Oxidation of 2-Chlorophenol in Water by Ultrasound/Fenton Method

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ABSTRACT: One of the toxic and refractory pollutants formed during the color removal of fertilizer, chemical, and petroleum industrial effluents by chlorine is 2-chlorophenol (2-cp). The objective of this study is to investigate the effect of H_2O_2 and Fe^{2+} dosages on the decomposition of 2-cp using a coupled ultrasound/Fe^{2+}/H_2O_2 process. The extent of 2-cp decomposition and mineralization depends on the dosages of H_2O_2 and Fe^{2+}. More than 99% of 2-cp was decomposed and 86% of 2-cp was mineralized using the ultrasound/Fe^{2+}/H_2O_2 process at Fe^{2+} of 10 mg/L and H_2O_2 of 500 mg/L. Oxidation-reduction potential (ORP) monitoring is a useful method for determining the decomposition efficiency of the target compound. There was a slight increase in the ORP values with increasing Fe^{2+} dosages, and an apparent increase with increasing H_2O_2 dosages was observed. The major intermediate formed during the decomposition of 2-cp was 2-chloro-p-benzoquinone. It was also readily decomposed using the coupled ultrasound/Fe^{2+}/H_2O_2 process.

INTRODUCTION

Chlorophenols are the refractory compounds that have been detected during the manufacture of pesticides, bleaching of industrial wastewater, and chlorination of drinking water (Karlsson et al. 1995; Smeds et al. 1995). The chlorinated by-products, produced by the chlorination of industrial wastewater and drinking water, have led to several health risks to human beings, and give bad odor and taste (Minero et al. 1995; Muftikian et al. 1995). Removal of the refractory compounds becomes difficult and expensive when a very low level of these compounds is dealt with (Wu et al. 1992). In recent years, increasing attention has been focused on the ultrasonic process in wastewater treatment, owing to its greater efficiency in decomposing the refractory compounds (Kotronarou et al. 1991, 1992; Okouchi et al. 1992; Petrier et al. 1992; Serpone et al. 1992; Lin et al. 1996a,b). Earlier studies proposed that the influence of reaction parameters on the decomposition of 2-chlorophenol (2-cp) is in the order of ultrasonic amplitude > pH level > ionic strength > initial 2-cp concentration (Lin et al. 1996a,b, 1998; Ma and Lin 1998). Similar results on the effects of reaction parameters during the decomposition of the chlorinated compounds are also reported (Wu et al. 1992; Ku et al. 1996).

It is well known that ferrous-hydrogen peroxide (Fe^{2+}-H_2O_2) oxidation is the Fenton process. Hydrogen peroxide reacts with the ferrous ions in water and generates free hydroxyl radicals, which have a high oxidation potential and can oxidize a wide range of organic compounds. The Fenton process has been used for several decades to remove the hazardous organic compounds from industrial wastewater (Kochany and Bolton 1992; Huang et al. 1995; Zhu et al. 1996). To carry out the Fenton process efficiently, many authors illustrated that the pH level of the solution should be controlled between 2 and 4 (Sedlak and Andren 1991; Kochany and Bolton 1992; Huang et al. 1995).

The coupled ultrasonic process, such as ultrasound/H_2O_2 or ultrasound/O_2, increases the decomposition efficiency and reduces the time required for removing the pollutants. The coupled method has been shown to be efficient for the removal of hazardous organic compounds (Orzechowska et al. 1995; Lin et al. 1996a,b; Ku et al. 1997). In this study, decomposition of 2-cp using a coupled ultrasound/Fe^{2+}/H_2O_2 process was conducted in a laboratory-scale reactor. The objectives of this study are to investigate the effect of Fe^{2+} and H_2O_2 dosages on the decomposition efficiency of 2-cp and its intermediate (2-chloro-p-benzoquinone), and to establish a relationship between the oxidation-reduction potential (ORP) value and 2-cp decomposition efficiency.

MATERIALS AND METHODS

Materials

In this study, 2-cp was chosen as the target pollutant. Chemicals including 2-cp (C_6H_5OCl, Merck 802253, purity >99%), hydrogen peroxide (H_2O_2, Merck 8597, purity 30%), sodium perchlorate monohydrate ($NaClO_4$, Merck 6564, purity >99%), perchloric acid, ($HClO_4$, Feark Art.-Nr. 11935, purity 70%), sodium hydroxide (NaOH, Yakuri, test number 31511601, purity >99%), iron (II) sulfate ($FeSO_4 \cdot 7H_2O$, Feark Art.-Nr. 00686, purity >98%), anhydrous potassium carbonate (K_2CO_3, Katayama 2391, purity >99.5%), acetic anhydride [$(CH_3CO)_2O$, Katayama chemical 4957, purity >96%], n-hexane (C_6H_{14}, Fisher Scientific 2037776, purity >99.99%, ammoniummolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Riedel-de Haën 31402], and 2-chloro-p-benzoquinone (Chemical Abstract Services number 697-91-6, purity >99%) were reagent grade and used without further purification. Stock 2-cp solution of concentration 10,000 mg/L was prepared using deionized and distilled water generated from a Millipore purification system, and was stored in a brown Pyrex bottle.

Experimental Setting

The diagram of the experimental setup used in this study has been already described in our earlier papers (Lin et al. 1996a,b, 1998; Ma and Lin 1998). A sonicator (Microson XL-2020, Heat System, 0-500 W), operated at 20 kHz and 160 W power output, was used in this study. The double amplitude at the titanium tip (part. number 419) of the standard horn (part. number 200, 1/2 in. diameter) is maintained at 120 μm. Working volume of the Pyrex-glass reactor was 1 L. The reactor was equipped with a water jacket. The rate at which 2-cp solution circulated from the reactor to the sonication cell is 500 mL/min. Therefore, the cycle time between the reactor and the sonication cell was 2 min. Reaction temperature was maintained at 25°C using a circulating temperature controller. All of the experiments were carried out under the initial con-

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centration of 100 mg/L of 2-cp and pH 3. Ionic strength was maintained approximately constant at 0.1 N by the addition of 50 mL of 2 N $NaClO_4$. To investigate the effect of H_2O_2 and Fe^{2+} concentration on the decomposition of 2-cp, the experiments were initiated by adding 0, 10, 50, 100, 200, and 500 mg/L of H_2O_2 and 0.5, 1, 2, 5, and 10 mg/L of Fe^{2+} in 2-cp wastewater. An ORP sensor was introduced into the solution; hence, the profiles of ORP were monitored on-line using an ORP meter (TK ORP-96A, Tank Co., Taiwan). Prior to the experiment, the ORP meter was rechecked by a standard solution of 220 mV.

Extraction Procedures

Liquid-liquid extraction was performed to extract 2-cp and its intermediates. Five milliliters of the sample was collected from the reactor, and was acidified to bring the pH values to less than 2 using perchloric acid (1 N). About 0.4 g of K_2CO_3 and 1 mL of acetic anhydride were added into the bottle, and the mixture was shaken vigorously for 30 min. Then, 1 mL n-hexane was added into the bottle, and it was shaken vigorously for another 30 min. The upper hexane layer of the extracted sample was injected into the gas chromatography/electron ionization detector (HP 1800A GC/EID).

Instrumental Analysis

This study followed the procedures given in the 19th edition of "Standard methods for examination of water and wastewater" ("Standard" 1995). Analysis of 2-cp and its intermediates was performed with a 30 m × 0.25 mm inside diameter DB-5 capillary column (J & W Scientific, Folsom, Calif.). Highly (99.99%) pure helium (1 mL/min) was used as the carrier gas. The column was heated from 50°C (holding time of 3 min) to 250°C (holding time of 3 min) at a ramp of 10°C/min. The temperatures of the injector and detector were 250°C and 280°C, respectively. The mass spectrometer was operated at −70 eV and scanned from 30 to 425 amu at 1 scan/s. H_2O_2 was estimated using a KI titration method (Kormann et al. 1988). When the organic compound was readily oxidized to carbon dioxide, it was estimated that this compound was mineralized. Hence, the mineralization of 2-cp was investigated by the removal of dissolved organic carbon (DOC). Profiles of DOC concentration were monitored using a total organic carbon analyzer (ASTRO 2001, System 2). A description of the analytical methods used in this study and their minimum detection limits (MDL) are given in Table 1. In this study, the concentrations of 2-cp chosen for constructing the calibration curve were in the range of 0.625 to 100 mg/L. The MDL of 2-cp is 0.22 mg/L.

RESULTS AND DISCUSSION

Impact of Coupled Process on 2-cp Decomposition

In the present work, a simulated lab-scale wastewater was prepared with an initial concentration of 2-cp of 100 mg/L. Three treatment methods, ultrasound, ultrasound/H_2O_2, and the Fenton process (Fe^{2+} of 5 mg/L and H_2O_2 of 200 mg/L), were conducted to decompose the 2-cp in the wastewater. The decomposition profiles are presented in Fig. 1. The total treatment period for the aforementioned process was 6 h. The pH value was maintained at 3 using H_2SO_4 and NaOH, and the ionic strength was adjusted to 0.1 N using $HClO_4$. A control test was carried out to study the vaporization of 2-cp during the reaction period (6 h). The condition for the control test was the same as that of the other three treatment processes, with a pH of 3, an ionic strength of 0.1 N, and a mixing rate of 150 rpm. The ultrasound condition was the same as that of the control test, but the ultrasonic wave was introduced into

TABLE 1. Analytical Methods

Parameter (1)	Reference (2)	Minimum detection limits (3)
2-cp	Liquid-liquid extraction GC/MS method[a]	0.22 mg/L
2-chloro-*p*-benzoquinone	Liquid-liquid extraction GC/MS method[a]	0.13 mg/L
Dissolved organic carbon	Wet oxidation method[a]	0.14 mg/L
Hydrogen peroxide	Iodometric titration[b]	0.27 mg/L
pH	Electrometric method[a]	—
ORP	Oxidation-reduction potential measurement in clean water[a]	—

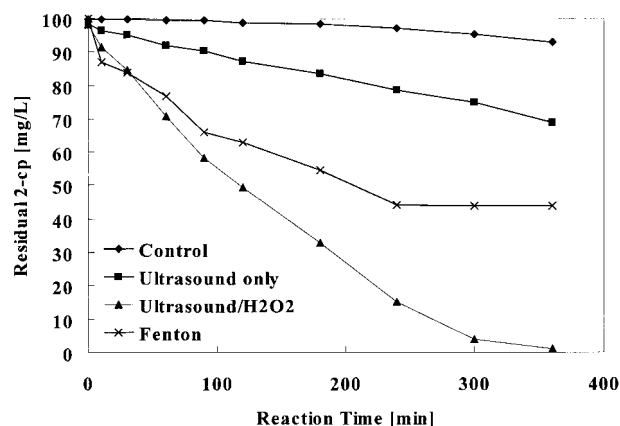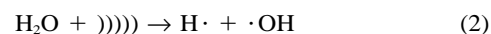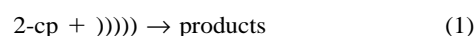[a]"Standard" (1995).
[b]Kormann et al. (1988).

FIG. 1. Decomposition Kinetics of 2-Chlorophenol in Water: Control and Comparison of Treatment Methods

the solution at an amplitude of 120 μm. The ultrasound/H_2O_2 condition was the same as that of the ultrasound condition, but 200 mg/L of H_2O_2 was added into the solution. For the Fenton method, the condition was the same as that of the control test, but 5 mg/L of Fe^{2+} and 200 mg/L of H_2O_2 were added into the solution. It was noted that less than 7% of 2-cp was vaporized for 6 h. When the 2-cp was decomposed using the ultrasound/Fe^{2+}/H_2O_2 process, the reaction was carried out for 90 min; hence, the effect of 2-cp vaporization (less than 1.8%) on the decomposition of 2-cp was insignificant. When the ultrasonic process was applied for the decomposition of 2-cp, it was observed that only 31% of 2-cp was decomposed during the reaction period of 6 h. However, more than 99% of 2-cp was decomposed when the ultrasonic process combined with H_2O_2 of 200 mg/L was performed. Wu et al. (1992) proposed that the target contaminant present in the water can be directly decomposed in the cavities [(1)] or oxidized by free radicals [(3)]. If the organic compound exists in molecular form, it can vaporize into the cavitation bubbles produced by the ultrasonic process and it is cleaved thermally; outside of the bubbles, it reacts with the hydroxyl radicals cleaved from water molecules (Ku et al. 1997). Therefore, in this study, it was assumed that two reaction mechanisms were possible for the decomposition of 2-cp. The mechanisms are represented by (1) and (3). Many researchers proposed that in the absence of H_2O_2, 2-cp is decomposed directly in the high temperature and pressure cavitation area (Kotronarou et al. 1992; Serpone et al. 1992; Wu et al. 1992). In the presence of H_2O_2, 2-cp is decomposed thermally in the cavitation area, and by the hydroxyl radicals or other free radicals in the bulk-liquid phase. Thus, a better decomposition efficiency of 2-cp can be obtained. A similar result was observed in this study

$$2\text{-cp} +))))) \rightarrow \text{products} \qquad (1)$$

$$H_2O +))))) \rightarrow H\cdot + \cdot OH \qquad (2)$$

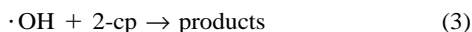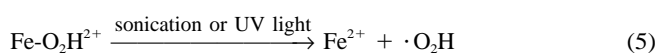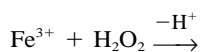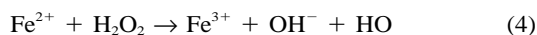$$\cdot OH + 2\text{-}cp \rightarrow products \qquad (3)$$

Fig. 1 also shows the decomposition of 2-cp using the Fenton process only. More than 56% of 2-cp was decomposed by the Fenton process. In the comparison of the results shown in Fig. 1, the Fenton process was found to be better than the ultrasonic process for decomposing 2-cp. Even though the Fenton and ultrasound/H_2O_2 processes showed a better efficiency in the decomposition of 2-cp, the 6 h reaction period was too long for application in a real wastewater treatment plant. Therefore, further investigation is necessary to reduce the treatment time.

Zhu et al. (1996) proposed that when H_2O_2 was added into an aqueous system containing the organic substances and Fe^{2+}, complex redox reactions would take place. The mechanism of the reaction is shown in (5). The mechanism by which hydroxyl radicals are generated from the H_2O_2 during the Fenton process is a common one. When Fe^{3+} is present in the solution, it reacts with H_2O_2 and produces a complex intermediate Fe-O_2H^{2+}. The complex intermediate, Fe-O_2H^{2+}, can be isolated as Fe^{2+} and the O_2H radical either by sonication or by ultraviolet (UV) light, as shown in (5). The isolated Fe^{2+} reacts with H_2O_2 and again produces the hydroxyl radical

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO \qquad (4)$$

$$Fe^{3+} + H_2O_2 \xrightarrow{-H^+}$$

$$Fe\text{-}O_2H^{2+} \xrightarrow{\text{sonication or UV light}} Fe^{2+} + \cdot O_2H \qquad (5)$$

From the above explanation, it is estimated that the coupled ultrasound/Fe^{2+}/H_2O_2 process can significantly enhance the decomposition of 2-cp, due to the high concentration of hydroxyl radicals that could be observed. Therefore, the present work was carried out to investigate the efficiency of 2-cp decomposition for different dosages of Fe^{2+} and H_2O_2 by the coupled ultrasound/Fe^{2+}/H_2O_2 process.

Effect of Fenton's Reagent on 2-cp Decomposition

The application of ultrasonic-wave energy on the decomposition of 2-cp was demonstrated, and the results were presented in our earlier studies (Lin et al. 1996a,b; Ma and Lin 1998). The performance of an ultrasound/Fe^{2+}/H_2O_2 process can be understood from Figs. 2(a)–2(c). These figures display the extent of 2-cp decomposition (represented as residual 2-cp in mg/L) for various dosages of Fe^{2+} with H_2O_2 concentrations of 0, 50, and 500 mg/L.

Figs. 2(a)–2(c) reveal that H_2O_2 significantly influences the 2-cp decomposition. The extent of 2-cp decomposition by the coupled ultrasound/Fe^{2+}/H_2O_2 process for various dosages of Fe^{2+} without H_2O_2 is between 30% and 65% in 90 min [Fig. 2(a)]. However, 80%–99% and more than 99% of 2-cp are decomposed with the H_2O_2 dosages of 50 and 500 mg/L, respectively [Figs. 2(b) and 2(c)]. With 10 mg/L of Fe^{2+} and 500 mg/L of H_2O_2, there was no 2-cp detected for the first minute. Therefore, only four curves are shown in Fig. 2(c). Based on the results shown in these three figures, a significant difference is observed during the decomposition of 2-cp with or without H_2O_2. It is also noted that the 2-cp rapidly decomposed when the applied H_2O_2 dosage was 500 mg/L. As shown by (4) and (5), the concentration of hydroxyl radicals increases with an increase of H_2O_2 dosage. It has been proposed that the higher the dosage of H_2O_2, the higher the concentration of hydroxyl radicals produced; this phenomenon increases the decomposition efficiency of the target compound. Fig. 2(c) demonstrates the importance of H_2O_2 in the solution. Comparing the results shown in Figs. 1 and 2(c), it is obvious that the ultrasound/Fe^{2+}/H_2O_2 process is more efficient than the other processes for the decomposition of 2-cp.
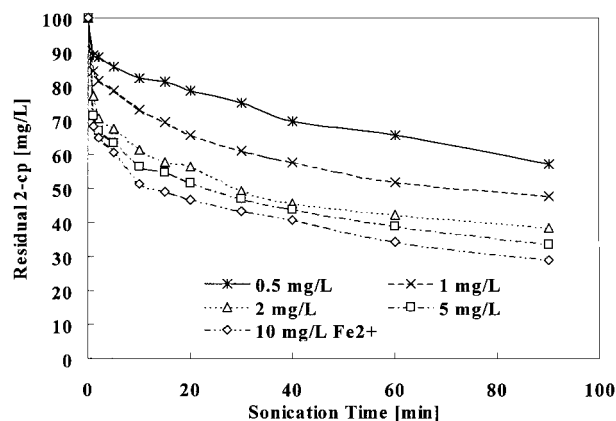

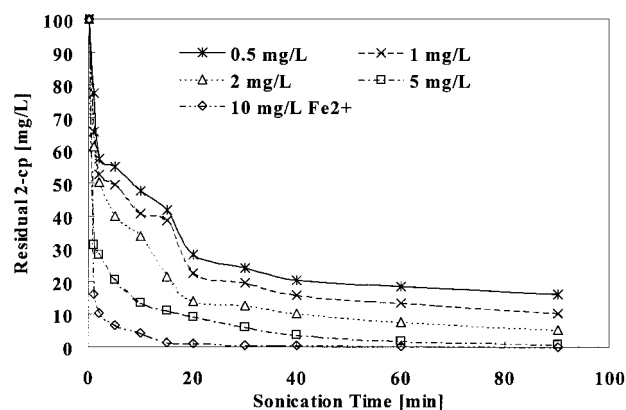**FIG. 2(a).** Decomposition Kinetics of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Absence of H_2O_2

FIG. 2(b). Decomposition Kinetics of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Presence of 50 mg/L of H_2O_2
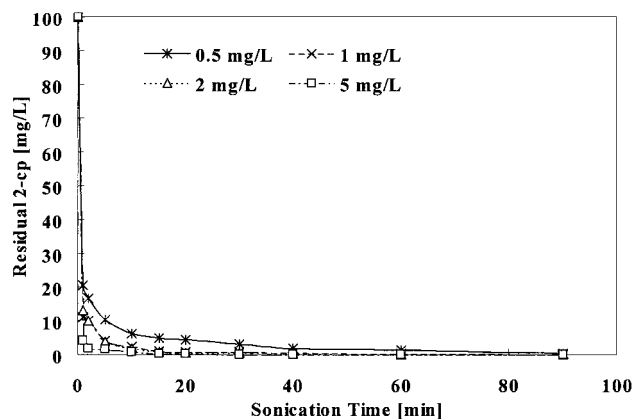

FIG. 2(c). Decomposition Kinetics of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Presence of 500 mg/L of H_2O_2

To further understand the contributions of the oxidants Fe^{2+} and H_2O_2 on the decomposition of 2-cp, the data from several recent studies (Puhakka et al. 1992; Wu et al. 1992; Minero et al. 1995; Ku et al. 1996, 1997; Lin et al. 1996a,b) are summarized in Table 2. From the table, it is clear that ultrasound, H_2O_2, or Fe^{2+} alone cannot decompose the refractory compounds efficiently within a short period. However, there is good agreement that the coupled process—that is, ultrasound/Fe^{2+}/H_2O_2 or UV/TiO_2—can efficiently decompose refractory compounds within a short period. In fact, more than 99% of the refractory compounds disappeared with the initial 20 min (Wu et al. 1992; Minero et al. 1995). A similar phenomenon was observed in this study [Fig. 2(c)]. Puhakka et al. (1992) used an aerobic biological treatment process to degrade 74 mg/L of pentachlorophenol (PCP). The result showed that the time

TABLE 2. Comparison of Degradation of Organic Materials by Different Treatment Methods

Authors (1)	Method (2)	Key test conditions (3)	Efficiency (4)	Time (5)
Lin et al. (1996a)	US/O_2, US/H_2O_2	US frequency 20 kHz, 2-cp 100 mg/L, H_2O_2 200 mg/L, and pH 7	26%, 49%	6 h, 6 h
Lin et al. (1996b)	US/Fe^{2+}, US/H_2O_2	US frequency 20 kHz, 2-cp 100 mg/L, H_2O_2 200 mg/L, pH 3, and Fe^{2+} 100 mg/L	40%, >99%	6 h, 6 h
Ku et al. (1996)	UV/TiO_2	UV intensity 22.5 W/m², 2-cp 10 mg/L, TiO_2 2 g/L, and pH 3	>99%	200 min
Ku et al. (1997)	US	US frequency 20 kHz, 2-cp 12 mg/L, and pH 3	>99%	20 h
Wu et al. (1992)	US	US frequency 20 kHz, CCl_4 46.7–130 mg/L, and 25°C	>96%	6 min
Puhakka et al. (1992)	Aerobic biotechnology	DO 3 mg/L, 21–25°C, pH 7.0–7.5, and PCP 74 mg/L	>99%	Three months
Minero et al. (1995)	UV, UV/TiO_2	UV intensity 23.9 W/m², PCP 10 mg/L, and TiO_2 0.1 g/L	>99%, >99%	70 min, 20 min
This study	US/Fe^{2+}, US/Fenton	US frequency 20 kHz, 2-cp 100 mg/L, pH 3, Fe^{2+} 1–10 mg/L, and H_2O_2 0–500 mg/L	40–70%, >99%	90 min, 10–90 min

Note: US = ultrasound, UV = ultraviolet light, and DO = dissolved oxygen.

taken for the complete degradation of PCP was three months. Compared with the advanced oxidation processes, the disadvantages of the biological process are its long treatment time and incubation time; if the biological microorganisms are acclimated, it can be used to treat refractory compounds continuously. For advanced oxidation processes, it is understood that high treatment efficiency and treatment time reduction can be achieved. However, the economic consideration and sedimentation problem caused by chemicals should be noticed.

Effect of Fenton's Reagent on ORP Profiles

The measurement of the ORP value is the key parameter in determining the oxidation power of an oxidative process (Doong and Wu 1993; Wareham et al. 1993; Chang et al. 1995). In this study, variations in the ORP values were monitored during the reaction, and a relationship was established between the ORP values and the concentration of Fe^{2+} and H_2O_2. Figs. 3(a)−3(c) show the change in the ORP values with various dosages of Fe^{2+} and 0, 50, and 500 mg/L of H_2O_2, respectively. The initial ORP value for each reaction condition was 395 mV, and the total treatment time was 90 min. From Figs. 3(a)−3(c), it is understood that the profiles in the ORP values during the reaction are affected by the various dosages of Fe^{2+}. In Fig. 3(a), the reaction is initiated at pH 3, an ionic strength of 0.1 N, and in the presence of oxygen without H_2O_2. This process is referred to as the ultrasound/Fe^{2+} process. It is obvious that there was a sudden increase in the ORP value when Fe^{2+} was added into the solution, and then the ORP value decreased. Also, there was a slight increase in the ORP values with the further increase of Fe^{2+} dosage. From (4) and (5), it is understood that the generation of hydroxyl radicals increases with increasing dosage of Fe^{2+}. Hence, the higher the Fe^{2+} dosage applied, the higher the ORP values during the overall reaction.
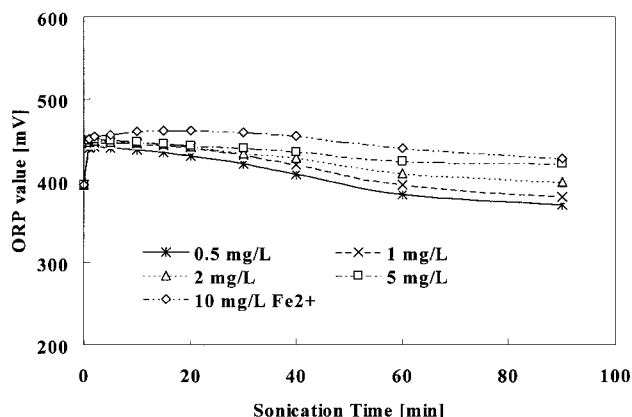
FIG. 3(a).   Kinetics of ORP Values during Decomposition of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Absence of H_2O_2
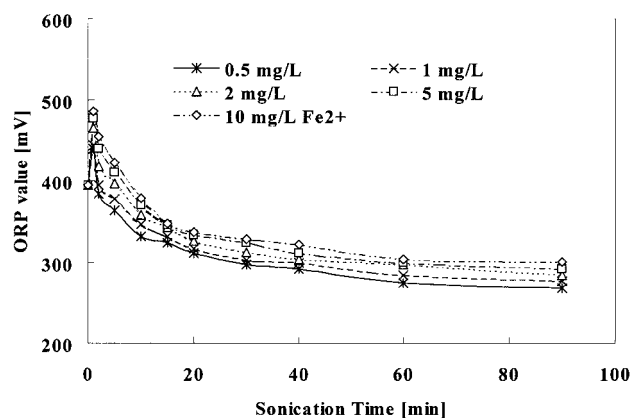
FIG. 3(b).   Kinetics of ORP Values during Decomposition of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Presence of 50 mg/L of H_2O_2
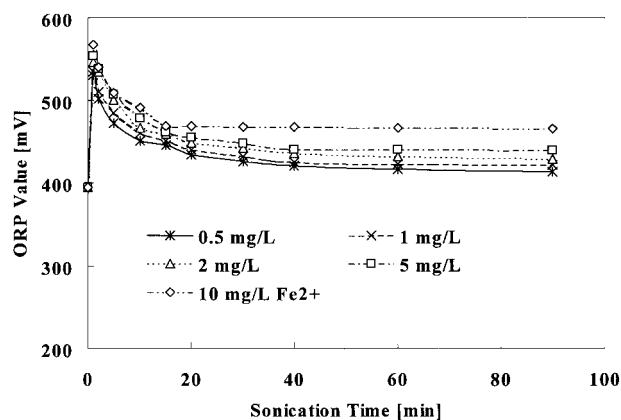
FIG. 3(c).   Kinetics of ORP Values during Decomposition of 2-Chlorophenol in Water for Various Dosages of Fe^{2+} in Presence of 500 mg/L of H_2O_2

Figs. 3(a)−3(c) also show the influence of H_2O_2 dosages on the ORP values. These figures show that the ORP values increase by the addition of oxidants (Fe^{2+} and/or H_2O_2) into the 2-cp solution. Since 2-cp is decomposed either by the Fenton process or by the ultrasonic process, the concentration of hydroxyl radicals in solution is decreased due to the reaction between the organic compound and the hydroxyl radicals. Thus, the ORP values declined steeply. This phenomenon is shown in both Fig. 3(b) and Fig. 3(c). Fig. 3(a) reveals that there is no significant increase in the ORP values with an increase in the concentration of Fe^{2+}. Two milligrams per liter of Fe^{2+} without H_2O_2 increases the ORP value initially to 53 mV [Fig. 3(a)]. However, for the same Fe^{2+} dosage with 50 and 500 mg/L of H_2O_2, the increase in the initial ORP values is 70 mV [Fig. 3(b)] and 151 mV [Fig. 3(c)], respectively. The above result illustrates that the addition of Fe^{2+} alone cannot

significantly enhance the oxidation power. Also, the oxidation power of the ultrasound/Fe^{2+} process is not sufficient to decompose the 2-cp effectively. This is in agreement with the result presented in Fig. 2(a), which shows that only 30%–65% of 2-cp is decomposed using the ultrasound/Fe^{2+} process.

Fig. 3(a) shows that the ORP values are in the range of 400–450 mV during the decomposition of 2-cp by the ultrasound/Fenton process. There is a slight change (near 10%) in the ORP values during the reaction even though the ORP value monitoring technique has been used to estimate the decomposition efficiency of 2-cp. Poziomek et al. (1995) combined the ultrasonic process and other methods such as measuring the pH level and chloride concentration for monitoring the decrease in chlorinated pollutant concentration. A good relationship between the decomposition of the target compound and the chloride concentration or pH level was found. When the target compound was decomposed, there was an increase in the chloride concentration and a decrease in the pH level. The authors proposed that combining the ultrasound process with other methods is a very useful in-situ technique for effective remediation. Orzechowska et al. (1995) also combined the ultrasound process with other measurement methods such as pH, conductivity, and chloride concentration for measuring the degradation of chlorinated hydrocarbons in water. The authors proposed that combining sonication with commercially available measurement methods is a powerful technique for determining specific pollutants in water. Liu et al. (1995) proposed that an ultrasonic wave frequency of 1.1 MHz was used to study sonoluminescence in air-saturated water for monitoring the concentration of dissolved oxygen (DO). The experimental results show that the anions in the simulated waters have no influence on the sonoluminescence intensity measured. Based on the results, a new type of DO monitoring method could be developed.

As mentioned above, it is interesting to assess the feasibility of an ORP value monitoring technique for estimating the decomposition of 2-cp. A relationship between the ORP ratio and

FIG. 4. Relationship between ORP Ratio and Percentage of 2-Chlorophenol Decomposition for Various H_2O_2 Dosages

the percentage of decomposition of 2-cp is plotted in Fig. 4. The ORP ratio is defined by the following equation:

$$\text{ORP ratio} = [(ORP)_t - (ORP)_0]/(ORP)_0 \qquad (6)$$

where $(ORP)_t$ = ORP value measured at time t; and $(ORP)_0$ = initial ORP value.

When the ORP ratio is positive, the decomposition takes place with a higher oxidation power, which is due to the presence of more hydroxyl radicals produced by the addition of H_2O_2. On the other hand, if it is negative, this solution is still in an oxidative state, but the oxidation power is lower compared with the positive ORP ratio condition. In Fig. 4, the dosage of Fe^{2+} applied is 2 mg/L. It is obvious that there is a good relationship between the percentage of 2-cp decomposition and the ORP ratio for various H_2O_2 dosages. This fact indicates that the addition of H_2O_2 does increase the oxidation power of the reaction. This increased oxidation power is completely used for the decomposition of 2-cp. Since a linear relationship exists between the ORP ratio and the percentage of decomposition of 2-cp, the ORP ratio can be used to estimate the decomposition efficiency of 2-cp. Based on the above result, it is noted that when industrial wastewater is treated using an ultrasonic/Fenton process, the efficiency of the process could be easily determined by monitoring the ORP values.

Effect of Fenton's Reagent on H_2O_2 Utilization

It is known that the amount of H_2O_2 utilized depends upon the dosage of Fe^{2+} applied (Arnold et al. 1995; Miller et al. 1996; Zhu et al. 1996). An additional dosage of Fe^{2+} applied can react with H_2O_2 and produce larger amounts of hydroxyl radicals in the solution. Therefore, a higher ORP value and decomposition of 2-cp were observed. Table 3 shows the effect of various Fe^{2+} and H_2O_2 dosages applied in the decomposition of 2-cp and the utilization of H_2O_2. It was found that the extent of H_2O_2 utilization decreased with an increasing H_2O_2 concentration. At 0.5 mg/L of Fe^{2+}, more than 72% of H_2O_2 was utilized with an initial H_2O_2 dosage of 10 mg/L, but less than 40% was utilized with H_2O_2 of 500 mg/L. It is interesting to note that this result is in contrast to the extent of 2-cp decomposition. It was observed that at 50 mg/L of H_2O_2, an increase in Fe^{2+} from the low to high level (from 0.5 to 10 mg/L) resulted in an increase in H_2O_2 utilization by 3.2 mg/L. At 500 mg/L of H_2O_2, the increase in Fe^{2+} resulted in an increase in H_2O_2 utilization by 71.4 mg/L (Table 3). The decomposition of 2-cp by the ultrasound/Fenton process was between 80 and 100 mg/L at 50 mg/L of H_2O_2 [Fig. 2(b)], but those were decomposed completely at 500 mg/L of H_2O_2 applied [Fig. 2(c)]. The experimental result reflects that the decomposition of 2-cp depends on the amount of H_2O_2 utilized. Similar observations are made by several researchers during the removal of refractory compounds (Lin et al. 1996a; Miller et al. 1996; Werderitsch et al. 1996; Zhu et al. 1996).

Table 3 also presents the low percentages of H_2O_2 utilization (22%–43%) with the large dosages of H_2O_2 applied. This reveals that the H_2O_2 is not completely used in the decomposi-

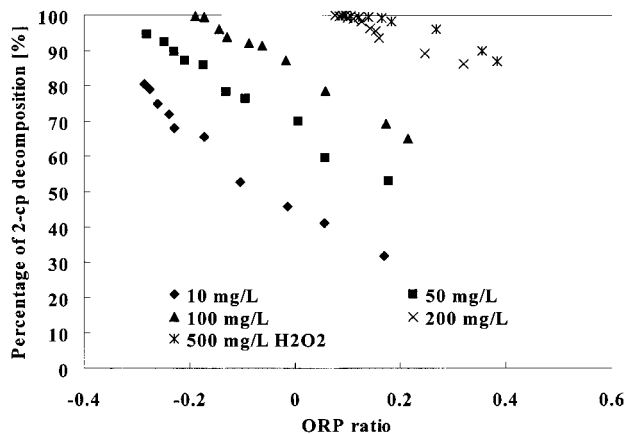**TABLE 3. Comparison of Amounts of 2-cp Decomposed and H_2O_2 Utilized at Various Concentrations of Fe^{2+} and H_2O_2**

Parameter (1)	Fe^{2+} = 0.5 mg/L Initial H_2O_2 Concentration (mg/L)					Fe^{2+} = 10 mg/L Initial H_2O_2 Concentration (mg/L)				
	10 (2)	50 (3)	100 (4)	200 (5)	500 (6)	10 (7)	50 (8)	100 (9)	200 (10)	500 (11)
2-cp Decomposed (mg/L)	68.9	83.9	96.2	99.3	99.8	93.3	100[a]	100[a]	100[a]	100[a]
H_2O_2 Utilized (mg/L)	7.2	42.6	56.4	73.5	122.6	8.5	45.8	72.80	135.4	194.0
2-cp Decomposed/H_2O_2 utilized (mol/mol)	2.54	0.53	0.45	0.37	0.21	2.92	0.58	0.35	0.19	0.13

[a]Residual 2-cp was lower than the minimum detection limit.

tion of 2-cp. Therefore, it is not necessary to add a large amount of oxidant into the solution to slightly increase the efficiency of 2-cp decomposition. Arnold et al. (1995) reported that lowering the ratio of $FeSO_4$ and H_2O_2 should improve the reaction efficiency because there would be less Fe^{2+} competing with atrazine for hydroxyl radicals. While acetone is treated by the UV/H_2O_2, Stefan et al. (1996) postulated that a higher H_2O_2 concentration becomes a strong scavenger for OH radicals, and hence the initial rate of acetone degradation decreases. Therefore, choosing an optimal dosage of H_2O_2 and Fe^{2+} is an important step for decomposing the 2-cp efficiency at a low cost.

It was observed that at an Fe^{2+} concentration of 10 mg/L, there was a slight increase in 2-cp decomposition with increasing H_2O_2 concentrations. In addition, the extent of 2-cp decomposition by H_2O_2 utilization was in the range of 0.13–2.92, while the additions of H_2O_2 were decreased from 500 mg/L to 10 mg/L. This fact reveals that the amounts of 2-cp decomposition resulting in each milligram of utilized H_2O_2 decrease with increasing initial H_2O_2 dosages. Similar results were observed in other studies (Arnold et al. 1995; Stefan et al. 1996; Zhu et al. 1996). For a fixed amount of H_2O_2 of 10 mg/L, the ratio of 2-cp decomposition by each milligram of H_2O_2 utilization was excellent (9.6–11.0 mg of 2-cp per milligram of H_2O_2). However, the percentages of 2-cp decomposition in the ultrasound/Fenton process were undesirable (ranging from 68.9% to 93.3%). Thus, for a high decomposition efficiency of 2-cp, a high concentration of Fe^{2+} is required.

Effect of Fenton's Reagent on 2-cp Mineralization

The goal of applying the ultrasound/Fe^{2+}/H_2O_2 process is to degrade the 2-cp completely and convert it into a nonhazardous product, e.g., CO_2 (Wu et al. 1992; Ku et al. 1996). In this study, mineralization of 2-cp was represented by the decrease of DOC concentration. Ding et al. (1995) concluded that the high selectivity to CO_2 was obtained based on the
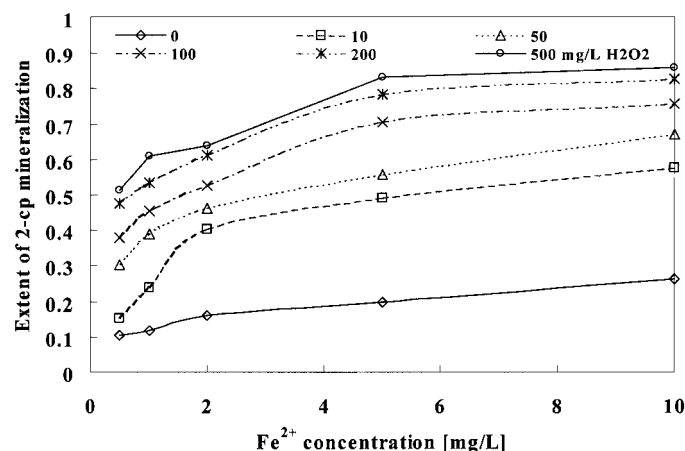

FIG. 5. Mineralization Kinetics of 2-Chlorophenol Decomposition for Various Dosages of H_2O_2 and Fe^{2+} in Coupled Ultrasound/Fenton Process

similar values for CO_2 production and total organic carbon (TOC) reduction. Ku et al. (1996) proposed that the reduction of DOC is a good sign of the mineralization of the refractory compounds. Fig. 5 shows the profiles of 2-cp mineralization at various dosages of H_2O_2 and Fe^{2+} applied. The higher the dosages of H_2O_2 and Fe^{2+} applied, the higher the mineralization of 2-cp. Apparently, 86% of 2-cp was mineralized while 10 mg/L of Fe^{2+} and 500 mg/L of H_2O_2 were added into the 2-cp solution. At this condition, 2-cp was not detected within the first minute of the reaction (MDL of 2-cp is 0.22 mg/L). This revealed that the 2-cp was decomposed completely when a high dosage of H_2O_2 was applied. Unfortunately, only 25% of the initially added H_2O_2 was utilized in the reaction. From Table 3, it is obvious that a higher amount of H_2O_2 is utilized when 50 mg/L of H_2O_2 is added. In addition, this condition has led to the complete decomposition of 2-cp.

Table 4 summarizes the results of 2-cp mineralization for various applied dosages of Fe^{2+} and H_2O_2. It shows the effect of low and high concentrations of H_2O_2 (10–500 mg/L) on the mineralization of 2-cp. The extent of DOC reduction increases with an increasing dosage of either H_2O_2 or Fe^{2+}. A slight increase in DOC reduction is found in Table 4, while the dosage of H_2O_2 is greater than 200 mg/L. Table 4 also shows the ratio of 2-cp decomposition to DOC reduction (or 2-cp mineralization) at various dosages of Fe^{2+} and H_2O_2 applied. Prior to the reaction, the concentration of 2-cp was 100 mg/L and the DOC concentration was 56.25 mg/L. The ratio of 2-cp decomposition to mineralization at the initial time was 1.78 mg/mg. This ratio can be used as a key parameter to reveal the relationship between the concentrations of 2-cp and the intermediates produced in the reaction. Since a higher ratio was observed from the result of 2-cp decomposition in the ultrasound/Fenton process, it is understood that the 2-cp was readily decomposed but DOC reduction was slow. This is due to the formation of several intermediates. As shown in Table 4, for a fixed dosage of Fe^{2+}, the ratio of 2-cp decomposition to DOC reduction decreases with increasing dosages of H_2O_2. This reveals that the 2-cp is decomposed more readily at a high dosage of H_2O_2 than at a low level. Also, low amounts of intermediates are produced for a high dosage of H_2O_2. On the other hand, for a fixed dosage of H_2O_2, the ratio of 2-cp decomposition to DOC reduction decreases with increasing dosages of Fe^{2+}. From Figs. 2(a)–2(c), it is obvious that the oxidation power increases with increasing concentrations of oxidants. Therefore, it is concluded that the 2-cp can be efficiently decomposed and the intermediates can be further decomposed when the oxidation power is high. Based on the above explanation, the optimal Fe^{2+} and H_2O_2 dosages were observed as 10 and 50 mg/L, respectively, owing to the high extent of 2-cp decomposition, H_2O_2 utilization, and a good extent of DOC reduction.

Intermediates and Reaction Pathways

In all of the experiments, seven types of intermediates (4-chloro-1,3-benzendiol; 2-chloro-5-methyl-phenol; 2-chloro-6-methyl-phenol; 4-chloro-3-methyl-phenol; 2-chloro-p-hydro-

TABLE 4. Comparison of Amounts of 2-cp Mineralized at Various Concentrations of Fe^{2+} and H_2O_2

| Parameter (1)	Fe^{2+} = 0.5 mg/L Initial H_2O_2 Concentration (mg/L)					Fe^{2+} = 10 mg/L Initial H_2O_2 Concentration (mg/L)				
	10 (2)	50 (3)	100 (4)	200 (5)	500 (6)	10 (7)	50 (8)	100 (9)	200 (10)	500 (11)
2-cp Mineralized (mg/L)	8.7	17.1	21.4	26.8	28.9	32.5	37.8	42.7	46.6	48.5
Removal ratio (DOC/DOC_0)	0.15	0.30	0.38	0.47	0.51	0.58	0.67	0.76	0.83	0.86
2-cp Decomposed/2-cp mineralized (mol/mol)	4.45	2.76	2.53	2.08	1.94	1.61	1.49	1.32	1.21	1.16

Note: DOC = dissolved organic carbon.
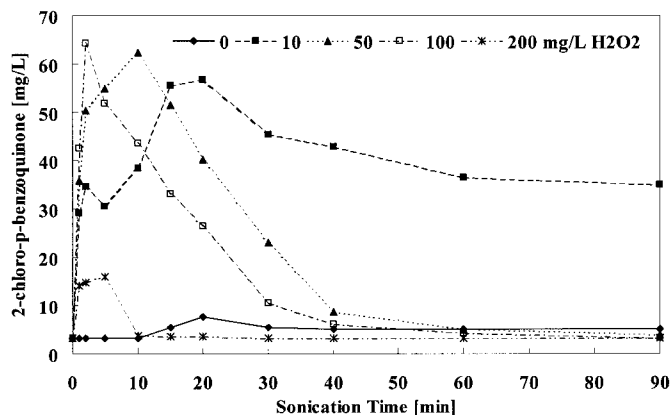
FIG. 6. Kinetics of 2-Chloro-*p*-Benzoquinone for Various H$_2$O$_2$ Concentrations during Decomposition of 2-cp by Ultrasound/ Fenton Process (Fe^{2+}: 5 mg/L)

quinone; 2-chloro-*p*-benzoquinone; and 2,6-dichloro-2, 5-cyclohexadiene-1, 4-dione) were observed. Huang et al. (1995) found that the reaction between the hydroxyl radical reacts with phenol in the ortho- and para- positions. In our earlier study (Ma and Lin 1998), based on the presence of these seven types of intermediates, two different reaction mechanisms— that is, para- and meta- position reactions—were developed during the decomposition of 2-cp. It was found that the para-position reaction was the major pathway of the reaction, due to the higher concentration of intermediates observed in the para- position reaction. Further, 2-chloro-*p*-benzoquinone was the major intermediate. Several authors also noted that the chlorinated benzoquinone is the major intermediate during the decomposition of chlorophenols using chemical processes (Kotronarou et al. 1992; Serpone et al. 1992; Minero et al. 1995; Stefan et al. 1996).

The effect of H$_2$O$_2$ dosages on the formation of an intermediate (2-chloro-*p*-benzoquinone) at 5 mg/L of Fe^{2+} and various dosages of H$_2$O$_2$ applied is presented in Fig. 6. This figure shows that the concentration of 2-chloro-*p*-benzoquinone is low for the Fe^{2+} dosage of 5 mg/L without H$_2$O$_2$. When the dosages of H$_2$O$_2$ are in the range of 10–100 mg/L, there is an increase in the formation of 2-choro-*p*-benzoquinone. It is also observed that the concentration of 2-chloro-*p*-benzoquinone in the solution increased with an increase of H$_2$O$_2$. This is explained by the fact that as the concentration of H$_2$O$_2$ increases, the oxidation power of the solution also increases. However, at the dosage of H$_2$O$_2$ of 200 mg/L, the formation of 2-chloro-*p*-benzoquinone was lower than that of H$_2$O$_2$ of 100 mg/L. At H$_2$O$_2$ of 500 mg/L, there was no 2-chloro-*p*-benzoquinone detected in the solution. This reveals that the hydroxyl radical decomposes the 2-cp as well as the intermediates. Scheck and Frimmel (1995) used the UV/H$_2$O$_2$/O$_2$ process for the removal of phenol and salicylic acid. Since a key intermediate in this study was 2-chloro-*p*-benzoquinone, the importance of hydroxylation of the aromatic ring has been confirmed. Also, since mineralization is indicated by the loss of DOC in solution, it is expected that the ring of 2-chloro-*p*-benzoquinone is cleaved and the hydrocarbon by-products are eventually oxidized to CO$_2$.

CONCLUSIONS

The effect of various dosages of H$_2$O$_2$ and Fe^{2+} on the decomposition of 2-cp in an ultrasound/Fe^{2+}/H$_2$O$_2$ method was investigated in this study. It is found that the ultrasound/Fe^{2+}/H$_2$O$_2$ method is a more promising and effective method than the ultrasound or the Fenton method for the decomposition of 2-cp. At Fe^{2+} of 0.5 mg/L without H$_2$O$_2$, less than 31% of 2-cp and 10% of DOC was removed. However, more than 99%

of 2-cp and 86% of DOC was removed at Fe^{2+} of 10 mg/L and H$_2$O$_2$ of 500 mg/L. Experimental results indicate that the technique of ORP value monitoring can be effectively used to estimate the decomposition efficiency of 2-cp. Considering the extent of 2-cp decomposition, DOC reduction, and H$_2$O$_2$ utilization, it was concluded that an Fe^{2+} dosage of 10 mg/L and H$_2$O$_2$ dosage of 50 mg/L was the optimal condition. The concentration of 2-chloro-*p*-benzoquinone, which was the major intermediate in the reaction, was affected by the applied dosages of H$_2$O$_2$. Since the H$_2$O$_2$ dosage applied in the reaction was greater than 200 mg/L, both the 2-cp and its intermediate were effectively decomposed.

ACKNOWLEDGMENTS

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