



## Original Article

# Microwave/H<sub>2</sub>O<sub>2</sub> Efficiency in Pentachlorophenol Removal from Aqueous Solutions

Ghorban Asgari (PhD)<sup>a</sup>, AbdolMotaleb Seidmohammadi (PhD)<sup>b</sup>, Afsane Chavoshani (MSc)<sup>c\*</sup>, Ali Reza Rahmani (PhD)<sup>b</sup>

<sup>a</sup> Social Determinants of Health Research Center (SDHRC), Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

<sup>b</sup> Research Center for Health Sciences, Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

<sup>c</sup> Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

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### \* Correspondence

Afsane Chavoshani (MSc)

Tel1: +98 831 7250071

Tel2: +98 937 4548889

E-mail: chavoshani.afsane@yahoo.com

## ABSTRACT

**Background:** Pentachlorophenol (PCP) is one of the most fungicides and pesticides. Acute and chronic poisoning from PCP may be occurred by dermal absorption, and respiration or ingestion. With respect to health and environmental effects of PCP, many methods were considered regarding its removal. Microwave assisted other methods are environmental friendly, safety, and economical method, consequently, in this study; microwave assisted with hydrogen peroxide (MW/H<sub>2</sub>O<sub>2</sub>) was used for PCP removal from aquatic solutions.

**Methods:** The possible of PCP removal was considered by application of a modified domestic microwave. PCP removal rate was considered under different factors such as H<sub>2</sub>O<sub>2</sub> dose (0.01, 0.02, 0.1, 0.2, 0.3 mol/L), PCP concentration (100,200, 300, 400, 500, 750, 1000 mg/L), pH (3, 7, 11), energy intensity (180,450, 600W), COD (344mg/L), and scavenger testes (0.02 mol/L from each of Tert- butyl alcohol (TBA), NaCl, NaHCO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>). The concentration changes of PCP were determined using spectrophotometer and HPLC spectra, respectively.

**Results:** The best PCP removal was obtained in condition of pH 11, 0.2 mol/L H<sub>2</sub>O<sub>2</sub> and 600 W energy intensity. Moreover, COD removal in this condition was 83%. Results obtained from radical scavengers indicated that OH<sup>•</sup> had only an initiator role, and had not a dominant role, and order reaction was in first order.

**Conclusion:** The results of microwave/H<sub>2</sub>O<sub>2</sub> application showed that this process is suitable for removal of PCP and other chlorinated organic compounds in alkaline pH.

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## Introduction

Pentachlorophenol (PCP) is widely used in the wood preserving industry and agriculture as a fungicide, pesticide and herbicide. The poisoning of PCP may be occurred by dermal absorption, respiration, ingestion, peripheral neuropathy and other problems related to nerve damage (neurotoxicity)<sup>1</sup>. PCP is a significant contaminant of soil, surface, and groundwater especially around sawmills and wood preserving facilities<sup>2-5</sup>. Researchers using a mathematical model calculated that 96.5% of PCP is in soil, 2.5% in water, 1% in air, and less than 1% in suspended sediments and organisms in aquatic environments<sup>1</sup>. Therefore, PCP removal from aquatic solution is necessary, especially from alkaline wastewater.

Nowadays, environmental researchers have considered the sustainable methods for refractory contaminants removal. Aqueous H<sub>2</sub>O<sub>2</sub> is an ecologically sustainable oxidant with high oxidation potential and water as the only by-product. However, oxidation with H<sub>2</sub>O<sub>2</sub> requires prior activation for radical production<sup>7</sup>. Recently, the application of microwave

heating in combination with hydrogen peroxide (MW/H<sub>2</sub>O<sub>2</sub>) for pollutants treatment has shown to be an efficient oxidation technology<sup>6</sup>. MW/H<sub>2</sub>O<sub>2</sub> process has showed high degradation efficiency, because it generates active species of hydroxyl and other radicals with a redox potential. Usually, MW/H<sub>2</sub>O<sub>2</sub> has no need of catalyst separation and no potential risk of environmental pollution, compared to some hybrid MW systems<sup>6,8,9</sup>.

In this study, due to an environmental-friendly as well as highly efficient method and low existence of specific work in this condition, analysis of the PCP removal was performed by MW/H<sub>2</sub>O<sub>2</sub> technology.

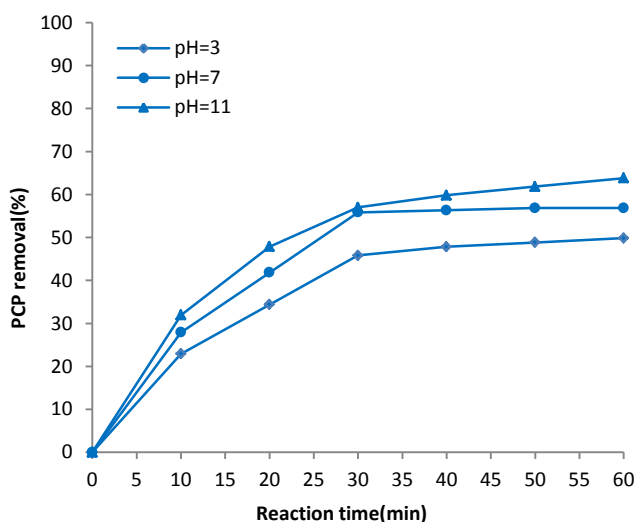
## Methods

Sodium salt PCP, which is the sodium salt of PCP (C<sub>6</sub>Cl<sub>5</sub>ONa) with 98% purity, was used without further purification. The characteristics of the PCP included of boiling point: 309-310C<sup>°</sup>, mass molar: 288.32g/mol. The PCP solu-

tion was prepared by dissolving PCP in NaOH solution to accelerate its dissolution<sup>1</sup>. And hydrogen peroxide (30% w/w). Under atmospheric pressure, all of the experiments were performed and triplicated in modified domestic microwave oven. Detail modifications of MW were performed as follows: drilled a hole in the upper oven wall and then attached an aluminum tube of the same diameter to the hole. The possible of PCP removal was considered by a reactor placed to domestic microwave. PCP removal rate was considered under different factors such as H<sub>2</sub>O<sub>2</sub> dose (0.01, 0.02, 0.1, 0.2, 0.3 mol/L), PCP dose (100, 200, 300, 400, 500, 750, 1000 mg/L), pH (3, 7, 11), energy intensity (180, 450, 600W), COD (344 mg/L), and scavenger testes (0.02 mol/L from each of Tert- butyl alcohol (TBA), NaCl, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>). A Thermometer GENWAY Medal 2003 was utilized to detect variation of solution temperature during degradation process. The leakage of MW oven was measured at 20 cm distance from the aperture. Concentration changes of PCP were determined using spectrophotometer according to (APHA, 2005)<sup>11</sup>, and HPLC spectra. HPLC (Part Number.WATO54275 with dimension of 4.6 mm×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 and detection wavelengths of UV was 254 nm<sup>12</sup>. 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<sup>6</sup>.

## Results

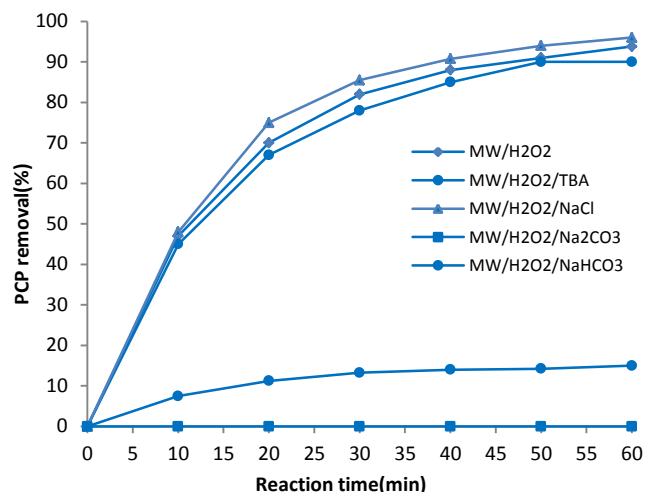
Removal of PCP in MW/H<sub>2</sub>O<sub>2</sub> in pHs of 3, 7 and 11 and reaction time 60 min was obtained 46, 56 and 64%, respectively (Figure 1). The results shown that alkaline pH could sharply accelerate PCP degradation in MW/H<sub>2</sub>O<sub>2</sub> system. Therefore, alkaline pH could slightly speeds up PCP degradation in MW/H<sub>2</sub>O<sub>2</sub> process.



**Figure 1:** Effect of pH on PCP removal ( $C_0=100\text{mg/L}$ ,  $\text{H}_2\text{O}_2=0.02\text{mol/L}$ ,  $E=450\text{W}$ )

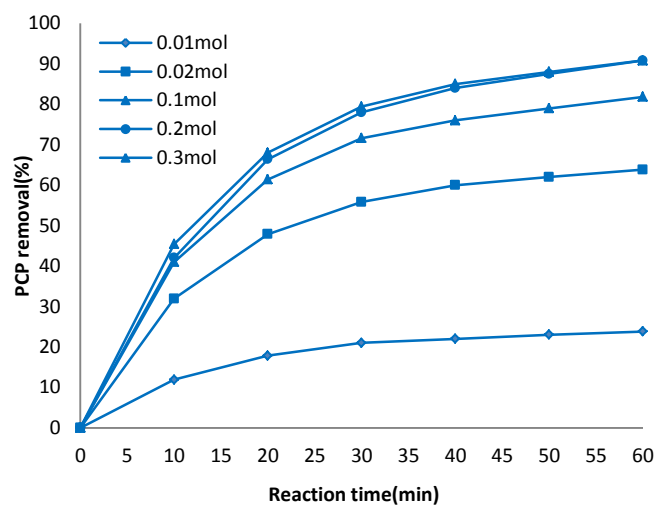
To scavenge all possible OH<sup>•</sup>, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, scavengers test was performed by 0.02mol/L from each of TBA, NaCl, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>. Results from experiments indicated that the degradation percentage in MW/H<sub>2</sub>O<sub>2</sub>/NaCl, MW/H<sub>2</sub>O<sub>2</sub>/TBA, MW/H<sub>2</sub>O<sub>2</sub>/NaHCO<sub>3</sub>, and MW/H<sub>2</sub>O<sub>2</sub>/Na<sub>2</sub>CO<sub>3</sub> was obtained 96, 90, 15, and 0% respectively, whereas in MW/H<sub>2</sub>O<sub>2</sub> degradation percentage was attained 93.82%

(Figure 2). Thus, in the MW/H<sub>2</sub>O<sub>2</sub>/NaCl process the PCP removal rate was increased.



**Figure 2:** Effect of radical scavengers on PCP removal ( $C_0=100\text{mg/L}$ ,  $\text{pH}=11$ ,  $\text{H}_2\text{O}_2=0.02\text{mol/L}$ ,  $E=600\text{W}$ , 0.02mol/L from each of radical scavengers)

PCP removal efficiency for 0.01, 0.02, 0.1, 0.2, and 0.3 mol/L of hydrogen peroxide was 23.82, 63.82, 81.82, 90.82, and 90.82% at 60 min respectively (Figure 3). PCP removal was stabled in doses of 0.2 and 0.3 mol/L. Therefore, H<sub>2</sub>O<sub>2</sub> dose of 0.2 mol/L was selected and used as optimal dose.



**Figure 3:** Effect of H<sub>2</sub>O<sub>2</sub> dose on PCP removal ( $C_0=100\text{mg/L}$ ,  $\text{pH}=11$ ,  $E=600\text{W}$ )

The test results shown in Figure 4 indicated that degradation rate of PCP gradually increased by increasing the microwave power from 180 to 600W. Amount of PCP removal in MW/H<sub>2</sub>O<sub>2</sub> with energy intensity of 180, 450, and 600 W was 32, 86 and 93%, respectively (Figure 4). Subsequently, the microwave irradiation of 600 W was chosen for further experiments.

Amount of PCP removal for 100, 200, 300, 400, 500, 750 and 1000 mg/L by MW/H<sub>2</sub>O<sub>2</sub> was obtained 93.82, 92, 91, 90, 89, 88 and 87%, respectively (data was not shown). Increasing PCP concentration had a negligible role in decreasing efficiency of process (approximately 7%), consequently, selection of 1000 mg/l as optimal dose was not economic and PCP concentration of 100 mg/l used for further experiments.

In addition, COD removal was 83% (data was not shown). The de-chlorination of PCP by the MW/H<sub>2</sub>O<sub>2</sub> process follows first-order kinetic (Figure 5). According to  $-\ln(C/C_0)=kt$  equation (where;  $C_0$  and  $C$ =PCP concentration (mg/l) at 0 and  $t$  time,  $t$  = reaction time (min) and  $k$ = reaction constant (min<sup>-1</sup>) respectively),  $k$  H<sub>2</sub>O<sub>2</sub> only and  $k$  MW/H<sub>2</sub>O<sub>2</sub> in 60 min was 0.0035 and 0.044min<sup>-1</sup> respectively ( $P=0.002$ ).

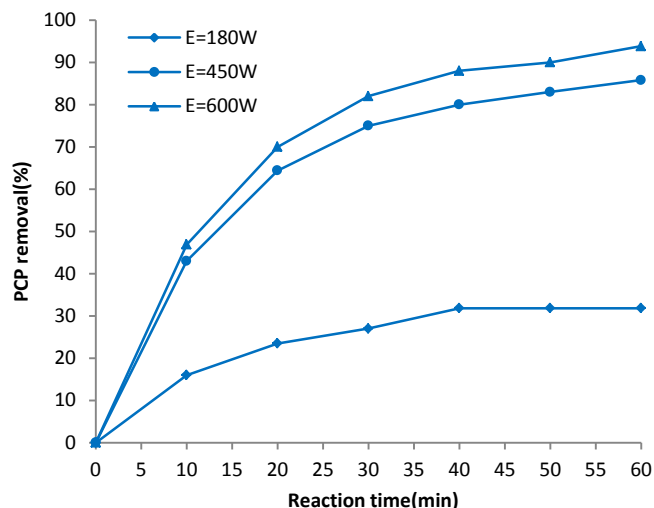


Figure 4: Effect of energy on PCP removal ( $C_0=100$ mg/L,  $pH=11$ ,  $H_2O_2=0.2$ mol/L,  $E=180,450, 600$ W)

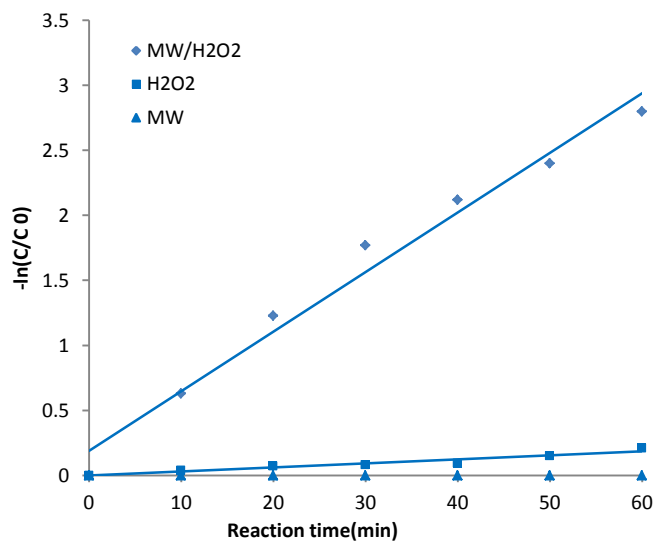


Figure 5: Reaction kinetics ( $C_0=100$ mg/L,  $H_2O_2=0.2$ mol/L,  $E=600$ W,  $pH=11$ )

## Discussion

Wastewater pH is one of the factors that effects on organic degradation. Degradation of PCP by MW/H<sub>2</sub>O<sub>2</sub> system in a broad pH range, from acidic to alkaline conditions, was initially studied. According to previous studies phenolic compounds, in alkaline pH, are in anionic state and absorb microwave more than other pHs, also under alkaline pH activated oxygen decomposed from hydrogen peroxide has a significant role for PCP removal<sup>6,13</sup>.

Formation of hydroxyl radicals, in advanced oxidation process (AOPs) such as MW/H<sub>2</sub>O<sub>2</sub>, was always considered to be the main agent in organic removal. "AOPs have considerable similarities due to the participation of hydroxyl radicals in most mechanisms that are operative during the reaction, but hydroxyl radicals are extremely unstable and

reactive because of their high reactivity"<sup>14</sup>. It seems that in MW/H<sub>2</sub>O<sub>2</sub> and at alkaline pH, OH<sup>•</sup> is activation initiator and is not dominant radical. According to Hong et al. results activated O<sub>2</sub> is dominant<sup>6</sup>.

In this study, results of OH<sup>•</sup> scavenger indicated that at least the main attack toward PCP was not OH<sup>•</sup> and NaCl had a catalytic role for extra H<sub>2</sub>O<sub>2</sub> and producing O<sub>2</sub><sup>6,15</sup>. However, TBA test had a negligible role for decreasing PCP removal. Decreasing effect of chloride and TBA on degradation has been observed in AOPs systems which are mainly based on OH<sup>•</sup> radicals<sup>16</sup>. Because decreasing PCP removal under application of Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> for quenching H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> was significant, according to other studies the main attack toward PCP was done by H<sub>2</sub>O<sub>2</sub> and activated O<sub>2</sub> from it and OH<sup>•</sup> was only an initiator radical<sup>17</sup>. Decomposition rate of PCP can express as an indirect reaction with OH<sup>•</sup>, because OH<sup>•</sup> is unstable and immediately able to converted to other radicals<sup>8</sup>. It seems that H<sub>2</sub>O<sub>2</sub> can be activated by MW to initiate other radicals at high pH under the effect of hydroxyl radical. But application of Na<sub>2</sub>CO<sub>3</sub> (as H<sub>2</sub>O<sub>2</sub> scavenger) showed that MW alone was not suitable for PCP removal and addition of H<sub>2</sub>O<sub>2</sub> dose during MW process enhances the rate of PCP degradation, except when the radical scavenging effect of H<sub>2</sub>O<sub>2</sub> is dominant<sup>17</sup>. However, at high concentrations of H<sub>2</sub>O<sub>2</sub> the increase in PCP removal started decreasing. This is because at high concentrations, the solution has a self-quenching of OH<sup>•</sup> radicals by extra amounts of H<sub>2</sub>O<sub>2</sub> to produce HO<sub>2</sub><sup>•</sup> radicals. The existences of extra H<sub>2</sub>O<sub>2</sub> as a scavenger of OH<sup>•</sup> radicals have also an effect in the removal efficiency<sup>18</sup>.

According to our results increasing PCP concentration had a negligible role in decreasing efficiency of process and MW/H<sub>2</sub>O<sub>2</sub> process was able to remove high PCP concentrations. Study of Chang et al. has shown that MW/Fenton was able to remove 99% of 500, 1000, 1500, and 2000 mg/l of isopropyl alcohol<sup>19</sup>. Besides, pollutants such as phenol, aromatic hydrocarbons and PCP with 1000, 5000, and 10000 concentrations can be removed in amount of 98, 96 and 92%, respectively<sup>20</sup>. These amounts are much higher than commonly adopted in attractive AOPs<sup>21</sup>. It is because of high efficiency of processes integrated with MW and non-thermal effects in these processes. The HPLC spectra indicated that major PCP informed to CO<sub>2</sub> and HCl. The HPLC spectra and COD results showed a similar trend in mineralization and the lack of toxic intermediates and by products<sup>8,22</sup>.

Energy intensity was very important for PCP removal. In this study, with increasing energy, the amount of final temperature increased. These results revealed that H<sub>2</sub>O<sub>2</sub> could be converted to OH<sup>•</sup> and other radicals by microwave energy resulting in a considerable enhancement in the reaction rates. Thus, the microwave irradiation of 600W was chosen throughout the experiments. Therefore, a high energy power input (and a high electrical field strength) with microwave is more efficient than a low energy input. However, efficiency can only increase to a limited value, and sometimes no further increase of the efficiency and absorption of microwave energy is observed<sup>23</sup>. Degradation of organic materials is not always increased with increasing microwave power, because characteristic of organic compounds and oxidants is effective for absorption of microwave energy<sup>24,25</sup>. Reaction kinetic allows the overall comparison between the different AOPs tested<sup>14</sup>. In our study the reaction kinetics of MW/H<sub>2</sub>O<sub>2</sub> was

12.57 times higher than H<sub>2</sub>O<sub>2</sub> only. Conclusively MW radiation was suitable for H<sub>2</sub>O<sub>2</sub> reaction and increasing PCP removal.

## Conclusions

MW/H<sub>2</sub>O<sub>2</sub> process could efficiently degrade refractory substrates at strong alkaline pH, via radical production. The microwave degradation has many advantages such as convenience, safety, economy and high efficiency, and provides a simple and rapid method for H<sub>2</sub>O<sub>2</sub> activation to generate radicals in aqueous solution using microwave energy. MW/H<sub>2</sub>O<sub>2</sub> process was able to remove high PCP concentrations. Addition of H<sub>2</sub>O<sub>2</sub> dose during MW process enhances the rate of PCP degradation, except when the radical scavenging effect of H<sub>2</sub>O<sub>2</sub>. Results obtained from radical scavengers showed that OH<sup>•</sup> had only an initiator role, and had not a dominant role, and order reaction was in first order. Accordingly this method has a better prospect in future for removal of other chlorinated organic compounds in alkaline pH.

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## Conflict of interest statement

The authors have no conflict of interests to declare.

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