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

Esrafil Asgari, Mohammad Aghanaghad, Heshmatollah Nourmoradi, Bayram Hashemzadeh, Rahim Aali

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, \( \text{H}_2\text{O}_2 \) 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, \( \text{H}_2\text{O}_2 \) concentration 13.5 mM, current density 5 mA cm\(^{-2}\), and reaction time 20 min. The optimum \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) 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 \( \text{H}_2\text{O}_2/\text{Fe}^{2+} \) 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 (BODS) 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
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, \( \text{H}_2\text{O}_2 \) is electrochemically produced by a graphite cathode electrode, but in indirect way, \( \text{H}_2\text{O}_2 \) is manually poured into the reactor. In both these methods, the reactive hydroxyl radicals (\( \cdot\text{OH} \)) are produced, because of the reaction between \textit{in-situ} generated \( \text{Fe}^{2+} \) and \( \text{H}_2\text{O}_2 \). 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 ~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, \( \text{H}_2\text{O}_2 \) concentration, average oxidation state (AOS), and reaction time were explored in the process.

2. Material and methods
All chemicals including \( \text{H}_2\text{O}_2 \) (17% w/w), HCl, NaOH, K\(_\text{2}\)MnO\(_\text{4}\), H\(_2\)SO\(_4\), Ag\(_2\)SO\(_4\), HgSO\(_4\), K\(_\text{2}\)Cr\(_2\)O\(_7\), Na\(_2\)S\(_2\)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 m\(^3\) 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>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity, ( \mu\text{S cm}^{-1} )</td>
<td>2,958</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
</tr>
<tr>
<td>TSS, mg L(^{-1})</td>
<td>385</td>
</tr>
<tr>
<td>COD, mg L(^{-1})</td>
<td>4,574</td>
</tr>
<tr>
<td>TOC, mg L(^{-1})</td>
<td>2,290</td>
</tr>
<tr>
<td>( \text{BOD}_5 ), mg L(^{-1})</td>
<td>1,060</td>
</tr>
<tr>
<td>( \text{BOD}_5/\text{COD} )</td>
<td>0.23</td>
</tr>
<tr>
<td>( \text{Cl}^- ), mg L(^{-1})</td>
<td>308</td>
</tr>
</tbody>
</table>

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 mm × 20 cm × 2.5 cm (thickness × length × 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 \( \text{H}_2\text{O}_2 \) 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
were conducted in duplicate by 300 mL of the wastewater at room temperature (25°C). The experimental runs were listed in Table 2. Biodegradability (BOD/COD) experiments were carried out at the optimum situations achieved in the first steps of the study. The increment value of BOD/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 BOD 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) 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 Fe3+.

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.

Fe2+ + H2O2 → Fe3+ + •OH + OH–

(1)

At pH of 6–9, Fe2+ ions are the notable form of Fe in the solution, thus the ratio of Fe2+/Fe3+ is decreased. According to Eq. (2), Fe2+ 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)3 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].

Fe3+ + H2O2 → Fe3+ + ‘OOH + H+

(2)

2Fe(OH)3 + 0.5H2O2 + 0.5O2 → ‘OH + Fe3O4 + 2H2O

(3)

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>
<thead>
<tr>
<th>No.</th>
<th>Experimantal run</th>
<th>pH</th>
<th>H2O2 content (mM)</th>
<th>Current density (mA cm–2)</th>
<th>Reaction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Effect of wastewater pH</td>
<td>3–9</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Effect of H2O2 content</td>
<td>a*</td>
<td>0–18</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Effect of current density</td>
<td>a*</td>
<td>b*</td>
<td>0–20</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Effect of reaction time</td>
<td>a*</td>
<td>b*</td>
<td>c*</td>
<td>5–40</td>
</tr>
</tbody>
</table>

a*, b*, and c* are the optimum values achieved at the earlier stage of the experimental runs.
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 Fe$^{2+}$ ions and the progress of the 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 H$_2$O$_2$ 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 Fe$^{2+}$ 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 Fe$^{2+}$ > H$_2$O$_2$ > 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 Fe$^{2+}$ 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 H$_2$O$_2$/Fe$^{2+}$, and consequently diminished the COD removal efficiency. Moreover, H$_2$O$_2$ molecules are degraded by hydroxyl radicals according to Eq. (4) [16]. The optimum H$_2$O$_2$/Fe$^{2+}$ 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
of Fe\textsuperscript{2+} 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 H\textsubscript{2}O\textsubscript{2} was determined at optimum pH, H\textsubscript{2}O\textsubscript{2} 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 H\textsubscript{2}O\textsubscript{2} at the optimum COD and TOC removal condition, was achieved at H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{2+} molar ratio of 2. The highest COD and TOC removal at a contact time of 20 min can be associated to H\textsubscript{2}O\textsubscript{2}/Fe\textsuperscript{2+} ratio at the optimum condition. On the other hand, the lowest level of residual H\textsubscript{2}O\textsubscript{2} (9.74 mM) occurred at reaction time 20 min. The increase in residual H\textsubscript{2}O\textsubscript{2} can be related to the electrochemical production of H\textsubscript{2}O\textsubscript{2} 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 H\textsubscript{2}O\textsubscript{2}. 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 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\textsuperscript{-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 (BOD\textsubscript{5}/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 BOD\textsubscript{5}/COD was enhanced from 0.23 (for the raw wastewater) to 0.39 (for the treated ones). But, the BOD\textsubscript{5}/COD was then diminished as time went forward up to 40 min. The low BOD\textsubscript{5}/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 BOD\textsubscript{5}/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
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):

\[
UED(t) = \frac{A \times V \times t}{10 \times C_i \eta(t)}
\]

(8)

where, UED is the unit energy demand for each m\(^3\) of wastewater (kWh kg\(^{-1}\) COD removed). \(C_i\) and \(\eta\) are the initial COD concentration (kg m\(^{-3}\)) 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, NaSO\(_4\), CaCO\(_3\), 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, NaSO\(_4\), CaCO\(_3\), 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 •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 •OH and \(O_2•\).

4. Conclusion

The maximum removal of COD (88%) and TOC (80.8%) was achieved at electrical current 5 mA cm\(^{-2}\), pH 4, H\(_2\)O\(_2\) 13.4 mM, and reaction time 20 min. The EFP increased the BOD\(_5\) 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.

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References


