Application of Electro-Fenton (EF) Process to the Removal of Pentachlorophenol from Aqueous Solutions

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Abstract
Pentachlorophenol (PCP) is a very hazardous compound which enters into the environment by industries such as refineries and petrochemicals. As its biological degradation is very slow, this use may cause the pollution of soils and groundwater; with the recent emergence of pentachlorophenol contamination as an important drinking water quality issue, finding an easy, economical, and useful method to remove it has been attracted interest. In this study, the performance of an electro-Fenton process (EFP) for the elimination of PCP from an aquatic environment was evaluated. The effects of important operational variables such as reaction time, pH, the applied voltage, and the distance between the electrodes on the degradation of solution were investigated. The maximum PCP removal was obtained at a distance of 3 cm, a pH of 3, a voltage of 24 volt, and the treatment time of 40 min. This study demonstrated that the distance between the electrodes, pH, the applied voltage, and the treatment time have significant effects on the electron-Fenton process and this process is suitable for the treatment of PCP-polluted waste waters.

Keywords: PCP, Electro-Fenton Process, Aquatic Environment, Biological Degradation

1. Introduction
Chlorophenols have been introduced into the environment through their use as bookends (Li et al., 2011). Due to five chlorines on pentachlorophenol (PCP) structure, it is the most toxic agent of chlorophenols (Lan et al., 2008). PCP is one of the widespread environmental contaminants in soils, surface, and ground water. It is a probable carcinogen and has been placed on the pollutant priority list (EPA, 1980). The main use of pentachlorophenol is as pesticides, disinfectant, and wood preservatives (Kumar et al., 2008). Chlorophenols in general have been used in the petrochemical industry (oil/gas industry, refineries, and production of basic chemicals) and are useful as an anti-algal and anti-fungal agent in industrial boilers and cooling systems due to their biocide properties. PCP has been added to petrochemical drilling fluids to arrest polysaccharide and starch fermentation (Nordin, 2004, Zaidi et al., 2003, and Jones 1981). These applications of PCP introduce it to industrial wastewater, which causes water and air pollutions. Phenolic compounds have long been recognized as one of the most recalcitrant and persistent substances in petroleum refinery effluents. Due to the improper disposal of

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industrial wastes containing PCP and its persistence, PCP still remains in the environment, although PCP has been banned since 1984. Owing to its potent cytotoxicity, an effective technology for rapid degradation of PCP is needed to decrease its high toxic risk for both human and the environment (Shih et al., 2010).

Since PCP could cause adverse effects on the digestive, nervous, and respiratory systems, as well as leading to cancer and interfering with the normal function of thyroid, based on the researches of International Programs on Chemical Safety (IPCS) (1987, 1989), it is necessary to find an effective method to treat the PCP waste or pollution (Zhang et al., 2007).

Researchers have tried many different methods such as low-temperature pyrolysis (Thuan et al., 2012), sorption using coal fly ash from a Portuguese thermal power plant (Martins et al., 2007), the surfactant-enhanced filtration through low-pressure thin film composite membranes (Kumar et al., 2009), the immobilization of horseradish peroxidase by electrospun fibrous membranes (Niu et al., 2013), the immobilization of laccase by Cu²⁺ chelate affinity interaction on surficially modified magnetic silica particles (Wang et al., 2012), the effects of inoculation with phanerochaete chrysosporium on remediation (Zhen et al., 2011), and the Fenton’s oxidation of pentachlorophenol (Zimbron et al., 2009) to treat PCP waste. In addition to these methods, biological methods are also among other studied areas (Zhang et al., 2007).

Furthermore, Electro-Fenton method is used for the removal of many kinds of recalcitrant pollutants; the treatment of landfill leachate (Atmaca, 2009), phenol degradation (Pimental et al., 2008), the effect of UV light on acetaminophen degradation in the electro-Fenton process (Su et al., 2013), chemical oxygen demand (COD), and color removal from landfill leachate (Daud et al., 2013), synthetic dyes in wastewater treatment (Peralta-Hernández et al., 2009), cyanide from aquatic environments in the presence of interfering humic acids (Samarghandi et al., 2013), nitrate in aqueous solutions for Fe electrodes (Seid Mohammadi et al., 2013), highly formaldehyde-polluted industrial waste water (Bagheri et al., 2012), p-nitrophenol (Lei Zhoua et al., 2014) and azinphos-methyl (Ozcan et al., 2013) are among the works carried out in this context.

Owing to the simplicity of the process and lack of toxicity of the reagents, an advanced oxidation process (AOP) using Fenton’s reagent is the best technology for the degradation of a large number of hazardous and organic pollutants (Nidheesh et al., 2012). AOP is based on highly reactive radicals, including the hydroxyl radical (OH⁺). This radical reacts rapidly and non-selectively with almost all electron-rich organic compounds (Glaze, 1987 and Stasinakis, 2008).

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^+; \quad k = 76 \text{ mol} \text{l}^{-1} \text{s}^{-1}
\]  

(1)

Two days electro-chemical methods were used for the treatment of organic materials having a high toxicity and low biological degradability (Naumczyk et al., 1996). Electro-Fenton (EF) method, which is the combination of FO and electro-coagulation, has shown good results in the treatment of strong wastewaters.

There are two different types of electro-Fenton (EF) processes; in the first one, Fenton’s reagents (Fe (II) and H₂O₂) are added from outside; in this case anode material should have a high catalytic activity. In the other one, H₂O₂ is added from outside and sacrificial cast iron anodes are used for providing Fe (II) (Atmaca, 2009).

In this study, a second type of Electro-Fenton process was used to study electro-Fenton advanced oxidation process for the removal of pentachlorophenol in aqueous solutions.
In the electron-Fenton method used herein, Fe (II) ions are generated from sacrificial anodes and can also be regenerate by the following reactions, which promote the efficiency of this method (Atmaca, 2009):

\[
\begin{align*}
H_2O_2 + Fe^{3+} & \rightarrow Fe^{2+} + HO_2^- + H^+ \quad (2) \\
Fe^{3+} + HO_2^- & \rightarrow Fe^{2+} + H^+ + O_2 \quad (3) \\
Fe^{3+} + e^- & \rightarrow Fe^{2+} \quad (4)
\end{align*}
\]

There are many interfere reactions which can decrease the removal efficiency. In this situation, hydrogen peroxide is used for oxidizing Fe^{2+} and HO_2^- (Bagheri et al., 2012):

\[
\begin{align*}
H_2O_2 + OH^- & \rightarrow HO_2^- + H_2O \quad (5) \\
Fe^{2+} + HO_2^- & \rightarrow Fe^{3+} + HO_2 
\end{align*}
\]

Furthermore, at a high current density, some reactions such as oxygen production at anode and hydrogen at cathode may happen, which causes the limitation of the efficiency of removal (Zhang et al., 2007):

\[
\begin{align*}
2H_2O_2 & \rightarrow 4H^+ + O_2 + 4e^- \quad (7) \\
2H^+ + 2e^- & \rightarrow H_2 \quad (8)
\end{align*}
\]

As described above, the electron-Fenton process and its reactions are very complex; thus finding the optimum operating conditions is of great importance to enhance the removal efficiency.

In this study, proper operating conditions, including the distance between the electrodes, pH, the applied voltage, and treatment time were determined. In this case, the removal efficiency was evaluated by means of COD analysis.

2. Experimental

2.1. Chemicals

Pentachlorophenol 98.5% and H_2O_2 (30%, Merck) were used as purchased. Sodium sulfate 99.5% was used as an electrolyte. The pH of the solutions was adjusted using concentrated sulfuric acid (H_2SO_4) and sodium hydroxide (0.1 M). All the solutions in this study were prepared with distilled water. Concentrated hydrochloric acid was used for electrode washing. The reagent concentrations used in each experiment are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCP concentration</td>
<td>15 (mg/l)</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>152 (mg/l)</td>
</tr>
<tr>
<td>H_2O_2 concentration</td>
<td>200 (mmol/l)</td>
</tr>
<tr>
<td>Sodium sulfate concentration</td>
<td>2000 (mg/l)</td>
</tr>
</tbody>
</table>
2.2. Electrochemical cell

The experiments were carried out at room temperature (25± 2 °C) in a divided double-electrode electrochemical cell which consists of 400 ml glass beaker with an internal diameter of 8.8 cm and is equipped with vertical electrodes. The cathode and anode were pieces of steal (st37) having an effective area of 1.5 cm², which were plunged in to the cell. A DC power supply which used for providing reasonable voltage was connected to the electrodes. The solutions were stirred with a magnetic stirrer continually at a suitable speed so that the vortex was not created to keep the homogeneity of the electrolyte concentration (Figure 1). A 250 ml solution was prepared by knowing the initial PCP concentration (15 mg/l) and sodium sulfate was then added as the electrolyte (2000 mg/l). The initial pH of the solutions was set by the addition of concentrated H₂SO₄ or sodium hydroxide (0.1 M). The pH was measured by a digital pH meter calibrated with a standard buffer at pH values of 4.01 and 7.01. The conductivity of the medium was fixed by the addition of Na₂SO₄ (2000 mg/l) and then the 250 ml sample was transferred into the electron-Fenton reactor. After the addition of the required amount of H₂O₂, the EF experiment was started. During the experiments, samples were taken after 10, 20, 30, 40, and 60 minutes in order to find the optimum treatment time for the PCP removal. The results of COD analyses were compared to find and select the best treatment time. For finding the optimum distance between the electrodes, the experiment was repeated for the distances of 2.5, 3.0, 3.5, and 4.0 cm at a constant treatment time and the results were compared to find the best distance. Figure 2 displays the steps needed to be carried out for each sample. The same procedures were repeated for obtaining the optimum pH and applied voltage. The pH values of the solutions were 2, 3, 4, and 5 and the applied voltages were 12, 18, 24, and 27 volt.

![Figure 1](image_url)

Experimental apparatus.
2.3. Analysis procedures

COD values of the samples were determined by using open reflux method by a standard method (APHA, 1992). For this purpose, a sample was refluxed in a strongly acidic solution with a known excess of potassium dichromate (K₂Cr₂O₇). After digestion, the unreduced K₂Cr₂O₇ remained in the solution was titrated with ferrous ammonium sulfate to find the amount of K₂Cr₂O₇ consumed and the oxidizable matter was calculated in terms of oxygen equivalent; a 2-hr reflux time was used. The efficiencies of PCP degradation and COD removal were defined as follows:

\[
COD \text{ removal efficiency} = \frac{\Delta [COD]}{COD_0} = \left(\frac{[COD_i] - [COD_f]}{COD_0}\right) \times 100
\]  

(9)

where, \([COD]_0\) and \([COD]_f\) are the COD concentrations in the solution at the beginning and end of each reaction respectively. At the end, the analysis and the comparison of results were carried out using office software.

3. Results and discussion

In the electron-Fenton method, many useful or intervention reactions can take place, which are possible to be controlled by using proper operating conditions such as treatment time, pH, applied voltage, and the distance between the electrodes. Therefore, this study was focused on the determination of optimum values of these parameters.

3.1. Effect of the distance between the electrodes

Figure 3 shows the effect of distance between the electrodes on the removal efficiency of COD. Accordingly, if the distance between the electrodes in this method is selected between 3 cm and 3.5
cm, this causes a 4% increase in the removal efficiency and gives rise to energy consumption and operational cost of the method. Thus the minimum distances should be selected [23]. The optimum distance between the electrodes was 3 cm, which resulted in 68% of COD removal at a pH of 3, voltage of 15 volt, an \( \text{H}_2\text{O}_2 \) concentration of 150 mmol/l, and a treatment time of 60 min. The distance between the electrodes is an important operation condition for the electrodes which affects the removal of pollutants. Decreasing the distance between the electrodes leads to a decrease in the ohmic drop through the electrolyte and then decreases the cell voltage and energy consumption. In the study performed by Nidheesh et al., (2012) and Cheng-Chun et al., (2007), a similar result was observed. Increasing the distance between the electrodes, however, significantly gives rise to energy expenses of the method (Atmaca, 2009). The removal efficiency of the electron-Fenton process was less for the distances less than 3 cm. This is because of the easier oxidation of electro-regenerated Fe\(^{2+}\) to Fe\(^{3+}\) at the anode. However, it is necessary to keep an appropriate distance between the electrodes for the installation and avoidance of short circuit between the anode and cathode (Lan et al., 2008).

**Figure 3**

Effects of the distances between the electrodes on COD removal efficiencies (test conditions: pH=3, voltage=24, \( \text{H}_2\text{O}_2 = 150 \text{ mmol/l} \), time=40 min, and PCP concentration=15mg/l).

### 3.2. Effect of treatment time on PCP removal efficiency

Figure 4 displays the effect of treatment time on the removal efficiency of COD for PCP. The best removal efficiencies were obtained when the treatment time was 40 minutes. COD were achieved 86.84% removal efficiency. Lin and Chang (2000) reported that the treatment time is required to complete the oxidation reaction largely due to the dosage of \( \text{H}_2\text{O}_2 \). As seen in Figure 4, the removal efficiency increases by increasing the reaction time from 10 to 40 minutes. In this case, by increasing the reaction time, it will complete the reaction. Other important results observed in Figure 4 show that the efficiency of the process decreases by increasing the reaction time from 40 to 60 minutes, due to hydrogen peroxide consumption and an increase in the solution temperature. In other words, reactions accrued faster by increasing the electrochemical cell temperature and reactant could be converted faster due to the high kinetic rate of this process. When the system temperature exceeds 25 °C, the following reactions may be dominant and hydrogen peroxide decomposition may also occur. In the
study performed by Bagheri et al., 2012 and Pereira and Zaiat, 2009, similar results were also observed:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \]  
(10)

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 (g) + 2\text{H}_2\text{O} \]  
(11)

**Figure 4**

Effects of the reaction time on the efficiency of PCP removal (test conditions: pH=3, voltage=24, H\textsubscript{2}O\textsubscript{2}= 200 mmol/l, distance between electrodes=3 cm, and PCP concentration= 15 mg/l).

### 3.3. Effect of pH on PCP removal efficiency

Although Fenton process was performed in an acidic medium, changes in the pH of the medium are one of the most important factors affecting the process. Figure 5 shows the effect of pH on the PCP removal efficiency in the electron-Fenton process. As seen in Figure 5, the best PCP removal efficiency (86.38%) at an H\textsubscript{2}O\textsubscript{2} concentration of 200 mmole/l, voltage of 24 volt, a treatment time of 40 minutes, and a PCP concentration of 15 mg/l was observed at a pH value of 3. For the experiment with a pH value higher than 3, the removal efficiency decreased to 43%. A similar result was observed elsewhere (Atmaca, 2009; Samarghandi et al., 2013; Nidheesh et al., 2012). Higher pH values cause iron species to precipitate as ferric hydroxides. Moreover, at lower pH values, catalysts may be deactivated because H\textsubscript{2}O\textsubscript{2} and iron species form stable complexes. Therefore, the oxidation efficiency decreases. Hydrogen peroxide will be converted to H\textsubscript{2}O as given in the following equation at low pH values and the H\textsubscript{2}O\textsubscript{2} concentration will thus be reduced.

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \]  
(12)

Due to the formation of oxonium ion (H\textsubscript{3}O\textsubscript{2}\textsuperscript{+}, as in Equation 13), the efficiency of the process may decrease. An oxonium ion makes peroxide electrophilic to enhance its stability and substantially reduces the reactivity with Fe\textsuperscript{3+} ion (Nidheesh et al., 2012; Arjunan et al., 2012; Ramirez et al., 2008).

\[ \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_3\text{O}_2\textsuperscript{+} \]  
(13)
When the pH in the reactor rises, electro-coagulation starts in the reactor due to the conversion of Fe$^{2+}$ and Fe$^{3+}$ to Fe (OH)$_n$ type structures (Nidheesh et al., 2012; Atmaca, 2009). At pH values higher than 3, the rate of Fenton’s reaction Equation 1 is slower than that of the reactions described by Equations 3 and 4; in this situation, by limiting the Fenton’s reaction, the concentration of Fe$^{2+}$ increases by decreasing the concentration of Fe$^{3+}$ and the settlement and management of Fe$^{2+}$ are more difficult than that of Fe$^{3+}$ (Nidesh et al., 2012). At very low pH values (<3), hydrogen ion acts as ‘OH scavengers (Arjunan et al., 2012).

![Figure 5](image-url)

**Figure 5**

Effects of pH on PCP removal efficiency (reaction time=40 min, voltage=24, H$_2$O$_2$= 200 mmol/l, distance between electrodes=3 cm, and PCP concentration=15 mg/l).

### 3.4. Effect of voltage on PCP removal efficiency

Another important operation parameter of the electron-Fenton method is the amount of voltage applied to the electrodes. As described by Panizza et al. (2009), higher applied voltage leads to the generation of higher amounts of hydroxyl radicals from Fenton’s reaction (Equation 1) (Panizza et al., 2009).

As the applied voltage increases, the removal efficiency of PCP improves. In electrochemical systems, higher applied current density is proportional to higher applied voltage. At higher current, the following reaction (Equation 14) is dominant in the electrochemical cell and by increasing the electro-regeneration of ferrous ions from ferric ion, the efficiency of Fenton chain reactions will increase (Nidesh et al., 2012; Cheng-Chang et al., 2007).

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (14)
\]

Under applying high voltage, the obtained removal efficiency increased considerably due to the formation of higher hydroxyl radical amount. Thus increasing Fe$^{2+}$ ions and hydroxyl radical amount resulted in higher removal efficiency (Samarghandi et al., 2013). Therefore, the applied voltage in the experiment should be determined. For this special purpose, the different observed results are illustrated in Figure 6. As can be seen, the removal efficiency enhances by increasing the applied voltage. In the study performed by Samarghandi et al., (2013) and Panizza et al., (2009), similar results were also observed.
4. Conclusions

The electro-Fenton process is nowadays used for organic pollutant removal from wastewater. Different arrangements of electrolytic reactors were used for this type of process. The results of running the process under different experimental conditions showed that the removal of PCP was affected by the distance between the electrode, pH, applied voltage, and treatment time, because Fe$^{2+}$ and 'OH, and subsequently the oxidation rate, were influenced by this operational parameters. Therefore, these parameters should be selected more precisely. Electro-Fenton process was found successful for the treatment of PCP. According to the results obtained, the optimum operating conditions of the process for the treatment of PCP can be summarized as the an initial pH of 3, applied voltage of 24 v, the distance between the electrode of 3 cm, and the treatment time of 40 min. Under these conditions, a COD removal efficiency of 86.84% can be reached. Electron-Fenton method can be used as an operational process for the removal of PCP and similar components from industrial wastewater. The following items have been identified as subjects for further research activities:

- PCP removal from aqueous solution by electron-Fenton oxidation combined with ultrasonic irradiation;
- Kinetic study of Electro-Fenton reactions;
- Theoretical study of the effects of ultrasonic and ultraviolet power on PCP removal efficiency in Sono-Electro-Fenton and photo-Electro-Fenton method;
- Repeating this process for real wastewater and investigating the removal efficiency of electro-Fenton for the removal of PCP in the presence of other pollutants.

Acknowledgments

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Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOP</td>
<td>Advance oxidation process</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>EF</td>
<td>Electro-Fenton</td>
</tr>
<tr>
<td>FO</td>
<td>Fenton oxidation</td>
</tr>
<tr>
<td>PCP</td>
<td>Pentachlorophenol</td>
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</table>

References


