

Pentachlorophenol Removal by Persulfate and Microwave Processes Coupled from Aqueous Environments

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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 (SO_4^-) 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 pentachlorophenol removal by persulfate and microwave processes coupled (MW/SPS) from aqueous environments 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 0.02 mol L^{-1} and microwave irradiation power of 600 W 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 showed that used the combination of microwave/persulfate processes is applicable for the removal of pentachlorophenol from aqueous solutions.

Key words: Pentachlorophenol, oxidation process, microwave, persulfate, PCP

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 *et al.*, 1985; Jorgen and Schepens, 1993). The clinical features of acute and chronic PCP poisoning can be classified systematically into effects on the skin, metabolism (fever), the hematopoietic tissue, the central and peripheral nervous system, the kidney and the gastrointestinal tract, the respiratory system (Fisher, 1990; Jorens and Schepens, 1993) and Asthma such as Isosianat (Barkhordari *et al.*, 2011). Exposure to PCP has also been associated with

aplastic anemia, leukemia, other blood disorders and neurotoxicity (Stehly and Hayton, 1990; Fisher, 1991). Now a days, 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^\cdot and other free radicals. In the last two decades, studies on chemical oxidation by ozone, $\text{H}_2\text{O}_2/\text{UV}$, Fenton's reaction, Photo-Fenton process, ultrasonic irradiation and TiO_2 -mediated heterogeneous photocatalysis suggested the effectiveness of AOPs for phenolic compounds removal (Olmez-Hanci *et al.*, 2013; Taghavi *et al.*, 2013). Recently, AOPs based on microwave and sulfate radical (SO_4^-) have created great scientific interest due to its high efficiency in the degradation and mineralization of recalcitrant and/or

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toxic organic pollutants (Liang *et al.*, 2008; Yang *et al.*, 2009a). Now a 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 *et al.*, 2011). So that in this study for removal of PCP from synthetic wastewaters, MW/SPS was used.

MATERIALS AND METHODS

Sodium salt PCP which is the sodium salt of PCP (C_6Cl_5ONa) purchased from Aldrich (its purity was 98%) and was used without further purification. The characteristics of the PCP included of boiling point: $309310^{\circ}C$, mass molar: $288.32 \text{ g mol}^{-1}$ (Fig. 1).

Under atmospheric pressure, all of the experiments were performed and triplicated in modified domestic microwave oven (2450 MHz, M2330 DN, SAMSUNG Co and output power of 100-850 W) (Fig. 2). 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, 1000 mg L^{-1}) 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^{-1}) and with adjusted pH (3, 7 and 11) were put into a reactor. The degradation rate of PCP was calculated according to the following equation: 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. 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

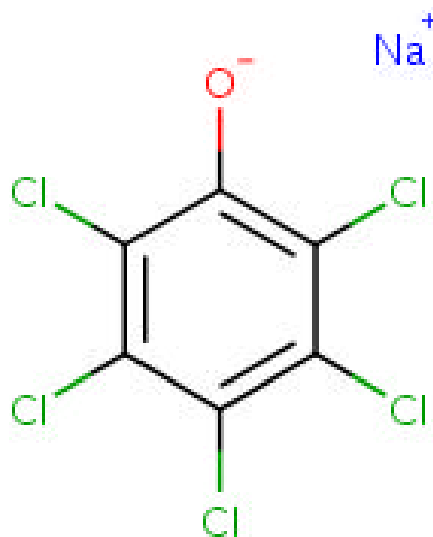


Fig. 1: Chemical structure of PCP

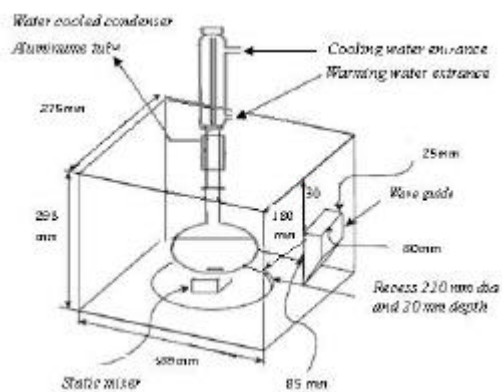


Fig. 2: Schematic diagram of modified microwave system

4.6×250 mm and column of symmetry C18-50 μm) method was performed with an acetonitrile/water 60:40 (v/v) as mobile phase at a flow rate of 1 mL min^{-1} and detection wavelengths of UV was 254 nm. Amount of injected samples was $10 \mu\text{L}$ at $25^{\circ}C$, pH = 7 and time of 7min. 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 *et al.*, 2012):

$$\mu = C_0 - C_t / C_0 \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Effect of pH: Degradation of PCP by MW/SPS system in a broad pH range, from acidic to alkaline conditions was initially studied (Fig. 3). In our study the values of k in

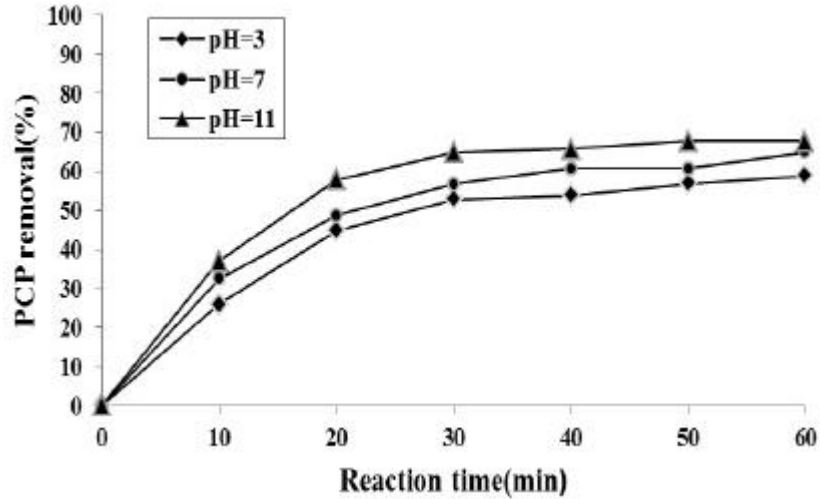


Fig. 3: Effect of pH on PCP removal ($C_0 = 100 \text{ mg L}^{-1}$, SPS = 0.01 mol L^{-1} , E = 600 W)

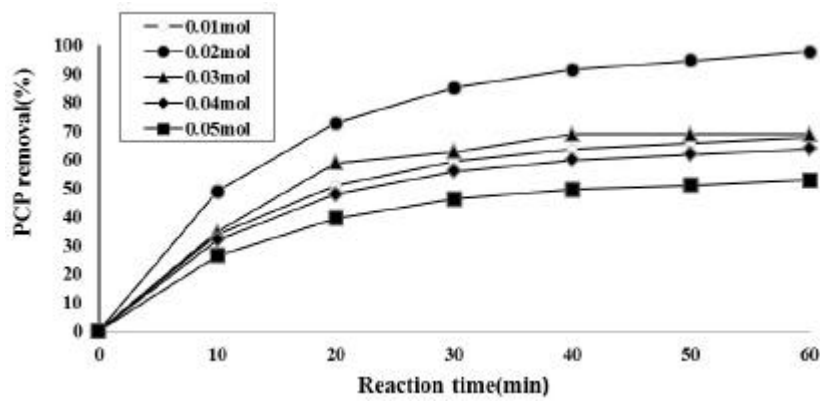
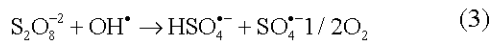
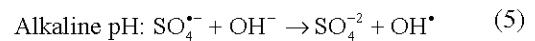
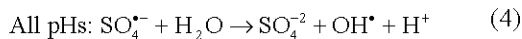


Fig. 4: Effect of SPS dose on PCP removal ($C_0 = 100 \text{ mg L}^{-1}$, pH = 11, E = 600 W)

pH = 3, 7 and 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 a higher oxidation potential than acidic conditions. The effect of basicity on persulfate reactivity was discussed by Furman *et al.* (2010) and the persulfate can be activated to initiate sulfate radical at high pH, under the effect of hydroxyl radical (Eq. 3) (Ocampo, 2009) (Fig. 4):



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

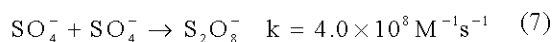
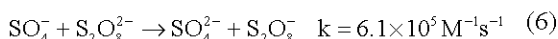


Both $\text{SO}_4^{\bullet-}$ and OH^\bullet are possibility responsible for degradation of organic contaminants and other radicals may produce depending on pH conditions. Other studies showed that in pH = 3-10, amount of hydroxyl radical is more than sulfate radical but in pH >11 amount of sulfate radical is more than hydroxyl (Liang *et al.*, 2007; Neppolian *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, Amr *et al.* (2013) reported that a high pH (11) is favored in the removal of Phenol from wastewater using persulfate oxidation (Amr *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 *et al.*, 2012).

Effect of persulfate concentration: The effect of the initial persulfate concentration persulfate did not effect on enhance PCP degradation. On PCP (100 mg L⁻¹) removals was examined at five PCP degradation rate almost was decreased 45% when concentrations of persulfate (0.01, 0.02, 0.03, 0.04, 0.05 mol L⁻¹) and at 600 W. From Fig. 4, it is observed that PCP removal rates increased with increasing persulfate concentration (0.01-0.02 mol L⁻¹). PCP removal was complete after 60 min of reaction. But when increasing the initial persulfate concentration from 0.02-0.05.

According to Eq. 7 and 8, it can be found that condition of extra SPS has a negative effect on SO₄⁻ production, because it changes SO₄⁻ radicals trend to anions of SO₄²⁻ and S₂O₈⁻. Therefore, removal efficiency of organic compounds is decreased (Liang *et al.*, 2007). The decrease in pH values to = 2.5 mol L⁻¹ 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 0.02-0.05 mol L⁻¹. An extremely high initial persulfate concentration generated a higher amount of SO₄⁻ that may reduce PCP oxidation according to the following equations:



during examinations, even by using buffer phosphate are a consequence of the sulfate radical formation and their accumulation. Also, other researchers confirm these results (Shih *et al.*, 2012).

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, 600 W with optimal temperatures 80, 100 and 105°C, respectively) whereas the degradation rate did not change for higher power (>600 W). So, the microwave irradiation of 600 W was chosen throughout the experiments. According other

studies with increasing energy, amount of Final Temperature (TF) was increased (Costa *et al.*, 2009). These results revealed that persulfate could be considerable enhancement in the reaction rates (Nuechter *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 have been attributed to “specific” or “non-thermal” microwave effects (Tellez *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 *et al.*, 2009; Hong *et al.*, 2012).

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 1000 mg L⁻¹) was studied by the MW/SPS system under microwave power of 600 W (Fig. 6). In this study the values of PCP removal were between 98-90%. Because effect of increasing PCP concentration had an ineligible role (8%) on efficiency removal and selection of 1000 mg L⁻¹ PCP wasn't economic, therefore 100 mg L⁻¹ 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 500-12000 mg L⁻¹ of ammonia with efficiencies above 95% (Lin *et al.*, 2009). So that, increasing of no 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 *et al.*, 2003; Lang *et al.*, 2007; Yang *et al.*, 2009b).

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 (SO₄⁻ vs. OH⁻) under 0.04 M of TBA by observing the differences in radical reactivates (i.e., radical scavengers. This method has been successfully employed to distinguish SO₄⁻ vs. OH⁻ activity

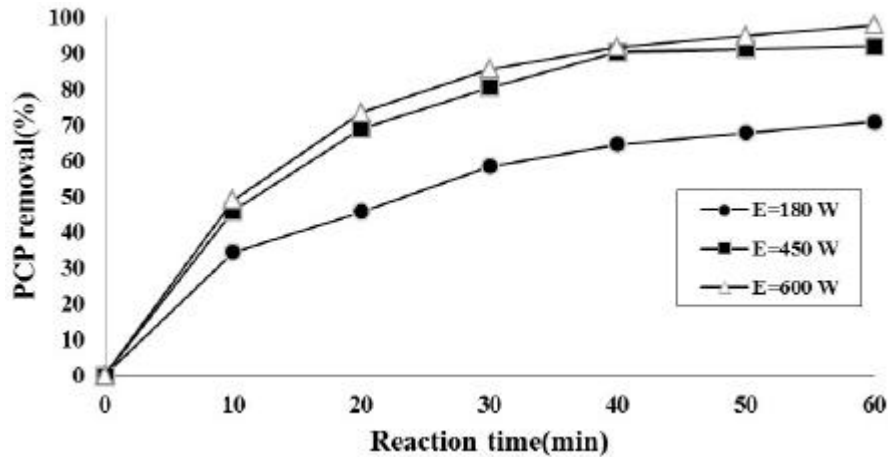


Fig. 5: Effect of energy on PCP removal ($C_0 = 100 \text{ mg L}^{-1}$, $\text{pH} = 11$, $\text{SPS} = 0.02 \text{ mol L}^{-1}$, $E = 180, 450, 600 \text{ W}$)

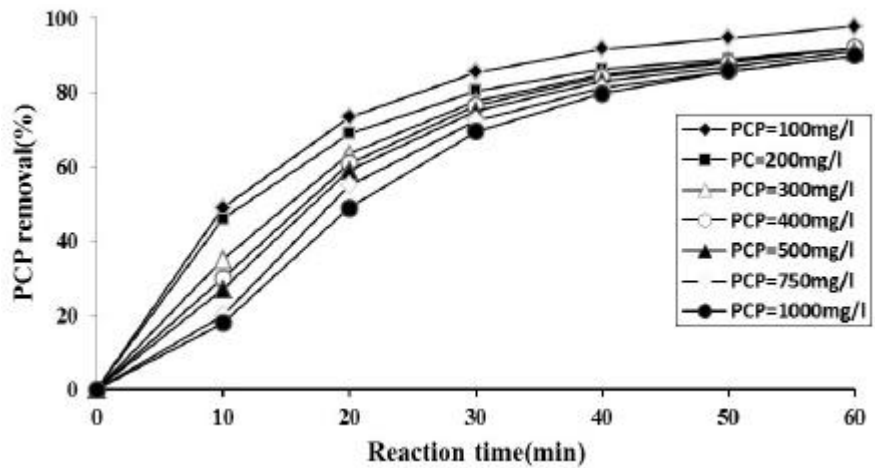
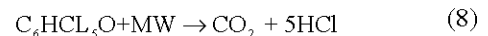


Fig. 6: Effect of PCP concentration ($\text{pH} = 11$, $\text{SPS} = 0.02 \text{ mol L}^{-1}$, $E = 600 \text{ W}$)

in an activated persulfate system (Anipsitakis *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 *et al.*, 2006). As shown in Table 1 with the addition of TBA the % change in k (i.e., inhibition) at $\text{pH} 11$ and 0.04 mol L^{-1} of TBA was between -31-46%. However, when the TBA was introduced into the degradation systems, the degradation rate was only decreased slightly. This result demonstrated 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, 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 SO_4^\cdot system (Liang *et al.*, 2007).

Comparison of PCP and COD removal Several mechanisms have been proposed in explaining the organic degradation based AOPs. $\text{PCP} = 100 \text{ mg L}^{-1}$; $\text{COD} = 344 \text{ mg L}^{-1}$; $\text{pH} = 11$, $\text{S}_2\text{O}_8^{2-} = 0.02 \text{ mol L}^{-1}$ 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 CO_2 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 CO_2 and HCl immediately (Eq 8). 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:



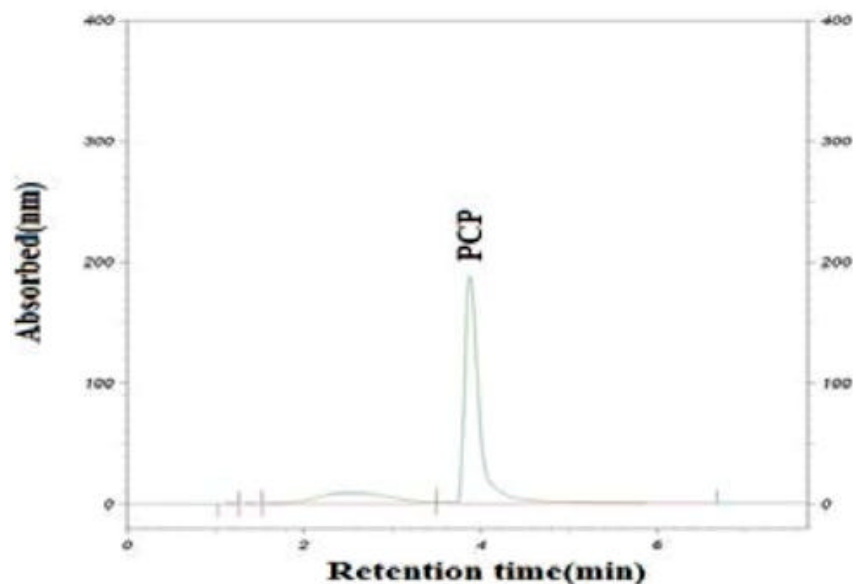


Fig. 7: Coparison of PCP and COD removal in MW/SPS ($C_0 = 100 \text{ mg L}^{-1}$, $\text{COD} = 344 \text{ mg L}^{-1}$ $\text{pH} = 11$, $\text{SPS} = -0.02 \text{ mol L}^{-1}$, $E = 600 \text{ W}$)

Table 1: Summary of radical identification experiments

| Time (min) | K (min^{-1}) | | Change in K with TBA (%) |
|------------|-------------------------|----------|--------------------------|
| | No alcohol | With TBA | |
| 10 | 0.230 | 0.160 | -31 |
| 20 | 0.125 | 0.059 | -32 |
| 30 | 0.058 | 0.085 | -46 |

$R^2 = 97\%$

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 *et al.*, 2003).

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 H_2O and CO_2 . 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 SO_4^- and an indirect reaction with OH^\ominus radical because SO_4^- 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 SO_4^- in aqueous solution using microwave energy. As SO_4^- is an active and

environment friendly oxidant, it will have great importance in the fields of Green Chemistry, environmental protection and other related fields.

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