Removal of phenol from steel wastewater by combined electrocoagulation with photo-Fenton

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ABSTRACT

Phenol and its derivatives are available in various industries such as refineries, coking plants, steel mills, drugs, pesticides, paints, plastics, explosives and herbicides industries. This substance is carcinogenic and highly toxic to humans. The purpose of the study was to investigate the removal of phenol from wastewater of the steel industry using the electrocoagulation–photo-Fenton (EC-PF) process. Phenol and chemical oxygen demand (COD) removal efficiency were investigated using the parameters pH, Fe²⁺/H₂O₂, reaction time and current density. The highest removal efficiency rates of phenol and COD were 100 and 98%, respectively, for real wastewater under optimal conditions of pH = 4, current density = 1.5 mA/cm², Fe²⁺/H₂O₂ = 1.5 and reaction time of 25 min. Combination of the two effective methods for the removal of phenol and COD, photocatalytic electrocoagulation photo-Fenton process is a suitable alternative for the removal of organic pollutants in industry wastewater because of the low consumption of chemicals, absence of sludge and other side products, and its high efficiency.

Key words | electrocoagulation, phenol, photo-Fenton, steel plant

INTRODUCTION

One widespread form of organic chemical pollutant is phenol and its compounds, which are found in industrial wastewater (Malakootian et al. 2017). These compounds are very dangerous because of their high toxicity and harmful impact on the environment. High concentrations of phenol and its compounds are commonly found in effluent from oil refineries and industries such as petrochemicals, ceramics, coke and steel, coal conversion processes, resin manufacturing, drugs, pesticides, plastics, explosives and herbicides industries (Alizadeh et al. 2018). The presence of phenol in drinking and irrigation water is a serious threat to the health of humans, animals, plants and microorganisms (Fajardo et al. 2018). Phenol is highly carcinogenic to humans and causes significant health concerns even at low concentrations (Farhadi et al. 2012). Its toxic effects include permeating cell membranes and cytoplasmic coagulation. The standard amount of phenol in drinking water is 0.5 mg, while the limit for effluent from industrial waste output is 1 mg/L. There are many methods for phenol removal, which include adsorption (Liu et al. 2018), chemical oxidation (Hernández-Francisco et al. 2017), biological methods (Priyadarshini & Bakthavatsalam 2016), distillation, extraction, ion exchange, membrane process, reverse osmosis and electrochemical techniques (Víctor-Ortega et al. 2016). Physical methods for removal of phenol are expensive and inefficient.

Presently, chemical methods are not used due to their disadvantages such as high maintenance costs, sludge issues and disposal problems. Electrooxidation methods are a good alternative for the treatment of organic pollutants (Farhadi et al. 2012). The conventional biological processes cannot be used for the complete treatment of industrial wastewater due to high toxicity and carcinogenicity, high chemical and physical resistance of the pollutants, and also, bacteria or fungi are sensitive to changes in the environmental parameters.

Electrocoagulation (EC) has been used in the treatment of urban wastewater (Yavuz & Ögutveren 2018), effluents of oil (Gobbi et al. 2018), dyes (Khemila et al. 2018), antibiotics (Baran et al. 2018), sulfate (Mamelkina et al. 2017) and cadmium (Malakootian et al. 2017). The EC process involves the formation of metallic hydroxides in the effluent by dissolving the electrodes (anodes), usually formed by iron or aluminum. A coagulant with no impurities or extra metal
produces less sludge as compared to other coagulants (Xu et al. 2018). The ions released from electrocoagulation allow the maximum removal of various forms of contaminants (Farhadi et al. 2012). During the EC process, metal hydroxides are formed. These flocks are of great magnitude and are effective in rapidly absorbing organic soluble compounds and colloidal particles (García-Segura et al. 2017). Also, if the potential of the anode is high enough, other reactions, such as direct oxidation of organic compounds, occur in the anode (Jaafarzadeh et al. 2016). The presence of hydroxyl (HO) radicals also increases the efficiency of organic pollutant removal (Aziz et al. 2016). EC is based on the formation of a coagulant made of anode, such as iron or aluminum, which has been oxidized due to the applied flock (Panikulam et al. 2018). When iron is used as an electrode material, three major reactions occur in the electrochemical reactor (Baran et al. 2018).

Advanced oxidation processes (AOPs) for wastewater treatment have been widely used, especially in cases where organic pollutants cannot be removed by physical, chemical or biological methods (Arshaad et al. 2018). The basis of the AOPs process is to produce HO radicals, which can react with most organic pollutants and then decompose them (Ayodele et al. 2012). Free radicals with organic molecules produce a constant reaction rate of 10⁻⁶–10⁻⁹ M¹⁻¹s⁻¹ (García & Hodaifa 2017). Between AOPs, Fenton-type reactions are the most effective methods which produce HO radicals by the reaction between ferrous ion and hydrogen peroxide. The advantages of these processes are the safe and biodegradable nature of reagents and relatively simple operation, as well as short reaction time and the absence of sludge production. The typical physical fields include the photo, electro, cavitation effect, and microwave, which corresponds to the photo-Fenton/Fenton-like processes, electro-Fenton-like processes, cavitation-Fenton-like processes, and sono-Fenton-like processes, respectively. The superiority of these processes is the complete destruction of pollutants into simple compounds, such as carbon dioxide and water. The role of photochemistry in a Fenton-like process is to provide energy using UV to reduce the catalyst loading and to enhance the catalytic capacity of the catalyst in Fenton-like processes.

The photo-Fenton (PF) process is one of the most studied AOPs and appears to be an attractive alternative for removing emerging contaminants. The simplified reaction sequence leading to the generation of HO radicals from hydrogen peroxide in the photo-Fenton processes is identified by Reactions (1) and (2), as follows (Clarizia et al. 2017):

\[
\text{Fe}^{3+} + \text{hv} + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{HO} + \text{H}^+ \tag{1}
\]

\[
\text{Fe}^{3+} + \text{HO}^* + \text{OH}^- \quad k = 53M^{-1}s^{-1} \tag{2}
\]

As shown in the equation, compounds like (M) have the ability to form a stable complex with Fe (III), which significantly increases UV absorption and photochemical reduction resulting in the production of Fe (II) ions (Equation (3)).

\[
[\text{Fe}^{2+}\text{M}] + \text{hv} \rightarrow [\text{Fe}^{2+}\text{L}]^* \rightarrow \text{Fe}^{2+} + \text{L}^* \tag{3}
\]

During the Fenton reaction, hydrogen peroxide is used by crumbling ions to produce HO radicals (Equation (4)):

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^* + \text{OH}^- \tag{4}
\]

This reaction is accomplished by the regeneration of iron ions mainly by reducing the production of ferric species with hydrogen peroxide (Equation (5)).

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO} + \text{H}^+ \tag{5}
\]

Iron ions are produced more rapidly. In addition, iron ions can be rapidly degraded by HO radicals (Equation (6)).

\[
\text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{OH}^- \tag{6}
\]

The efficiency of the Fenton process using UV rays is improved by increasing the production rate of OH by the photochemical reaction of Fe(OH)²⁺ (Equations (7) and (8)) and optical analysis of Fe³⁺ (Equations (9) and (10)) (Baran et al. 2018).

\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{OH}^* \tag{7}
\]

\[
\text{R(CO}_2\text{)}_n\text{Fe}^{3+} + \text{hv} \rightarrow \text{R(CO}_2\text{)}_n + \text{Fe(II)} \rightarrow \text{R}^* + \text{CO}_2 \tag{8}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^{2+} + \text{OH}^+ \tag{9}
\]

\[
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{OH}^+ \tag{10}
\]

The combined photochemical oxidation and EC process (Akyol et al. 2015), combined EC–electro flotation (Aoudj et al. 2017), EC with UV (Cotillas et al. 2014; Aziz et al. 2016; Jaafarzadeh et al. 2016), EC with sulfite (Xu et al. 2018) and the combination of Fenton and Nano composite (Arshaad et al. 2018) have been studied.
This paper examined the possibility of phenol removal by EC-PF compound, EC and PF, individually. Parametric effects such as initial pH, current density, molar ratio of Fe$^{2+}$/H$_2$O$_2$ and contact time on phenol and COD removal from steel plant effluents were investigated.

**MATERIAL AND METHODS**

**Materials**

In this study, samples of effluent obtained from the Steel Industry Factory located in Iran were used. They were collected in polypropylene bottles and taken to the laboratory for preservation at 4 °C before use. Table 1 summarizes the characteristics of the produced wastewater.

pH meter and temperature control system was used to maintain the reaction solution at a stable pH and temperature. The effect of pH with HNO$_3$ and NaOH solution (0.1 mol/L) was used and hydrogen peroxide (30%) was purchased from Merck.

**Electrocoagulation–photo-Fenton reactor**

The EC-PF reactor consisted of a Plexiglas vessel (1,000 mL) with four aluminum plate electrodes (1 mm thickness) and one 30-W (UV-C) mercury lamp (Philips) in a quartz sheath that was fitted with an aluminum cover in batch reactor (Khandegar & Saroha 2013). The distance between the anode and the cathode was 3 cm and the mode of electrode connection was bipolar. Certain amount of Na$_2$SO$_4$ (10 mg/L) was added as the only supporting electrolyte (Baran et al. 2018). In all the experiments, a magnetic stirrer (400 rpm) was used in the reactor to maintain monotonous concentration. The PF process was carried out under the conditions of pH = 2–10, molar ratio of Fe$^{2+}$/H$_2$O$_2$ = 1–5, contact times of 10–100 min, current densities of 1–10 mA/cm$^2$, and initial phenol concentrations of 50–200 mg/L.

**Analytical method**

The phenol test was determined by the 4-aminoantipyrine method using a spectrophotometric quartz cell in a UV-Vis spectrophotometer, COD (dichromatic closed reflux method) according to Standard Methods (APHA-AWWA et al. 2012). Energy consumption was calculated using an experimental formula (Equation (19)). The experiments were designed as one factorial planning to obtain the optimum parameters. The data were analyzed using the statistical software SPSS 17, descriptive-inferential statistics and T-test statistical test at significance level of $P \leq 0.05$ and the related figures were drawn using Excel software.

The percentages of phenol and COD removed were calculated using the following (Equation (11)):

$$R = \frac{[\text{input}] - [\text{output}]}{[\text{input}]} \times 100 \quad (11)$$

**RESULTS AND DISCUSSION**

**Effect of initial pH**

The efficiency of EC-PF process depends on several important factors, including pH, flow density, molar ratio of Fe$^{2+}$/H$_2$O$_2$ and initial concentrations of pollutants. pH affects the performance of oxidation and coagulation process. According to the results shown in Figure 1, at pH = 4, 100% removal of phenol and 98% removal of COD were achieved with the EC-PF process. Results further showed that increase in the pH to 5 caused a mild drop in the phenol removal efficiency. With increase the value of pH, removal efficiency of the linear was reduced. The reason for this is the aluminum electrodes, which, as a ligand with abandoned aluminum ions, form polymer compounds that can form monomeric or polymeric metal hydroxide ions. Oxygen levels of the anode in acidic environments (Equation (12)) are strong oxidizing organic molecules that reduce the production of H-bubbles in stable cadmium molecules and reduce their resistance to oxidation.

**Oxidation reaction in anode (Equation (12))**:

$$2\text{Al}^{3+} + 4\text{H}_2\text{O}(l) + \text{O}_2(\text{aq}) \rightarrow 2\text{Al(OH)}_3(s) + 2\text{H}^+\text{(aq)} \quad (12)$$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BOD</th>
<th>COD</th>
<th>TSS</th>
<th>TOC</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw WW</td>
<td>185</td>
<td>880</td>
<td>479.2</td>
<td>253</td>
<td>240</td>
<td>35</td>
<td>298</td>
<td>25</td>
<td>250</td>
<td>21</td>
<td>51</td>
</tr>
</tbody>
</table>
Reduction reaction in the cathode (Equation (13)):
\[ 2H^+_{(aq)} + 2e^- \rightarrow H_2(g) \] (13)

Overall reaction during electrolysis (Equation (14)):
\[ 2Al(s) + 4H_2O(l) + O_{2(aq)} \rightarrow 2Al(OH)_3(s) + 2H_2(g) \] (14)

On the other hand, H$_2$O$_2$ decomposes rapidly to hydrogen and out of the environment. In addition, hydrogen peroxide is converted to a high concentration at high concentrations of hydrogen ions, which forms an ion of electrophilic peroxides and reduces the reaction with iron (Yavuz & Ögutveren 2018). Triple iron is precipitated as Fe(OH)$_3$,$^{2+}$, and Fe ion is removed from the environment, resulting in a lowering of the pH-efficiency of EC-PF process. In acidic pH, the invasive effect of H$^+$ on OH$^-$ is much than that of OH$^-$ on OH$^-$. In addition, the catalytic behavior of iron is strongly influenced by pH (Song et al. 2017). In acidic pH, CO$_2$ is also released as a gas from water environments, causing the loss of HO radicals such as carbonates in alkaline environments.

**Contact time**

The highest percentage of phenol removal was observed at 25 min and pH = 4 with the EC-PF process (Figure 2). As the contact time was increased, the phenol removal efficiency increased significantly, particularly with 25 min and the remaining time increased. An insignificant increase was observed from 25 to 40 min, which can be attributed to higher energy consumption, leading to more clots in the
short term. As the amount of dissolved coagulants in the aluminum electrode increased, removal efficiency increased (Hakizimana et al. 2017). This might be due to the sufficient quantity of coagulant dissolving from the aluminum electrode to effectively reduce the double layer of the suspended metallic hydroxides and destabilize them. The released Al ions and hydroxyls from electrodes formed more hydroxide flocks, which would adsorb more pollutant particles as the time is extended. Although increase in the time further resulted in slight increases in removal efficiency, this would not be applied due to the high energy and electrode consumption (Khandegar & Saroha 2013).

Effect of molar Fe$^{2+}$/H$_2$O$_2$ ratio

As shown in Figure 3, the molar ratio of peroxide to iron Fe$^{2+}$/H$_2$O$_2$ = 1.5 at pH = 4 and a contact time of 25 min resulted in 100% removal of phenol and an increase in COD removal to 98% with the EC-PF process. At higher concentrations, however, the removal rate was reduced. Increase in the concentration of hydrogen peroxide led to an increase in HO radicals. In particular, in the presence of UV, the removal efficiency increased (Orbeci et al. 2014): acidic compounds formed by phenol oxidation react with the Fe$^0$ electrode (Equation (15)) and form a small amount of Fe$^{2+}$ in the aqueous phase, which is the main factor for the production of HO radicals (Equation (16)):

$$\begin{align*}
\text{Fe}^0 + 2\text{H}^+ &\rightarrow \text{Fe}^{2+} + \text{H}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^* 
\end{align*}$$

(15) (16)

With regard to the high oxidation potential of the reaction medium, Fe (II), Fe (III) and hydroxide oxides (FeO, Fe$_2$O$_3$, Fe$_3$O$_4$ and FeOOH) can form on a solid surface (Clarizia et al. 2017).

In proportions higher than molar ratio of Fe$^{2+}$/H$_2$O$_2$ = 1.5, scavenger radicals that reduce removal efficiency are produced. Hydrogen peroxide reduces the excess HO radicals in the solution and reduces the reaction speed.

Equation (17) shows the reaction of hydrogen peroxide and corresponding ions (M):

$$(\text{M}^{n+}) + \text{H}_2\text{O}_2 \rightarrow (\text{M}^{n+1}) + \text{OH}^- + \text{OH}^0$$

(17)

In the PF process (Equation (18)), the re-reduction of Fe$^{2+}$ occurs, after which the oxidation of H$_2$O$_2$ again produces a new OH. As a result, the oxidation of organic pollutants is accelerated.

$$\text{Fe}^{3+} + \text{H}_2\text{O}_, hv \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}^*$$

(18)

Effect of current density

Current density is the most important parameter for controlling the reaction speed of the electrochemical reactor in all electrochemical processes (Hakizimana et al. 2017).

The optimum current density of 1.5 mA/cm$^2$ was achieved in the EC-PF process for removal of 100% phenol and 98% COD at a concentration of H$_2$O$_2$/Fe$^{2+} = 1.5$ in pH = 4 and 25 min (Figure 4). As the current density increased, the phenol removal efficiency increased. This increased the oxidation potential by increasing the potential difference, which resulted in increased clot production and, consequently, reduction of phenol. However, by increasing the current density, 1.5 mA/cm$^2$, the efficiency is reduced, which may be related to the polarization and inactivation of the electrodes. According to other studies, the higher
reaction time with constant density increases the phenol removal efficiency and decreases the energy consumption of the iron electrode (An et al. 2017).

Energy consumption

Specifically, an efficient process for industries should be economically viable and operational. The main operating cost of EC-PF is related to the amount of electrical energy consumed during the process. Therefore, the electric energy consumption (E) (Equation (19)) was determined using the formula (Fajardo et al. 2015):

$$E = \frac{UI_{\text{EC-PF}}}{V}$$

where $E$ is the electrical energy in Wh, $U$ is the cell voltage in volt (V), $I$ is the current density in ampere (A) and $t_{\text{EC-PF}}$ is the time of the EC-PF process per hour. According to the results (Table 2), the minimum energy consumption was due to the COD reduction rate of the EC-PF process.

Kinetic studies of the COD removal

The rate of phenol decomposition in processes based on the pseudo-second-order reaction model was matched (Equation (20)).

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e}$$

where $k$ (g/mg min) is the constant rate of the pseudo-second-order equation (Thokchom et al. 2015), $q_e$ is the maximum adsorption capacity and $q_t$ is the amount of adsorption at time $t$ (An et al. 2017). Correlation coefficients for the pseudo-second-order kinetic model obtained in EC-PF reactor studies were above 0.99. These results indicate that the adsorption model of three processes conform to the pseudo-second-order kinetic model.

The concentration of phenol was measured at different times and the time charts were plotted for all three systems (Figure 5). Due to the EC-PF process and the simultaneous presence of Fe, H_{2}O_{2} and UV together with EC, the phenol oxidation rate was significantly increased.

Table 2 | Energy consumption in the various processes under optimal conditions

<table>
<thead>
<tr>
<th>Kind of process</th>
<th>COD removal</th>
<th>Energy consumption (kWh/kg COD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC-PF</td>
<td>97</td>
<td>23.45</td>
</tr>
<tr>
<td>EC</td>
<td>87</td>
<td>34.63</td>
</tr>
<tr>
<td>PF</td>
<td>91</td>
<td>29.15</td>
</tr>
</tbody>
</table>

Figure 4 | Effect of current density on phenol and COD removal efficiency by PF single, EC single and EC-PF (Fe^{2+}/H_2O_2 = 1.5, pH = 4, t = 25 min).

Figure 5 | Pseudo-second-order equation plot with contact time.
CONCLUSIONS

The results of this study showed that the best efficiency of phenol and COD removal using EC-PF are 100 and 97%, respectively, under optimal conditions (Fe$^{2+}$/H$_2$O$_2$ = 1.5, pH = 4, current density = 1.5 mA/cm$^2$ and time = 25 min). At optimal conditions, the power requirement of PF, EC and EC-PF were 23.45, 34.63 and 29.15 kWh/kg COD, respectively. The results also showed that the pseudo-second-order equation is more consistent with the experimental results. From the results, it is clear that the EC-PF process is an effective process for the removal of organic materials like phenol from water considering its greater removal efficiency and more economic cost in comparison with other removal processes.

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