

original article

# Application of several advanced oxidation processes for degradation of 4-chlorophenol from aqueous solution

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## ABSTRACT

**Aims:** In this work, degradation of 4-chlorophenol (4-CP) was investigated in aqueous solutions using several oxidation systems involving ultraviolet (UV)/H<sub>2</sub>O<sub>2</sub>, microwave (MW)/H<sub>2</sub>O<sub>2</sub>, and ultrasonic (US)/Fenton systems.

**Materials and Methods:** Three pilot plant reactors consist of a photolytic reactor, a modified domestic MW, and an US bath reactor of 22 kHz frequency were constructed and separately used in batch mode. The effects of several operation parameters such as pH of the solution ranging 3-10, H<sub>2</sub>O<sub>2</sub> initial concentration ranging from 0.005 to 0.2 mol/l, and reaction time were examined. Concentration changes of 4-CP were determined using a spectrophotometer at an absorption wavelength of 500 nm.

**Results:** The results show that the oxidation rate was influenced by many factors, such as the pH value, reaction times, and the amount of H<sub>2</sub>O<sub>2</sub> concentration. The optimum conditions obtained for the best degradation rate were pH = 7, H<sub>2</sub>O<sub>2</sub> concentration of about 0.05 mol/l and pH = 10, H<sub>2</sub>O<sub>2</sub> concentration of about 0.1 mol/l for UV/H<sub>2</sub>O<sub>2</sub> and MW/H<sub>2</sub>O<sub>2</sub> system, respectively. For US/Fenton system, the highest 4-CP degradation was achieved in pH = 3, H<sub>2</sub>O<sub>2</sub> concentration of about 0.05 mol/l in the percent of 0.025 mmol Fe/l. The highest 4-CP removal rate in optimum conditions of pH and concentration of H<sub>2</sub>O<sub>2</sub>, in UV/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub>, and US/Fenton systems was >99% over the retention time of 40 min, 85% after 180 min, and >99% after 40 min, respectively.

**Conclusion:** Based on the results of this study, the UV/H<sub>2</sub>O<sub>2</sub> and US/H<sub>2</sub>O<sub>2</sub> are successfully applicable for degradation of 4-CP in aqueous solution. Also, the kinetic study represented that the US/H<sub>2</sub>O<sub>2</sub> is capable of removing 4-CP slightly rather than UV/H<sub>2</sub>O<sub>2</sub> process.

**Key words:** Advanced oxidation processes, Fenton, microwave, ultrasound, ultraviolet, 4-chlorophenol

## INTRODUCTION

Aromatic compounds are common pollutants that can be present in the effluent of different industries in concentrations ranging from trace quantities to thousands of milligrams per liter. Most of these compounds are toxic and have been classified as hazardous pollutants.<sup>[1,2]</sup> Hence, the degradation

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of these pollutants in wastewater streams has emerged as an important concern during last decades.<sup>[3-6]</sup> Phenol compounds, such as 4-chlorophenol (4-CP), have been extensively applied in refineries, petrochemical industries, pesticides and herbicides production industries, antimicrobial agent manufacturers, production of compounds like 2-benzyl-4-chlorophenol, and industrial wood preservatives.<sup>[1,7,8]</sup> 4-CP is toxic and largely non-biodegradable, posing serious risks to the environment, particularly when released into natural waters. This material may enter human body through skin, breathing, and digestion and as a toxic and corrosive chemical, it causes the irritation of eyes, skin, throat, and nose, cough, wheezing, and respiratory problems. Long exposure to this chemical results in headaches, exhaustion, anxiety, liver and kidney disorders, paresis, nausea, and finally coma and death.<sup>[8]</sup> Therefore, it is important to efficiently remove or degrade this aqueous pollutant before the wastewater is discharged into receiving waters. Advanced oxidation processes (AOPs) are interesting alternatives for the destruction of organic pollutants in industrial wastewater.<sup>[3,4,9]</sup> The reason for the use of AOPs processes is due to the inability of conventional processes to treat highly polluted toxic water. Generally, these processes involving *in situ* production of hydroxyl radicals (OH<sup>•</sup>) as main oxidizing agents that are responsible for the degradation and mineralization of the organic compounds to ingredients can be generated via a number of aqueous treatment scenarios including O<sub>3</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, ultrasonic, MW, and Fenton processes.<sup>[1,6,10]</sup> Especially, UV/H<sub>2</sub>O<sub>2</sub> system involving the formation of hydroxyl radicals through photolysis of H<sub>2</sub>O<sub>2</sub> got noticed of the researchers due to its cost-effectiveness and production of a reliable source of radicals.<sup>[11]</sup> The most acceptable mechanism for H<sub>2</sub>O<sub>2</sub> is its decomposition into hydroxyl radicals which is shown in Eq. 1:<sup>[5]</sup>



During UV-based AOPs, organic compounds are oxidized in two ways. Some organic chemicals absorb UV light directly, and absorption of this high-energy radiation can cause degradation of chemical bonds and subsequent breakdown of the organic contaminant.<sup>[3,12]</sup> However, some hazardous organic compounds are hard to degrade by direct UV photolysis. Therefore, addition of H<sub>2</sub>O<sub>2</sub> to the UV process creates AOPs conditions, often increasing the rate of contaminant degradation significantly.<sup>[13]</sup> H<sub>2</sub>O<sub>2</sub> absorbs UV light and breaks down into OH radicals, degrading the contaminant via OH radical oxidation.<sup>[10]</sup> Recently, MW irradiations which are generally used to synthesize chemical materials, have been considered an option for destruction of hazard organic compounds.<sup>[11,14]</sup> MW irradiations are electromagnetic non-ionizing radiation with frequencies between 300 GHz and 300 MHz. To do so, MW irradiations have been widely used in synthesis or degradation of organic compounds with varied properties and also in industry, medicine, chemistry, pharmacy, etc., due to its certain properties.<sup>[15]</sup> Effects of MW radiations in chemical reactions

are a combination of thermal effects such as excessive heat and hot spots and non-thermal effects such as increase in molecular movements and field fixation.<sup>[6]</sup>

Ultrasound is another method of AOPs which is effective in oxidizing organic compound in water and wastewater either as the single means of treatment or in combination with other methods.<sup>[1,2]</sup> In recent years, increasing attention has been attended on the US treatment due to its greater efficiency in decomposing refractory compounds, additional chemicals are not needed, and the operation costs lower than that of other treatment methods.<sup>[1,2,16]</sup> The AOP-based ultrasound processes are one of the two different views have so far been published.<sup>[1,16]</sup> The first mechanism is pyrolysis in the cavitation bubble which is expected to be the main reaction path for the degradation of polar organic compounds. The second mechanism is the generation of reactive radicals, i.e., HO<sub>2</sub><sup>•</sup>, OH<sup>•</sup>, and H<sup>•</sup> in the cavitation bubbles which gradually decompose the polar organic compounds.<sup>[1]</sup> Another chemical oxidation process that has been widely applied in the treatment of non-biodegradable wastewater treatment is the Fenton reaction.<sup>[17]</sup> During Fenton process, in the presence of Fe<sup>(II)</sup> or Fe<sup>(III)</sup>, H<sub>2</sub>O<sub>2</sub> is decomposed and produces OH<sup>•</sup> and OH<sup>-</sup>. However, Fenton system has two limitations. The first is that Fenton reactions generally produce a large amount of iron sludge. The second observed limitation is a slow reduction of ferric ions by H<sub>2</sub>O<sub>2</sub> in their application.<sup>[17,18]</sup> Also, a combination of US irradiation with Fe<sup>(II)</sup> or Fe<sup>(III)</sup>, the so-called US-Fenton process, is a promising process which represents an efficient and cheap method for industrial wastewater treatment.<sup>[19]</sup>

The main goal of this study was to evaluate the degradation of 4-CP in aqueous solutions using different AOPs including UV/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub>, and US/Fenton. To facilitate these, the effects of pH, H<sub>2</sub>O<sub>2</sub> dose, and reaction time were also evaluated.

## MATERIALS AND METHODS

### Reagents

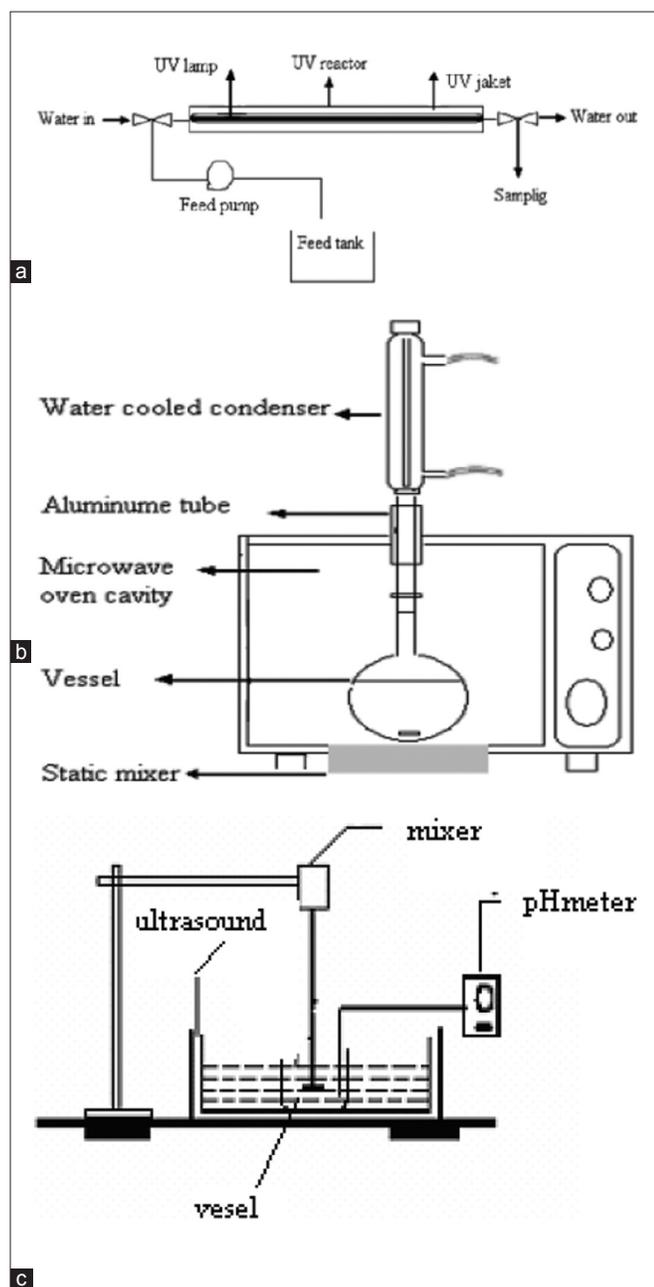
The 4-CP (C<sub>6</sub>H<sub>5</sub>ClO), NH<sub>4</sub>OH 0.5 N, KH<sub>2</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, 4-aminoantipyrine, potassium ferricyanide with 99.9% purity, and hydrogen peroxide solution (30% w/w) in stable form were all analytical grade and purchased from Merck chemical company, Pakan Ab, Co': City, state (if USA), and country. All reagents employed were not subjected to any further treatment. Water used throughout the experiments was ultrapure deionized water.

### Experimental set-up

In this study, three laboratory-scale pilot plants were used in a batch mode. The experiment with UV was done in a cylindrical reactor with 2.5 l volume and was made from stainless steel (Pakan Ab, Co). This experimental device is shown in Figure 1a. Irradiation was achieved using UV lamp (low-pressure mercury vapor lamp of 55 W, radiation

flux used for only degradation of 253.7 nm, and irradiation intensity equal to 50,000  $\mu\text{W}/\text{cm}^2$  from Philips Company) which was immersed in the glass tube.

The experiments with MW-assisted  $\text{H}_2\text{O}_2$  were conducted in an experimental installation designed on the basis of a modified MW oven with cooling system (2450 MHz, SAMSUNG Co.). Figure 1b shows a detailed diagram of the experimental device. It was modified to prevent liquid evaporation through installing a reflux still in the MW. The power used by the device was adjusted at 180 W. Fenton's reagent and US/Fenton experiments were consisted of



**Figure 1:** Schematic diagram of several oxidation systems: (a) Ultraviolet/ $\text{H}_2\text{O}_2$ , (b) microwave/ $\text{H}_2\text{O}_2$ , and (c) ultrasonic/Fenton

a digital US system (CD-4820, China) equipped with a stainless steel tank with effective volume of 2.5 l and frequency of 42 kHz [Figure 1c]. The solution was mixed by means of an automatic mixer. The reactor was equipped with a pH meter and temperature was controlled by thermometer.

### Experimental methodology

In UV processes (UV and UV/ $\text{H}_2\text{O}_2$ ), the reactor was fed with 2.5 l of a 4-CP solution with an initial concentration of 100 mg/l. Also, the studied pH variable was ranging from 3 to 10 and the influence of the amount of  $\text{H}_2\text{O}_2$  ranging from 0.005 to 0.2 mol/l. Finally, the effect of UV irradiation without the addition of  $\text{H}_2\text{O}_2$  on optimum pH value was studied. MW processes (MW and MW/ $\text{H}_2\text{O}_2$ ) were done with the special glass vessel filled with 150 ml aqueous solution of 4-CP (initial concentration of 100 mg/l, pH = 7, and different amount of  $\text{H}_2\text{O}_2$  [ranging from 0.005 to 0.2 mol/l] and ignited to MW oven by adjusting the MW power at 180 W. Then, the optimum concentration of  $\text{H}_2\text{O}_2$  was added to the vessel in different pH value between 3 and 10 by the addition of 0.1 M sulfuric acid solution in the same power with first stage. Finally, the effect of MW irradiation alone on optimum pH value was evaluated.

In US/Fenton experiments, the reactor was always charged with 1 l of an aqueous solution of 4-CP, with an initial concentration of 100 mg/l. The pH of the solution varied between 3 and 10. The influence of various concentrations of  $\text{H}_2\text{O}_2$  (from 0.1 to 0.01 mol/l) and pH was studied at constant concentration of 0.025 mmol  $\text{Fe}^{(II)}/\text{l}$ .

### Analytical methods

Samples were taken at appropriate time intervals from the reaction vessel and pipetted into 10 ml glass vials. The samples were immediately analyzed to avoid further reaction. Concentration changes of p-chlorophenol were determined using spectrophotometry (Spectronic 20 D from Milton Ray Company) which was read at 500 nm.<sup>[20]</sup>

## RESULTS

### UV/ $\text{H}_2\text{O}_2$ system

#### Effect of the amount of $\text{H}_2\text{O}_2$

Figure 2 shows the percent degradation of 4-CP as a function of the irradiation time at different initial doses of  $\text{H}_2\text{O}_2$ . As shown, the degradation rate of 4-CP first increased when  $\text{H}_2\text{O}_2$  concentration increased; however, its effect is negative for  $\text{H}_2\text{O}_2$  concentrations higher than 0.05 mol/l. The photolysis of 4-CP in the absence of  $\text{H}_2\text{O}_2$  gave rather moderate results and resulted in a slow degradation of 4-CP. As can be seen from Figure 2, when  $\text{H}_2\text{O}_2$  was added to UV irradiated solutions at optimum  $\text{H}_2\text{O}_2$  initial concentration of 0.05 mol/l, the percent degradation of 4-CP at 40 min was >99%. The direct irradiation results showed that the

degradation of 4-CP was 62% at same time in UV system without H<sub>2</sub>O<sub>2</sub>.

### Effect of pH of solution

Figure 3 illustrates the effect of pH of solution in degradation rates of 4-CP using UV/H<sub>2</sub>O<sub>2</sub> system. A maximum degradation of >99% was obtained at pH = 3 and 7 in less than 40 min. For pH values above 10, the 4-CP degradation fairly decreased.

### MW/H<sub>2</sub>O<sub>2</sub> system

#### Effect of the amount of H<sub>2</sub>O<sub>2</sub>

The effects of various initial H<sub>2</sub>O<sub>2</sub> concentrations for degrading 4-CP by MW/H<sub>2</sub>O<sub>2</sub> in the power irradiation of 180 W and neutral pH are shown in Figure 4. It has been seen from Figure 4 that the degradation rates of 4-CP increased

in the presence of H<sub>2</sub>O<sub>2</sub> and influenced by its dosages. As can be seen from Figure 4, the maximum degradation of 4-CP was 59% when system was carried out in the presence of an optimal H<sub>2</sub>O<sub>2</sub> concentration of 0.1 mol/l at 180 W MW powers. The direct irradiation results showed that the degradation of 4-CP was 7% after 180 min irradiation time in MW system without H<sub>2</sub>O<sub>2</sub>.

### Effect of pH of solution

The dependence of degradation rates on initial pH values was studied in different pH values (3, 7, and 10). It can be seen from Figure 5 that the initial pH has relatively effect on the 4-CP degradation rates. At the alkaline medium, degradation rates increased more than 80%.

### US/Fenton system

#### Effect of the amount of H<sub>2</sub>O<sub>2</sub>

Figure 6 clearly indicates the effect of H<sub>2</sub>O<sub>2</sub> concentration on degradation efficiency of 4-CP using US/Fenton process at a solution of pH = 3 and initial concentration of Fe<sup>+2</sup> = 0.025 mmol/l. From this Figure, the degrading rate of 4-CP was 8% when US used without H<sub>2</sub>O<sub>2</sub>. Figure 6 also shows that a significant enhancement of degradation efficiency was verified when the H<sub>2</sub>O<sub>2</sub> concentration was increased from 0.01 to 0.1 mol/l. However, the highest 4-CP removal efficiency was achieved at H<sub>2</sub>O<sub>2</sub> = 0.05 mol/l.

### Effect of pH of solution

Figure 7 illustrates the influence of the pH value during the use of the US/Fenton process. A maximum degradation of 99% was obtained with the system US/H<sub>2</sub>O<sub>2</sub>/Fe<sup>(II)</sup> at pH = 3.

### Degradation rate

The degradation of 4-CP by different types of oxidation processes followed first-order rate decay kinetics according to the following relationship as shown in Figure 8.

$$\ln \frac{C}{C_0} = -Kt \quad (1)$$

where C and C<sub>0</sub> are the 4-CP concentrations at 0 and t time and K is the expected pseudo-first-order rate constant. The rate constants were 0.137, 0.012, and 0.138 min for UV/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub>, and US/Fenton, respectively. Optimum conditions of processes were used to illustrate first-order changes.

## DISCUSSION

Various AOPs such as UV/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub>, and US/Fenton have been investigated and compared for degrading 4-CP in aqua solution. In UV/H<sub>2</sub>O<sub>2</sub> system, the degradation of organic material likes other pollutants in UV light in presence of H<sub>2</sub>O<sub>2</sub> in coordinate with the reaction of hydroxyl radicals generated upon photolysis of H<sub>2</sub>O<sub>2</sub> which is shown in Eq. 2.<sup>[5]</sup>

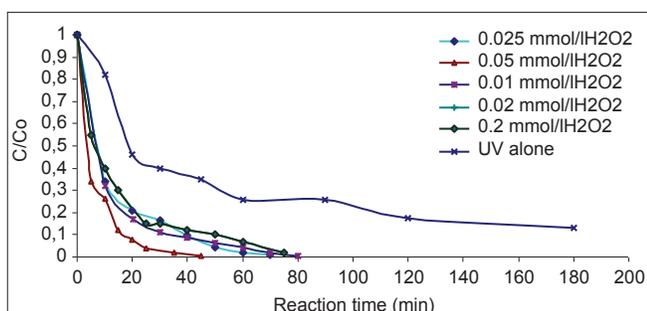


Figure 2: Effect of initial hydrogen peroxide concentration in ultraviolet/H<sub>2</sub>O<sub>2</sub> system

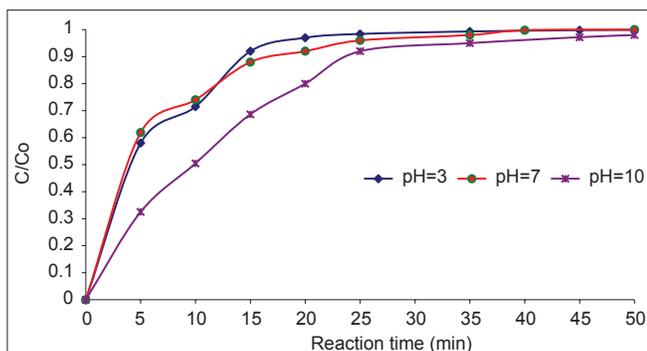


Figure 3: Effect of pH of solution in ultraviolet/H<sub>2</sub>O<sub>2</sub> system

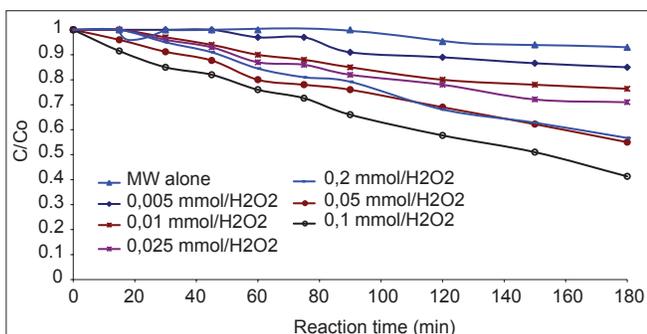
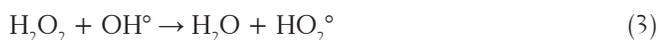


Figure 4: Effect of initial hydrogen peroxide concentration in microwave/H<sub>2</sub>O<sub>2</sub> system



Furthermore, in photochemical oxidation process, an initial  $H_2O_2$  concentration plays an important role for degrading organic pollutants. It should be added at an optimal concentration to achieve the best degradation. This is clearly shown in Figure 2. As shown, the enhancement of 4-CP degradation by addition of  $H_2O_2$  is due to the increase in the hydroxyl radical concentration.<sup>[11]</sup> At low concentration,  $H_2O_2$  cannot generate enough hydroxyl radical; therefore, the removal rate was minimum. Addition of  $H_2O_2$  greater than optimal concentration did not increase the respective maximum degradation. This behavior may be explained due to auto-decomposition of  $H_2O_2$  to oxygen and water and/or self-quenching of OH radicals by added amounts of  $H_2O_2$ <sup>[21]</sup> to produce  $HO_2^\circ$  radicals according to Eqs. 3-7.<sup>[3,6,21]</sup>



As a result, there is a critical  $H_2O_2$  concentration for the degradation of 4-CP in UV/ $H_2O_2$  process. The same behavior was reported by other literature that there is a

relationship between the initial concentrations of  $H_2O_2$  and the degradation effectiveness of organic pollutants in aqua solution.<sup>[6,11,21]</sup> The pH affects photochemical oxidation processes both directly and indirectly via it influences the production of OH radicals. The results of pH affected 4-CP degradation using UV/ $H_2O_2$  system in this study illustrated that the removal rates were not noticeably affected according to Figure 3. However, 4-CP degradation percent is increased in the acidic and neural pH solution. This may be because there is a greater facility in the generation of free radicals  $OH^\circ$  at these pH values.<sup>[5]</sup>

MW irradiation has been profitably applied in chemical engineering. The effect of MW irradiation in organic synthesis is a combination of thermal effects such as superheating, hot spots formation, polarization, and spin alignment.<sup>[6,11]</sup> Like other AOP processes, the addition of  $H_2O_2$  could have enhanced the degradation of 4-CP in MW/ $H_2O_2$  system as shown in Figure 5. However, the 4-CP removal rate seriously depends on initial  $H_2O_2$  concentration. To do so, the degradation of 4-CP was improved in the presence of  $H_2O_2$  and influenced by the dosage of  $H_2O_2$ . Most of the decomposition resulted from this process is related to generation of hydroxyl and oxygen radicals from dissolved oxygen resulting from  $H_2O_2$  dosage. Also, like UV/ $H_2O_2$  systems, with increase in initial  $H_2O_2$  concentration above the optimal dosage, the 4-CP removal rate decreased due to that  $H_2O_2$  acts as a quencher and consumes the free produced

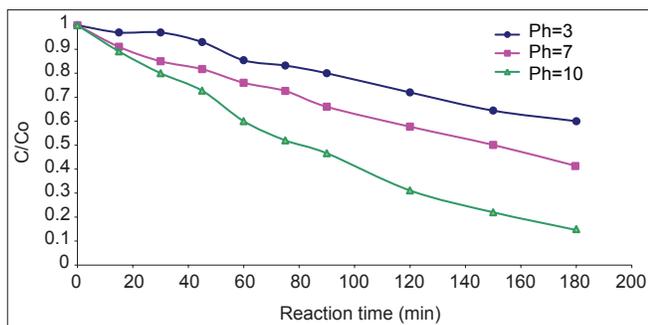


Figure 5: Effect of pH of solution in microwave/ $H_2O_2$  system

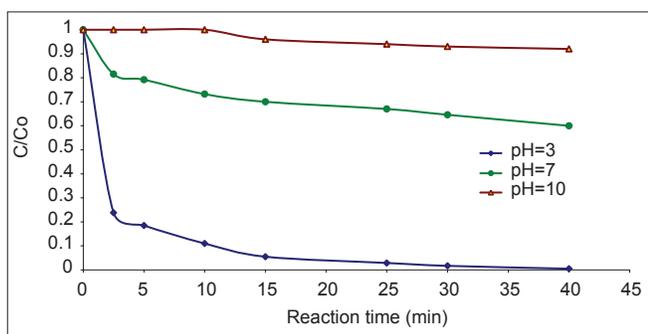


Figure 7: Effect of pH of solution in ultrasonic/Fenton system

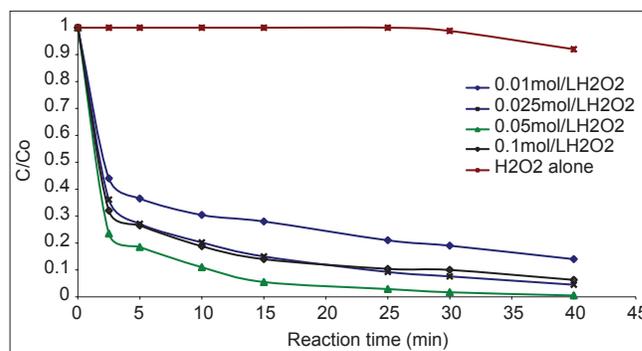


Figure 6: Effect of initial hydrogen peroxide concentration in ultrasonic/Fenton system

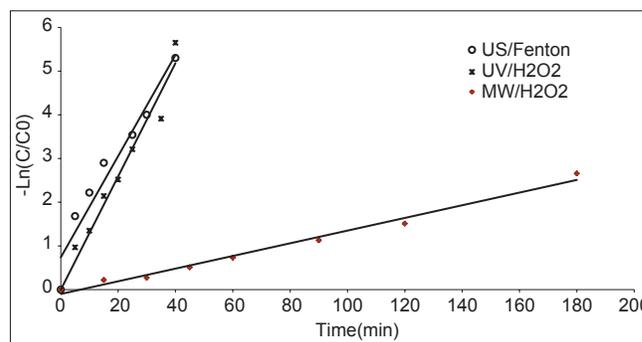
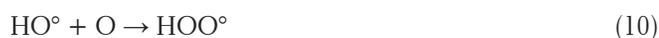


Figure 8: First-order plot for degradation of 4-chlorophenol using different oxidation processes

radicals.<sup>[19,22]</sup> In MW/H<sub>2</sub>O<sub>2</sub> process, the 4-CP degradation rate is strongly dependent on pH of solution [Figure 5]. As shown, the removal percentage of 4-CP in alkaline pH medium was rather more than that in acidic and neutral media. There were two main reasons: The first one was the higher generation of hydroxyl radicals, and the second one was the possibility of better absorption of MW irradiation with 4-CP due to the presence of anions.<sup>[19,22]</sup> Other published results in this regard indicated that the removal rate for degradation of 4-CP depended on pH of the solution and removal rate increased in acidic (pH = 2) and even more in alkaline (pH = 10) solution.<sup>[6]</sup>

In US system, US irradiation induces the formation of free radicals as a consequence of cavitation. The thermal decomposition of the water vapor and O<sub>2</sub> in a cavitation bubble leads to the formation of HO° and H° radicals as well as O atoms and HOO° radicals<sup>[16]</sup> (Eqs. 8-11).



H<sub>2</sub>O<sub>2</sub> will be formed outside the hot bubbles or at the cooler interface as a consequence of hydroxyl and hydroperoxyl recombination.<sup>[22]</sup> However, the production of H<sub>2</sub>O<sub>2</sub> would not be expected to be enhanced at low frequency. This is clearly shown in Figure 7. As can be seen, 4-CP is only partially removed by US treatment alone with about 7% removal being recorded after 180 min. As shown, with increase of H<sub>2</sub>O<sub>2</sub> in constant amount of Fe, 4-CP removal increased and reaches from 80% to 99% with increase of H<sub>2</sub>O<sub>2</sub> from 0.01 to 0.05 mmol/l. This is related with the fact that iron is an effective oxidation catalyst for several classes of organics capable of degrading the organic radicals formed through reactions of free radicals with the organic substrate, and readily decomposes H<sub>2</sub>O<sub>2</sub> to regenerate more hydroxyl radicals, hence promoting the oxidation of the organic substrate. In addition, the results shown in Figure 7 revealed that the removal rate of 4-CP in acidic pH region was largely more than that in alkaline and neutral regions. The reason is that Fe<sup>(II)</sup> is in a solution state at pH less than 3 and colloidal Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O at pH between 3 and 5, while it sediments in alkaline region at pH more than 5. High pH causes the formation of hydrated iron and ferric species which, in turn, causes rapid decomposition of H<sub>2</sub>O<sub>2</sub> into oxygen and water and consequently, no hydroxyl radical is generated. However, ferrous ion in acidic region of the solution is more than the other regions and this enhances the oxidizing power of hydroxyl radicals.<sup>[2,5,16,23]</sup>

The comparison of first-order kinetics constant showed that UV/H<sub>2</sub>O<sub>2</sub> and US/Fenton processes had a significant accelerating effect on the 4-CP oxidation rate. This is clearly

illustrated in Figure 8. The processes indicating highest rate constant (k) was observed in US/Fenton and UV/H<sub>2</sub>O<sub>2</sub>, approximately 11.5 and 11.4 times higher than the MW/H<sub>2</sub>O<sub>2</sub> and 35 and 34.5 times higher than MW only.

## CONCLUSIONS

On investigating the effect of several AOPs technology for the removing of 4-CP, it was found that degradation rate of 4-CP depends on various factors such as pH, concentration of H<sub>2</sub>O<sub>2</sub> as an oxidant, and reaction time. The optimum conditions for operating UV/H<sub>2</sub>O<sub>2</sub>, MW/H<sub>2</sub>O<sub>2</sub>, and US/Fenton systems were achieved at concentrations of 0.05, 0.1, and 0.05 mol H<sub>2</sub>O<sub>2</sub>/l, respectively. Considering the above results, UV/H<sub>2</sub>O<sub>2</sub> and US/Fenton systems are suggested as appropriate methods for removal of 4-CP in sewage of chemical and petrochemical industries.

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