazard. Mater.*, 237 (2012) 147–152.
- [4] M. Panizza, A. Barbucci, M. Delucchi, M. Carpanese, A. Giuliano, M. Cataldo-Hernández, G. Cerisola, Electro-Fenton degradation of anionic surfactants, *Sep. Purif. Technol.*, 118 (2013) 394–398.
- [5] M. Solak, M. Kılıç, Y. Hüseyin, A. Şencan, Removal of suspended solids and turbidity from marble processing wastewaters by electrocoagulation: comparison of electrode materials and electrode connection systems, *J. Hazard. Mater.*, 172 (2009) 345–352.
- [6] G. Moussavi, R. Khosravi, M. Farzadkia, Removal of petroleum hydrocarbons from contaminated groundwater using an electrocoagulation process: batch and continuous experiments, *Desalination*, 278 (2011) 288–294.

- [7] J. Casado, Towards industrial implementation of electro-Fenton and derived technologies for wastewater treatment: a review, *J. Environ. Chem. Eng.*, 7 (2018) 102823.
- [8] WEF, APHA, Standard Methods for the Examination of Water and Wastewater, Water Environment Federation, American Public Health Association, Washington, DC, USA, 2005.
- [9] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, *Appl. Catal., B*, 166 (2015) 603–643.
- [10] H.M. Bui, X.-T. Bui, Degradation of Complex Organic Pollutants in Wastewater by Homogeneous Electro-Fenton, X.T. Bui, C. Chiemchaisri, T. Fujioka, S. Varjani, Eds., *Water and Wastewater Treatment Technologies, Energy, Environment, and Sustainability*, Springer, Singapore, 2019, pp. 145–166.
- [11] E. Brillas, Electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton treatments of organics in waters using a boron-doped diamond anode: a review, *J. Mex. Chem. Soc.*, 58 (2014) 239–255.
- [12] P. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: an overview, *Desalination*, 299 (2012) 1–15.
- [13] C.A. Martínez-Huitle, M.A. Rodrigo, O. Scialdone, *Electrochemical Water and Wastewater Treatment*, Butterworth-Heinemann, 2018, pp. 193–221.
- [14] P. Ma, H. Ma, A. Galia, S. Sabatino, O. Scialdone, Reduction of oxygen to H₂O₂ at carbon felt cathode in undivided cells. Effect of the ratio between the anode and the cathode surfaces and of other operative parameters, *Sep. Purif. Technol.*, 208 (2019) 116–122.
- [15] A. El-Ghenymy, S. Garcia-Segura, R.M. Rodríguez, E. Brillas, M.S. El Begrani, B.A. Abdelouahid, Optimization of the electro-Fenton and solar photoelectro-Fenton treatments of sulfanilic acid solutions using a pre-pilot flow plant by response surface methodology, *J. Hazard. Mater.*, 221 (2012) 288–297.
- [16] A. Módenes, F. Espinoza-Quiñones, F. Borba, D. Manenti, Performance evaluation of an integrated photo-Fenton–electrocoagulation process applied to pollutant removal from tannery effluent in batch system, *Chem. Eng. J.*, 197 (2012) 1–9.
- [17] F. Deng, O. Garcia-Rodríguez, H. Olvera-Vargas, S. Qiu, O. Lefebvre, J. Yang, Iron-foam as a heterogeneous catalyst in the presence of tripolyphosphate electrolyte for improving electro-Fenton oxidation capability, *Electrochim. Acta*, 272 (2018) 176–183.
- [18] H. Zhuang, S. Shan, C. Fang, Y. Song, X. Xue, Advanced treatment of paper mill wastewater using electro-fenton process with novel catalytic particle electrodes, *Bioresources*, 13 (2018) 4175–4186.
- [19] H. Monteil, Y. Péchaud, N. Oturan, M.A. Oturan, A review on efficiency and cost effectiveness of electro-and bio-electro-Fenton processes: application to the treatment of pharmaceutical pollutants in water, *Chem. Eng. J.*, 376 (2018) 119577.
- [20] O. Rozas, D. Contreras, M.A. Mondaca, M. Pérez-Moya, H.D. Mansilla, Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions, *J. Hazard. Mater.*, 177 (2010) 1025–1030.
- [21] M.A. Oturan, P. Nidheesh, M. Zhou, Electrochemical advanced oxidation processes for the abatement of persistent organic pollutants, *Chemosphere*, 209 (2018) 17–19.
- [22] V. Poza-Nogueiras, E. Rosales, M. Pazos, M.Á. Sanromán, Current advances and trends in electro-Fenton process using heterogeneous catalysts—a review, *Chemosphere*, 201 (2018) 399–416.
- [23] T. Sruthi, R. Gandhimathi, S. Ramesh, P. Nidheesh, Stabilized landfill leachate treatment using heterogeneous Fenton and electro-Fenton processes, *Chemosphere*, 210 (2018) 38–43.
- [24] S.O. Ganiyu, M. Zhou, C.A. Martínez-Huitle, Heterogeneous electro-Fenton and photoelectro-Fenton processes: a critical review of fundamental principles and application for water/wastewater treatment, *Appl. Catal., B*, 235 (2018) 103–129.
- [25] U. Kurt, O. Apaydin, M.T. Gonullu, Reduction of COD in wastewater from an organized tannery industrial region by Electro-Fenton process, *J. Hazard. Mater.*, 143 (2007) 33–40.
- [26] G. Moussavi, M. Aqanaghad, Performance evaluation of electro-Fenton process for pretreatment and biodegradability improvement of a pesticide manufacturing plant effluent, *Sustainable Environ. Res.*, 25 (2015) 249–254.
- [27] Y. Long, Y. Feng, X. Li, N. Suo, H. Chen, Z. Wang, Y. Yu, Removal of diclofenac by three-dimensional electro-Fenton-persulfate (3D electro-Fenton-PS), *Chemosphere*, 219 (2019) 1024–1031.