COMPARISON OF DIFFERENT ADVANCED OXIDATION PROCESSES DEGRADING P-CHLOROPHENOL IN AQUEOUS SOLUTION

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ABSTRACT

In present study, degradation of p-chlorophenol using several oxidation systems involving advanced oxidation processes such as ultraviolet/H_2O_2, microwave/H_2O_2 and both in the absence of hydrogen peroxide in batch mode by photolytic pilot plant and modified domestic microwave oven was evaluated. The oxidation rate was influenced by many factors, such as the pH value, the amount of hydrogen peroxide, irradiation time and microwave power. The optimum conditions obtained for the best degradation rate were pH=7 and H_2O_2 concentration of 0.05 mol/L for ultraviolet/H_2O_2 system and pH=10.5, H_2O_2 concentration of about 0.1 mol/L and microwave irradiation power of about 600W for microwave/H_2O_2 system at constant p-chlorophenol concentration. The degradation of p-chlorophenol by different types of oxidation processes followed first order rate decay kinetics. The rate constants were 0.137, 0.012, 0.02 and 0.004/min[1] for ultraviolet/H_2O_2, microwave/H_2O_2, ultraviolet and microwave irradiation alone. Finally a comparison of the specific energy consumption showed that ultraviolet/H_2O_2 process reduced the energy consumption by at least 67% compared with the microwave/H_2O_2 process.

Keywords: Degradation rate, p-chlorophenol, Ultraviolet/H_2O_2, Microwave/H_2O_2, Microwave irradiation

INTRODUCTION

Advanced oxidation processes (AOPs) have been successful in treating most of the refractory organic compounds present in polluted water. The reason for the use of AOPs is due to the inability of conventional processes to treat highly contaminated toxic water. In AOPs, the hydroxyl radicals (OH°) are generated in the solution and these are responsible for the oxidation and mineralization of the organic compounds to water and carbon dioxide. In recent years, different advanced oxidation processes, which produce hydroxyl radicals, i.e. O_3/UV, O_3/H_2O_2 and UV/H_2O_2 etc., have been applied in wastewater treatment (Prousek, 1996; Birgit and Gerhard, 1999; Ghaly *et al*., 2001).

Microwave (MW) assisted system, another type of AOPs process, has been developed over than 30 years since in 1975 (Ta *et al*., 2006). During the last two decades, microwave irradiation has widely been applied in environmental and medical fields as a more effective, easier and cheaper extraction technique in comparison with traditional methods. The applications of microwave energy to enhance chemical reactions are well known (Eskilsson and Klund, 2000; Jung *et al*., 2004). Moreover, microwave irradiation was reported as an alternative to waste treatment (Caddick, 1995; Airton *et al*, 2000).

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One of the most important members of chlorophenols from environmental and health view, is ρ-chlorophenol. This pollutant is introduced into the environment through various human activities such as waste incineration, uncontrolled use of wood preservatives, pesticides, fungicides and herbicides, as well as via bleaching of pulp with chlorine, chlorination of drinking water and wastewater and from break down of phenoxy herbicides such as 2, 4-dichlorophenoxyacetic acid (Mangat and Elefsiniotis, 1999; Contrerasa *et al*., 2003; Tarighian *et al*., 2003; Sahinkaya and Dilek, 2006). p-chlorophenol is also a product of anaerobic degradation of more highly chlorinated phenols, such as pentachlorophenol which have been used extensively for preservation of lumber (Buitron *et al*., 2005). The reported levels of chlorophenols in contaminated environments range from 150µg/L to 100–200 mg/L (Sahinkaya and Dilek, 2007). However, small amounts of these compounds (at ppb to ppm) can be tasted in water (Poulopoulos *et al*., 2007).

Lately, much research have been carried out on treating chlorophenols by using AOP_S; however, there has been little research comparing AOPs including MW and UV based processes.

The results reported by Ghaley et al (2001) showed that the degradation rate of p-chlorophenol was strongly accelerated by the photochemical oxidation processes. The photo-Fenton process, the combination of homogeneous systems of $UV/H_2O_2/Fe$ compounds, produced the highest photochemical elimination rate for p-chlorophenol. Zhihui *et al* (2005a) similarly reported that microwave irradiation can greatly enhance the efficiencies of AOPs on the degradation of p-chlorophenol. These results suggest that operating different advanced oxidation processes on wastewater treatment should be considered in degrading refractory compounds.

The main goal of this study was to investigate the degradation of p-chlorophenol in aqueous synthetic wastewater using different photochemical processes including UV/H_2O_2 and MW/H_2O_2. The effects of the pH, hydrogen peroxide dose, energy consumption and irradiation time were also evaluated.

MATERIALS AND METHODS

p-chlorophenol (C_6H_5ClO), NH_4OH 0.5 N, KH_2PO_4, K_2HPO_4, 4-aminoantipyrine, potassium ferricyanide and hydrogen peroxide solution (30% w/w) in stable form, were all analytical grade and purchased from Merck Chemical Company. All reagents employed were not subjected to any further treatment. Water used throughout the experiments was ultrapure deionized water.

All experiments with UV/H_2O_2 system were performed in a batch reactor. The sketch of the experimental set-up used in the study is shown in Fig. 1. The reactor was cylindrical with 2.5 l volume and was made from stainless steel. Irradiation was achieved by using UV lamp (low pressure mercury vapour lamp of 55 W, radiation flux used for only degradation of 253.7 nm from Philips Company) which was immersed in the glass tube. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system.
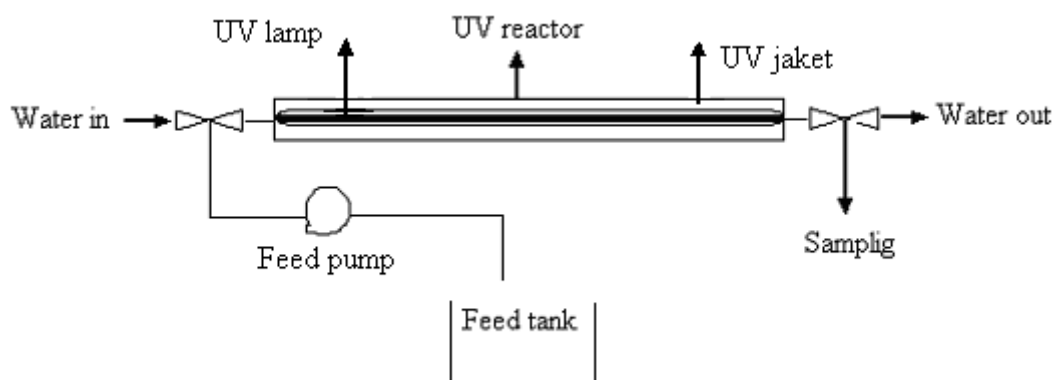

Fig. 1: Schematic diagram of photolytic oxidation system experimental set-up

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For runs using UV/H_2O_2 system, synthetic aqueous solution containing 100 mg/L p-chlorophenol constant concentration was prepared in ultrapure deionized water as solvent. First, hydrogen peroxide at different concentrations (ranging from 0.005-0.2 molar) was mixed very well with the p-chlorophenol solution in the storage tank. The pH of the solution was maintained constant at neutral pH value before the beginning of each run. Second, the p-chlorophenol solution was set at the optimum dosage of hydrogen peroxide and different pH value between 3 and 10.5 by the addition of a 1 N sulfuric acid or/and sodium hydroxide solution before startup. Experiments with microwave irradiation were carried out in a modified domestic microwave oven with cooling system (2450MHz, SAMSUNG Co.) according to Fig. 2.
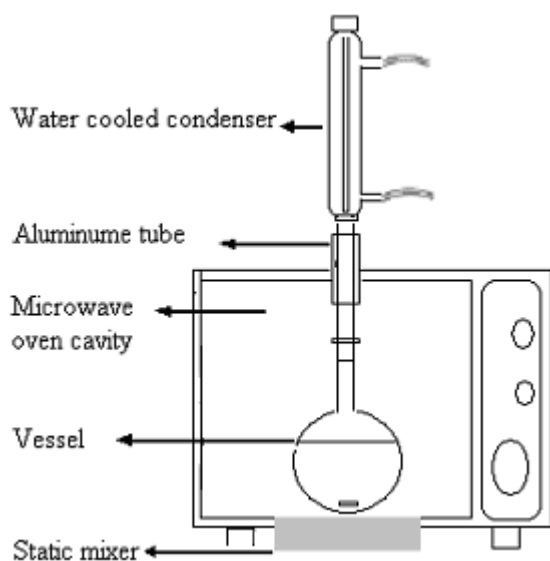

Fig. 2: Schematic diagram of modified microwave system

For experiments, first of all, the special glass vessel was filled with 500 mL aqueous solution of p-chlorophenol (initial concentration of 100 mg/L, pH=7 and different amounts of H_2O_2 (ranging from 0.005-0.2 Molar) and ignited to microwave oven by adjusting the microwave power at 180W. Then, the optimum concentration of H_2O_2 was added to the vessel in different pH values between 3 and 10.5 by the addition of a 1N sulfuric acid or/and sodium hydroxide solution in the same power as with the first stage.

In another stage, different microwave powers, (300 and 600 W) were adjusted in the optimal concentration of H_2O_2 and pH value. Samples were taken at appropriate time intervals from the reaction vessel with a 10 mL syringe and pipetted in to glass vials. Finally, the processes of UV photolysis and microwave irradiation without the addition of hydrogen peroxide on optimal pH value for the degradation of p-chlorophenol were monitored separately. The samples were immediately analyzed to avoid further reaction. Concentration changes of p-chlorophenol were determined using spectrophotometer (Spectronic 20D) according to (APHA, 2005).

RESULTS
UV/H_2O_2 process
Effect of the amount of H_2O_2
Fig. 3 illustrates the percent degradation of p-chlorophenol as a function of the irradiation time at different doses of H_2O_2 input. By addition of H_2O_2, the degradation rate of p-chlorophenol first increased when hydrogen peroxide concentration increased, however the effect of peroxide is negative for hydrogen peroxide concentrations higher than 0.05 mol/L. The p-chlorophenol degradation rate was higher than that obtained from direct photolysis. As can be seen from Fig.3, the percent degradation of p-chlorophenol at 40 min was 62% in a direct photolysis experiment and was >99% at the same time when the photolysis was carried out in the presence of an optimal hydrogen peroxide concentration of 0.05 mol/L.
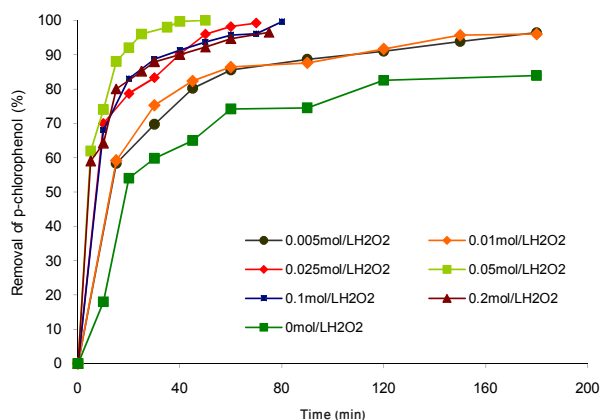

Fig. 3: Degradation of p-chlorophenol with UV/ H_2O_2 system. The effect of initial hydrogen peroxide concentration (C_o=100mg/L, pH=7)

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Effect of pH

Fig. 4 shows the effect of pH during UV/H_2O_2 process. A maximum degradation of >99% was obtained at pH=3 and pH=7 in less than 40 min. For pH values above 10.5, the p-chlorophenol degradation relatively decreased.
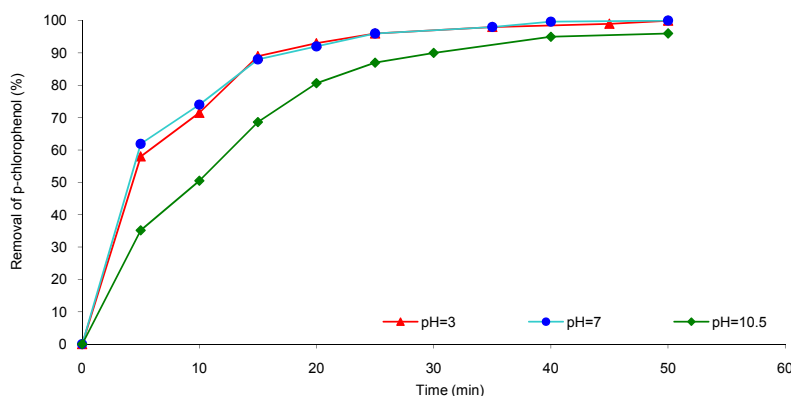
MW/H_2O_2 process

Fig. 4: p-chlorophenol degradation as a function of the pH value by using UV/H_2O_2 processes
($C_{\circ}$=100mg/L, H_2O_2=0.05mol/L)

Effect of the amount of H_2O_2

The effects of different H_2O_2 concentrations (0–0.2 mol/L) in the degradation of constant p-chlorophenol concentration by MW/H_2O_2 in the power irradiation of 180W and neutral pH are shown in Fig. 5. The direct irradiation results showed that the degradation of p-chlorophenol was 7% after 180 min irradiation time in MW system without H_2O_2. The degradation of p-chlorophenol increased in the presence of H_2O_2 and influenced by its dosages. With the addition of H_2O_2 >0.1 mol/L, the percent degradation of p-chlorophenol decreased. The maximum degradation of p-chlorophenol was 59% at 180 min irradiation time when the microwave was carried out in the presence of an optimal hydrogen peroxide concentration of 0.1 mol/L at 180W microwave power.
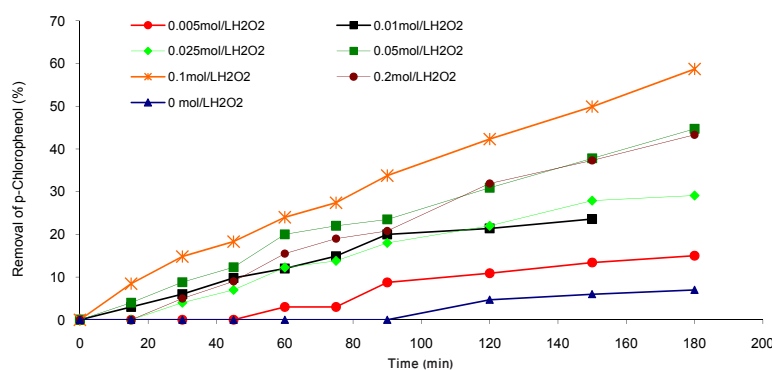

Fig. 5: Degradation of p-chlorophenol with MW/H_2O_2 system. The effect of initial hydrogen peroxide concentration [$C_{\circ}$ =100mg/L, pH=7 and MW power=180W]

Effect of initial pH

The effects of initial pH on the MW/H_2O_2 in degradation rates of p-chlorophenol were investigated. As illustrated in Fig.6, the degradation reactions were enhanced in an alkaline medium.
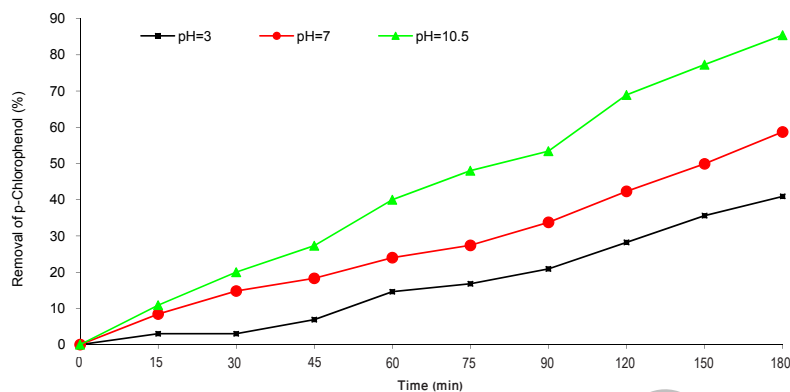
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Fig. 6: p-chlorophenol degradation as a function of the pH value by using MW/H_2O_2 processes
[$C_\circ$ =100mg/L, H_2O_2=0.05mol/L, MW power =180W]

Effect of microwave power irradiation

The results of different microwave powers in the optimum amount of H_2O_2 and pH value are shown in Fig.7. As can be seen, along with the increase in the microwave power, the degradation rate of p-chlorophenol was increased. Also, the percent degradation of p-chlorophenol at 180 min irradiation time was 93% in 600 W and 85.4% at the same time when the microwave was adjusted in the power of 180W.
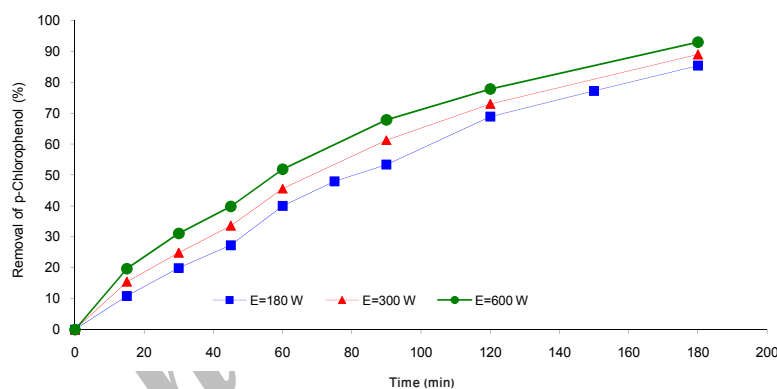

Fig.7: p-chlorophenol degradation as a function of the microwave power irradiation by using MW/H_2O_2 processes
[$C_\circ$ =100mg/L, H_2O_2=0.05mol/L, pH=10.5]

Degradation rate

The reduction of p-chlorophenol by different types of oxidation processes followed first order rate decay kinetics according to the following relationship as shown in Fig. 8.
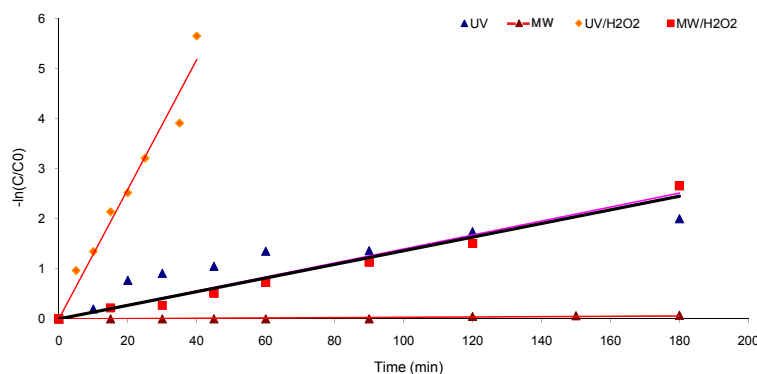
$$\mathrm{Ln} \frac{C}{C_0} = -Kt \tag{1}$$

Fig. 8: First order plot for degradation of p-chlorophenol by using different oxidation processes

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In which $C_°$ and C are the p-chlorophenol concentrations at 0 and t time and $K_°$ is the expected pseudo-first-order rate constant. The rate constants were 0.137, 0.012, 0.02 and 0.004 min^{-1} for UV/H_2O_2, MW/H_2O_2, UV and MW, respectively. Optimum conditions of processes were used to illustrate first order changes.

Comparison of the specific energy consumption
Fig. 9 presents a rough comparison of the energy required to remove 1 kg of p-chlorophenol by UV/H_2O_2 and MW/H_2O_2 processes. The conditions of two above mentioned processes were: total UV power of 55 W, percent degradation of p-chlorophenol 99.65%, reaction time 45 min, and total MW-power of 600 W, percent degradation of p-chlorophenol 93%, and reaction times 180 min.
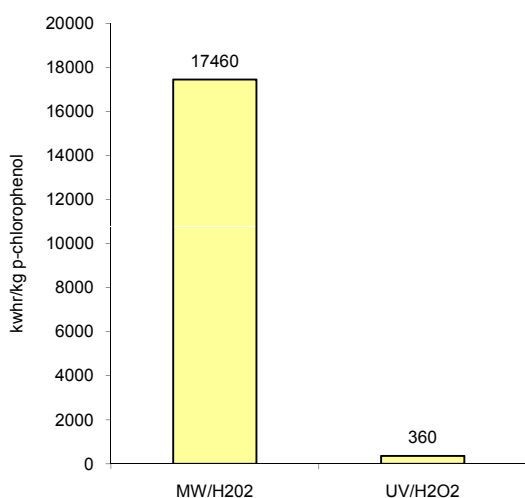

Fig.9: Comparison of the specific energy consumption

$$H_2O_2 + hv \rightarrow 2OH \qquad (2)$$

DISCUSSION

Different advanced oxidation processes (UV and MW only, UV/H_2O_2 and MW/H_2O_2) have been investigated and compared for the degradation of p-chlorophenol in aqueous solution. Although direct photolysis by UV radiation can relatively reduce p-chlorophenol initial concentration, the combination of UV and a little amount of H_2O_2 enhanced strongly the efficiency of degradation of p-chlorophenol. In the UV/H_2O_2 processes hydroxyl radicals, the dominant oxidizing species

in the photocatalytic process (Zhihui *et al.*, 2005a; Ghaly *et al.*, 2001) are formed according to Eq. 2.

Initial H_2O_2 concentration plays an important role in oxidation process. It should be added at an optimal concentration to achieve the best degradation. Addition of H_2O_2 exceeding than optimal concentration did not improve the respective maximum degradation. This is clearly shown in Fig.3. This behavior may be explained due to two reasons from findings of other studies. First of all, auto-decomposition of H_2O_2 to oxygen and water and the recombination of OH radicals (Ghaly *et al.*, 2001) and secondly, OH radicals react with H_2O_2 and H_2O_2 itself contributes to the OH scavenging capacity (Buxton *et al.*, 1998). The same behavior was reported by other literature that there is a relationship between the amounts of hydrogen peroxide and the degradation efficiency of organic material (Zhihui *et al.*, 2005a). This provide further support to earlier work that by addition of H_2O_2, the degradation rate of p-chlorophenol at 100 mg/L first increased when hydrogen peroxide concentration increased. However, the effect of peroxide is negative for hydrogen peroxide concentrations higher than 0.02 mol/L for which the p-chlorophenol degradation rate was even lower than that obtained from direct photolysis (Ghaly *et a*l., 2001).

The results of pH effects in the UV/H_2O_2 process in present study indicated that the degradation percent were not considerably affected according to Fig.4. However, degradation of p-chlorophenol is accelerated in an acidic and neutral pH medium. This can be perhaps because the decomposition of hydrogen peroxide to oxygen and water occurs at high pH values. The findings of other researches have shown that pH affects the oxidation of organic substances both directly and indirectly and it influences the generation of OH radicals and thus the oxidation efficiency (Ghaly *et al.*, 2001).

Microwave irradiation has been successfully applied in organic chemistry (Hoz *et al.*, 2005). The effect of microwave irradiation in organic synthesis is a combination of thermal effects i.e. superheating, hot spots formation, polarization, and spin alignment (Loupy, 2002). Similar to UV/

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H_2O_2 process the addition of hydrogen peroxide can enhance the degradation of p-chlorophenol in MW/H_2O_2 system up to certain concentration of H_2O_2 as shown in Fig.5. Most of the decomposition resulted from this process is related to generation of hydroxyl and oxygen radicals from dissolved oxygen in the samples. The concentration of OH radicals could be enhanced by the addition of hydrogen peroxide (Prousek, 1996; Loupy, 2002).

Similarly, Zhihui *et al*. (2005a) have shown that the degradation of 4-chlorophenol was increased in the presence of H_2O_2 and influenced by the dosages of H_2O_2. p-chlorophenol degradation is also strongly dependent on pH in MW/H_2O_2 process (Fig.6). Degradation reactions were enhanced in the alkaline medium. This behavior can be explained by more hydroxide ions (OH^-) in the solution producing more hydroxyl radicals (Ta *et al*., 2006). Also the results of other study reported that degradation reactions were enhanced at low and high initial pH values (Zhihui *et al*., 2005b). As seen from Fig.7, the p-chlorophenol reduction seemed to be more pronounced with increase in the MW input power as shown by increasing degradation percent when MW power was increased from 180 to 600W. Compared to UV/H_2O_2, p-chlorophenol could not be oxidized by microwave alone because energy of MW radiation is considerably lower than that of UV radiation, it is not sufficient to disrupt bonds of common organic molecules (Loupy, 2002).

The comparison of first order kinetics constant showed that UV/H_2O_2 process had a significant accelerating effect on the p-chlorophenol oxidation rate. This is clearly illustrated in Fig.8. The process indicating highest k is UV/H_2O_2, approximately 11.5 times higher than the MW/H_2O_2 and 34.5 times higher than MW only. The experimental data in this study showed that not only UV/H_2O_2 process had a significant accelerating effect on the rate of oxidation of p-chlorophenol than other types of oxidation processes, but also this process is more economical with an energy reduction of 67% over than the MW/H_2O_2 process as shown in Fig. 9.

The present study indicates that UV/H_2O_2 process has high potential in treating aqueous solutions containing p-chlorophenol. Also, these findings suggest that microwave irradiation in the presence of hydrogen peroxide can greatly enhance the efficiencies of AOPs on the degradation of p-chlorophenol. Hence, it is recommended to continue the study with use of high and moderate pressure UV lamps, influence of different initial p-chlorophenol concentrations, application of microwave assisted UV process and detail assessment of economical aspects.

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