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Keywords: *pentachlorophenol, oxidation process, microwave, persulfate.*

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Abstract- Pentachlorophenol (PCP) is one of the most pollutants frequently used in fungicides and pesticides. Its toxicity is due to intervention with oxidative phosphorylation. Acute and chronic PCP poisoning are approved in human and other living organisms. Recently, AOPs based on microwave and sulfate radical (SO₄^{•-}) have created many great scientific interests due to its high efficiency in the degradation and mineralization of recalcitrant and/or toxic organic pollutants. So that in this study for removal of PCP from wastewater, microwave/persulfate(MW/SPS) was used. The effects of operational parameters such as pH of solution, the power of microwave radiations and the amount of persulfate concentration were studied. Spectrophotometer and HPLC instruments were used for determining the concentration of PCP. The experimental results showed that the removal of PCP was influenced by many factors, such as the pH value, the amount of persulfate and microwave power. The optimum conditions for the best removal rate were obtained at pH=11, a persulfate concentration of 0.02mol/L and microwave irradiation power of 600W for MW/SPS system at constant PCP concentration. Also, obtained results showed that the removal of PCP by MW/SPS and MW alone were follow first order rate decay kinetics and the rate constants were 0.093 and 0.00066 min⁻¹, respectively.

The results of MW/SPS application showed that this processe had suitable efficiency for removal of refractory pollutants and COD and also was cleared that persulfate had high oxidation power.

Keywords: pentachlorophenol, oxidation process, microwave, persulfate.

I. INTRODUCTION

Pentachlorophenol (PCP) is one of the most pollutants frequently used in fungicides and pesticides for wood protection. Its toxicity is due to intervention with oxidative phosphorylation. Acute and chronic poisoning may happen by dermal absorption, inhalation or ingestion. Quantitative determination of PCP in urine and serum is useful to detect its professional or subclinical exposure (Zischke, Arthur et al. 1985, Jorens and Schepens 1993). The clinical

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features of acute and chronic PCP poisoning can be classified systematically into effects on the skin, metabolism (fever), the hematopoietic tissue, the respiratory system, the central and peripheral nervous system, the kidney and the gastrointestinal tract-(Warwick Fisher 1990, Jorens and Schepens 1993).

Exposure to PCP has also been associated with aplastic anemia, leukemia, other blood disorders and neurotoxicity(Stehly and Hayton 1990, Fisher 1991). Nowadays, environmental researchers have considered the sustainable methods for refractory contaminants removal. The inability of conventional treatment processes to remove PCP has stimulated the development and investigation of advanced oxidation processes (AOPs) based on the formation of high active oxidizing species such as HO[•] and other free radicals. In the last two decades, studies on chemical oxidation by ozone, H₂O₂/UV, Fenton's reaction, photo-Fenton process ,ultrasonic irradiation and TiO₂-mediated heterogeneous photocatalysis suggested the effectiveness of AOPs for phenolic compounds removal(Olmez-Hanci, Arslan-Alaton et al. 2013). Recently, AOPs based on microwave and sulfate radical (SO₄^{•-}) have created great scientific interest due to its high efficiency in the degradation and mineralization of recalcitrant and/or toxic organic pollutants(Liang, Huang et al. 2008, Yang, Wang et al. 2009). Now days, microwave assisted Process has been developed as green chemistry. it is able to reduce or eliminate negative environmental impacts(Anastas and Warner 2000). The use of this system involves the reduction of waste products, non-toxic components, and improved efficiency(Tellez, Alquisira et al. 2011). So that in this study for removal of PCP from Synthetic wastewaters, MW/SPS was used.

II. MATERIALS AND EXPERIMENTAL METHODS

Sodium salt PCP, which is the sodium salt of PCP (C₆C₁₅ONa) purchased from Aldrich (its purity was 98%) and was used without further purification. The characteristics of the PCP included of boiling point: 309-310C⁰, mass molar: 288.32g/mol(Fig.1).

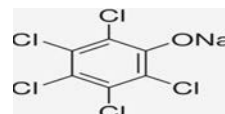


Figure 1 : Chemical structure of PCP

Under atmospheric pressure, all of the experiments were performed and triplicated in modified domestic microwave oven (2450MHz, M2330 DN, SAMSUNG Co, and output power of 100 to 850 W) (Figure2). Detail modifications of MW were presented as follows: drilled a hole in the upper oven wall and then attached an aluminum tube of the same diameter to the hole then equipped with cooling system and a glass reactor with 500 mL volume. Then Samples were taken at suitable time intervals (10 min) from the reaction reactor with a 10 mL syringe and pipetted in to glass vials. Besides, a Thermometer GENWAY Medal 2003 was utilized to detect variation of solution temperature during degradation process. The leakage of MW oven is measured at 20 cm distance from the aperture.

The PCP solution (100,200,300,400, 500, 750, 1000mg/l) prepared by dissolving PCP in NaOH solution to increase its dissolution solution and adding SPS powders (0.01, 0.02, 0.03, 0.04, 0.05 mol/l) and with adjusted pH (3,7and 11) were put into a reactor. The degradation rate of PCP was calculated according to the following equation:

$$\mu = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Where:

C_t is the concentration of the PCP after MW irradiation;
 C_0 is the concentration of the PCP before MW irradiation.
 PCP was oxidized by the following methods:

- Microwave irradiation method (MW)
- Microwave/persulfate method (MW/SPS)

After setting interval time for degradation, samples were drawn for the analysis. Concentration changes of PCP were determined using spectrophotometer according to (APHA, 2005). In the end for identification of oxidation intermediates HPLC spectra and COD methods were used. The measurement with modified HPLC (Part Number.WATO54275 with dimension of 4.6 mm×250 mm and column of symmetry C18-50 μ m) method was performed with an acetonitrile/water 60:40 (v/v) as mobile phase at a flow rate of 1mL/min and detection wavelengths of UV was 254 nm. Amount of injected samples was 10 μ l at 25C^o, pH=7 and time of 7minutes. COD was determined using potassium dichromate solution as oxidizer in a strong acid medium, then by titration step using ferrous ammonium sulfate as the reducing agent and Ferroin as the indicator(Hong, Yuan et al. 2012).

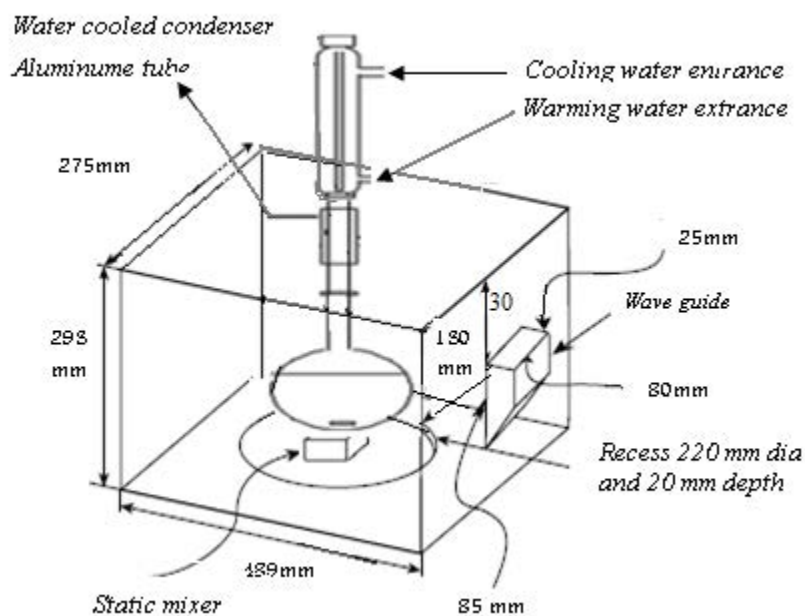


Figure 2 : schematic diagram of modified microwave system

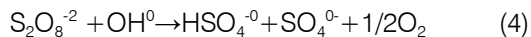
III. RESULTS AND DISCUSSION

a) Effect of pH

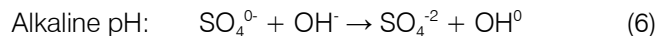
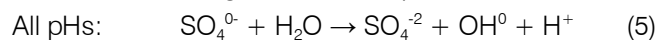
Degradation of PCP by MW/SPS system in a broad pH range, from acidic to alkaline conditions, was initially studied (Fig3). In our study the values of k in pH= 3,7and 11 was 54%, 64% and 67% respectively. The observed degradation rate was highest at pH 11.

The Phenomena of PCP removal are attributed to the ability of MW to initiate sulfate and hydroxyl radical formation at high pH. These radicals at extreme alkaline pH have an higher oxidation potential than acidic conditions .The effect of basicity on persulfate reactivity was discussed by Furman et al(Furman, Teel et al. 2010) and the persulfate can be activated to initiate

sulfate radical at high pH, under the effect of hydroxyl radical (Eq. 4)(Ocampo 2009).



In general and according to experimental conditions following reactions are performed:



Both $\text{SO}_4^{\cdot-}$ and OH^0 are possibility responsible for degradation of organic contaminants and other radicals may produce depending on pH conditions. other studies showed that in pH=3-10, amount of hydroxyl radical is more than sulfate radical ,But in pH>11 amount of sulfate radical is more than hydroxyl(Liang, Wang et al. 2007, Neppolian, Doronila et

al. 2010). The difference between our work and previous studies could partly attribute to pH>10. It was also possible that substrates with distinct physico-chemical characterization could show different degradation behaviors in alkaline SPS system. Furthermore, Abu Amr et al reported that a high pH (11) is favored in the removal of Phenol from wastewater using persulfate oxidation(Abu Amr, Aziz et al. 2013). The most of results showed organic removal efficiencies were highly depended on pH values and the efficiencies were dropped sharply with decreasing pH values. For higher pH values (above 11), the efficiencies of removal were relatively high. The complex pH effect may be associated with the fact that the total radical concentration and fractions of the different radicals were varied with pH changes (Gao, Gao et al. 2012).

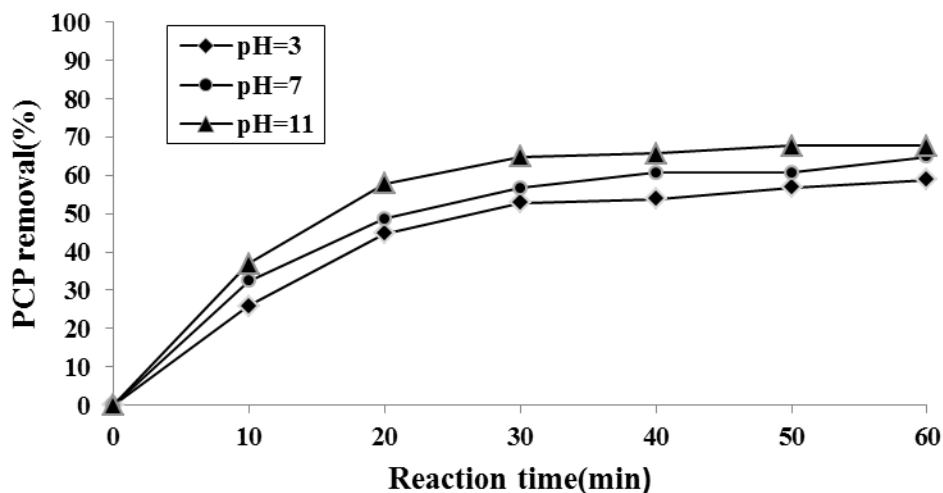
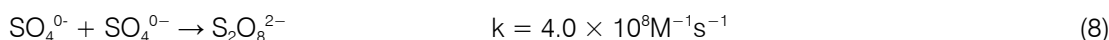
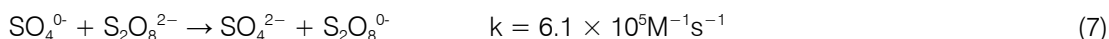


Figure 3 : Effect of pH on PCP removal ($C_0=100\text{mg/L}$, $\text{SPS}=0.01\text{mol/l}$, $E=600\text{W}$)

b) Effect of persulfate concentration

The effect of the initial persulfate concentration on PCP (100 mg/L) removals was examined at five concentrations of persulfate (0.01, 0.02, 0.03, 0.04, 0.05 mol/l) and at 600W. From Fig. 4 it is observed that PCP removal rates increased with increasing persulfate concentration (0.01 to 0.02 mol/l). PCP removal was complete after 60 min of reaction. But when increasing the initial persulfate concentration from 0.02 to 0.05

mol/l under MW reaction conditions, increase of persulfate did not effect on enhance PCP degradation. PCP degradation rate almost was decreased 45% when the initial persulfate concentration was increased from 0.02 mol/l to 0.05 mol/l. An extremely high initial persulfate concentration generated a higher amount of $\text{SO}_4^{\cdot-}$ that may reduce PCP oxidation according to the following equations (Olmez-Hanci, Arslan-Alaton et al. 2013):



According to Eqs. (7) and (8), it can be found that condition of extra SPS has a negative effect on $\text{SO}_4^{\cdot-}$ production, because it changes $\text{SO}_4^{\cdot-}$ radicals trend to anions of SO_4^{2-} and $\text{S}_2\text{O}_8^{\cdot-}$. Therefore removal efficiency of organic compounds is decreased (Liang, Wang et al. 2007). The decrease in pH values to ≤ 2.5

during examinations, even by using buffer phosphate, are a consequence of the sulfate radicals formation and their accumulation (Olmez-Hanci, Arslan-Alaton et al. 2013). Also, other researchers confirm these results (Shih, Putra et al. 2012).

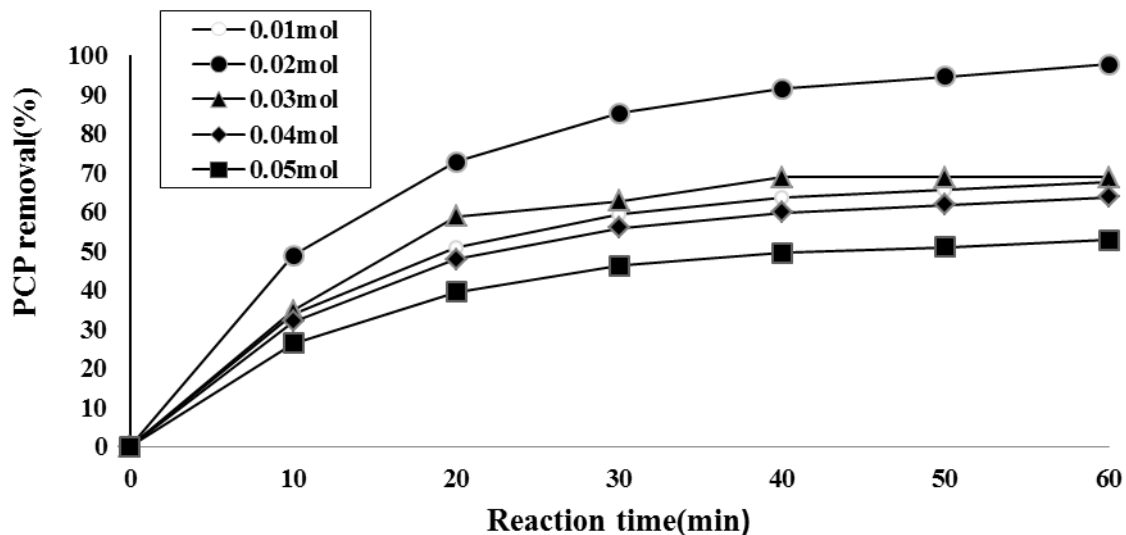


Figure 4 : Effect of SPS dose on PCP removal ($C_0=100\text{mg/L}$, $\text{pH}=11$, $E=600\text{W}$)

c) Effect of different microwave energy on decomposition of PCP

The test results shown in Fig. 5 indicated that degradation rate of PCP gradually increased with increasing energy intensity (180,450,600W with optimal temperatures 80, 100, and 105C° respectively); whereas the degradation rate did not changed for higher power (>600 W). So the microwave irradiation of 600W was chosen throughout the experiments. According other studies with increasing energy, amount of final temperature (T_f) was increased(Costa, Santos et al. 2009). These results revealed that persulfate could be

converted to $\text{SO}_4^{\cdot-}$ radicals by MW energy resulting in a considerable enhancement in the reaction rates(Nuechter, Mueller et al. 2003). It was noted that the organic compounds removal by MW/SPS system was higher than conventional heat/SPS (CH/SPS) - system. This effects has been attributed to “specific” or “non-thermal” microwave effects(Tellez, Alquisira et al. 2011) and existence of hot spots. It seems that it be the more possible cause of the reaction rate enhancement observed in works under microwave irradiation. However, it is necessary to more study in this field(Costa, Santos et al. 2009, Hong, Yuan et al. 2012).

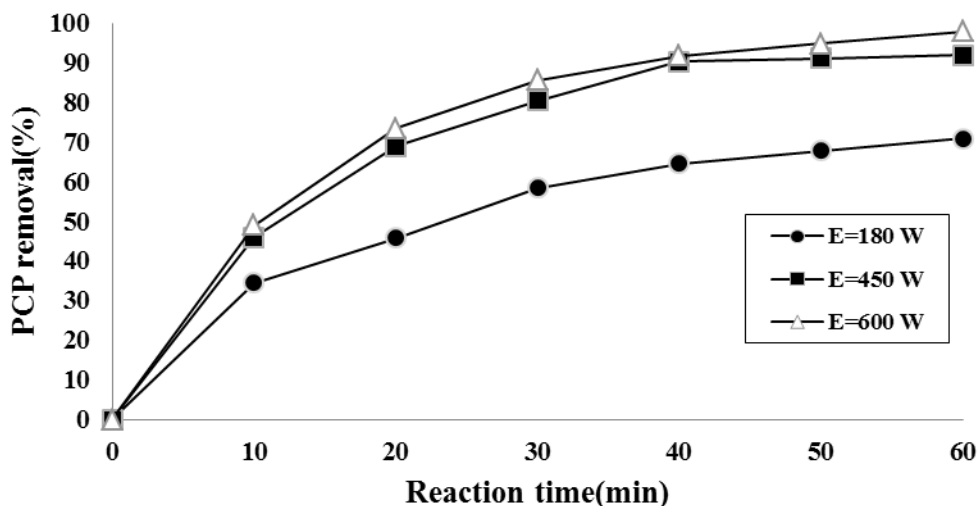


Figure 5 : Effect of energy on PCP removal ($C_0=100\text{mg/L}$, $\text{pH}=11$, $\text{SPS}=0.02\text{mol/L}$, $E=180,450,600\text{W}$)

d) *Effect of PCP concentration*

High PCP concentrations were subjected to MW/SPS. In this study effect of PCP concentration (100, 200, 300, 400, 500, 750 and 1000mg/l) was studied by the MW/SPS system under microwave power of 600 W (Fig. 6). In this study the values of PCP removal was between 98% to 90%. Because effect of increasing PCP concentration had an ineligibile role (8%) on efficiency removal and selection of 1000mg/l PCP wasn't economic, therefore 100mg/l was chosen as optimal concentration. Also, the direct degradation results showed that the removal of PCP was 2% in MW system without SPS after 60 min of MW irradiation. The removal of PCP by MW/SPS and MW alone were follow first order

rate decay kinetics and the rate constants were 0.093 and 0.00066 min⁻¹, respectively. Today it is observed that processes integrated with MW have high efficiency in removal of pollutants such as phenol, aromatic hydrocarbon and PCPs. For example, this process is able to remove 500 to 12000 mg/l of ammonia with efficiencies above 95% (Lin, Yuan et al. 2009). So that, increasing of non polar organic materials cannot decrease process efficiency. Also other Previous studies confirm that microwave process is very effective for removal of heavy metals, COD and color from waste water effluent (Ramon, Valero et al. 2003, Zhang, Li et al. 2007, Yang, Wang et al. 2009).

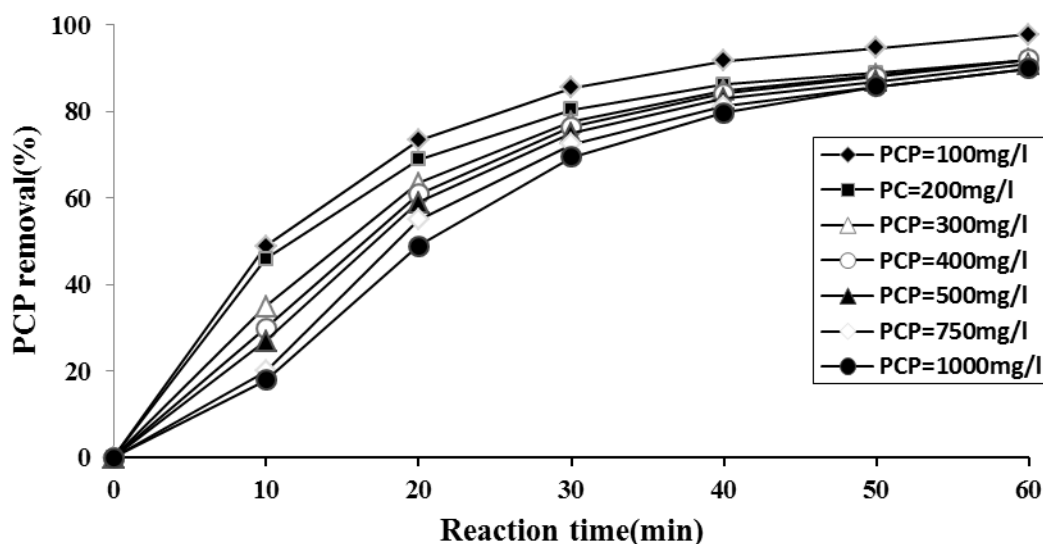


Figure 6 : Effect of PCP concentration (pH=11, SPS=0.02mol/L, E=600W)

e) *Identification of Predominate Radical Species Under Tba Molar Constant*

Table 1 shows that the addition of TBA resulted in slightly decreases (i.e., inhibition) in the PCP degradation rate when compared to without TBA conditions. Inhibition was 15% at pH 11. Radical inhibition experiments were conducted to identify the main radical oxidant ($\text{SO}_4^{\cdot-}$ vs. OH^\cdot) under 0.04M of TBA by observing the differences in radical reactivities (i.e., radical scavengers. This method has been successfully employed to distinguish $\text{SO}_4^{\cdot-}$ vs. OH^\cdot activity in an activated persulfate system (Anipsitakis, Dionysiou et al. 2006). When comparing k in the presence of alcohol scavengers to those observed without alcohols, the decreases of k due to the addition of the alcohol (% change in $k = ((k \text{ (with alcohol)} / k \text{ (without alcohol)}) - 1) \times 100$) were calculated (Liang, Wang et al. 2006). As shown in Table 1 with the addition of TBA the % change in k (i.e., inhibition) at pH 11 and 0.04 mol/l of TBA was between -31 to -46%. However, when the TBA was introduced into the

degradation systems, the degradation rate was only decreased slightly. This result demonstrated $\text{SO}_4^{\cdot-}$ was the dominate active species generated in the MW/SPS system, while OH^\cdot played a minor role in this process for PCP removal. Usually, $\text{SO}_4^{\cdot-}$ is more selective for electron transfer reactions than is OH^\cdot . So, it is seen that the reactivity of $\text{OH}^\cdot/\text{TBA}$ system is near 400–1900-fold greater than that of $\text{SO}_4^{\cdot-}$ system (Liang, Wang et al. 2007).

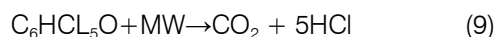
Table 1 : Summary of radical identification experiments

Time (min)	K (min ⁻¹)				% change in K with TBA
	No alcohol	R ²	With TBA	R ²	
10	0.23	97%	0.16	97%	-31
20	0.125		0.059		-32
30	0.058		0.085		-46

f) Comparison of PCP and COD removal

Several mechanisms have been proposed in explaining the organic degradation based AOPs. PCP = 100 mg/L; COD = 344mg/l; pH = 11, S₂O₈²⁻ = 0.02mol/l were analyzed by HPLC and COD method after 0, 10, 20 and 30 min treatment. From Fig 7 it is clear that mainly aromatic intermediates could be detected via HPLC analyses, namely CO₂ and HCL. The reaction degradation can be demonstrated by the products and intermediates shown in the HPLC spectra. COD degradation rate indicated that PCP completely

transformed into CO₂ and HCl immediately (Eq.9). Also, The HPLC spectra and COD results showed a similar trend in mineralization and the lack of toxic intermediates and by products in this process.



In fact, MW/SPS method provides very good results in efficiency of COD removal and reduces the analysis time from 2 h in standard method to some min for any type of sample (Ramon, Valero et al. 2003).

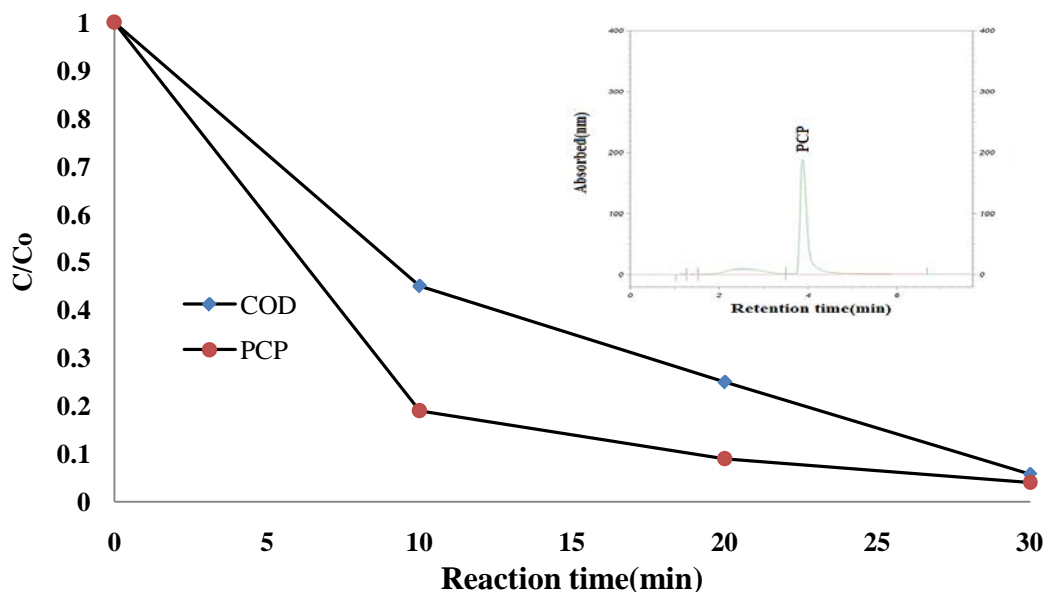


Figure 7 : Comparison of PCP and COD removal in MW/SPS (C₀ = 100mg/L, COD = 344 mg/l pH = 11, SPS = 0.02mol/L, E = 600W)

IV. CONCLUSION

Advanced Oxidation Processes represent a powerful treatment for refractory and/or toxic pollutants wastewaters. Microwave irradiation was particularly effective on COD removal as well as on the oxidation of PCP and eventually leading to mineralization of the compounds into H₂O and CO₂. Addition of SPS, above a required amount, was a limitation for increasing PCP removal. The kinetic analysis showed that a direct reaction of PCP removal with SO₄⁰⁻ and an indirect reaction with OH⁰ radical, because SO₄⁰⁻ radical was dominant in this process. The removal of PCP by MW/SPS and MW alone were follow first order rate

decay kinetics and the rate constants of MW/SPS were 140 times higher than MW alone. This work provides a simple and rapid method for persulfate activation to produce SO₄⁰⁻ in aqueous solution using microwave energy. As SO₄⁰⁻ is an active and environment friendly oxidant, it will have great importance in the fields of green chemistry, environmental protection, and other related fields.

V. ACKNOWLEDGMENTS

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REFERENCES RÉFÉRENCES REFERENCIAS

1. Abu Amr, S. S., et al. (2013). Pretreatment of stabilized leachate using Ozone/Persulfate oxidation process. *Chemical Engineering Journal*.
2. Anastas, P. T. and J. C. Warner (2000). *Green chemistry: theory and practice*, Oxford University Press, USA.
3. Anipsitakis, G. P., et al. (2006). Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions. *Environmental science & technology*, 40, 1000-1007.
4. Costa, C., et al. (2009). Microwave-assisted rapid decomposition of persulfate. *European Polymer Journal*, 45, 2011-2016.
5. Fisher, B. (1991). Pentachlorophenol: toxicology and environmental fate. *Journal of pesticide reform: a publication of the Northwest Coalition for Alternatives to Pesticides*, 11,1-5.
6. Furman, O. S., et al. (2010). Effect of basicity on persulfate reactivity. *Journal of Environmental Engineering* 137, 241-247.
7. Gao, Y.-q., et al. (2012). Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chemical Engineering Journal*, 195-196, 248-253.
8. Hong, J., et al. (2012). Efficient degradation of Rhodamine B in microwave-H₂O₂ system at alkaline pH. *Chemical Engineering Journal*, 191, 364-65.
10. Jorens, P. G. and P. J. C. Schepens (1993). Human pentachlorophenol poisoning. *Human & experimental toxicology*, 12, 479-495.
11. Liang, C., et al. (2008). Potential for activated persulfate degradation of BTEX contamination. *Water research*, 42, 4091-4100.
12. Liang, C., et al. (2007). Influence of pH on persulfate oxidation of TCE at ambient temperatures. *Chemosphere*, 66, 106-113.
13. Liang, C., et al. (2006). Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 C. *Science of the total environment*, 370, 271-277.
14. Lin, L., et al. (2009). Removal of ammonia nitrogen in wastewater by microwave radiation. *Journal of hazardous materials*, 161, 1063-1068.
15. Neppolian, B., et al. (2010). Sonochemical oxidation of arsenic (III) to arsenic (V) using potassium peroxydisulfate as an oxidizing agent. *Water Research*, 44, 3687-3695.
16. Nuechter, M., et al. (2003). Microwave-Assisted Chemical Reactions. *Chemical engineering & technology*, 26, 1207-1216.
17. Ocampo, A. M. (2009). *Persulfate activation by organic compounds*, Washington State University.
18. Olmez-Hanci, T., et al. (2013). Bisphenol A Treatment by the Hot Persulfate Process: Oxidation Products and Acute Toxicity. *Journal of hazardous materials*, 263, 283-290.
19. Ramon, R., et al. (2003). Rapid determination of chemical oxygen demand using a focused microwave heating system featuring temperature control. *Analytica chimica acta*, 491, 99-109.
20. Shih, Y.-J., et al. (2012). Mineralization and deflourization of 2, 2, 3, 3-tetrafluoro-1-propanol (TFP) by UV/persulfate oxidation and sequential adsorption. *Chemosphere*, 89, 1262-1266.
21. Stehly, G. R. and W. L. Hayton (1990). Effect of pH on the accumulation kinetics of pentachlorophenol in goldfish. *Archives of environmental contamination and toxicology*, 19, 464-470.
22. Tellez, H. M., et al. (2011). Comparative Kinetic Study and Microwaves Non-Thermal Effects on the Formation of Poly (amic acid) 4, 4'-(Hexafluoroisopropylidene) diphthalic Anhydride (6FDA) and 4, 4'-(Hexafluoroisopropylidene) bis (p-phenyleneoxy) dianiline (BAPHF). Reaction Activated by Microwave, Ultrasound and Conventional Heating. *International journal of molecular sciences* 12, 6703-6721.
23. Warwick Fisher, S. (1990). The pH dependent accumulation of PCP in aquatic microcosms with sediment. *Aquatic toxicology*, 18, 199-217.
24. Yang, S., et al. (2009). A novel advanced oxidation process to degrade organic pollutants in wastewater: Microwave-activated persulfate oxidation. *Journal of environmental sciences*, 21, 1175-1180.
25. Yang, Y., et al. (2009). Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater: *Journal of hazardous materials*, 168, 238-245.
26. Zhang, X., et al. (2007). Microwave assisted photocatalytic degradation of high concentration azo dye Reactive Brilliant Red X-3B with microwave electrodeless lamp as light source. *Dyes and pigments*, 74, 536-544.
27. Zischke, J. A., et al. (1985). Effects of pentachlorophenol on invertebrates and fish in outdoor experimental channels. *Aquatic toxicology*, 7, 37-58.