WASTEWATER

2-Chlorophenol Oxidation by Ultrasound/H₂O₂ in Aqueous Solution: Models and Kinetics

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ABSTRACT

The effect of varying reaction parameters on the decomposition of 2-chlorophenol (2-cp) and removal of total organic carbon (TOC) using the ultrasound/H_2O_2 process was investigated. The decomposition of 2-cp was found to be a first-order reaction. The experimental results showed that decomposition of 2-cp using the ultrasound/H_2O_2 process was more effective than that using the ultrasound or H_2O_2 alone. At pH 3, the efficiency of 2-cp decomposition was better than 99%, but that of TOC removal was only 63% after 360 min of reaction. We detected two intermediate compounds, i.e., 2-chloro-hydroquinone and 2-chloro-*p*-benzoquinone, during the reaction. With increasing ionic strength, the extent of 2-cp decomposition was remarkably enhanced. However, the removal of TOC was found to be nearly independent of the ionic strength. The extent of 2-cp decomposition was also enhanced by the addition of catalysts ($FeSO_4$, or Fe_2O_3/Al_2O_3), but this effect was insignificant compared with that of the addition of H_2O_2. The extent of 2-cp decomposition at a small initial concentration of 2-cp was more rapid than that at a greater one concentration.

Key Words: 2-chlorophenol, first-order reaction, intermediate, ultrasound

I. Introduction

The ultrasound has gained great attention in the field of the hazardous wastewater treatment as the sole means of treatment with ozonation or UV irradiation (Kotronarou *et al.*, 1991, 1992a, 1992b; Lin *et al.*, 1996a, 1996b; Ku *et al.*, 1997). Sonication of water induces the formation of cavitation bubbles (Apfel, 1981; Berlan and Mason, 1992; Cum *et al.*, 1992; Mason *et al.*, 1992). These bubbles, filled with vapor and dissolved gases, pulsate, grow, and implode violently when they reach a critical resonant size. At the end of the compression phase, the internal temperature can reach several thousand degrees K, and the pressure can reach several hundred bars. Thermal cleavage results from these high temperatures and pressures, and the water molecule is cleaved into the H and OH radicals (Petrier *et al.*, 1992a, 1992b). Although the steady-state concentration of the OH radical is 10^{-10}–10^{-12} M, the oxidation reaction between the OH radicals and organic molecules is still practical. The OH radical is an extremely powerful oxidant, of which the coefficients of rates with organic molecules are generally in the range of 10^9–10^{10} $M^{-1}S^{-1}$ (Glaze and Kang, 1989).

Ultrasonic irradiation has shown adequate efficiency in the decomposition of organic pollutants present in water, such as *p*-nitrophenol (PNP) (Kotronarou *et al.*, 1991), hydrogen sulfide (Kotronarou *et al.*, 1992a), parathion (Kotronarou *et al.*, 1992b), chlorophenol (Lin *et al.*, 1996a, 1996b), pentachlorophenol (Petrier *et al.*, 1992a), and phenol (Okouchi *et al.*, 1992; Serpone *et al.*, 1992). The parameters affecting pollutant removal by means of ultrasonic oxidation include the ultrasound frequency and power supply (Kotronarou *et al.*, 1992a; Lin *et al.*, 1996b), saturated gas in the aqueous solution (Petrier *et al.*, 1992a), catalyst (Okouchi *et al.*, 1992), pH (Ku *et al.*, 1996a, 1996b), ionic strength (Lin *et al.*, 1996a, 1996b), and the properties of the contaminants (Kotronarou *et al.*, 1991; Ku *et al.*, 1997). Increasing of the frequency results in collapsing bubbles which release less energy but in a shorter period of time. The effect of the ultrasound frequency on the change of oxidation rate was found to be significant (Petrier *et al.*, 1992b). The rate of oxidation of H_2S was found to be proportional to the ultrasonic power (Kotronarou *et al.*, 1992b). The ambient gases, such as O_2, N_2, and Ar, were found to be directly affected by the high temperature reached during the collapse of the bubbles

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(Petrier *et al.*, 1992a). For the purpose of cavitation-induced degradation of phenol, it was found to be profitable to enhance the degradation of phenol and the formation of H_2O_2 by introducing pure oxygen (Okouchi *et al.*, 1992). Okouchi *et al.* (1992) also proposed that the degradation rate of phenol can be increased by adding Fe^{2+} and MnO_2 into the aqueous phenol solution. In sonochemical oxidation of phenol in air-equilibrated aqueous media under various pH values, three principal intermediate species were detected at pH 3, but no intermediate species were detected at pH 12 (Serpone *et al.*, 1992). The rate of decay of PNP with sonication depended on the initial concentration of PNP (Kotronarou *et al.*, 1991). Concerning the kinetics of the ultrasonic reactions, several researchers have proposed that the reaction kinetics follow either first- (Okouchi *et al.*, 1992; Serpone *et al.*, 1992) or zero-order (Ionescu and Popa, 1992) kinetic models.

The objective of this work was to study the effect of varying reaction parameters on the decomposition of 2-chlorophenol (2-cp) using the coupled ultrasound/H_2O_2 process. The effects of these parameters on the mineralization of 2-cp, represented by total organic carbon (TOC) removal, was also studied. Furthermore, we have inferred the kinetic models to describe the decomposition rate of 2-cp.

II. Experimental Sections

1. Materials

In this study, we chose 2-cp (C_6H_5OCl, Merck, 802253, purity >99%) as the target pollutant. The most important factor of 2-cp is its *pKa* value (8.49 at 25 °C). The value affects the type of 2-cp in solution (Ku *et al.*, 1997). Reagents, including hydrogen peroxide (H_2O_2, Merck 8597, purity 30%), sodium perchlorate monohydrate ($NaClO_4 \cdot H_2O$, Merck 6564, purity >99%), perchloric acid, ($HClO_4$, FEARK Art.-Nr. 11935, purity 70%), sodium hydroxide (NaOH, YAKURI, Test No. 31511601, purity >99%), and ferrous sulfate ($FeSO_4 \cdot 7H_2O$, FEARK Art.-Nr. 00686, purity >98%), were used without further purification. Stock 2-cp solution for further dilution was prepared using deionized water from a Millipore purification system at 10,000 mg/L, and properly stored to prevent any effect due to sunlight.

2. Apparatus

The experiment was conducted with a sonicator (Microson XL-2020, Heat System Ltd., USA, 0-500 W) operated at 20 kHz and a power output equal to 160

W. The double amplitude at the titanium tip (Part. No. 419) of the standard horn (Part. No. 200, 1/2" d) was adjusted to 120 μm (126.5 W/cm² of tip). The volume of the solution was 1 L in a mixing flask with a water jacket. The solution was circulated to the sonication cell at a rate of 500 mL/min by a circulating pump. Pure oxygen was continuously introduced into the flask so that the dissolved oxygen was kept at 30-32 mg/L to enhance the reaction rate and the amount of H_2O_2 produced (Okouchi *et al.*, 1992). The reaction temperature of the solution was controlled at 25 °C using a circulating temperature controller. Aqueous 2-cp solution was prepared with distilled and deionized water, and the initial pH value was adjusted using $HClO_4$ (1 N) and NaOH (1 N).

3. Parameters

The parameters considered in this work were the concentration of H_2O_2, initial pH value, ionic strength, catalyst addition, and the initial concentration of 2-cp. The initial concentrations of H_2O_2 were 0, 100, 200, and 500 mg/L. The initial pH was adjusted to 3, 5, 7, 9, and 11, and kept constant. The ionic strength of the aqueous solution was adjusted to 0.001, 0.01, and 0.1 M using $NaClO_4$. $FeSO_4$ and Fe_2O_3/Al_2O_3 were used as the only catalysts in the ultrasonic irradiation. The initial concentrations of the 2-cp solutions were 10 and 100 mg/L, and they were prepared from the stock solution.

4. Analysis Determinations

The gas chromatography/mass spectrometry (HP 1800A GCD, USA, with DB-5 column, 30 m × 0.25 mm i.d.) technique was employed to analyze 2-cp and its intermediates. The samples were analyzed using a liquid-liquid extraction procedure. Each sample collected from a treated 2-cp solution was 5 mL, in volume, acidified to a pH of less than 2 using perchloric acid, gently extracted with n-hexane for 30 min, and then injected into the GCD. An initial oven temperature of 50 °C was held for 3 min, increased to 250 °C at 10 °C/min, and then held for 3 min. The temperatures of the injector and detector were 250 and 280 °C, respectively. The method detection limit (MDL) of the analyses of the 2-cp and 2-chloro-*p*-benzoquinone was 0.22 and 0.13 mg/L, respectively. The recovery of the 2-cp was 98±4% with seven times analyses. The concentration of TOC was determined with a TOC analyzer (ASTRO 2001, USA). The MDL of the analysis of TOC was 0.14 mg/L. Analysis of H_2O_2 was performed by means of an iodometric titration with phenylarsine oxide solutions.

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III. Results

1. Effect of H_2O_2

Hydrogen peroxide used as an oxidant was added into the sample solution to study the effect of the oxidant with the ultrasonic process. With sonication, H_2O is known to decompose in collapsing cavitation bubbles to yield OH radicals (Kotronarou *et al.*, 1992b; Lin *et al.*, 1996a, 1996b; Apfel, 1981; Berlan and Mason, 1992; Cum *et al.*, 1992; Mason *et al.*, 1992; Wu *et al.*, 1992). These radicals diffuse into the bulk liquid and increase the radical concentrations in the solution; thus, they enhance the decomposition rate of organic matter (James *et al.*, 1995). However, we added H_2O_2 into the solution to increase the concentration of the OH radicals (Wu *et al.*, 1992) as shown below. Figure 1 shows typical changes of the aqueous 2-cp concentration as $[2\text{-cp}]/[2\text{-cp}]_0$, where $[2\text{-cp}]_t$ and $[2\text{-cp}]_0$ are the 2-cp concentrations at a given irradiation time t and at the initial time. The pH value was determined to be at 7 and the ionic strength 0.1 M. Moreover, we did not introduce any pure oxygen into the aqueous 2-cp solution in this test.

According to Fig. 1, the addition of H_2O_2 increased the decomposition efficiency of 2-cp. After 360 min reaction, the extent of 2-cp decomposition in the control test, i.e., without H_2O_2 addition, was only 31 %; it increased to 38% with a dosage of H_2O_2 of 100 mg/L, to 46% with 200 mg/L H_2O_2 and to 47% with 500 mg/L H_2O_2. However, there was no significant difference between the results for 200 mg/L and 500 mg/L H_2O_2. Because the concentration of OH radicals was saturated, the additional H_2O_2 failed to increase the amount of OH radicals; thus, the addition of more H_2O_2 was of no use to the reaction. According to the results of this experiment, the most effective concentration of H_2O_2 was 200 mg/L. However, Fig. 1 also shows that the efficiency of 2-cp decomposition with 200 mg/L H_2O_2 alone was not good enough. In a sonochemistry study, it was reported (Lin *et al.*, 1996a) that the effect of varying the H_2O_2 concentration on the decomposition of organic compound was insignificant. Our results show that the addition of the H_2O_2 oxidant had almost no effect upon 2-cp decomposition. Based on the efficiency of 2-cp decomposition using various processes, it was concluded that the coupled ultrasound/H_2O_2 process resulted in greater 2-cp decomposition than did the process with ultrasound alone.

2. Effect of pH
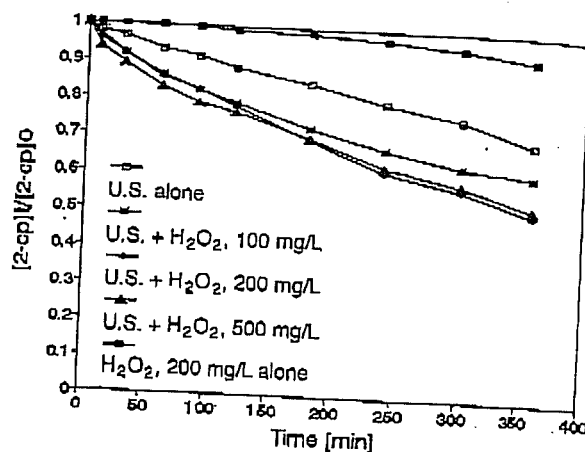
During the reaction, we controlled the pH values

Fig. 1. Comparison of the effect of H_2O_2 concentration on 2-cp decomposition using the ultrasound/H_2O_2 process (U.S. denotes ultrasound).

by means of a factitious process. The effect of varying the initial pH values on the decomposition of 2-cp vs. the irradiation time is shown in Fig. 2(a), which indicates that a smaller pH value was more effective. The extent of 2-cp decomposition reached 99% at pH 3, 85% at pH 5, and 62% at pH 7. For the samples controlled at pH 9 and 11, the extent of 2-cp decomposition was only 22 and 15%, respectively. The obvious variation among the results were due to the dissociation constant, i.e., pK_a value of 2-cp (8.49 at 25 °C). If the pH value of solution was lower than 8.49, 2-cp existed in molecular form in the solution. In contrast, 2-cp existed in ionic form if the pH value was greater than 8.49. We can write an equation to show the correlation between the molecular and ionic 2-cp as Eq. (1). Furthermore, we can calculate the ratio of [molecular 2-cp]/[ionic 2-cp] under varying pH values based upon Eq (2):

$$Molecular\ 2\text{-}cp \xrightarrow{K_a} Ionic\ 2\text{-}cp + H^+ \qquad (1)$$
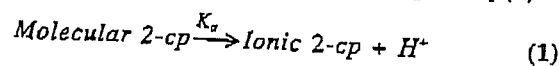
$$\frac{[molecular\ 2\text{-}cp]}{[ionic\ 2\text{-}cp]} = \frac{[H^+]}{K_a}. \qquad (2)$$

In our study, we adjusted the initial pH value to 3, 5, 7, 9, and 11. Almost all the 2-cp solutions were either in ionic form when the pH value was 11, or in molecular form when the pH values were 3 and 5. At pH 7, 97% of the 2-cp existed in molecular form and 3% in ionic form. If the initial pH value of the solution was 9, 24% of the 2-cp was in molecular form and 76% in ionic form. The ionic 2-cp could not vaporize into cavitation bubbles; they could react only outside the bubble film with OH radicals cleaved from water molecules. However, the molecular 2-cp could vaporize into cavitation bubbles and oxidize both inside by

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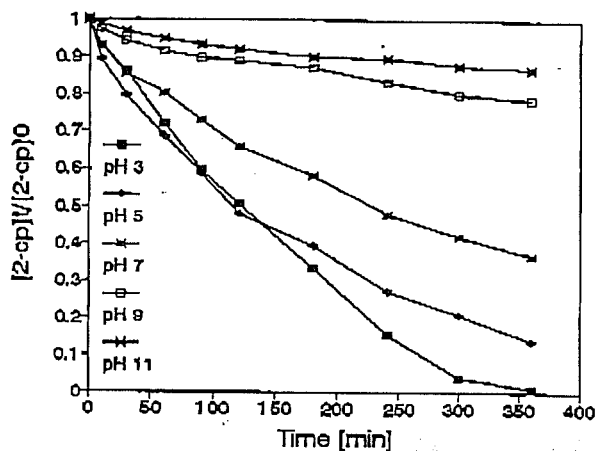
(a)
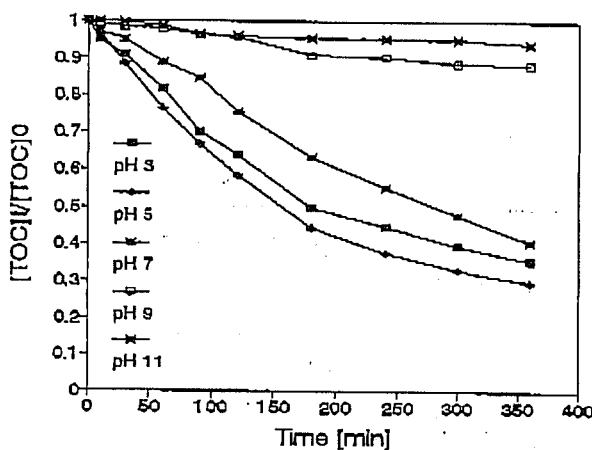
(b)

Fig. 2. (a) Comparison of the effect of pH values on 2-cp decomposition using the ultrasound/H₂O₂ process. (b) Comparison of the effect of pH values on TOC removal using the ultrasound/H₂O₂ process.

thermal cleavage and outside with the OH radicals. Hence, a lower initial pH value (especially when it was less than the pK_a) was more effective for 2-cp decomposition.

In the present study, the wastewater sample was prepared by preparing 2-cp with distilled and deionized water (without other carbonium-containing species). Therefore, one way to assess the efficiency of 2-cp mineralization was to measure the decrease of TOC concentration (James *et al.*, 1995). Figure 2(b) shows the change of TOC concentration vs. reaction time at different pH values; these results resemble those of 2-cp decomposition. The extent of 2-cp mineralization was better at a lower pH value than at a higher one. This fact indicates that TOC removal lagged behind

degradation of 2-cp (relative to Fig. 2(a)).

3. Effect of Ionic Strength

Only a few researchers have investigated the effect of varying the ionic strength on the removal of organic compounds using the ultrasonic process (Apfel, 1981; Ku *et al.*, 1997; Wu *et al.*, 1992). Similar to the pH value, the ionic strength influences the state of organic compounds in aqueous solution. The effect of varying the ionic strength on 2-cp decomposition and mineralization using the ultrasound/H₂O₂ process is shown in Fig. 3(a) and (b). James *et al.* (1995) proposed that the humic acid molecule can either be a rigid or flexible sphere, rod-like, or a flat plate depending on the ionic strength. A greater ionic strength causes the humic acid molecule to have a spherical form; as a result, other compounds or oxidants can react with humic acid more easily due to its larger surface area (James *et al.*, 1995; Bose and Reckhow, 1997). Therefore, we assumed that
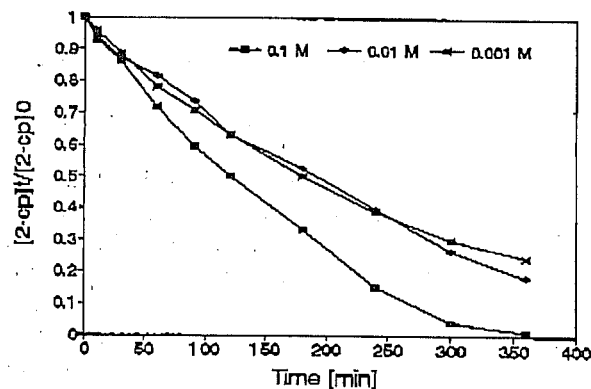
(a)
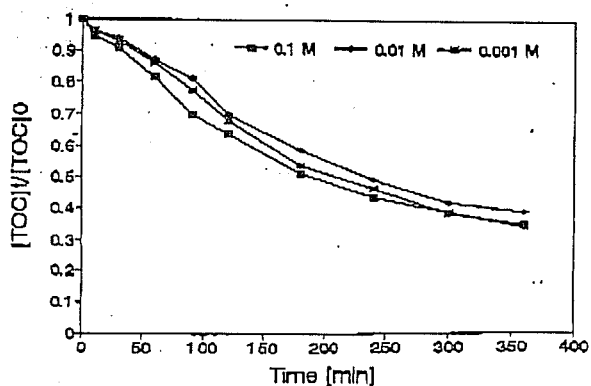
(b)

Fig. 3. (a) Comparison of the effect of ionic strength on 2-cp decomposition using the ultrasound/H₂O₂ process. (b) Comparison of the effect of ionic strength on TOC removal using the ultrasound/H₂O₂ process.

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this phenomenon could be used in our study owing to the similar result induced by ionic strength. In addition, we estimated that the ionic strength would affect the form of 2-cp.

The concentration of the ionic strength had an important impact on the 2-cp decomposition rate. The results plotted in Fig. 3(a) and (b) demonstrate that varying the ionic strength did affect the characteristics of the 2-cp. The larger the ionic strength of the solution, the larger the extent of 2-cp decomposition using the ultrasound/H_2O_2 process (Fig. 3(a)). More than 99% of the 2-cp had decomposed at an ionic strength of 0.1 M after reaction for 360 min. In addition, only 81% and 75% of the 2-cp decomposed at an ionic strength of 0.01 and 0.001 M, respectively. That is, the extent of 2-cp decomposition in the ionic strength range of 0.01 and 0.001 M did not significantly vary because the concentration of $NaClO_4$ was low. According to the results for TOC removal (Fig. 3(b)), the extent of 2-cp mineralization was almost independent of the ionic strength of the solution. The extent of 2-cp mineralization decreased with increasing ionic strength. Thermal cleavage and/or addition/substitution reactions were more important if the ionic strength increased.
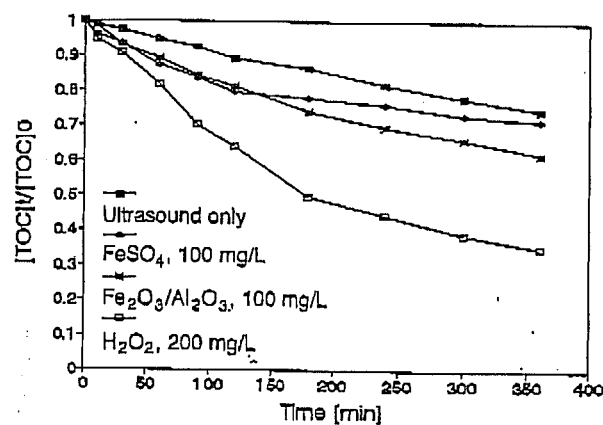
4. Effect of Catalysts

Okouchi *et al.* (1992) investigated the effects of coexisting substances, such as OH radicals and cavitation bubbles, on the decomposition of phenol using ultrasound. They proposed that the degradation rates of phenol increased with the addition of Fe^{2+}. We consider Fe^{2+} to be a catalyst. Petrier *et al.* (1992a) proposed that hydrogen peroxide was efficiently formed under aerobic conditions at a high ultrasound frequency. The Fenton oxidation reaction, requiring the addition of both Fe^{2+} and H_2O_2, is also efficient in destroying organic pollutants. To distinguish our reactions from the Fenton oxidation reaction, we examined the effect of catalysts ($FeSO_4$ and Fe_2O_3/Al_2O_3) on the decomposition of 2-cp using ultrasound only, i.e., without the addition of H_2O_2.

The effect of the catalyst type on 2-cp decomposition and mineralization using ultrasonic irradiation are shown in Fig. 4(a) and (b). Only 25% of the 2-cp were decomposed using ultrasound only. The extent of 2-cp decomposition reached 40% after 360 min of reaction when $FeSO_4$ was added into the solution. Furthermore, the extent of 2-cp decomposition reached 47% when Fe_2O_3/Al_2O_3 was added into the solution. However, the extent of 2-cp decomposition with the addition of $FeSO_4$ or Fe_2O_3/Al_2O_3 was lower than that with the addition of H_2O_2. More than 99% of the 2-
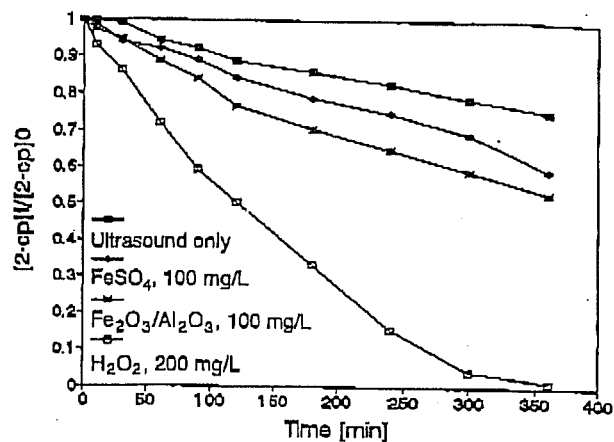
(a)

(b)

Fig. 4. (a) Comparison of the effects of various added catalysts on 2-cp decomposition using the ultrasound/H_2O_2 process. (b) Comparison of the effects of various added catalysts on TOC removal using the ultrasound/H_2O_2 process.

cp had been decomposed after 360 min of sonication using the ultrasound/H_2O_2 process. The results of TOC removal resemble those of 2-cp decomposition. In summary, the amount of H_2O_2 produced by ultrasound irradiation only was inadequate. However, the coupled ultrasound/H_2O_2 process could produce enough amounts of OH radicals; thus, it had an excellent efficiency in 2-cp decomposition. The extent of 2-cp decomposition using ultrasound was somewhat enhanced by the addition of $FeSO_4$ or Fe_2O_3/Al_2O_3.

5. Effect of Initial Concentration of 2-cp

Figure 5 shows the impact of varying the initial 2-cp concentration on the decomposition of 2-cp using the coupled ultrasound/H_2O_2 process. The extent of 2-cp decomposition depended on the initial concentra-
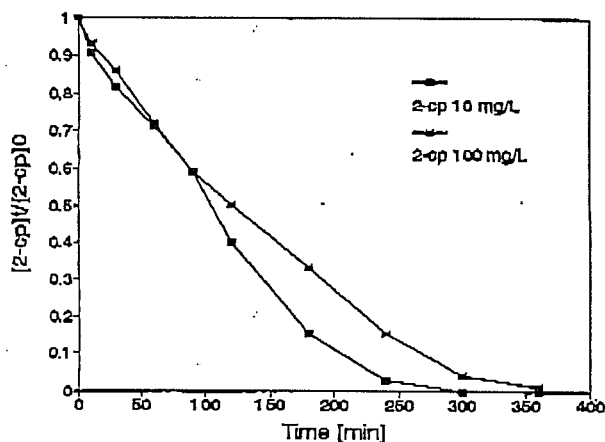
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Fig. 5. Comparison of the effect of 2-cp initial concentration on 2-cp decomposition using the ultrasound/H_2O_2 process.

tion of 2-cp. It was observed that with 200 mg/L H_2O_2, the 2-cp concentration increased from a low to a high level (10-100 mg/L), which resulted in a 15% decrease in 2-cp decomposition. These results resemble those reported by Kotronarou et al. (1991, 1992a, 1992b), namely, that the rate of contaminant destruction due to sonication decreased with an increasing initial concentration of the organic compound. Ionescu and Popa (1992) also found a similar result for the pollutant destruction with the sonication.

6. Reaction Pathway

Under the conditions of pH 3, ionic strength 0.1 M, and 200 mg/L H_2O_2, the efficiency of 2-cp decomposition was 99% but the removal of TOC was only 63%; a similar situation occurred under other pH conditions. This phenomenon shows that the 2-cp decomposition to CO_2 was incomplete. Some intermediate compounds were formed during the reaction. From analyses of the intermediates, we detected the formation of 2-chloro-hydroquinone and 2-chloro-p-benzoquinone. In addition, 2-chloro-p-benzoquinone was the major product formed based upon its abundance in the total ion chromatogram result. Huang et al. (1995) proposed that the reaction between OH radicals and phenol often took place in the ortho- and para-positions. However, we found that the OH radicals were attached to the para-position within the decomposed of 2-cp. If the OH radical attached to the para-position, 2-cp could be connected with an OH radical, which then produced 2-chloro-hydroquinone. We maintained aerobic conditions by introducing pure oxygen into the aqueous solution. The addition of pure oxygen increased the concentration of the OH radicals, and the pure oxygen reacted with compounds containing the

hydroxyl group (Anderson and Hites, 1996). The pure O_2 attached to the OH functional group sites (Kotronarou et al., 1992b; Serpone et al., 1992; Stefan et al., 1996) and transformed 2-chloro-hydroquinone into 2-chloro-p-benzoquinone. Based on these obvious results, we show the pathway of 2-cp decomposition in Fig. 6.

7. Development of Model

The advanced oxidation process represents the mineralization of organic pollutants in water due to OH radical oxidation. Several authors (Kotronarou et al., 1992a; Petrier et al., 1992a; Serpone et al., 1992; Ionescu and Popa, 1992) have reported that ultrasonic irradiation can oxidize various organic pollutants by cleaving water molecules and H_2O_2 into OH and H radicals. These reactive free radicals generated by ultrasound then reacted with other molecules or radicals. In our experiment, it was observed that the addition of H_2O_2 and the introduction of pure oxygen enhanced the formation of reactive radicals. A series of chain reactions shown occurred as follows:
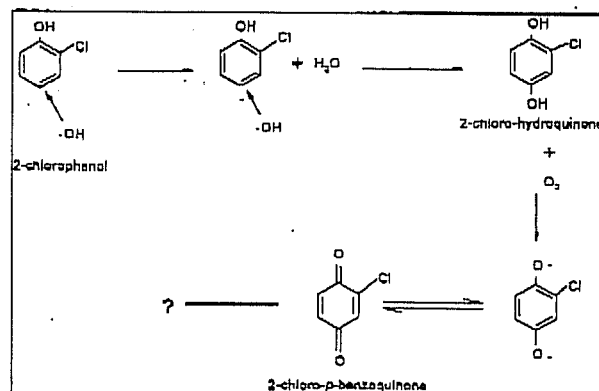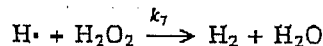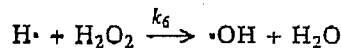
$$H_2O +))))) \xrightarrow{k_1} H\cdot + \cdot OH$$

$$2\cdot OH \xrightarrow{k_2} H_2O_2$$

$$H\cdot + \cdot OH \xrightarrow{k_3} H_2O$$

$$H\cdot + O_2 \xrightarrow{k_4} HO_2\cdot$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{k_5} H_2O_2 + O_2$$

$$H\cdot + H_2O_2 \xrightarrow{k_6} \cdot OH + H_2O$$

$$H\cdot + H_2O_2 \xrightarrow{k_7} H_2 + H_2O$$
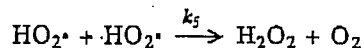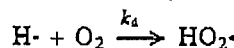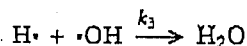
Fig. 6. Reaction pathway of 2-chlorophenol degradation using the ultrasound/H_2O_2 process.

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Table 1. Changes of Ratios of the H₂O₂ Concentration from the Beginning of the Experiment of the End

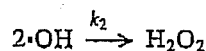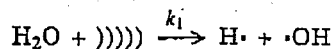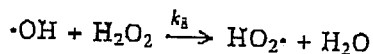| H₂O₂	Initial concentration of H_2O_2 (mg/L)	Final concentration of H_2O_2 (mg/L)	Change of ratio (%)
100 mg/l	104.30	90.12	-13.60
200 mg/l	205.35	210.73	2.62
500 mg/l	505.12	513.80	1.72
pH			
3	210.24	196.09	-6.73
5	209.39	206.84	-1.22
7	197.27	195.92	-0.68
9	203.21	205.87	1.31
11	198.61	203.64	2.53
Ionic strength			
0.1 M	210.24	196.09	-6.73
0.01 M	205.35	218.81	6.55
0.001 M	204.67	201.96	-1.32
Initial concentration			
100 mg/l	210.24	196.09	-6.73
10 mg/l	211.41	204.62	-3.21

$$\cdot OH + H_2O_2 \xrightarrow{k_a} HO_2 \cdot + H_2O$$

The OH radical generated by ultrasound is an extremely powerful oxidant. The rate constants of reactions between OH radicals and organic molecules are in the range of 10^6-10^{10} $M^{-1}S^{-1}$ (Glaze and Kang, 1989). However, the reaction mechanisms of organic compounds with ultrasound are complex. These reaction mechanisms, such as thermal cleavage and OH radical oxidation, have been investigated (Kotronarou *et al.*, 1991, 1992b; Okouchi *et al.*, 1992; Serpone *et al.*, 1992). Intermediates, such as chlorinated benzoquinone, catechol, and hydroquinone, have been studied and proposed recently (Kotronarou *et al.*, 1992b; Okouchi *et al.*, 1992; Serpone *et al.*, 1992; Wu *et al.*, 1992). Owing to the complexity of the decomposition of 2-cp, a simplified and irreversible reaction was used in this study to express the appearance of the intermediates. We denoted that the reaction rate constant was k_9:

$$\cdot OH + 2\text{-}cp \xrightarrow{k_9} \longrightarrow \longrightarrow \text{products.}$$
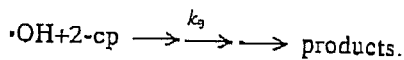
The decomposition rate of 2-cp is given in Eq. (3):

$$\frac{-d[2-cp]}{dt} = k_9[2-cp][\cdot OH] . \tag{3}$$

To simplify these complex mathematical equations, some assumptions were made based on the experimental conditions used in this study.

(1) In the aqueous solution, the volume of the reactor was not greatly changed; therefore, the

H_2O concentration ([H₂O]) could be kept constant.

(2) By controlling the ultrasound amplitude, i.e., by keeping the power supply constant, the parameter of ultrasound variation would be kept constant.

(3) Oxygen was introduced into the solution continuously, and the concentration of the dissolved oxygen was in the range of 30-32 mg/L; that is, [O₂] was constant.

(4) The reactor was an open system; assuming that the producing H₂ diffused into air, the amount of [H₂] would be 0.

(5) The change of the H₂O₂ concentration was insignificant; therefore, the concentration of H₂O₂ was assumed to be constant. To evaluate this assumption, we analyzed the change of H₂O₂ under different conditions with only one compound, H₂O₂, reacting with the field of ultrasound cavitation bubbles.

Based on the data shown in Table 1, we postulate that the change of H₂O₂ in the reaction lasted for 360 min. We found that the change of H₂O₂ was insignificant, so this assumption was correct. By combining and rearranging, we can rewrite Eq. (3) either as Eq. (4) if the 2-cp decomposition followed the first-order equation, or as Eq. (5) if it followed the α-order (α between 0 and 1) equation:

$$\frac{-d[2-cp]}{dt} = k[2-cp] \tag{4}$$

$$\frac{-d[2-cp]}{dt} = k[2-cp]^{\alpha} . \tag{5}$$

2-Chlorophenol Oxidation by Ultrasound/H_2O_2

Table 2. Proposed Kinetic Models of 2-cp Decomposition Using the Ultrasound/H_2O_2 Process

	Between zero- and first-order			First-order	
	α	k, min^{-1}	R^2	k', min^{-1}	R^2
pH					
3	0.475	2.88×10^{-2}	0.999	1.17×10^{-2}	0.921
5	0.999	1.20×10^{-7}	0.995	5.32×10^{-3}	0.994
7	0.999	5.00×10^{-3}	0.992	2.70×10^{-3}	0.993
9	0.880	1.60×10^{-4}	0.951	6.21×10^{-4}	0.955
11	0.975	1.36×10^{-5}	0.917	3.70×10^{-4}	0.916
Ion strength					
0.1M	0.475	2.88×10^{-2}	0.999	1.17×10^{-2}	0.921
0.01M	0.507	1.52×10^{-2}	0.997	4.50×10^{-3}	0.979
0.001M	0.960	1.87×10^{-4}	0.999	3.97×10^{-3}	0.999
Catalyst					
None	0.947	5.43×10^{-5}	0.987	8.02×10^{-4}	0.989
$FeSO_4$	0.992	1.44×10^{-5}	0.993	1.33×10^{-3}	0.981
Fe_2O_3/Al_2O_3	0.408	1.08×10^{-2}	0.989	1.88×10^{-2}	0.992
H_2O_2	0.475	2.88×10^{-2}	0.999	1.17×10^{-2}	0.921
Initial concentration					
100 mg/L	0.475	2.88×10^{-2}	0.999	1.17×10^{-2}	0.921
10 mg/L	0.302	2.00×10^{-2}	0.993	1.36×10^{-2}	0.913

8. Verification of the Experiment

In the present study, we prepared wastewater containing 100 mg/L (7.78×10^{-4} M) of 2-cp, and treated the wastewater using the coupled ultrasound/H_2O_2 process. We will fit the experimental data with the α- and first-order equation in this section. Integrating Eqs. (4) and (5), we can derive Eqs. (6) and (7), which show the change of 2-cp at different times:

$$-\ln\frac{[2-cp]}{[2-cp]_0} = kt \qquad (6)$$

$$[2-cp]_0^{1-\alpha}-[2-cp]^{1-\alpha}=kt. \qquad (7)$$

where

t	= variable reaction time, min;
$[2-cp]$	= the concentration of 2-chlorophenol at time t, mg/L;
$[2-cp]_0$	= the initial concentration of 2-chlorophenol, mg/L;
α	= the factor of kinetic order ($0<\alpha<1$);
k, k'	= the reaction rate constant modeled by α- and first-order, min^{-1}.

Linear regression was used to fit the values of $-\ln([2-cp]_t/[2-cp]_0)$ vs. t with the first-order equation. Nonlinear regression was used to fit those values using the computational method of the statistical analysis system with the α-order equation. The data for the kinetic constant with varying conditions of pH, ionic strength, catalyst addition, and initial concentration of 2-cp are listed in Table 2. With the α-order equation, the squared correlation coefficient of determination, R^2, is generally close to 1. This is somewhat worse than that obtained with the first-order equation, especially when α is far away from 1, e.g., under the conditions of pH 3, ionic strength 0.1 M, and an initial 2-cp concentration of 10 mg/L. Though the α-order kinetics have good fitting results, the kinetic constant (k) is closely related to the value of α. For different values of α, the values of k are not comparable. The different orders of kinetic equations reveal the different reaction pathways. Hence, when we compared the effects of different reaction conditions on the removal of organic compounds, we had to compare them using the same order. Furthermore, when the value of α is close to 1, the difference of simulated equation between the α- and first-order equations is insignificant. Since the first-order equation fits better the experimental data reported in this paper, we focused on the result of the first-order equation.

In the few cases where the α value approaches 0.90, the α-order equation can make up for the inadequacy of the first-order equation. Accordingly, the kinetics of 2-cp decomposition can be satisfactorily described using the α- and/or first-order equations.

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The results of the present investigation enable us to better understand the kinetics of 2-cp oxidation using the ultrasound process. In fact, after identification of the intermediates, i.e., hydroquinone and 2-chloro-*p*-benzoquinone, during the reaction, the reaction mechanism could be shown clearly. The α-order kinetic model shows a sufficient simulated change of 2-cp decomposition (R^2 values between 0.92-1.00). However, it is not very profitable to compare the results obtained under different reaction conditions. In fact, the values of k were not correlative to the extents of 2-cp decomposition or mineralization. Therefore, we suggest application of the first-order equation to describe the 2-cp decomposition process.

VI. Conclusions

This study has demonstrated that the coupled ultrasound/H_2O_2 process is a powerful method for the decomposition of 2-cp in wastewater. The decomposition efficiency of 2-cp is strongly influenced by both the pH value of the water sample and the addition of an oxidant. However, it was found to be insignificantly influenced either by the ionic strength or the initial concentration of 2-cp. In contrast, since the dosage of H_2O_2 was greater than 200 mg/L, it was observed that adding H_2O_2 had only a negligible effect upon the decomposition of 2-cp. Finally, it was found that mathematical modeling of the ultrasonic chemical reaction via a series of elementary reactions appeared to fit the first-order equation well.

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References

Anderson, P. N. and R. A. Hites (1996) System to measure relative rate constants of semivolatile organic compounds with hydroxyl radicals. *Environ. Sci. Technol.*, 30, 301-306.

Apfel, R. E. (1981) Acoustic cavitation prediction. *J. Acoust. Soc. Am.*, Acoustical Society of America. 69, 1624-1633.

Berlan, J. and T. J. Mason (1992) Sonochemistry: from research laboratories to industrial plants. *Ultrasonics*, 30, 203-212.

Bose, P. and D. A. Reckhow (1997) Modeling pH and ionic strength effects on proton and calcium complexation of fulvic acid: a tool for drinking water-NOM studies. *Environ. Sci. Technol.*, 31, 765-770.

Cum, G., G. Galli, R. Gallo, and A. Spadaro (1992) Role of frequency in the ultrasonic activation of chemical reactions. *Ultrasonics*, 30, 267-270.

Glaze, W. H. and J. W. Kang (1989) Advanced oxidation process. Description of a kinetic model for the oxidation of hazardous materials in aqueous media with ozone and hydrogen peroxide in a semibatch reactor. *J. Ind. Eng. Chem. Res.*, 28, 1573-1580.

Huang, C. P., C. S. Shu, C. W. Chen, and C. Dong (1995) Electrochemically generated Fenton's reagent for the removal of chlorophenols in water. First Workshop on Drinking Water Management and Treatment Technologies, Taipei, Taiwan, R.O.C.

Ionescu, S. G. and N. Popa (1992) Kinetics of FeSO₄ sonolytic oxidation in aqueous solutions. *Revue Roumaine de Chimie*, 37, 747-753.

James, H. E., P. Catharina, N. Maria, and A. Bert (1995) Potentiometric titrations of humic substances: do ionic strength effects depend on the molecular weight? *Environ. Sci. Technol.*, 29, 622-628.

Kotronarou, A., G. Mills, and M. R. Hoffmann (1991) Ultrasonic irradiation of *p*-nitrophenol in aqueous solution. *J. of Phys. Chem.*, 95, 3630-3638.

Kotronarou, A., G. Mills, and M. R. Hoffmann (1992a) Oxidation of hydrogen sulfide in aqueous solution by ultrasonic irradiation. *Environ. Sci. Technol.*, 26, 2420-2428.

Kotronarou, A., G. Mills, and M. R. Hoffmann (1992b) Decomposition of parathion in aqueous solution by ultrasonic irradiation. *Environ. Sci. Technol.*, 26, 1460-1462.

Ku, Y., K. Y. Chen, and K. C. Lee (1997) Ultrasonic destruction of 2-chlorophenol in aqueous solution. *Wat. Res.*, 31, 929-935.

Lin, J. G., C. N. Chang, and J. R. Wu (1996a) Decomposition of 2-chlorophenol in aqueous solution by ultrasound/H_2O_2 process. *Wat. Sci. & Tech.*, 33, 75-81.

Lin, J. G., C. N. Chang, J. R. Wu, and Y. S. Ma (1996b) Enhancement of decomposition of 2-chlorophenol with ultrasound/H_2O_2 process. *Wat. Sci. & Tech.*, 34, 41-48.

Mason, T. J., J. P. Lorimer, and D. M. Bates (1992) Quantifying sonochemistry: casting some light on a 'black art'. *Ultrasonics*, 30, 40-43.

Okouchi, S., O. Nojima, and T. Arai (1992) Cavitation-induced degradation of phenol by ultrasound. *Wat. Sci. & Tech.*, 26, 2053-2056.

Petrier, C., M. Micolle, G. Merlin, J. L. Luche, and G. Reverdy (1992a) Characteristics of pentachlorophenate degradation in aqueous solution by means of ultrasound. *Environ. Sci. Technol.*, 26, 1639-1642.

Petrier, C., A. Jeunet, J. L. Luche, and G. Reverdy (1992b) Unexpected frequency effects on the rate of oxidative process induced by ultrasound. *J. Am. Chem. Soc.*, 114, 3148-3150.

Serpone, N., R. Terzian, P. Colarusso, C. Minero, E. Pelizzetti, and H. Hidaka (1992) Sonochemical oxidation of phenol and three of its intermediate products in aqueous media: catechol, hydroquinone, and benzoquinone. kinetic and mechanistic aspects. *Research on Chemical Intermediates*, 18, 183-202.

Stefan, M. I., A. R. Hoy, and J. R. Bolton (1996) Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. *Environ. Sci. Technol.*, 30, 2382-2390.

Wu, J. M., H. S. Huang, and C. D. Livengood (1992) Ultrasonic destruction of chlorinated compounds in aqueous solution. *Environmental Progress*, 11, 195-201.