



ENHANCEMENT OF DECOMPOSITION OF 2-CHLOROPHENOL WITH ULTRASOUND/H₂O₂ PROCESS

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ABSTRACT

We investigated the effects of pH, ionic strength, catalyst, and initial concentration on both decomposition of 2-chlorophenol (2-cp) and removal of total organic carbon (TOC) in aqueous solution with ultrasonic amplitude 120 μm and H₂O₂ (200 mg/l). When the initial concentrations of 2-cp was 100 mg/l and the pH was controlled at 3, the rate of 2-cp decomposition was enhanced up to 6.6-fold and TOC removal up to 9.8-fold over pH controlled at 11. At pH 3, the efficiency of decomposition of 2-cp was 99% but the removal of TOC was only 63%; a similar situation applied at pH 7 and 11. Hence intermediate compounds were produced and 2-cp was not completely mineralized. When the concentration of ionic strength was increased from 0.001 to 0.1 M, the rate of 2-cp decomposition was enhanced only 0.3-fold, whereas the TOC removal was not enhanced. In comparison of the effects of pH and ionic strength, pH had greater influence on both 2-cp decomposition and TOC removal than ionic strength. The effect of a catalyst (FeSO₄) on decomposition of 2-cp was insignificant comparing with direct addition of H₂O₂. The reaction rate at a smaller initial concentration of 2-cp (10 mg/l) was more rapid than at a greater one (100 mg/l). The rate of 2-cp decomposition and TOC removal appeared to follow pseudo-first-order reaction kinetics. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Catalyst; 2-chlorophenol; decomposition; ionic strength; pH; pseudo-first-order kinetics; TOC removal; ultrasound/H₂O₂ process.

INTRODUCTION

Ultrasound has gained great attention in the field of hazardous wastewater treatment. Several authors (Kotronarou *et al.*, 1991; Okouchi *et al.*, 1992; Petrier *et al.*, 1992a; Serpone *et al.*, 1992) reported that ultrasonic irradiation can oxidize various organic pollutants by cleaving water molecules to OH radicals. The parameters that effect ultrasonic oxidation include ultrasound frequency and power supply (or intensity), saturated gas in the aqueous solution, catalyst, pH, temperature and ionic strength, and initial concentration of contaminants.

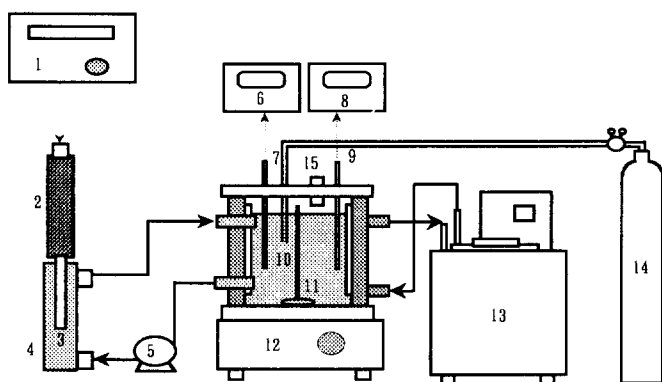
Oxidative processes induced by ultrasound are enhanced when a high frequency is used by comparison with a small frequency. Hydrogen peroxide was formed in larger amounts at 514 kHz than at 20 kHz (Petrier *et al.*, 1992b). For the cavitation-induced degradation of phenol the rate of formation of H_2O_2 was enhanced with oxygen, and addition of Fe^{2+} and MnO_2 into the aqueous phenol solution increased rates of degradation of phenol (Okouchi *et al.*, 1992). For the sonochemical oxidation of phenol in air-equilibrated aqueous media at varied pH, Serpone *et al.* (1992) found three principal intermediate species to be formed at pH 3, but no intermediate species were detected at pH 12. The rate of decay of *p*-nitrophenol (PNP) with sonification depended on the initial concentration of PNP (Kotronarou *et al.*, 1991). About the kinetics of ultrasonic reactions several researchers proposed that the reaction follows either first-order (Serpone *et al.*, 1992; Okouchi *et al.*, 1992) or zero-order (Ionescu and Popa, 1992) kinetic models.

Lin *et al.* (1996) reported that an ultrasound/ H_2O_2 process with ultrasonic amplitude 120 μm and H_2O_2 (200 mg/l) gave more efficient decomposition than ultrasound alone, although the decomposition of 2-cp was effective with ultrasound at a greater amplitude. The process, without addition of catalyst, was purged with oxygen and tested at constant ion strength (0.1 M). In the present work, we investigated further the parameters not only pH but also ionic strength, catalyst, and initial concentration of 2-cp in the decomposition of 2-cp. The effect of these parameters on mineralization of 2-cp, represented by removal of total organic carbon (TOC), was also examined. The kinetics of 2-cp decomposition and mineralization in the ultrasound/ H_2O_2 process are described with a pseudo-first-order model.

EXPERIMENTAL SECTION

Apparatus

The experiment was conducted with a sonicator (Microson XL-2020, Heat System Ltd., USA) operated at 20 kHz. A schematic drawing of the reactor appears in Figure 1. The volume of solution was 1 l in a mixing flask, and was circulated to the sonication cell at a rate 500 ml/min. The double amplitude was adjusted at 120 μm , corresponding to a power output 160 W. Oxygen was continuously purged into the flask so that the dissolved oxygen was kept at 30–32 mg/l. The temperature of the solution was controlled at 25°C with a constant temperature circulator. Aqueous 2-cp solution was prepared with deionized water and the reaction was initiated on addition of H_2O_2 (200 mg/l).



1. sonicator, 2. horn, 3. tip, 4. flowing reactor, 5. pump, 6. DO meter, 7. DO sensor, 8. pH meter, 9. pH sensor, 10. mixing flask, 11. stirring bar, 12. stirrer, 13. temperature circulator, 14. O_2 bomb, 15. sampling port.

Figure 1. Schematic of apparatus.

Parameters

The parameters considered in this work are pH, ionic strength, catalyst, and initial concentration. The pH was controlled at 3, 7 and 11 with HClO_4 and NaOH . The ionic strength of the aqueous solution was adjusted to 0.1, 0.01 and 0.001 M with NaClO_4 . FeSO_4 was used as catalyst in ultrasonic irradiation without addition of H_2O_2 . The initial concentrations of 2-cp used in this work were 100 and 10 mg/l.

Analysis

Ten aqueous samples, collected between 0 and 360 min of reaction duration, were tested for analysis of 2-cp and TOC. The concentrations of 2-cp were analyzed with hexane/water extraction and GC/ECD (HP 5890II, USA); a capillary column DB1 (0.32 mm i.d. x 15 m) was used. The temperatures of the injection port were 150°C and of the oven, initially 50°C for 3 min, then increased to 250°C at a ramp rate 20°C/min, held there 2 min. The detector temperature was 300°C. Total organic carbon was determined with a TOC analyzer (Astro 2001 system 2, USA).

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the decomposition of 2-cp vs. time is shown in Fig. 2. (a), for which the ionic strength was adjusted to 0.1 M without addition of catalyst. The results indicate that a smaller pH value is more effective. The decomposition of 2-cp attained 99% at pH 3, and 62% at pH 7. For a sample controlled at pH 11, the extent of 2-cp decomposition was only 15%. The obvious variation among these values arises because the pK_a value of 2-cp is 8.49 at 25°C. Almost all 2-cp compound is in the ionic form when the pH exceeds 8.49, but in a molecular form when pH is less than pK_a . The fraction in the molecular state of 2-cp was larger when the pH was smaller. The 2-cp ions do not vaporize into the cavitation bubbles; they can react only outside of the bubble film with the OH radicals cleaved from water. However, in the molecular state 2-cp can vaporize into cavitation bubbles and react both inside by thermal cleavage and outside with OH radicals as an oxidation reaction (Chen *et al.*, 1994). Hence a smaller pH (especially less than pK_a) was effective for decomposition.

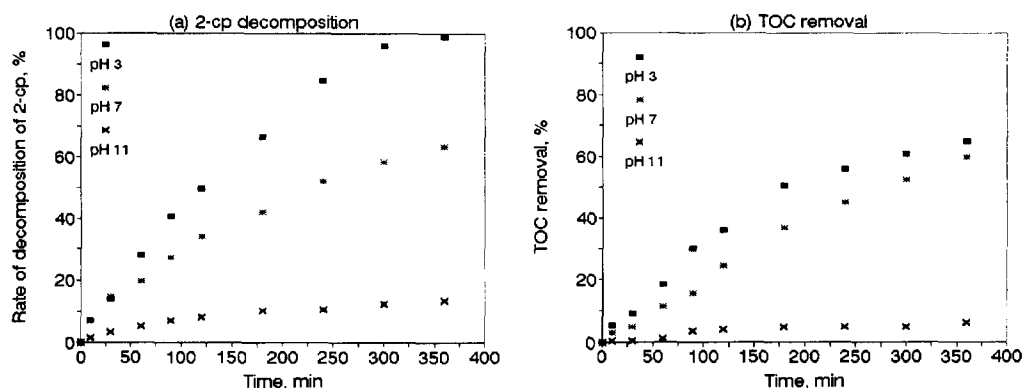


Figure 2. Effects of pH on 2-cp decomposition and TOC removal. (2-cp conc. = 100 mg/l, ionic strength = 0.1 M, and H_2O_2 conc. = 200 mg/l).

We prepared wastewater by adding only 2-cp; therefore the determination of removal of TOC indicated the mineralization of 2-cp. The concentration of TOC vs. reaction duration at varied pH (Fig. 2 (b)) indicates that TOC removal lagged behind degradation of 2-cp relative to Fig. 2 (a). At pH 3, the efficiency of decomposition of 2-cp was 99% but the removal of TOC was only 63%; a similar situation applied at pH 7 and 11. Hence intermediate compounds were produced and 2-cp was not completely mineralized.

Effect of ionic strength

Few researchers have investigated the effect of ionic strength on ultrasound. Like pH, the ionic strength has an influence on the state of organic compounds in aqueous solution. According to results of the effect of pH discussed in the above section, we varied the concentration of ionic strength to be 0.1, 0.01, and 0.001 M and controlled the pH at 3. The effect of ionic strength on the ultrasound/H₂O₂ process is shown in Fig. 3. The results show that varying the ionic strength affected the characteristics. The larger the ionic strength of the solution, the larger was the rate of 2-cp decomposition in the ultrasound/H₂O₂ process (Fig. 3 (a)). The 2-cp decomposition was 99% with ionic strength 0.1M at 360 min of reaction, 81% with 0.01 M and 75% with 0.001 M. The rates of 2-cp decomposition with both 0.01 and 0.001 M ionic strength did not differ significantly. According to the results of TOC removal (Fig. 3. (b)), the rate of mineralization was mostly independent of the ionic strength of the solution. A greater ionic strength significantly enhanced the rate of 2-cp decomposition with ultrasound/H₂O₂ process, while it enhanced the rate of mineralization only slightly. This result revealed that the reaction mechanisms of ultrasound/H₂O₂ process varied with varied ionic strength of the solution varied. Thus, the mechanism was dependent on the ionic strength of the solution.

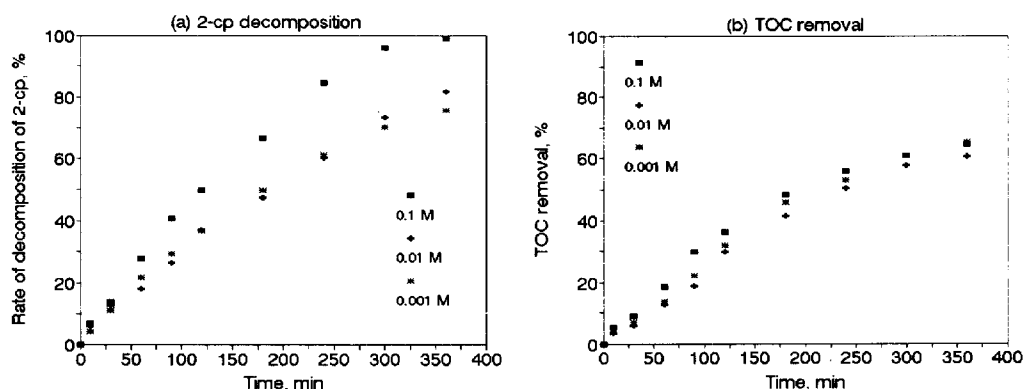


Figure 3. Effects of ionic strength on 2-cp decomposition and TOC removal. (2-cp conc. = 100 mg/l, pH = 3, and H₂O₂ conc. = 200 mg/l).

Table 1. Improvement of ultrasound/H₂O₂ process with varied pH and ionic strength

	Extent of 2-cp decomposition	Improvement - fold***	TOC removal	Improvement - fold***
pH*				
3	0.99	7.62	0.65	10.83
7	0.63	4.85	0.60	10.00
11	0.13	1.00	0.06	1.00
Ion strength**				
0.1 M	0.99	1.30	0.65	1.00
0.01 M	0.82	1.08	0.61	0.94
0.001 M	0.76	1.00	0.65	1.00

*Ion strength was adjusted at 0.1 M.

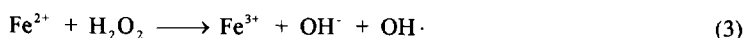
**pH was controlled at 3.

***Improvement over pH 11 or ion strength 0.001 M.

The improvement in the ultrasound/H₂O₂ process is shown in Table 1. When pH was controlled at 3 the rate of 2-cp decomposition was enhanced up to 6.6-fold and TOC removal up to 9.8-fold over pH controlled at 11. As the ionic strength increased from 0.001 to 0.1 M, the rate of 2-cp decomposition was enhanced only 0.3-fold, whereas the TOC removal was not enhanced. Comparing both parameters, pH had a greater influence on either 2-cp decomposition or TOC removal than ionic strength.

Effect of catalyst

Okouchi *et al.* (1992) investigated the effects of coexisting substances on phenol degradation with ultrasound. They discovered that the rates of degradation were increased on addition of Fe^{2+} . We call Fe^{2+} a catalyst. Sonification of water generates radicals: the water molecule is cleaved to OH and H radicals (eq 1). Hydrogen peroxide is one product resulting from recombination of hydroxyl radicals (eq 2). Petrier *et al.* (1992b) showed that hydrogen peroxide is efficiently formed under oxygen at high frequency. The Fenton oxidation reaction (eq 3), requiring addition of both Fe^{2+} and H_2O_2 to aqueous solution, is also efficient to destruct organic pollutants. To distinguish from the Fenton oxidation reaction, we examined the effect of catalyst (FeSO_4) on decomposition of 2-cp with ultrasound only, without addition of H_2O_2 .



The effect of catalyst on 2-cp decomposition with ultrasound irradiation is shown in Figure 4. With FeSO_4 as catalyst, the 2-cp decomposition was 40% at 360 min of reaction; while the blank (with ultrasound only) was 25%. However, the rate of 2-cp decomposition with addition of FeSO_4 was worse than with addition of 200 mg/l H_2O_2 , i.e. the ultrasound/ H_2O_2 process in which the extent of decomposition was 99%. A similar result was found for TOC removal. These results reveal that the production of H_2O_2 by ultrasound irradiation was inadequate; the small concentration of H_2O_2 limited the reaction of equation 3. Thus, ultrasound was somewhat enhanced for decomposition of 2-cp with addition of FeSO_4 . With the combination of ultrasound and the Fenton oxidation reaction, efficient decomposition of 2-cp is obtained. We are currently investigating the combination of ultrasound and Fenton oxidation reaction on decomposition of 2-cp; the results will be reported in the near future.

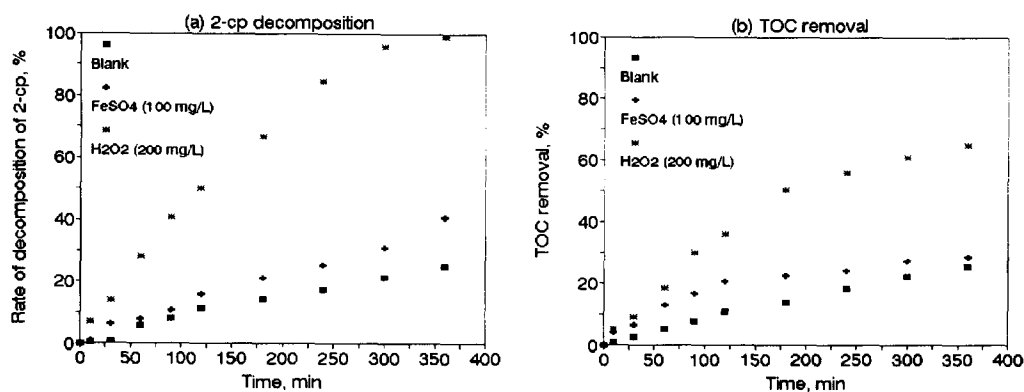


Figure 4. Effects of catalyst on 2-cp decomposition and TOC removal. (2-cp conc. = 100 mg/l, ionic strength = 0.1 M, and pH = 3).

Effect of concentration of 2-cp

The rate of 2-cp decomposition with ultrasound/ H_2O_2 process at varied initial TOC concentrations (100 and 10 mg/l) is shown in Fig. 5. The decomposition of 2-cp depended on the initial concentration of 2-cp. The extent of 2-cp decomposition was almost 100% with initial concentration of 2-cp 10 mg/l at 240 min of reaction, and 85% with 2-cp 100 mg/l. According to a first-order kinetic model, the rate coefficient for the reaction was $1.17 \times 10^{-2} \text{ min}^{-1}$ with 100 mg/l 2-cp, and $1.36 \times 10^{-2} \text{ min}^{-1}$ with 10 mg/l 2-cp. The rate

coefficient of sonification was increased when the initial concentration of 2-cp in aqueous solution was decreased. These results resembled those of Kotronarou *et al.* (1991); they investigated ultrasonic irradiation of p-nitrophenol (PNP) in aqueous solution, and indicated that the first-order rate coefficient increased from $6.17 \times 10^{-5} \text{ s}^{-1}$ at $[\text{PNP}]_i = 1 \text{ mM}$ to $0.37 \times 10^{-2} \text{ s}^{-1}$ at $[\text{PNP}]_i = 10 \text{ }\mu\text{M}$.

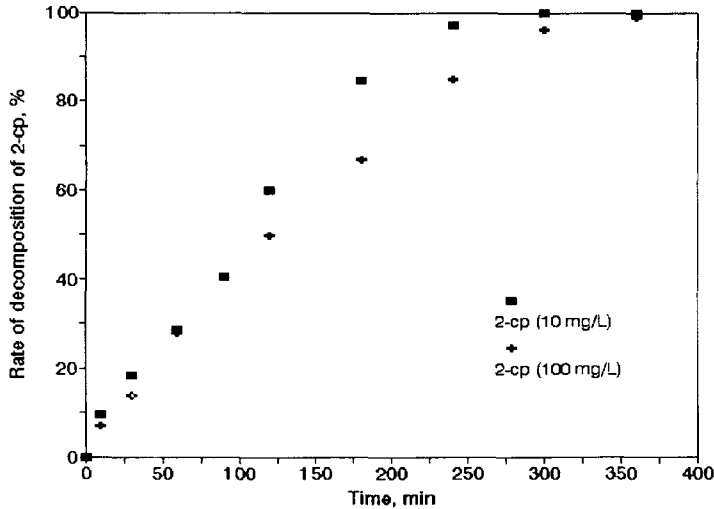


Figure 5. Effect of 2-cp concentration on its decomposition. (ionic strength = 0.1 M, pH = 3, and H_2O_2 conc. = 200 mg/l).

Kinetics

Recent work shows that ultrasonic oxidation is complicated, including thermal cleavage, OH radical oxidation, substitution, elimination, or addition reaction (Okouchi *et al.*, 1992; Kotronarou *et al.*, 1991; Petrier *et al.*, 1992b and Serpone *et al.* 1992). Okouchi *et al.* (1992) investigated degradation of phenol with ultrasonic irradiation, which was regarded as a pseudo-first-order reaction. In analyzing the experimental results, a simplified model of pseudo-first order (eq 4) was applied to simulate kinetic data obtained from experiments on both 2-cp decomposition and TOC removal with ultrasound/ H_2O_2 process.

$$C = C_0 e^{-kt} \quad (4)$$

in which

t = variable reaction duration,

C = the concentration of 2-chlorophenol or TOC at time t

C_0 = the initial concentration of 2-chlorophenol or TOC,

k = reaction rate coefficient.

The resulting values of k for pH, ionic strength, catalyst, and initial concentration of 2-cp are listed in Table 2. The squared correlation coefficient of the determination, R^2 , generally was nearly unity, greater than 0.9 for varied values of each parameter. Thus, the kinetics of 2-cp decomposition and TOC removal are satisfactorily described with this model.

Table 2. Values of k in the proposed pseudo first-order model

	2-cp decomposition		TOC removal	
	k, min ⁻¹	R ²	k, min ⁻¹	R ²
pH				
3	1.17 x 10 ⁻²	0.92	3.04 x 10 ⁻³	0.98
7	2.70 x 10 ⁻³	0.99	2.56 x 10 ⁻³	1.00
11	3.70 x 10 ⁻⁴	0.92	1.75 x 10 ⁻⁴	0.84
Ionic strength				
0.1 M	1.17 x 10 ⁻²	0.92	3.04 x 10 ⁻³	0.98
0.01 M	4.50 x 10 ⁻³	0.98	3.07 x 10 ⁻³	0.99
0.001 M	3.97 x 10 ⁻³	1.00	2.79 x 10 ⁻³	0.99
Catalyst				
Blank	8.02 x 10 ⁻⁴	0.99	8.09 x 10 ⁻⁴	1.00
FeSO ₄ (100 mg/L)	1.33 x 10 ⁻³	0.98	8.66 x 10 ⁻⁴	0.89
H ₂ O ₂ (200 mg/L)	1.17 x 10 ⁻²	0.92	3.04 x 10 ⁻³	0.98
Initial concentration				
100 mg/L	1.17 x 10 ⁻²	0.92		
10 mg/L	1.36 x 10 ⁻²	0.91		

CONCLUSIONS

In this work, we investigated the parameters of pH, ionic strength, catalyst, and initial concentration of 2-cp on decomposition of 2-cp and removal of TOC with the ultrasound/H₂O₂ process. When the pH was controlled at 3 the rate of 2-cp decomposition was enhanced up to 6.6-fold and TOC removal up to 9.8-fold over pH controlled at 11. At pH 3, the efficiency of decomposition of 2-cp was 99% but the removal of TOC was only 63%; a similar situation applied at pH 7 and 11. Hence intermediate compounds were produced and 2-cp was not completely mineralized. With ionic strength 0.1 M, the 2-cp decomposition was found to be 99% after 360 min of reaction, 81% with 0.01 M and 75% with 0.001 M. As the ionic strength increased from 0.001 to 0.1 M, the rate of 2-cp decomposition was enhanced only 0.3-fold, but the TOC removal was not enhanced. This result reveals that the reaction mechanisms of ultrasound/H₂O₂ process depend on the ionic strength of the solution. Comparing the effect of pH and ionic strength, pH had a greater influence on both 2-cp decomposition and TOC removal than ionic strength. With FeSO₄ as catalyst, the 2-cp decomposition was 40% at 360 min of reaction; while the blank (with ultrasound only) was 25%. However, the effect of FeSO₄ on decomposition of 2-cp was insignificant compared with direct addition of H₂O₂. A similar result was found for TOC removal. The reaction at a smaller initial concentration of 2-cp (10 mg/l) was more rapid than at a greater one (100 mg/l). The 2-cp decomposition and TOC removal appeared to follow pseudo-first-order reaction kinetics.

ACKNOWLEDGMENTS

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