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Effect of UV light on pentachlorophenol removal in the electro-Fenton process

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Abstract

Background: This research studied the effect of UV light on pentachlorophenol (PCP) removal in the electro-Fenton (EF) process.

Methods: PCP was used as the pollutant in this study. The effects of Fenton's reagent, i.e. hydrogen peroxide concentration, solution pH, and treatment time by EF (EF) and photoelectro-Fenton (PEF) processes, were studied to determine rates of PCP removal. The results showed that a better performance and a high removal efficiency were achieved by coupling UV radiation and the EF process.

Results: EF processes required more time to remove PCP, while after a reaction time of 10 minutes, the PEF achieved a removal efficiency of 90.4%; this value is higher than the maximum efficiency of the EF process (83.44% after 40 minutes). The kinetic mechanisms of both processes were examined and compared. The rate constants at optimum conditions were 0.0455 and 0.0579 min^{-1} for EF and PEF processes, respectively.

Conclusion: Removal efficiency was obtained in the order of PEF > EF.

Keywords: Ultraviolet rays, Reaction Time, Kinetics.

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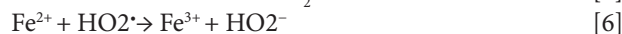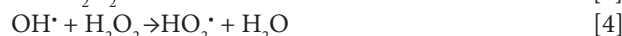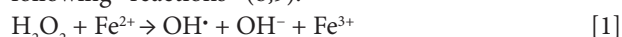
Introduction

The presence of phenol compounds in the environment has acute toxicity for mankind. Due to five chlorines on the pentachlorophenol (PCP) structure, it is the most toxic agent of chlorophenols (1). PCP can affect the nervous, digestive, and respiratory systems and lead to cancer in humans. It is used in pesticides, disinfectants, and wood preservatives (2). PCP remains in the environment because of the unsuitable disposal of industrial wastes containing PCP and its pertinacity. Thus, the treatment of phenolic pollutants before disposal is very important. It is necessary to find a highly effective method to treat PCP waste (3). Advanced oxidation processes (AOPs) are more efficient than conventional methods. They are able to oxidize and mineralize most organic compounds, including bio-recalcitrant ones, by producing highly reactive and non-selective oxidants called hydroxyl radicals (HO) (4). AOPs include two steps of oxidation: the formation of hydroxyl radicals, and the reaction of these radicals with an organic compound (5).

Conventional biological wastewater treatment processes are inefficient for the removal of recalcitrant organic compounds that are the main sources of pollutants in industrial effluent. The electro-Fenton (EF) process is known as a powerful and environmentally-friendly technology for the removal of this compound from wastewaters (6). In the EF process, highly oxidative hydroxyl radicals are formed from the reaction between H_2O_2 and Fe^{2+} (7). The Fenton process includes the following reactions (8,9):

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^{-} + Fe^{3+} \tag{1}$$
$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \tag{2}$$
$$R^{\bullet} + H_2O_2 \rightarrow ROH + OH^{\bullet} \tag{3}$$
$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{4}$$
$$Fe^{3+} + HO2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \tag{5}$$
$$Fe^{2+} + HO2^{\bullet} \rightarrow Fe^{3+} + HO2^{-} \tag{6}$$
$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{7}$$
$$H_2O_2 + Fe^{2+} \rightarrow FeO^{2+} + H_2O \tag{8}$$
$$FeO^{2+} + H_2O_2 \rightarrow O_2 + H_2O \tag{9}$$

In the Fenton process Fe^{2+} is consumed faster than it is produced. The EF method solved this problem by regenerating Fe^{2+} in the cathode according to the following reaction (10):

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{10}$$

The photoelectron-Fenton (PEF) process can regenerate a large amount of Fe^{2+} by solution irradiation with UV light by the following reaction (11):

$$(Fe-OH)^{2+} +hv \rightarrow Fe^{2+} +OH^{\bullet} \qquad [11]$$
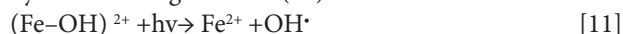
Furthermore, in the PEF mechanism, hydroxyl radicals can be produced from H_2O_2 in the presence of UV radiation (11,12):

$$H_2O_2 +hv \rightarrow 2OH^{\bullet} \qquad [12]$$

Recently, different usages for the EF process have been found, for example, the treatment of landfill leachate (13), phenol degradation (14), the effect of UV light on acetaminophen degradation in the EF process (15), COD and color removal from landfill leachate (16-18).

According to our previous study (19,20), PCP has been successfully removed in the EF and sonoelectro-Fenton processes, but the effect of UV light on PCP removal in the EF process has not yet been studied. Thus, the current study investigated the effects of UV radiation on PCP removal in the EF process. The influence of operating parameters such as H_2O_2 concentration, pH, and treatment time of PCP on degradation was investigated. The reaction kinetics were studied to find the removal mechanism and compare it with the EF results.

Methods

PCP 98.5% and H_2O_2 (30%) were purchased from Merck. Sodium sulfate 99.5% (used as an electrolyte), H_2SO_4, and NAOH were obtained from Merck. Concentrated hydrochloric acid was used for electrode washing. Chemical oxygen demand (COD) was determined using the open reflux method (21). The efficiencies of PCP degradation and COD removal were defined as:

COD removal efficiency = Δ [COD] $/COD_0$ = ([COD_f-COD_0] $/COD_0$) $\times 100$

where $[COD]_0$ and $[COD]_f$ are the COD concentrations in the solution at 0 minute and at the end of each reaction, respectively. A divided double-electrode electrochemical cell was used in this study. The reactor was a glass beaker with a volume of 400 mL. The cathodes and anodes of the reactors were a piece of steal (st37). The same experimental set-up as the EF process was used in the photoelectro-Fenton (PEF) process. The addition of eight UVC lamps with a frequency of 247 nm was used. The pH of the solutions was adjusted using concentrated sulfuric acid (H_2SO_4) and sodium hydroxide (0.1 M). A DC power supply used to provide reasonable voltage was connected to the electrodes, and 250 mL solution was prepared by determining the initial PCP concentration (15 mg/L) and then adding sodium sulfate as the electrolyte (2000 mg/L). The initial pH of the solutions was set. The conductivity of the medium was fixed by adding Na_2SO_4 (2000 mg/L). Then, 250 mL of sample was transferred to the E-F reactor. After adding the required amount of H_2O_2, 8-watt UVC lights were turned on and the PEF experiment was started. The EF set-up was the same as the PEF process but without UV lights.

Results

Figure 1 shows the effect of initial H_2O_2 concentration on PCP removal efficiency at a constant PCP concentration of 15 mg/L, voltage of 24 V, and pH = 3 after a reaction time of 40 minutes by EF and PEF processes. Under these operational conditions, the PCP removal efficiency rates in both processes were increased with increases in H_2O_2 concentration. The effect of pH (3–7) on PCP removal was studied using both processes, and the results are shown in Figure 2. Experiments were performed using an initial PCP concentration of 15 mg/L, reaction time of 40 minutes, and H_2O_2 concentration of 200 m mole/L. A voltage of 24 V was maintained for the EF and PEF processes. The effects of treatment time on PCP removal efficiency at an initial PCP concentration of 15 mg/L, pH of 3, and H_2O_2 concentration of 200 m mole/L at a voltage of 24 V in the EF and PEF processes are shown in Figure 3. In the kinetics study, the zero-, first-, and second-order models were analyzed separately to determine the behavior of PEF reactions. Modeling of PCP removal by pseudo-first-order, pseudo-second-order, and zero-order equations is shown in Figures 4, 5, and 6, respectively. The results indicate that the removal kinetics followed the
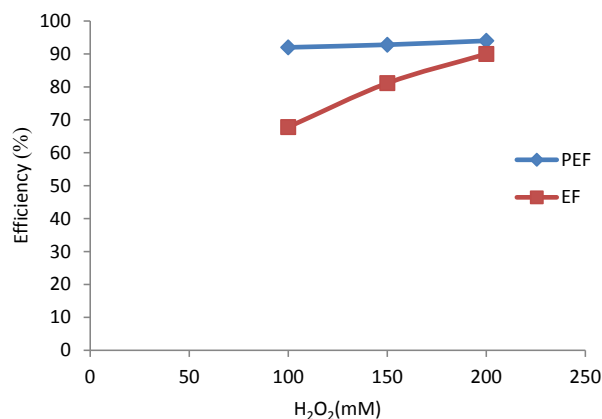
Figure 1. Effect of initial H_2O_2 concentration on PCP removal efficiency in the EF and PEF processes.
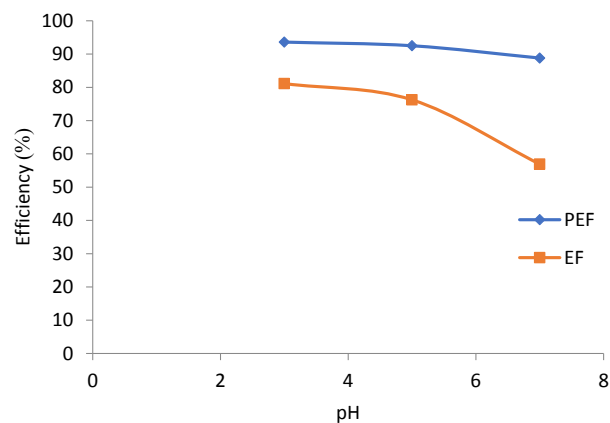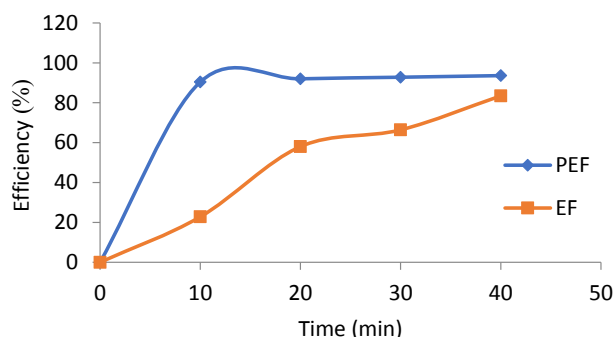

Figure 2. Effect of pH on PCP removal efficiency in the EF and PEF processes.
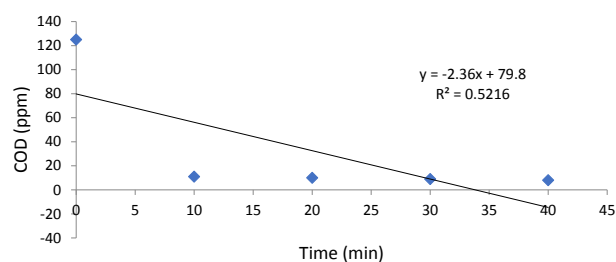
first-order reaction.
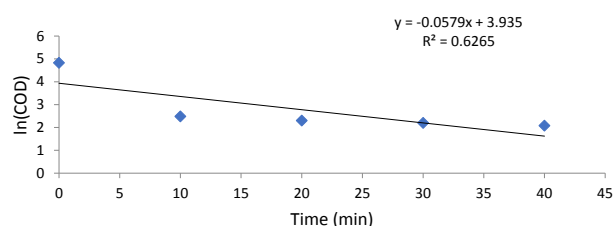
Discussion

Effect of H_2O_2 concentration

The highest removal of PCP presented at an H_2O_2 concentration of 200 mM in both processes. The maximum
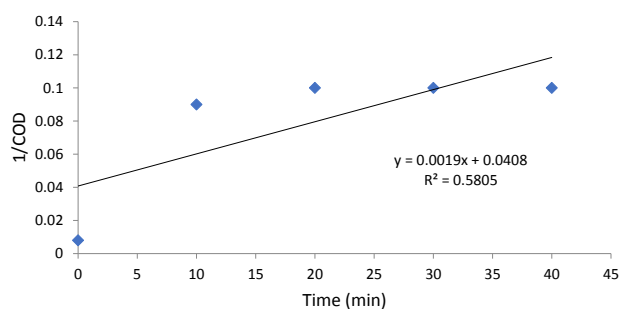

Figure 3. Effect of treatment time on PCP removal efficiency in the EF and PEF processes.

Figure 4. Zero-order kinetics modeling of PCP removal using PEF.

Figure 5. First-order kinetics modeling of PCP removal using PEF.

Figure 6. Second-order kinetic modeling of PCP removal using PEF.

PCP removal efficiency of 90% was observed in the EF process at the H_2O_2 concentration of 200 mM, while a removal efficiency of 92% was observed in the PEF at an H_2O_2 concentration of 100 mM. This phenomenon was due to an OH• production from reactions 11 and 12. The difference in PCP removal efficiency was insignificant in the PEF processes. Thus, high efficiency can be achieved by adding the lowest amount of H_2O_2 concentration in the PEF process, and it is economical. In the AOP, H_2O_2 is the main source of hydroxyl radical production according to reaction 1. The excess amount of H_2O_2 has a scavenger effect, so finding the lowest concentration of H_2O_2 for higher removal efficiency is very important (1,10,11,22). In the PEF process, UV light reduces the scavenging effect and generates a greater amount of hydroxyl radicals according to Eq. [12] (1). This result was observed in several other studies, including the effect of UV light on acetaminophen degradation in the EF process (10) and treatment of landfill leachate by PEF process (11).

Effect of pH

It is well known that advanced oxidation reactions occur in low pH values (13). Hydroxyl radicals have high oxidation ability in acidic mediums (1). The results showed that PCP removal efficiency is significantly affected by pH. The maximum PCP removal was observed at pH 3 (93.6% in PEF process). Increasing pH from 3 to 7 reduced the amount of PCP removed for both process. This is due to the reduction in hydroxyl oxidation potential in high pH values. At high pH values, ferric hydroxide was formed and caused the low generation of hydroxyl radicals (1,20). At higher pH values, electro-coagulation starts in the reactor because of the conversion of Fe^{2+} and Fe^{3+} to Fe (OH)n-type structures (1,13). Increasing pH to a value beyond 3 affected the removal efficiency because of the transformation of ferrous ions (Fe^{2+}) to ferric iron (Fe^{3+}). By adding UV light radiation to the EF process, it is possible to reduce Fe^{3+} to Fe^{2+} and generate hydroxyl radicals according to the following reaction (3):

$$Fe(OH)^{2+hv} \rightarrow Fe^{2+} + \cdot OH \qquad [13]$$

Hydroxyl radicals produced in these reactions are used for PCP removal at higher pH values. In this situation, PEF processes could be used at a near neutral pH and reduce the problems created by acidic effluent treatment (1). This result was observed in several other studies, including advanced oxidation of phenol by EF and SEF process (1), COD and color removal from synthetic textile wastewater by SEF process (22), and PCP removal by SEF (20).

Effect of treatment time

As shown in Figure 3, the PCP removal efficiency of the EF and PEF processes was increased by increasing the reaction time; in the PEF process, a removal efficiency of 90.4% was obtained after a reaction time of 10 minutes; this value is higher than the maximum efficiency of the EF process (83.44% after 40 minutes). These phenomena

can be a result of the greater amount of hydroxyl radical produced, according to Eq. [12] (1). In the studies of Babuponnusami et al (1), and Altin (11), similar results were observed.

Kinetics of pentachlorophenol removal
According to our previous studies, the removal of PCP by the EF process can be represented as (20):

PCP + OH• → Oxidation products   [14]

As described in our previous study, the zero-order, first-order, and second-order reaction kinetics, respectively, can be written as shown below, and the removal of PCP by the EF process followed the pseudo-first-order kinetics (20):

$C = C_0 - k_0 t$ [15]

$\ln C - \ln C_0 = -k_{app} t$ [16]

$1/C = 1/C_0 - Kt$ [17]

The correlation coefficients for the PCP removal kinetics of zero-, pseudo-first, and second order were 0.5216, 0.6265, and 0.5805, respectively. The comparison of the correlation coefficients indicated a good agreement between the removal kinetics and the pseudo-first order models. The results of zero-, first-, and second-order reaction kinetics for PCP removal in EF and PEF processes are summarized in Table 1.

Figure 7 shows the comparison of the results of the first-order kinetics models for both the EF and the PEF method, and it shows that the rate constants of the EF and PEF processes are 0.0455 and 0.0579, respectively. The same results were reported by other studies (1,10,20).

Conclusion
This study investigated the effects of UV radiation combined with EF for the removal of PCP from aqueous solutions. The results indicated that both the EF and PEF

Table 1. The regression coefficients for zero-, first-, and second-order kinetics

Oxidation process	Zero-order	First-order	Second-order
EF	0.9045	0.9707	0.9418
PEF	0.5216	0.6265	0.5805
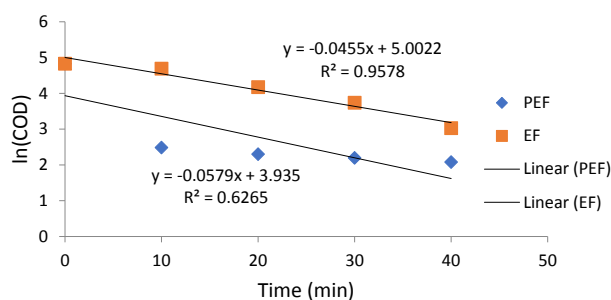
Figure 7. Pseudo-first-order kinetics plot under the EF and PEF processes under optimum conditions (H_2O_2=200 mM, voltage = 24 V, PCP=15 mg/L, and pH = 3)

processes were effective in removing PCP from wastewater. The effects of changing the H_2O_2 concentration was clearer in the PEF process than in the EF process. At low H_2O_2 injection amounts, adding UVA irradiation enhanced the PCP removal rate in the PEF process because of the greater production of OH• in the PEF process. Another advantage of combining UV and EF was that it could act at high pH values near the neutral pH and solve the problems associated with acidic effluent. From the kinetic studies, both processes followed the first-order reaction. The rate constant values at optimum conditions were equal to 0.0455 and 0.0579 min^{-1} for the EF and PEF processes, respectively. The following items are recommended as subjects for further research: studying the efficiency of PCP removal from aqueous solutions by sequential sono-photoelecro-Fenton; repeating this process for real wastewater.

Ethical issues
The authors have thoroughly observed ethical issues, including plagiarism, misconduct, data fabrication, and redundancy.

Competing interests
The authors declare that no competing interests exist.

Authors' contributions
All authors contributed equally to the study, and all authors participated in data acquisition, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

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