

## **Advanced oxidation of pentachlorophenol: A comparison between electro-Fenton, sono electro-Fenton processes**

Heidari, Z<sup>1</sup>, Motevasel, M<sup>1</sup>, Jaafarzadeh, N<sup>2</sup>

<sup>1</sup> *Department of Chemical E-engineering, Petroleum University of Technology, Abadan, Iran*

<sup>2</sup> *Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran*

### **Abstract:**

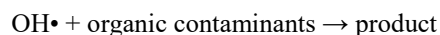
Pentachlorophenol (PCP) is a very hazardous compound that enters into the environment by industries such as refinery and petrochemical industry. As its biological degradation is very slow, this use may be caused pollution of soils and groundwater. Here we compare the results obtained by electro-Fenton and Sono-electro-Fenton treatment methods on the degradation of pentachlorophenol. Better performance arises from the coupling between ultrasound irradiation and the Electro Fenton process. The effect of operating parameters such as hydrogen peroxide concentration, solution pH and treatment time was studied. The results showed that Sono-E-F process was able to remove the higher amount of pentachlorophenol (PCP) by consuming the smallest amount of H<sub>2</sub>O<sub>2</sub> at least time in comparison with the E-F process. The PCP degradation kinetics was studied and compared for two processes.

**Keywords:** PCP; Sono- Electro Fenton; process; electro-Fenton; kinetic model

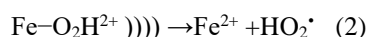
### **1. Introduction**

Pentachlorophenol (PCP) is a general biocide and has been used widely for a different purposes including agriculture and timber preservation. [1] PCP could cause negative effects on digestive system, nervous system and respiratory system, as well as Suspected to Carcinogenesis and interfering with the normal function of thyroid, therefore treatment of phenolic pollutants is required before the disposal and it is important to find an effective and economical method to treat the PCP waste or pollution [2]. PCP is a bio recalcitrant compound that enters into the environment by industries such as refinery and petrochemical industry. Various methods have been employed to removal PCP, low-temperature pyrolysis [3], the surfactant-enhanced filtration through low-pressure thin film composite membranes [4], immobilization of horseradish peroxidase by electro spun fibrous membranes [5], immobilization of laccase by Cu<sup>2+</sup>chelate affinity interaction on surface modified magnetic silica particles [6], the effects of inoculation with phanerochaete chrysosporium on remediation [7] and Fenton's oxidation of pentachlorophenol [8]. Besides these methods, biological method is one of the other studied areas [9]. Recently advance oxidation process has been developed for remediation of chlorophenols including: ozonation,

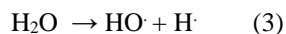
photooxidation, Fenton oxidation [10]. FO is one of the advanced oxidation processes (AOPs). This process based on hydroxyl radical's production by following reaction between H<sub>2</sub>O<sub>2</sub> and Fe (II) ions, [11]:



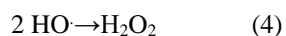
In the E-F method, due to the low solubility of oxygen in the water the production of H<sub>2</sub>O<sub>2</sub> is slow. In most promising type of E-F process that ferric ion is reduced to ferrous ion at the cathode; Fe<sup>2+</sup> regeneration is slow even at an optimal condition. Ultrasound is a usual and useful method of producing hydroxyl radicals, which is the key oxidant in AOPs [12]. Combination of ultrasound and electro-fenton can accelerate the regeneration of Fe<sup>2+</sup> from Fe-O<sub>2</sub>H<sup>2+</sup> that formed by the reaction of Fe<sup>3+</sup> with H<sub>2</sub>O<sub>2</sub> as given in the following reaction [13]:



Bubble cavitation is the main factor of degradation, which occurs by passing the ultrasound wave through a liquid. There are two different mechanisms for organic pollutant degradation based on their physicochemical properties: thermal decomposition which occurs by direct pyrolysis inside the cavitation bubbles, oxidation of the pollutants by OH radicals formed when the cavitation bubbles collapse. [14] Presence of ultrasonic in aqueous solutions leading to cleavage of the H-O bond in water to form hydroxyl radicals and hydrogen atoms according to the following reaction as the result of cavitation:



The fate of this two produce component is proportional to the reaction condition, the most usual reaction is dimerisation of the hydroxyl radical producing hydrogen peroxide and this reduces the amount of H<sub>2</sub>O<sub>2</sub> need to be added [15]:



Although several studies were carried out for the degradation of PCP but degradation by SEF process and comparison between this method and E-F process has not been addressed in the literature. Therefore, the aim of the present study was to compare the performance of electro-Fenton (EF), and sono-electro-Fenton (SEF) process for the degradation of pentachlorophenol. The influence of operating parameters such H<sub>2</sub>O<sub>2</sub> concentration, pH and treatment time of PCP on the degradation was investigated. The reaction kinetics was studied for find the degradation mechanism and compare with electro Fenton results.

## 2. Materials and methods

### 2.1. Materials

Pentachlorophenol 98.5%, H<sub>2</sub>O<sub>2</sub> (30%, Merck) was used as purchased. Sodium sulfate 99.5% is used as electrolyte; the PH of the solution was adjusted using concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (0.1 M). All the solution in this study was prepared with distilled water; concentrated hydrochloric acid was used for electrode washing. All chemicals that used in this study were of analytical grade and without any further purification.

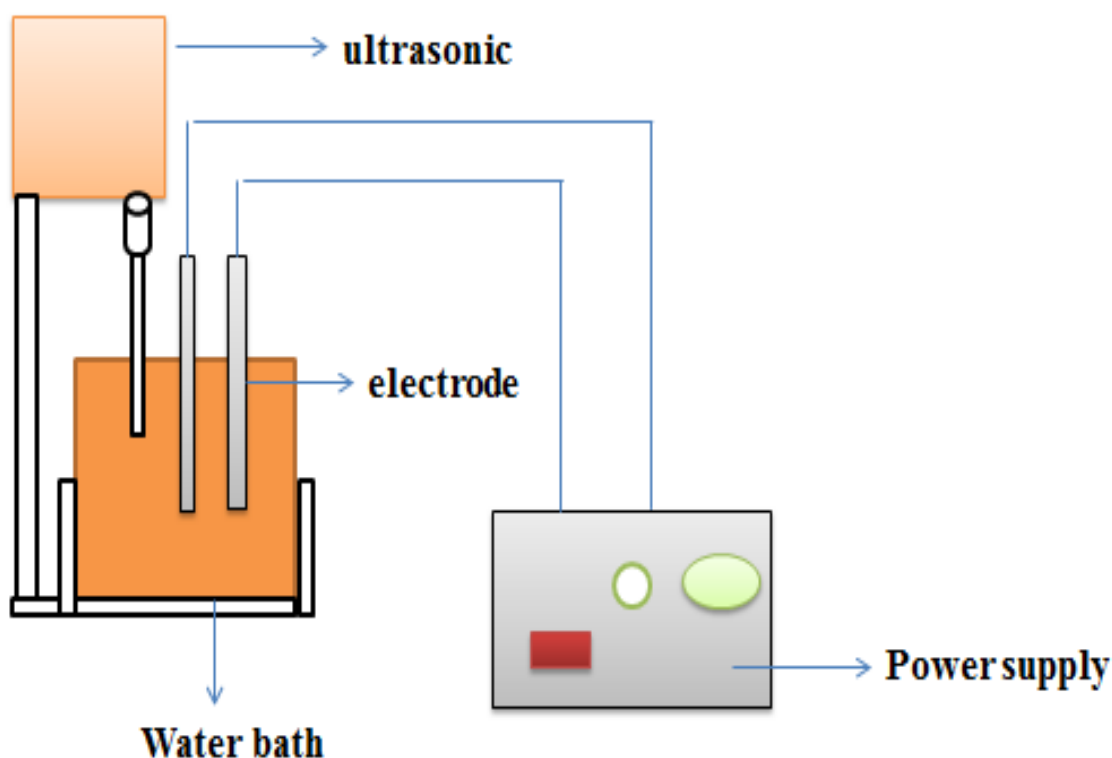
### 2.2 Electro-Fenton process (EF)

Experiment was done at room temperature (25°C) in a divided double- electrode electrochemical cell that consists of 400 ml glass beaker with the internal diameter of 8.8 cm, equipped with by vertically electrodes. The cathode and anode were a piece of steal (st37) having an effective area of 3 cm<sup>2</sup> which was plunged into the cell. A DC power supply which used for providing reasonable voltage was connected to the electrodes and the voltage was set at suitable value for each experiment. The solution was stirred with a magnetic stirrer continually by suitable rotation

per min so that the vortex was not created to keep homogeneity of electrolyte concentration. 250 ml solution was prepared by knowing the initial PCP concentration (15 mg/l) then sodium sulfate was added as electrolyte (2000mg/lit). The initial pH of solutions was set by the addition of concentrated H<sub>2</sub>SO<sub>4</sub> or sodium hydroxide (0.1 M). The PH was measured by digital PH meter calibrated with standard buffer at PH value of 4.01 and 7.01. The conductivity of the medium was fixed by addition of Na<sub>2</sub>SO<sub>4</sub> (2000mg/l) and then 250 ml sample was transferred in to the E-F reactor. After addition of required amount of H<sub>2</sub>O<sub>2</sub>, EF experiment was started. At the end of each experiment, the pH was adjusted to below 2 by H<sub>2</sub>SO<sub>4</sub> [16]

### 2.3 Sono-electro-Fenton process (SEF)

Sample Preparation was done the same as the E - Fenton method. After preparing a specific amount of the solution, it was subjected to ultrasonic wave. Sonication was carried out at 20 kHz in a power of 100 W by placing ¼ inch diameter sonic probe at the center of the sample. In order to control the temperature of the solution, the reactor was placed in the water bath. The temperature of the bath was monitored during the experiment to keep constant at room temperature (fig1).



**Figure1.** SEF Experimental apparatus

### 2.4 Analysis procedures

COD values of samples were determined by using open reflux method described in the standard method. In this case a sample was refluxed in strongly acid solution with a known excess of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). After digestion, the un reduced K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> that remained in the solution is titrated with ferrous ammonium sulfate to find the amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed and the oxidizable matter is calculated in terms of oxygen equivalent. 2-h reflux time was used. The efficiencies of PCP degradation and COD removal were defined as follows:

$$\text{COD removal efficiency} = \Delta [\text{COD}] / \text{COD}_0 = [\text{COD}_f - \text{COD}_0] / \text{COD}_0 * 100$$

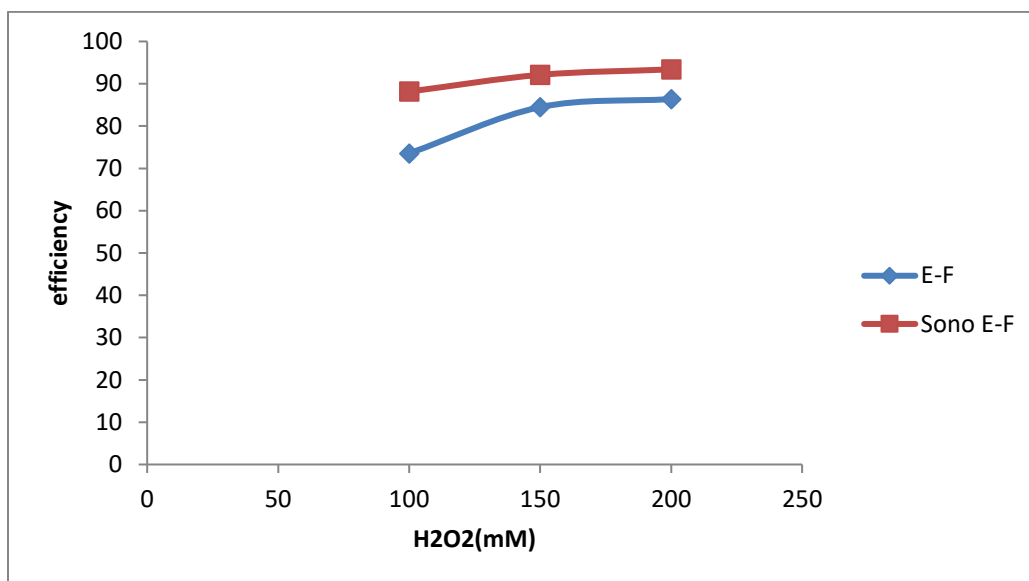
Where  $[\text{COD}]_0$  and  $[\text{COD}]_f$  are the COD concentrations in the solution at 0 min and end of each reaction, respectively. At the end the analysis and comparison of result was done using office software.

### 3. Results and discussion

Electro-Fenton and sono-electro-Fenton were carried out to investigate the effect of different operational parameters such as  $\text{H}_2\text{O}_2$  concentration, pH and treatment time on PCP degradation and COD removal. In this experimental study we were used the result of our optimization using Taguchi method in the past, the following sections described the results of this experimental study.

#### 3.1 Effect of $\text{H}_2\text{O}_2$

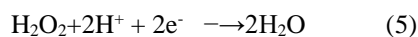
Fig. 2 shows the effect of initial  $\text{H}_2\text{O}_2$  concentration on PCP degradation by EF and SEF processes at a constant PCP concentration of 15 mg/L, voltage of 24v and at pH 3, after the reaction time of 40 min. As can be seen from the figure, the degradation of PCP and COD removal efficiency in both processes has the same pattern and it increased with increasing initial  $\text{H}_2\text{O}_2$  concentration. The maximum COD removal of 90% was observed for EF process with 200 mM of  $\text{H}_2\text{O}_2$ . In SEF processes, higher COD removal was observed for a low amount of  $\text{H}_2\text{O}_2$  concentration, because in SEF hydroxyl radical production was increased by increasing  $\text{H}_2\text{O}_2$  amount in accordance with Eq. (4). In Fenton process,  $\text{H}_2\text{O}_2$  is the main source of hydroxyl radical Production. But excess  $\text{H}_2\text{O}_2$  has a scavenging effect on Produced  $\text{OH}\cdot$  Furthermore the operational cost will be increased with rising  $\text{H}_2\text{O}_2$  consumption. [17], so finding the best  $\text{H}_2\text{O}_2$  concentration is an important in AOPs process. In SEF maximum COD removal efficiency was 94% at 200Mm  $\text{H}_2\text{O}_2$ . In SEF the increase in COD removal efficiency is due to the increase in hydroxyl radical's production, which is due to combination of ultrasound waves and Electro Fenton process. [13] This result was observed in several other studies, including: Advanced oxidation of phenol by EF and SEF process. [13], COD and color removal from synthetic textile wastewater by SEF process [16], Dye removal by SEF process. [14].



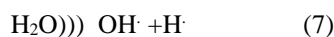
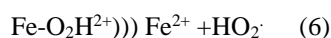
**Figure 2:** Effect of  $\text{H}_2\text{O}_2$  concentration on PCP removal efficiency (conditions: initial PCP concentration, 15 mg/L; initial pH, 3; voltage, 24 v; reaction time, 40 min).

### 3.2 Effect of pH

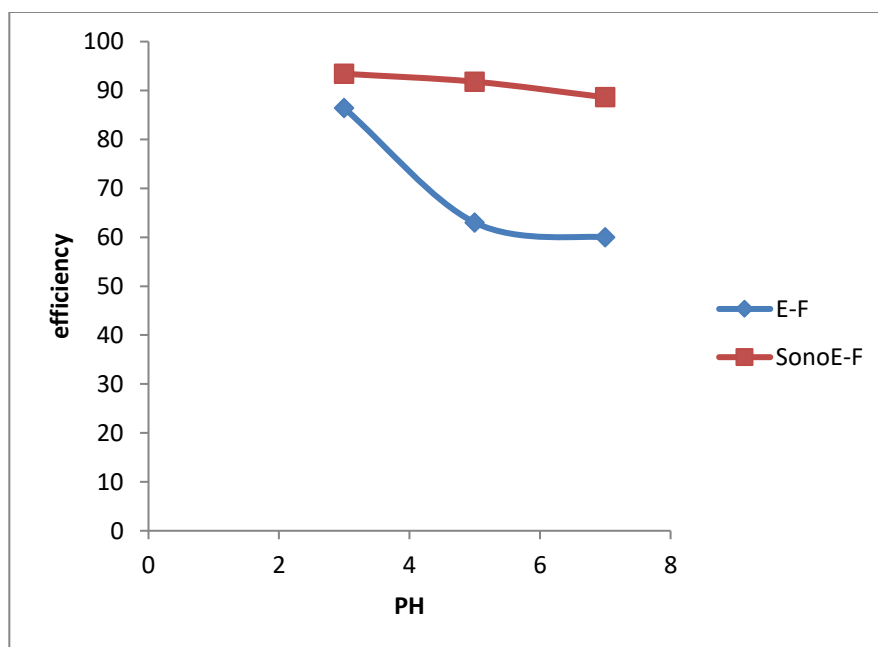
Although Fenton process was done in acidic medium Changes in the pH of the medium are one of the most important factors affecting the AOP process due to controls the H<sub>2</sub>O<sub>2</sub> and iron species. [18, 13] the influences of PH (3-7) on PCP removal were studied and figure 3 investigate the comparison between EF and SEF. The experiment were performed by using initial PCP concentration of 15 mg/L, voltage of 24v, H<sub>2</sub>O<sub>2</sub> concentration of 200mmol/l and treatment time of 40 min for both EF and SEF processes. According to the result PH had a significant effect on PCP removal efficiency. The maximum PCP removal was observed at PH 3. Increase in pH from 3 to 7 decreased the removal efficiencies of both processes because Higher pH values leading iron species to precipitate as ferric hydroxides. At lower PH values Hydrogen peroxide converted to H<sub>2</sub>O as given in the following Eq:



Due to formation of oxonium ion (H<sub>3</sub>O<sub>2</sub><sup>+</sup>), which makes peroxide electrophilic to enhance its stability and substantially reduces the reactivity with Fe<sup>2+</sup> ion, the efficiency of the process may decrease [18, 13] at higher pH values, electro-coagulation starts in the reactor because of the conversion of Fe<sup>2+</sup> and Fe<sup>3+</sup> to Fe(OH)<sub>n</sub> type structures [13, 11] The increase in pH beyond 3 affected the removal efficiency due to the transformation of ferrous ions (Fe<sup>2+</sup>) to ferric iron (Fe<sup>3+</sup>). However, addition of ultrasonic wave's irradiation provides the transformation of Fe<sup>3+</sup> to Fe<sup>2+</sup> (Eq. (2)) and generation of hydroxyl radicals as shown in Eq. (7). [13, 17]



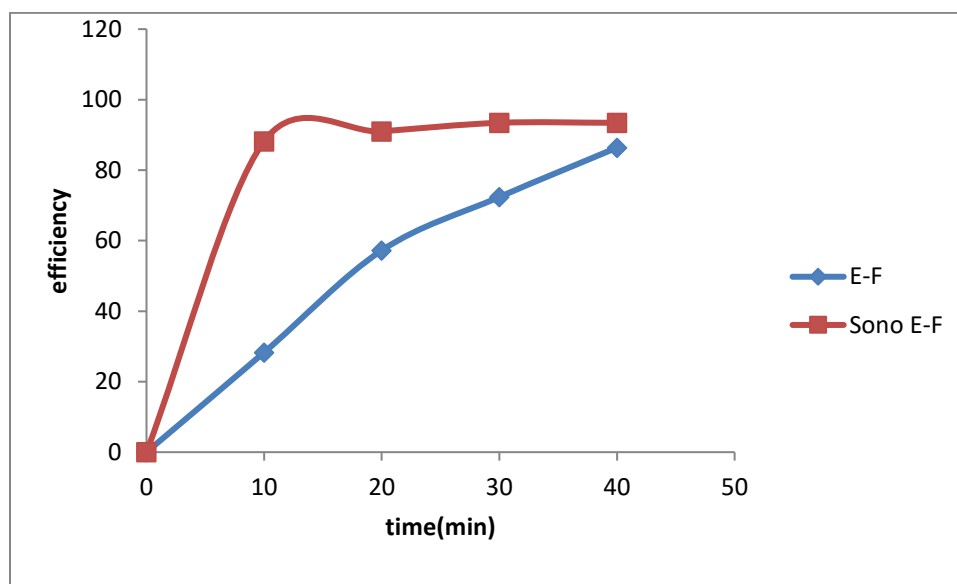
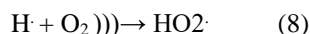
Hydroxyl radical produced in these reactions is used for PCP removal at higher pH. SEF processes could be used at near neutral pH range and reduce the problems associated with acidic effluent treatment. [13] This result was observed in several other studies, including: Advanced oxidation of phenol by EF and SEF process. [13], COD and color removal from synthetic textile wastewater by SEF process [17].



**Fig3.** Effect of pH on a PCP removal (conditions: initial PCP concentration, 15 mg/L; applied voltage, 24v; H<sub>2</sub>O<sub>2</sub> concentration, 200 mM; reaction time, 40 min).

### 3.3 Effect of treatment time

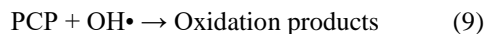
Figure 4 shows the variation of PCP removal efficiency with time for the two processes studied. The experiments were performed by using initial PCP concentration of 15 mg/L, voltage of 24v, H<sub>2</sub>O<sub>2</sub> concentration of 200mmol/l and PH values of 3for both EF and SEF processes. By increase the time the removal efficiency was increase to 40 min for two processes. The time required for the removal of PCP by SEF process was less than Electro Fenton due to the rapid production of hydroxyl radicals by ultrasound as shown in Eqs. (7) and (8).



**Figure4.** Showing % PCP removal under Sono-E-Fenton , E-Fenton process at optimum condition (initial PCP concentration, 15 mg/L; applied voltage,24v; H<sub>2</sub>O<sub>2</sub> concentration, 200 mM; PH, 3).

### 3.4 Removal kinetics

Kinetic modeling is the one approach to study the behavior of the EF and SEF reactions. Zero-, first- and second-order reaction kinetics was used to study PCP removal kinetics for EF and Sono-EF processes. The following equations investigate these model expressions. The removal of PCP by E-Fenton process can be represented as:



•OH does not accumulate in the solution because it is a very reactive species and its concentration takes a steady-state value during the experiment.

First-order reaction kinetics:

$$dC/dt = k_{abs} C [OH \cdot] \quad (10)$$

Since [•OH] is constant,  $k_{abs} [OH \cdot]$  is equal to  $k_{app}$ , Where  $k_{abs}$  and  $k_{app}$  are absolute and apparent rate constants, respectively. Equation (9) can be written as follows:

$$dc/dt = k_{app}C \quad (11)$$

$$\ln C - \ln C_0 = -k_{app}t \quad (12)$$

Zero-order reaction kinetics:

$$dc/dt = -k_0 \quad (13)$$

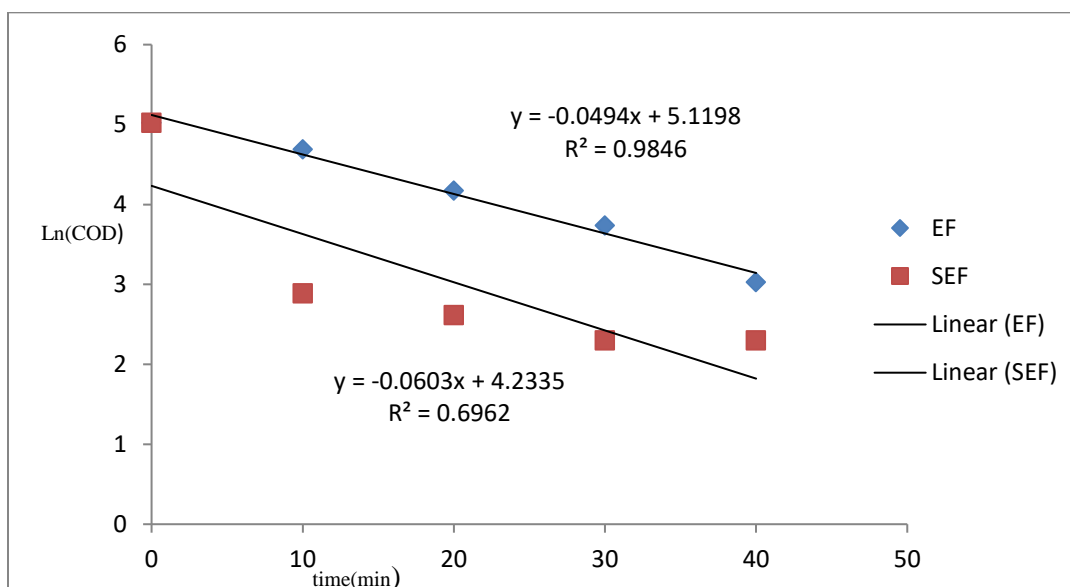
$$C = C_0 - k_0t \quad (14)$$

Second-order reaction kinetics:

$$dc/dt = -kC^2 \quad (15)$$

$$1/C = 1/C_0 - Kt \quad (16)$$

Where C and C<sub>0</sub> are local and initial concentration respectively and K is rate constant, [19, 20]. Regression analyses based on the zero-, first- and second order reaction kinetics for PCP removal in EF and sono-EF processes were investigated and the results were summarized in Table 1. Comparing the determination coefficient it can be seen that R<sup>2</sup> values based on the first-order reaction kinetics for PCP removal by EF and sono-EF processes were 0.9707 and 0.8929, respectively which were more than those based on the zero-order and the second-order models. So, the results showed that the removal kinetics of PCP followed the first-order kinetics mechanism (fig.5), this result was observed in several other studies, including: Photocatalytic degradation kinetics and mechanism of pentachlorophenol based on superoxide radicals [20].



**Figure 5:** Pseudo first order kinetic plot under Electro-Fenton, and Sono-Electro-Fenton process at optimum condition (H<sub>2</sub>O<sub>2</sub>=200mM, voltage =24v, PCP =15mg/l and PH=3)

**Table 1:** The regression coefficients for zero-, first and second-order kinetic and rate constants.

Oxidation process	Zero order	First order	Second order
EF	0.9045	0.9707	0.9418
SEF	0.5495	0.7793	0.7659

#### 4. Conclusion

The performance of electro-Fenton and sono-electro-Fenton processes on the PCP removal efficiency were studied and their results were compared. As a result of this experimental study, it can be concluded that the PCP removal is strongly dependent on initial pH and H<sub>2</sub>O<sub>2</sub> concentration. When EF process was coupled with sonication, the removal efficiency increased due to the more generation of oxidizing agents in Sono-EF process compared with EF process. In SEF process PCP can be removed at less time and less H<sub>2</sub>O<sub>2</sub> consumption compared with EF process and the SEF process can reduce the problems associated with acidic effluent treatment. From the removal kinetic analysis, the reaction order for the two processes followed the first-order kinetics. The following items have been identified as subjects for further research activities: PCP removal from aqueous solution by E-F oxidation combined with UV irradiation, theoretical study of the effects of ultrasonic and ultraviolet power on PCP removal efficiency in Sono-Electro-Fenton and photo-Electro-Fenton method, repeat this process for real waste water and investigation of removal efficiency of electro-Fenton for removal of PCP in the presence of other pollutants.

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#### References

- [1] T.C. Wang, G. Qu, J. Li, N. Luc, Kinetics studies on pentachlorophenol degradation in soil during pulsed discharge plasma process, *Journal of Electrostatics*, 71, 994-998, 2013.
- [2] J. Zhang, P. Ye, S. Chen, and W. Wang, Removal of pentachlorophenol by immobilized horseradish peroxidase, *Journal of International Biodeterioration & Biodegradation*, 59, 307-314, 2007.
- [3] N. T. Thuan, M. B. Chang, Investigation of the degradation of pentachlorophenol in sandy soil via low temperature pyrolysis, *Journal of Hazardous Materials* 229-230, 411-418, 2012.
- [4] Y. Kumar, K. M. Papat, H. Brahmabhatt, B. Ganguly, and A. Bhattacharya, pentachlorophenol removal from water using surfactant-enhanced filtration through low-pressure thin film composite membranes, *Journal of Hazardous Materials*, 154, 426-431, 2008.
- [5] J. Niu, J. Xu, Y. Dai, J. Xu, H. Guo, K. Sun, and R. Liuet, Immobilization of horseradish peroxidase by electrospun fibrous membranes for adsorption and degradation of pentachlorophenol in water, *Journal of Hazardous Materials*, 246-247, p.119-125, 2013.
- [6] Y. Wang, D. Zhang, F. Rong He, and X. Chun Chen, Immobilization of laccase by Cu<sup>2+</sup> chelate affinity interaction on surface modified magnetic silica particles and its use for the removal of pentachlorophenol, *Journal of Chinese Chemical Letters*, 23, 197-200, 2012.
- [7] Z., Yu, G. M., Zenga, Y. N. Chena, J. C. Zhanga, Y. Yua, H. Li, Z. F. Liu, and L. Tang, Effects of inoculation with *Phanerochaete chrysosporium* on remediation of pentachlorophenol-contaminated soil waste by composting, *Journal of Process Biochemistry*, 46, 1285-1291, 2011.
- [8] J. Zimbron, and K. F. Reardon, Fenton's oxidation of pentachlorophenol, *Journal of water Research*, 43, 1831-1840, 2009.
- [9] J. Zhang, P. Ye, S. Chen, and W. Wang, removal of pentachlorophenol by immobilized horseradish peroxidase, *Journal of International Biodeterioration & Biodegradation*, 59, 307-314, 2007.



- [10] Y. Li, Y. Zhang, J. Li, and X. Zheng, enhanced removal of pentachlorophenol by a novel composite: Nanoscale zero valent iron immobilized on organobentonite, *Environmental Pollution*, 159, 3744-3749, 2011.
- [11] E. Atmaca, Treatment of landfill leachate by using electro-Fenton method, *Journal of Hazardous Materials*, 163, 109–114, 2009.
- [12] W.H. Glaze, an overview of advanced oxidation processes: current status and kinetic models, *Journal of Chemical. Oxidation*, 2, 44-57,1994.
- [13] A. Babuponnusami, and K. Muthukumar, advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, *Journal of Chemical Engineering*, 183, 1–9, 2012.
- [14] S. N. Giray, D. Aktas, M. Dolaz, Y. Uysal, Removal of dye from real textile wastewater by sono-electro-Fenton oxidation process, *Journal of selçuk university natural and applied science*, 2014.
- [15] C. Petrier, A. Juenet, J-L. Luche, G. Reverdy, Unexpected frequency effects on the rate of oxidative processes induced by ultrasound, *Journal of Am. Chem. Soc.*, 114, 3148-3150, 1992.
- [16] Z.Heidari,M. Motavasel, N. jaafarzadeh, Application of Electro-Fenton (EF) process to the removal of pentachlorophenol from aqueous solutions, *Iranian Journal of Oil & Gas Science and Technology*, 4, 76-87, 2015.
- [17] S. Sahinkaya, COD and color removal from synthetic textile wastewater by ultrasound assisted electro-Fenton oxidation process, *Journal of Industrial and Engineering Chemistry*, 19, 601–605, 2013.
- [18] P.V, Nidheesh, and R. Gandhimathi, trends in electro-Fenton process for water and wastewater treatment: an overview, *Journal of Desalination*, 299, 1–15, 2012.
- [19] F., Javier Benitez, J.L. Acero, F.J. Real, F.J., J. Garc, Kinetics of photodegradation and ozonation of pentachlorophenol, *Journal of Chemosphere*, 51, 651–662,2003.
- [20] Y. Li, J. Niu, L. Yin, W Wang, Y. Bao, J. Chen, Y. Duan, Photocatalytic degradation kinetics and mechanism of pentachlorophenol based on superoxide radicals, *Journal of Environmental Sciences*, 23, 11, 1911–1918, 2011.