original article

4-Chlorophenol degradation with modified domestic microwave and hydrogen peroxide in aqueous solution

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ABSTRACT

Aims: This study was conducted for degradation of 4-chlorophenol by microwave (MW) radiations alone and in combination with hydrogen peroxide from aqueous solution.

Materials and Methods: A modified domestic microwave oven was used alone and in combination with hydrogen peroxide for removing 4-chlorophenol. Furthermore, the influences of pH value, irradiation time, the power of MW radiations, and the initial concentration of 4-chlorophenol were studied.

Results: It was shown that 4-chlorophenol removal efficiency extremely depend on the concentration of hydrogen peroxide, pH value, MW irradiation power and initial 4-chlorophenol concentration. The optimum conditions obtained for the best degradation rate were pH = 10.5, H_2O_2 concentration of about 0.1 mol/l, and MW irradiation power of about 600 W. Other result shows that the best degradation rate of 4-chlorophenol was obtained when initial 4-chlorophenol concentration was 50 mg/l. Also the amount of the specific energy consumption in this method was 17460 kwh/kg of the removed organic compound.

Conclusion: This result shows that MW irradiation in the presence of hydrogen peroxide can greatly enhance the degradation of 4-chlorophenol. However, the high consumption of energy for this method must be taken into consideration.

Key words: Advanced oxidation processes, hydroxyl radical, microwave, petrochemical wastewater, 4-chlorophenol

INTRODUCTION

The presence of toxic and refractory compounds in water resources and also the generation of sewage containing toxic and complex compounds limited the application of conventional water and wastewater treatment processes.[1] On the other hand, during the last two decades, environmental standards have been stricter due to the awareness increase of human health and ecological hazards related to environmental pollutants.[2] Among the broad range of organic materials, 4-chlorophenol is largely applied in refineries, petrochemical industries, pesticides and herbicides production industries, antimicrobial agents, production of compounds like 2-bezyl-4chlorophenol and acetophenrtidin, and wood preservatives. The concentration of 4-chlorophenol in industrial wastewater is in the range of 50-400 mg/l.[3-5]

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This organic compound with the chemical formula C_6H_5ClO is one of the chlorophenols in which chlorine replaces the hydrogen number 4 in benzene ring in phenol and is also available in the market with names p-chlorophenol, para-chlorophenol, and chloro-4-hydroxybenzene [Figure 1].[5] Its other specifications are the melting point of 43.2°C, the boiling point of 218.5°C, specific gravity of 1.265, and molecular weight of 128.56 g/mol.[5] This organic matter is water-soluble and relatively acidic. According to National Fire Protection Association (NFPA), the ranks of the 4-chlorophenol respecting to its health, flammability, and reactivity properties are 3, 1, and 0, respectively.[5]

4-chlorophenol may enter the human body through skin, breathing, and digestion and causes the irritation of eyes, skin, throat, and nose, cough, wheezing, and respiratory problems. Long exposure to this compound results in headaches, exhaustion, anxiety, liver and kidney disorders, paresis, nausea, and finally coma and death. Its LD_{50} is 670 mg/kg weight of the body.[5] The most important treatment methods for organic compounds such as chlorophenols are incineration, air striping, adsorption, wet oxidation, electrochemical, biological, and advanced oxidation processes.[6-13] Meanwhile, microwave (MW) radiations which are often used in chemical synthesis can be applied in degradation of organic materials.[2,14,15]

Microwave radiations are electromagnetic waves with wavelengths shorter than 1 m and larger than 1 mm and a frequency of 300 MHz to 300 GHz. It was first discovered by James Clerk Maxwell in 1864. MW radiations have been widely used in the synthesis or degradation of organic materials with varied properties and also in industry, medicine, chemistry, pharmacy, etc. due to their certain properties. Effects of MW radiations in chemical reactions are a combination of thermal effects like excessive heat and hot spots and non-thermal effect like increase in molecular movements.[9,16,17]

The effect of MW on the oxidation of 4-chlorophenol has not sufficiently been studied so far. However, the oxidation of 4-chlorophenol was examined using a modified domestic microwave oven alone and also along with ultraviolet (UV) radiations and without a chemical oxidant by Ai *et al*,[4] They represented that using MW or H_2O_2 as an oxidant alone could not remove 4-chlorophenol. However, a high removal rate was obtained using a combined UV/MW/H_2O_2 system. In the present study, MW radiations were used alone and with an oxidant (hydrogen peroxide) and the effect of different operational parameters on the efficiency of the process was studied for the first time in Iran.

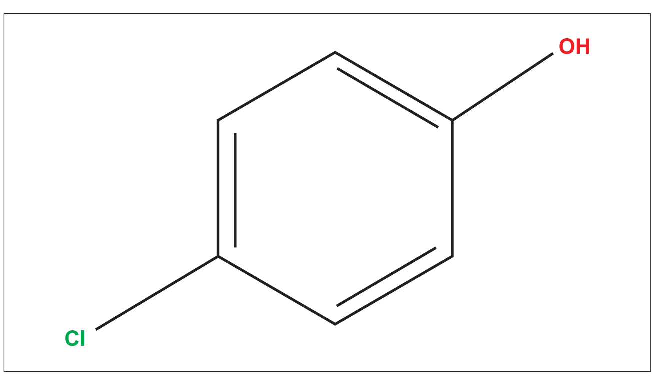

Figure 1: Spatial arrangement of 4-chlorophenol[5]

MATERIALS AND METHODS

Experiments with MW irradiation were carried out in a modified domestic microwave oven with a cooling system (2450 MHz, SAMSUNG Co. model M2349GN). Modification was done to prevent liquid evaporation through installing a reflux condenser apparatus in the microwave [Figure 2].

The stock solution of 4-chlorophenol with a concentration of 1000 mg/l was used for all procedures. For runs using the MW/H_2O_2 system, a fixed concentration of 4-chlorophenol in the neutral pH region was used with various concentrations of hydrogen peroxide. Then, the effect of other variables was examined by obtaining the optimum molar ratio of H_2O_2/4-chlorophenol. In this respect, after adjusting the pH of the solution, different amount of 4-chlorophenol and hydrogen peroxide were poured into a glass container of 500 ml. When the materials were sufficiently mixed by a magnetic stirrer, the container was put in the MW generator. Then, the reflux condenser was installed on the microwave and connected to water for cooling. Finally, the mixture was exposed to various radiations of the microwave and the samples of 1-10 ml were taken from the top of the container at specific intervals using a bubble pipette. The procedures of the experiment were as follows.

The effects of various concentrations of H_2O_2

Hydrogen peroxide with various concentrations of 0.2, 0.1, 0.05, 0.02, 0.01, and 0.005 mol/l was used to determine its

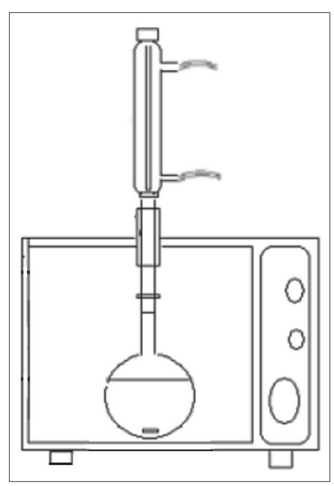

Figure 2: Schematic diagram of the modified MW pilot plant

optimum molar ratio. A fixed concentration of 4-chlorophenol (100 mg/l) in the neutral pH region and an energy of 180 W was used in order to assess the effect of initial concentration of hydrogen peroxide.

The effect of pH

Acidic, neutral, and alkaline pH regions of 3.5, 7, and 10.5 were preferred to determine pH changes in the fixed concentration of 4-chlorophenol at an energy of 180 W and optimum molar ratio of H_2O_2/4-chlorophenol. The adjustment of pH was done by 1-molar sodium hydroxide and sulfuric acid.

The effect of various amount of MW power

The removal rate of 4-chlorophenol was measured to determine the effect of MW power ranging from 180 to 900 W after specifying the optimum amount of pH and the optimum molar ratio of H_2O_2/4-chlorophenol.

The effect of initial concentration of 4-chlorophenol

Various concentrations of 4-chlorophenol (50, 100, 200, 400, and 500 mg/l) were examined to determine the effect of initial concentration of this organic compound in the MW/H_2O_2 system.

The role of MW alone

In one stage of the study, the role of MW alone in the degradation of 4-chlorophenol with a specific concentration, neutral pH, and energy of 180 W was studied to find the effect of hydrogen peroxide.

Determining specific energy consumption

Finally, the required energy for degradation of 1 kg of 4-chlorophenol (kwh/kg) in optimum conditions was specified using a power counter.

The samples were immediately analyzed to avoid further reaction. Concentration changes of p-chlorophenol were determined using a spectrophotometer (Spectronic 20D). The combination of 4-chlorophenol and 4-aminoantipyrine at pH = 7.9 ± 0.1 had a color reaction with potassium ferrocyanide. This color remained in the solution and the absorption was measured at 500 nm.[18]

RESULTS

The results on the effect of initial concentrations of H_2O_2 on 4-chlorophenol removal are shown in Figure 3. The direct irradiation results showed that the degradation of 4-chlorophenol was 7% after 180 min irradiation time in the MW system without H_2O_2. A maximum degradation of 4-chlorophenol was obtained when the H_2O_2 concentration reached 0.1 mol/l. With the addition of H_2O_2 > 0.1 mol/l, the percent degradation of 4-chlorophenol gradually decreased.

The effect of pH on the efficiency of the system is presented in Figure 4. The experiments showed that the removal rate of 4-chlorophenol in the alkaline pH region was rather more than in the acidic and neutral mediums.

The results on the effect of MW energy on the degradation of 4-chlorophenol are shown in Figure 5. As can be seen, along with the increase in the MW power, the degradation rate of 4-chlorophenol was increased.

Figure 6 presents the effects of initial concentrations of 4-chlorophenol on the effectiveness of the system. It can be seen that with increase of the initial concentration of 4-chlorophenol at an optimum condition 4-chlorophenol removal efficiency gradually decreased at different irradiation times.

The results on determining the reaction order showed that the degradation rate of 4-chlorophenol as a function of contact time was a first-order reaction (equation 1):

$$\ln(C/C_o) = -kt, \quad \text{(Eq. 1)}^{[19]}$$

where C and C_o are the 4-chlorophenol concentrations at irradiation times of 0 and *t*. *k* is the first-order reaction rate constant (l/min) and *t* is the irradiation time (min).

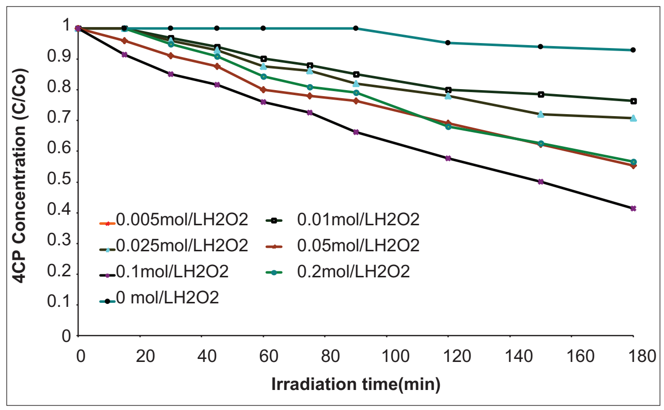

Figure 3: The effect of initial concentrations of H_2O_2 on the degradation of 4-chlorophenol in the MW/H_2O_2 system (Co=100 mg/l, pH=7)

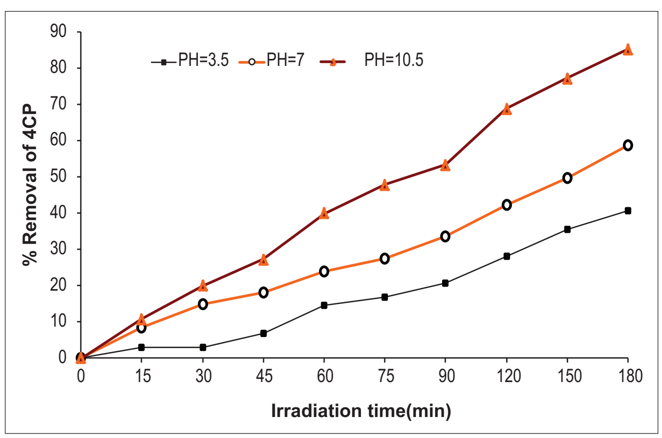

Figure 4: Degradation of 4-chlorophenol as a function of pH in the MW/H_2O_2 system (Co = 100 mg/l, H_2O_2 = 0.1M)

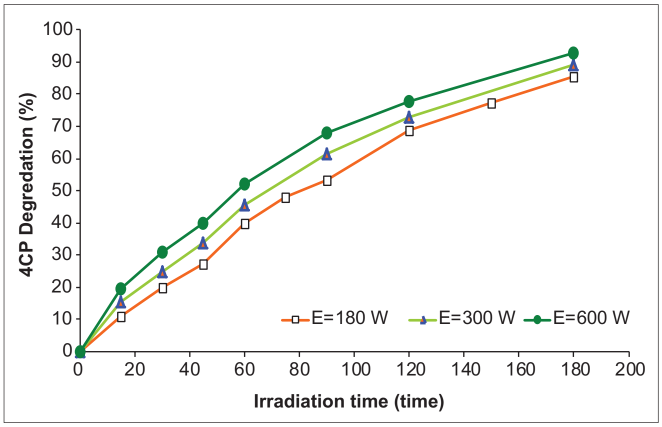

Figure 5: Comparison of the degradation rate of 4-chlorophenol at different levels of energy in the MW/H_2O_2 system (Co = 100 mg/l, pH = 10.5, H_2O_2 = 0.1M)

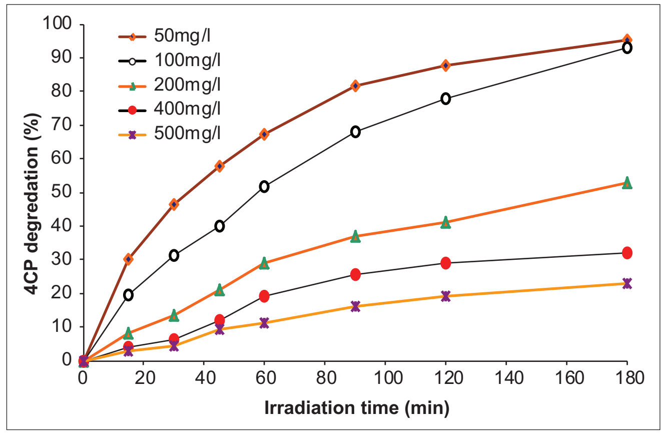

Figure 6: The effect of initial concentrations of 4-chlorophenol on the degradation of 4-chlorophenol in the MW/H_2O_2 system (Co = 100 mg/l, pH = 10)

The reaction rate constant in MW/H_2O_2 and MW systems under optimum conditions were 0.012 and 0.004, respectively.

In this study, the amount of energy consumption was also calculated (figure not shown). The results concluded that for removing 1 kg of 4-chlorophenol by MW/H_2O_2 approximately 17,460 W energy was consumed.

DISCUSSION

An advanced oxidation process using MW/H_2O_2 has been investigated for the degradation of 4-chlorophenol in aqueous solution. It was shown in Figure 3 that with the increase of initial hydrogen peroxide, the removal rate of 4-chlorophenol increased. The reason seemed to be the effect of MW radiations on H_2O_2 and the generation of hydroxyl radicals having an important role in oxidation of organic materials.[13,16,20] Therefore, as the concentration of H_2O_2 in the solution increased, the generation of hydroxyl radicals increased as well, which results in more oxidation of organic materials. The addition of H_2O_2 greater than the optimal concentration did not increase the respective maximum degradation. This behavior may be explained due to that high concentration of H_2O_2 which acts as a consumer of free radicals and decreased the concentration of these radicals.[17] The most removal rate of 4-chlorophenol was obtained in the neutral pH range, the MW energy of 180 W and the concentration of 0.1 molar in which 34% and 59% of the organic material was oxidized within 90 and 180 min, respectively. When the concentration of the oxidant increased to 0.2 molar, the removal of the organic material decreased to 44% within 180 min. Thus, the optimum molar ratio of 128 for H_2O_2/4-chlorophenol was used as a basis for doing other experiments.

The removal rate of 4-chlorophenol depends on the pH of the solution which influences the oxidation directly or indirectly. Furthermore, in chemical oxidation reactions, pH affects the oxidation efficiency through influencing the generation of hydroxyl radicals.[20] Similar to the photochemical oxidation reactions, the combined system of advanced oxidation and microwave generated the hydroxyl radical. Therefore, through generating the hydroxyl radical, the pH affected the efficiency of oxidation. The results showed that the removal rate of 4-chlorophenol in an alkaline pH medium was rather more than in the acidic and neutral regions [Figure 4]. There were two reasons for the above result. The first one is the higher generation of hydroxyl radicals, and the second one is the possibility of better absorption of MW radiations by 4-chlorophenol in the presence of anions.[3,4,13]

Most of the domestic microwave ovens can be used at different energy levels of 90-900 W. The results on the effect of MW energy on degradation of 4-chrophenol are shown in Figure 5. As shown, with the increase of MW power, the degradation rate of 4-chrophenol increased as the removal rate of 4-chlorophenol at 180 min for the different energy levels of 180, 360, and 600 comprised 85.4%, 89%, and 93%, respectively, in the MW/H_2O_2 system.

The results of the effect of initial concentrations of 4-chlorophenol on the efficiency of the system are shown in Figure 6. It was found that the degradation rate of 4-chrophenol decreased while its concentration increased as the removal rate of 81.7% occurred in the concentration of 50 mg/l after 90 min. The results [Figure 6] showed that MW radiations alone could only remove 7% of the 4-chlorophenol within 180 min which arouse from the MW heat. These results indicated the inefficiency of the MW radiations in the oxidation of the organic materials. A study using the MW system alone showed a removal rate of 2.5% for 4-chlorophenol within 120 min.[3]

The comparison of first-order kinetics constant showed that the MV/H_2O_2 process had a significant accelerating effect on the 4-chlorophenol oxidation rate. The process indicating highest k is MW/H_2O_2, approximately three times higher than the MW only.

The amount of energy consumption is one of the most important economical factors playing a significant role in the development of various units and acceptance or rejection of projects. Therefore, the amount of consumed energy consumption in optimum conditions in the MW/H_2O_2 system (E = 600 W, H_2O_2 = 0.1 M, pH = 10.5, contact time = 180 min, and the removal rate of 93%) was 17,460 kwh/kg for 4-chlorophenol removal.

CONCLUSION

The present study indicates that MW irradiation in the presence of hydrogen peroxide can greatly enhance the efficiencies of AOPs on the degradation of 4-chlorophenol. Also, it was found that the degradation rate of 4-chlorophenol using MW radiations depended on numerous factors including pH, concentration of hydrogen peroxide as an oxidant, molar ratio of H_2O_2/4-chlorophenol, MW power (W), and the initial concentration of the organic material.

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