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Magnitude of effect of reaction parameters on 2-chlorophenol decomposition by ultrasonic process

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Abstract

In the present work, decomposition of *o*-chlorophenol (2-cp) was carried out using an ultrasonic process. The extent of 2-cp decomposition depends on several parameters such as ultrasound wave energy (ultrasonic amplitude), addition of hydrogen peroxide (H_2O_2), pH value (H^+ concentration), ionic strength, and initial concentration of 2-cp. The experimental results showed that the decomposition of 2-cp was affected by the various reaction conditions. The profiles of 2-cp decomposition fitted well with the first-order kinetic equation. A linear relationship was obtained between the rate constants of 2-cp decomposition and the varying reaction parameters. The magnitude of effect of reaction parameters such as ultrasonic amplitude, H^+ concentration, ionic strength, H_2O_2 and 2-cp initial concentration on 2-cp decomposition were 0.60, 0.48, 0.19, 0.09 and −0.06, respectively.

Keywords: Ultrasonic-wave energy; *o*-Chlorophenol; Hydrogen peroxide; First-order kinetic equation

1. Introduction

It has been reported that the decomposition efficiency of organic compounds using sonication method was affected by the parameters such as pH value, reaction temperature, ionic strength, types of catalysts, and initial concentration of contaminant [1–6]. Therefore, it is interesting to study the magnitude of effect of reaction parameters on the decomposition of organic compounds. Ultrasonic oxidation is often applied for the destruction of refractory compounds because high decomposition efficiencies have been observed [4,5,7–11]. Sonochemical effects are due to the phenomenon of cavitation, which is the nucleation, and behaviour of bubbles in a liquid. Sonication of the water

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molecules leads to the formation of cavitation bubbles [12,13]. High temperature and high pressures cause the water molecules to cleave thermally into the atomic hydrogen and hydroxyl radicals [14–17]. These two radicals recombine to form either water or hydrogen molecules, or they react with oxygen molecules to yield hydroperoxide radicals and hydrogen peroxide. In wastewater treatment, a cavitation bubble may function as a microreactor, which destroys the volatile organic compounds [13].

The rate of the organic compound decomposition by chemical processes is generally fitted well with the first-order kinetic equation [1,2,10,11,18–20], and the rate constants are affected by the varying reaction conditions. Savage and Smith [18] have applied the Arrhenius model to investigate the effects of reaction parameters on the first-order rate constants during the oxidation of acetic acid. The experimental data showed that both concentration of acetic acid and temperature of the reaction play an important role in the oxidation of acetic acid. Huang and Hao [10] have also investigated that the Arrhenius model can be used to calculate the activated energy of the sonochemical reaction. The activated energy calculated for the degradation of 2-cp was 17.5 KJ mol^{-1}. The low activation energy value indicates that the oxidation was controlled by mass-transfer steps. Martin et al. [19] have developed a kinetic equation for the rate of degradation of 4-chlorophenol. This kinetic equation was shown to be a function of concentrations of 4-chlorophenol, ClO_3^-, and dissolved oxygen. Gruebel et al. [20] have proposed that the rate of oxidation of selenite by ultraviolet radiation in the presence of oxygen, titania, and light, was only a function of pH, light intensity, ionic strength, partial pressure of oxygen, and concentration of selenite.

In this study, *o*-chlorophenol (2-cp) was chosen as the target to study the decomposition using ultrasound process in the presence and absence of hydrogen peroxide (H_2O_2). The main objective of this work was to study the effects of reaction parameters on the decomposition of 2-cp and to investigate the factors influencing the reaction parameters.

2. Materials and methods

The 2-cp decomposition was carried out in a batch reactor. The reaction temperature was maintained at 25°C using a temperature controller. The diameter and the height of the reactor were 10.0 cm and 17.7 cm respectively and the reactor was covered by a water jacket. The schematic diagram of the apparatus has been described in our earlier report [4].

2.1. Reagents

All reagents used in this work were of analytical grade and used without further purification. A stock solution of 10 000 mg l^{-1} concentration of 2-cp was prepared using deionized and distilled water generated from a Millipore purification system, and was stored in a brown Pyrex bottle.

2.2. Experimental conditions

Effects of five reaction parameters such as ultrasonic amplitude, H_2O_2, pH, ionic strength and initial concentration of 2-cp on the decomposition of 2-cp were studied. A

sonicator (Microson XL-2020, Heat System, USA, 0–500 W), operated at 20 kHz, was used in this study. The double amplitude at the titanium tip (Part. No. 419) of the standard horn (Part. No. 200, 1/2 in. diameter) was adjusted between 0 and 120 μm, with respect to the power output of 0 to 126.5 W/cm^2 of tip. The concentrations of H_2O_2 were varied from 0 to 500 mg l^{-1}. Initial pH values were adjusted between 3 to 11 using H_2SO_4 and NaOH. Ionic strengths of the 2-cp solution were maintained in the range of 0.001 N to 0.1 N using $NaClO_4$. Initial concentrations of 2-cp solution were prepared in the range of 10 mg l^{-1} to 100 mg l^{-1}.

2.3. Analytic methods

The analysis of the samples was carried out according to the procedures given in the 18th edition of Standard Methods for Examination of Water and Wastewater [21]. The concentration of 2-cp was analyzed by a gas chromatograph equipped with a mass spectrometry detector (HP 1800A GCD). The analysis of 2-cp was performed with a 30 m × 0.25 mm i.d. DB-5 capillary column (J&W Scientific, Folsom, CA, USA). Pure helium gas with a flow rate of 1 ml min^{-1} was used as the carrier gas. The oven temperature program was as follows: increased from 50°C (holding time 3 min) to 250°C (holding time 3 min) at a rate of 10°C min^{-1}. The injector and detector temperatures were kept at 250°C and 280°C, respectively. After chromatographic separation, the samples were identified by mass spectrometry. The mass spectrometer was operated at 70 eV and scanned from 30 to 425 amu at one scan per second. Mineralization of 2-cp was represented by the removal of dissolved organic carbon (DOC) from the solution. The DOC concentrations were measured using a TOC analyzer (ASTRO 2001, USA). Each sample taken from the 2-cp solution after sonication was analyzed three times. The method detection limit (MDL) for the analysis of 2-cp was 0.22 mg l^{-1}. The recovery of 2-cp was 98 ± 4%. The MDL for the analysis of DOC was 0.14 mg l^{-1}.

3. Derivation of equation

Savage et al. [18] have evaluated an equation to describe the effect of reaction parameters on the decomposition of acetic acid and is shown by Eq. (1).

$$\text{Rate}(k) = A \times \exp(-E_a/RT) \times [\text{HOAc}]^a \times [O_2]^b \times [H_2O]^c \quad (1)$$

Constants a, b and c denote the magnitudes of the effect for reaction parameters during the decomposition of acetic acid, and A and E_a are the Arrhenius pre-exponential factor and activation energy, respectively.

In our study, a new equation (Eq. (2)) was derived from Eq. (1) to describe the effect of five reaction parameters on the decomposition of 2-cp. Since the reaction temperature was kept constant at 25°C, effect of temperature was ignored.

$$\text{Rate}(k) = A' \times [\text{ultrasonic amplitude}]^a \times [H_2O_2]^b \times [\text{pH}]^c \times [\text{ionic strength}]^d \times [2 - \text{cp initial conc.}]^e \quad (2)$$

Constants a, b, c, d, and e are the magnitudes of the effect of reaction parameters on the decomposition of 2-cp, and A' is a constant.

The magnitude of effect of ultrasonic amplitude was calculated by keeping the other four parameters (H_2O_2, pH, ionic strength and initial 2-cp concentration) constant. It has been found out that the change in the ultrasonic amplitude affects the decomposition of 2-cp, and the effects of other parameters were negligible. In a similar manner the magnitude of effect of other four parameters was calculated. The letter P denoted the parameters that were kept constant. Therefore, to calculate the magnitude of the effect of ultrasonic amplitude, Eq. (2) can be rewritten as

$$k = A' \times P \times [\text{amplitude}]^a \tag{3}$$

Taking natural logarithms on both sides, Eq. (3) becomes

$$\ln(k) = a \times \ln([\text{amplitude}]) + \ln(P) + \ln(A') \tag{4}$$

The magnitude of the effect for ultrasonic amplitude (a) was obtained by regression of rate constant and ultrasonic amplitude. The magnitude of the effect of other parameters was calculated in the same manner.

4. Results and discussion

In our earlier reports [4,5], it has been shown that the ultrasonic process has the potential to generate a large amount of heat or energy so that the target compound could be decomposed in the cavitation bubbles. Therefore, in this study, the energy was considered as the fundamental factor to represent the change in the concentration of 2-cp during the degradation.

4.1. Effects of ultrasonic energy input

Fig. 1 shows the effect of ultrasonic amplitudes (0 to 120 μm) on the decomposition of 2-cp by ultrasonic process. The experiment was carried out under the initial pH value of 7 and 2-cp concentration of 100 mg l^{-1}. The total treatment period for the above reaction was 90 min. In Fig. 1, unit of the horizontal axis was the product of output ultrasonic power and reaction time (kW h). When ultrasonic amplitude was kept at 120 μm, an output ultrasonic power of 165 W (or 126.5 W/cm^2 of tip) was produced from the sonicator. When the reaction was carried out for 90 min, it was observed that an ultrasonic energy of 0.24 kW h was introduced into the batch reactor. To investigate the influence of vaporization on 2-cp, a control test was also carried out (Fig. 1). The control test was conducted under the initial pH value of 7, reaction temperature of 25°C and 2-cp concentration of 100 mg l^{-1} without introducing any ultrasonic energy. The results revealed that the amount of 2-cp vaporized during the reaction period of 90 min is less than 2%. Therefore, it was understood that the concentration of 2-cp could be considered as a constant in the control test. When the ultrasonic energy was introduced into the reactor, it was obvious that there was a slight decrease in the 2-cp concentration with the increase of input energy (or reaction time). The decomposition of 2-cp was in

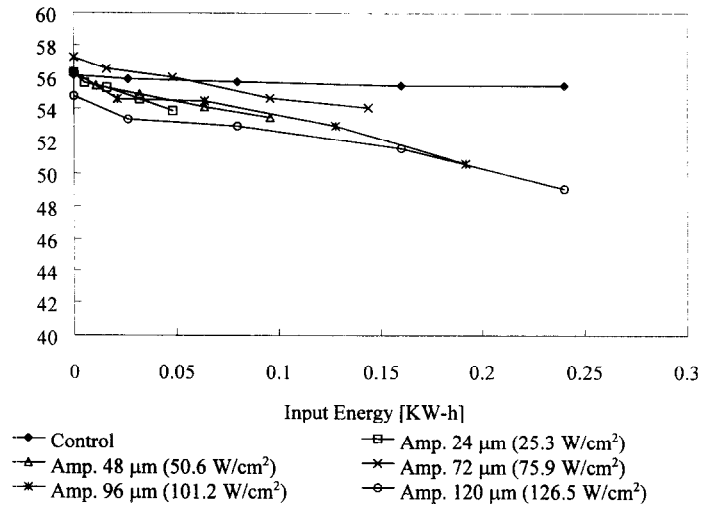

Fig. 1. Profiles of residual concentration of 2-cp for various amplitudes (initial 2-cp concentration of 100 mg l^{-1}, pH 7, and temperature 25°C).

the range of 4% to 11% when the ultrasonic amplitude was increased from 0 to 120 μm. Serpone et al. [3] have also studied the effect of ultrasonic energy on the decomposition of phenol. Their report reveals that the higher the ultrasonic power, the greater the decomposition of phenol.

On the basis of the above results, it was clear that the ultrasonic energy affects the decomposition of 2-cp and the magnitude of the effect of ultrasonic amplitude on the decomposition was calculated using Eq. (4). By the simple linear regression statistical analysis, the decomposition of 2-cp fitted well with a first-order kinetic equation. Table 1 presents the rate constants of 2-cp decomposition for various ultrasonic amplitudes, which is plotted in Fig. 2. The difference between the six experiments shown in Table 1 is due to the ultrasonic amplitude only (or the input energy). Based on the above fact, the constant P could be taken as 1 because 2-cp was decomposed only by the ultrasonic wave. Fig. 2 reveals that the magnitude of the effect of ultrasonic amplitude is 0.60 and constant A' is 5.95×10^{-5} min^{-1}. Huang and Hao [10] have studied the effect of energy intensity on the degradation of chlorophenols. When the output energy increased

Table 1
Rate constants of 2-cp decomposition for various ultrasonic amplitudes using ultrasonic process (initial 2-cp concentration of 100 mg l^{-1}, pH 7, and temperature 25°C)

	Ultrasonic amplitude (μm)					
	0	24	48	72	96	120
k ($\times 10^{-4}$ min^{-1})	1.3	4.5	5.4	6.2	10.5	11.2
R^2	0.87	0.98	0.97	0.98	0.95	0.96

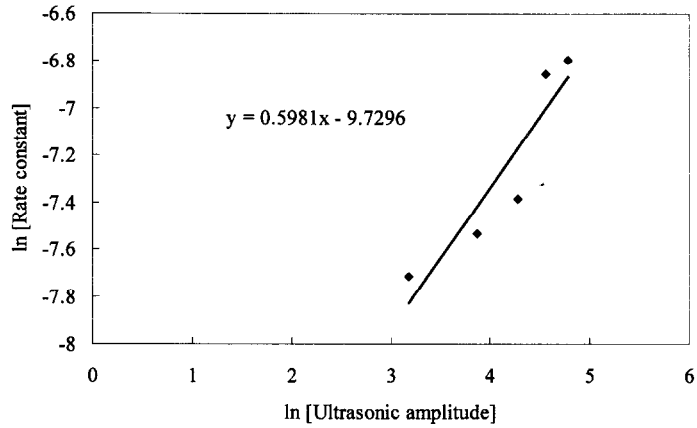

Fig. 2. Relationship between ultrasonic amplitude and decomposition rate of 2-cp (initial 2-cp concentration of 100 mg l^{-1}, pH 7, and temperature 25°C).

from 8 to 24 W/ml, the amount of mono-chlorophenol in the solution decreased exponentially with sonication time.

4.2. *Effects of H_2O_2 addition*

Several authors have proved that the hydroxyl radicals react with a wide range of organic compounds via oxidation mechanism [3–5,13]. If oxidants are added to the solution, it is expected that larger amounts of the hydroxyl radicals will be produced, and hence larger amounts of 2-cp will be removed. Fig. 3 illustrates the change in the carbon content (DOC) of 2-cp for different concentrations of H_2O_2. In this experiment, the ultrasonic amplitude was kept at 120 μm and the initial pH value was adjusted to 7.

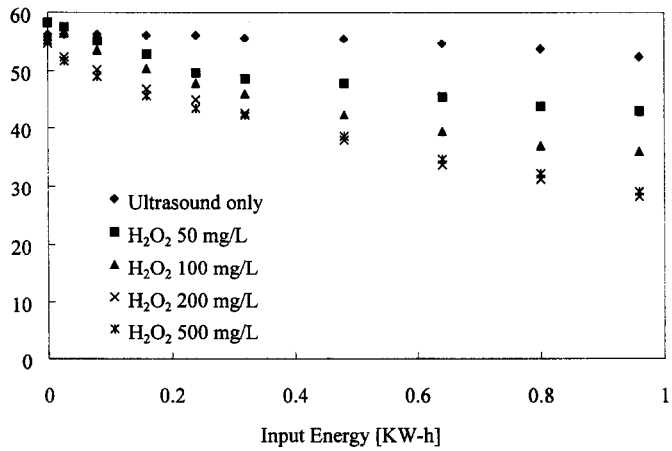

Fig. 3. Profiles of residual concentration of 2-cp for various concentrations of H_2O_2 (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, pH 7, and temperature 25°C).

In the control test, without H_2O_2 addition, it was observed that 7% of the 2-cp was decomposed for the reaction period of 6 h (0.99 kW h input energy). When the addition of the oxidant (H_2O_2) was increased, the extent of 2-cp decomposition also increased. Hence, it is proposed that increased H_2O_2 addition has the potential to raise the decomposition efficiency of 2-cp due to the formation of a large number of hydroxyl radicals. In contrast, Fig. 3 shows no significant difference was observed in 2-cp decomposition with H_2O_2 concentration of 200 mg l^{-1} (49%) and 500 mg l^{-1} (46%). Earlier studies have reported that after reaching a concentration limit, further increase in the concentration of H_2O_2 will not produce any effect on the decomposition of organic compounds [22–24]. In fact, the excess addition of H_2O_2 would cause the formation of hydroperoxide radicals that can act as scavengers of the hydroxyl radicals. Wu et al. [13] have investigated the effect of various concentrations of H_2O_2 on the decomposition of chlorinated compounds. The results suggested that there is no use in exceeding the concentration of H_2O_2 after a certain amount has been added into the solution. Gulyas et al. [22] have also proposed that ozone would react with the hydroxide ions and form some superoxide anion radicals and hydroperoxide radicals. Thus, it is important to obtain the optimal H_2O_2 concentration and pH value since a good decomposition efficiency of organic compounds is achieved [6,25].

Comparison of efficiency of 2-cp decomposition between a coupled ultrasound/H_2O_2 process and ultrasound process is shown in Fig. 3. Earlier reports also observed a similar result when a coupled process was carried out to decompose the organic compounds [26,27]. The rate constants of 2-cp decomposition for various concentrations of H_2O_2 are presented in Table 2. Fig. 3 shows that the rate constant increased when the concentration of H_2O_2 was increased from 0 to 200 mg l^{-1}. The rate constant for 500 mg l^{-1} concentration of H_2O_2 was less than that of 200 mg l^{-1}. The magnitude of the effect of H_2O_2 addition was calculated by procedures similar to those used for calculating the magnitude of effect of ultrasonic amplitude. Data are shown in Table 2 and are plotted in Fig. 4. It was found that the magnitude of the effect for H_2O_2 addition was 0.09.

4.3. Effects of pH

The pH is an important factor which affects the decomposition of target compounds using advanced oxidation processes, especially with ultrasonic process [1,3–6,28]. The pH affects the state of the organic compounds in aqueous solution. The acid–base dissociation constant (pK_a) of 2-cp at 25°C is 8.49. When the pH value is greater than

Table 2
Rate constants of 2-cp decomposition for various concentrations of H_2O_2 using ultrasound/H_2O_2 process (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, pH 7, and temperature 25°C)

	H_2O_2 (mg l^{-1})				
	0	10	100	200	500
k ($\times 10^{-3}$ min^{-1})	1.2	1.2	1.3	1.8	1.6
R^2	0.99	1.00	0.97	1.00	0.99

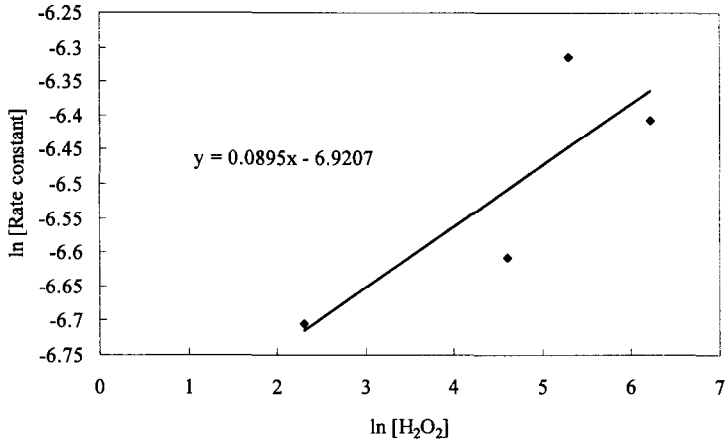

Fig. 4. Relationship between H_2O_2 concentration and decomposition rate of 2-cp (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, pH 7, and temperature 25°C).

the pK_a, almost all of the 2-cp is ionized in the solution. When the pH value is less than the pK_a, almost all of the 2-cp is in the molecular form. The percentage of the molecular or ionic form can be calculated using the following equations (Eqs. (5) and (6)). In this study, initial pH values were adjusted to 3, 5, 7, 9, and 11, respectively. Almost all 2-cp was in the ionic form when the pH value was 11 and in the molecular form when the pH value was 3 or 5. At the pH value of 7, 97% of 2-cp existed in molecular form and 3% in ionic form. At the initial pH value of 9, the molecular form and the ionic form of 2-cp were 24% and 76%, respectively.

$$\text{Molecular 2-cp} \xrightarrow{K_a} \text{Ionic 2-cp} + H^+ \tag{5}$$

$$\frac{\text{Molecular 2-cp}}{\text{Ionic 2-cp}} = \frac{[H^+]}{K_a} \tag{6}$$

Several researchers have reported that the state of the compound affects the reaction mechanism. The ionic form of the compound does not vaporize into the cavitation bubbles; it reacts at the outside of the bubble with the hydroxyl radicals cleaved from water molecules [6,13]. Therefore, under 120 μm ultrasonic amplitude and 200 mg l^{-1} H_2O_2 concentration, at the pH value of 9 and 11 only 22% and 15%, respectively, of the 2-cp was decomposed for the reaction period of 6 h (shown in Fig. 5). On the other hand at lower pH, the molecular form of 2-cp decomposes thermally in the cavitation area and also by the hydroxyl radicals or other free radicals in the bulk–liquid phase. Thus, a better decomposition efficiency of 2-cp can be obtained at lower pH values (3, 5, or 7). For the reaction period of 6 h, the decomposition ratios of 2-cp at pH 3, pH 5, and pH 7 were 99%, 87% and 63%, respectively (Fig. 5). Serpone et al. [3] have used the ultrasound process to decompose phenol at pH 3, 5.7 and 12. The authors have investigated that phenol could be decomposed more readily when the pH value was 3, and the decomposition of phenol was very slow at pH 12.

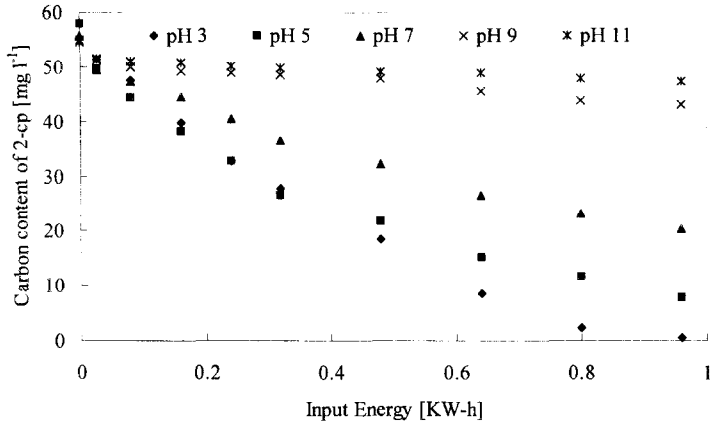

Fig. 5. Profiles of residual concentration of 2-cp for various pH values (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, ionic strength 0.1 N, and temperature 25°C).

The rate constants of 2-cp decomposition for various pH values are presented in Table 3. It is observed that there is a significant increase in the rate constant with decreasing pH values. The rate constant of 2-cp decomposition at pH 3 was almost 40 times greater than at pH 11. In addition, it was observed that the rate constants at pH 9 and pH 11 were similar. This result resembles the report of Kotronarou et al. [1]. Ku et al. [6] also used the ultrasound process to decompose 2-cp. The authors found that in the absence of H_2O_2, the decomposition rate constant decreased with the increase of pH value. While analyzing the regression of the 2-cp decomposition rate at a constant pH value, it is appropriate to estimate the concentration of hydrogen ion as independent. Fig. 6 shows that the magnitude of the effect of H^+ concentration is 0.48. When the concentration of hydrogen ion is expressed in terms of pH, this magnitude becomes −0.48. The negative number shows that as the pH level of the solution increases a negative effect is observed.

4.4. Effects of ionic strength

Studies have also been carried out on the effect of ionic strength on the decomposition of organic compounds using ultrasonic process [5,8]. Like pH, ionic strength also

Table 3
Rate constants of 2-cp decomposition for various pH values using ultrasound/H_2O_2 process (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, ionic strength 0.1 N, and temperature 25°C)

	pH				
	3	5	7	9	11
k ($\times 10^{-3}$ min^{-1})	11.5	5.3	2.4	0.5	0.3
R^2	0.92	0.99	0.99	0.95	0.91

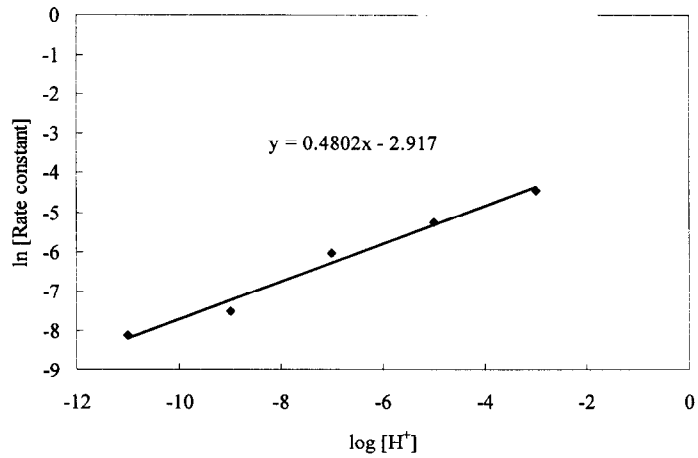

Fig. 6. Relationship between pH value and decomposition rate of 2-cp (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, ionic strength 0.1 N, and temperature 25°C).

affects the state of the target compound in aqueous solution. James et al. [29] have proposed that the humic acid molecule could either be a rigid or flexible sphere, rod-like, or a flat plate depending on the ionic strength. Greater ionic strength induces the humic acid molecule to be in a spherical form so that other compounds or oxidants could react with the humic acid more easily due to its larger surface area [29,30]. Therefore, this explanation is used in our study. The effect of various ionic strengths on the decomposition of 2-cp using the ultrasound/H_2O_2 process is shown in Fig. 7.

The pH value of the reaction was taken as 3 because the 2-cp decomposition efficiency was good at this value which is shown in Fig. 5. As explained above, the ionic strength variation affects the state of 2-cp and hence the extent of 2-cp decomposi-

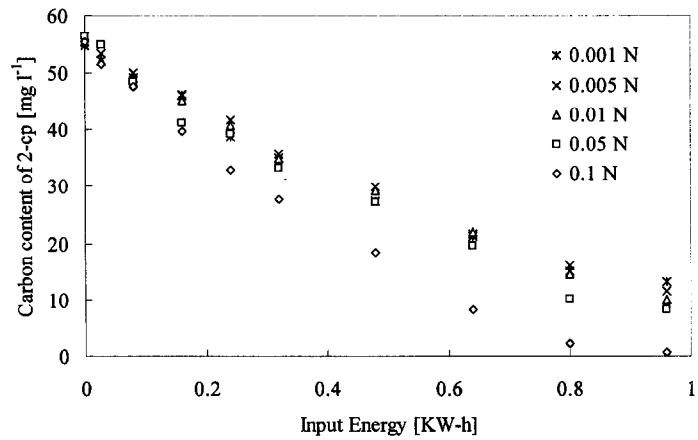

Fig. 7. Profiles of residual concentrations of 2-cp for various ionic strengths (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, and temperature 25°C).

Table 4
Rate constants of 2-cp decomposition for various ionic strengths using ultrasound/H_2O_2 process (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, and temperature 25°C)

	Ionic strength (N)				
	0.001	0.005	0.01	0.05	0.1
k ($\times 10^{-3}$ min^{-1})	4.1	4.3	4.5	5.3	11.5
R^2	0.99	0.99	0.98	0.98	0.92

tion. Fig. 7 shows that the decomposition of 2-cp increased from 76% to 85% when the ionic strength increased from 0.001 N to 0.05 N. However, more than 99% of 2-cp was decomposed at the ionic strength of 0.1 N for the reaction period of 6 h. This clearly shows that the ionic strength affects the extent of 2-cp decomposition. Several studies [4,29,30] also reported similar results.

The rate constants of 2-cp decomposition for various ionic strengths are given in Table 4. Fig. 7 reveals that the rate constant insignificantly increased when the ionic strength was increased from 0.001 N to 0.05 N. The rate constant of 2-cp decomposition at the ionic strength of 0.1 N was about 2.8 times of 0.001 N. Fig. 8 shows that the magnitude of effect of ionic strength is 0.19. Such a value shows that the influence of ionic strength is lesser than ultrasonic amplitude and pH value. A low correlation coefficient (R^2) value 0.63 was observed in Fig. 8, due to the dramatic increase of rate constant at the ionic strength of 0.1 N. If only the relationship between the rate constant of 2-cp decomposition and ionic strength of 0.001 N to 0.05 N had been taken into account then a good R^2 value of 0.97 would obtained.

4.5. Effects of 2-cp initial concentration

The initial concentration of the target compound has been found to affect the decomposition efficiency and the reaction rate [1,13]. Fig. 9 illustrates the profiles of

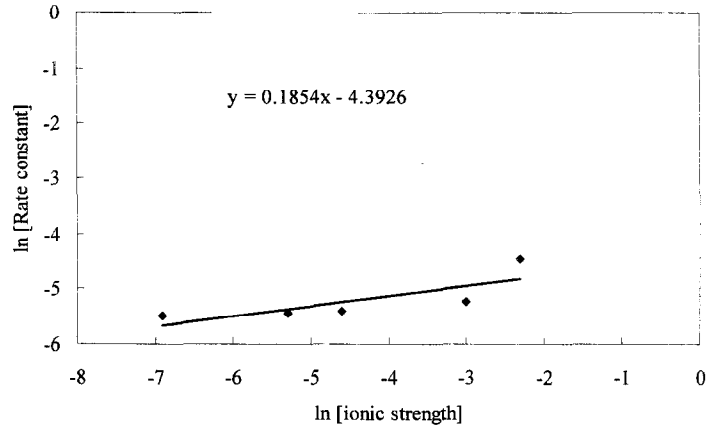

Fig. 8. Relationship between ionic strength and decomposition rate of 2-cp (initial 2-cp concentration of 100 mg l^{-1}, ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, and temperature 25°C).

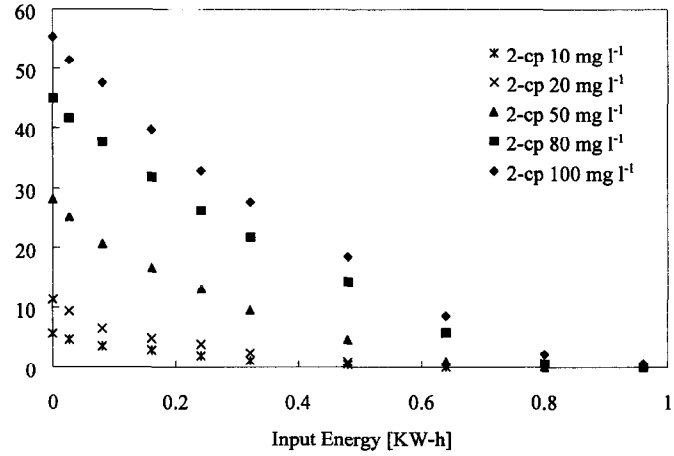

Fig. 9. Profiles of residual concentration of 2-cp for various initial concentrations of 2-cp (ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, ionic strength 0.1 N, and temperature 25°C).

2-cp decomposition for different 2-cp initial concentrations using the ultrasound/H_2O_2 process. The experiment was carried out at ultrasonic amplitude of 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH value of 3 and ionic strength of 0.1 N. It is apparent that more than 99% of 2-cp was decomposed when the initial concentrations of 2-cp were in the range of 10 to 100 mg l^{-1} with the input energy 0.99 kW h for the reaction period of 6 h. When the input energy was 0.5 kW h, the decomposition of 2-cp was greater than 99% for the 2-cp concentration of 10 mg l^{-1} but less than 65% for the 2-cp concentration of 100 mg l^{-1}. Kotronarou et al. [1] used the ultrasound process to decompose *p*-nitrophenol (PNP) with the ultrasonic frequency of 20 kHz and temperature of 30°C. The authors have found out that PNP decayed in the presence of ultrasound and the rate of PNP decay was found to be dependent on the initial concentration of PNP. Wu et al. [13] have also applied the ultrasound process to remove carbon tetrachloride by introducing the ultrasonic frequency of 20 kHz. It was found that carbon tetrachloride decomposition takes place more readily when the initial concentration of carbon tetrachloride is low.

The rate constants of 2-cp decomposition for various initial concentrations of 2-cp are presented in Table 5. The rate constant of 2-cp decomposition was not markedly increased with decreasing initial concentrations of 2-cp. Further, it was observed that the

Table 5
Rate constants of 2-cp decomposition for various initial concentrations of 2-cp using ultrasound/H_2O_2 process (ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, ionic strength 0.1 N, and temperature 25°C)

	Initial concentration of 2-cp (mg l^{-1})				
	10	20	50	80	100
k ($\times 10^{-3}$ min^{-1})	13.6	13.4	12.7	11.9	11.5
R^2	0.96	0.99	0.95	0.97	0.92

rate constant of 2-cp decomposition for the 2-cp concentration of 10 mg l^{-1} was 1.2 times the 100 mg l^{-1} concentration. Serpone et al. [11] have observed that the ultrasound process was effective to oxidize the 2-cp at the pH level of 5.7 and 2-cp initial concentration of 10 mg l^{-1}. The rate constant for the disappearance of 2-cp was $4.8 \pm 0.4 \times 10^{-3}$ min^{-1}. In this study, the rate constant for the decomposition of 2-cp was 13.6×10^{-3} min^{-1} for the pH value of 3 and 2-cp initial concentration of 10 mg l^{-1}. However, when the pH value was 5 and initial 2-cp concentration was 100 mg l^{-1}, the rate constant for 2-cp decomposition was 5.3×10^{-3} min^{-1} (shown in Table 3). This result is in agreement with the results of Serpone et al. [11].

The data in Table 5 were plotted in Fig. 10, and a linear plot represented a good fit (R^2 0.91) for the rate constants of 2-cp decomposition and its initial concentration. The magnitude of the effect of initial concentration of 2-cp was −0.06. The negative value indicates that the rate constant of 2-cp decomposition decreased with increasing initial concentrations of 2-cp. On the basis of the above results Eq. (2) can be expressed as

$$k = 5.95 \times 10^{-5}[\text{amplitude}]^{0.60} \times [H_2O_2]^{0.09} \times [\text{pH}]^{(-0.48)} \times [\text{ionic strength}]^{0.19} \times [\text{2-cp initial conc.}]^{(-0.06)} \quad (7)$$

Many researchers [11,19,20] have proposed that a greater value of magnitude indicated a greater effect on the decomposition. From Eq. (7), it is observed that the ultrasonic amplitude is the most important parameter that affects the decomposition of 2-cp by the ultrasound/H_2O_2 process. The ultrasonic amplitude affects the output energy of the sonicator. It is understood that a greater number of hydroxyl radicals and cavitation bubbles were generated when the higher ultrasonic amplitude was introduced [3–5,13]. Earlier reports have revealed that pH value is also an important parameter, which influences the removal of the target compounds [1,3–6,9]. In this work, the experimental data also showed that the pH value plays an important role on the decomposition of 2-cp. Excluding ultrasonic amplitude, the magnitude of effect of pH

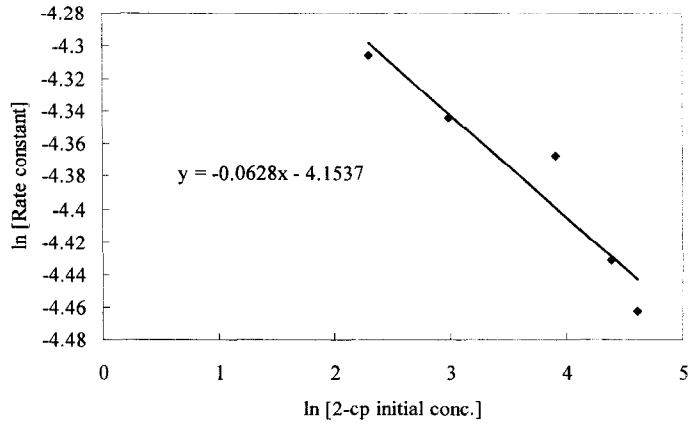

Fig. 10. Relationship between initial concentration of 2-cp and decomposition rate of 2-cp (ultrasonic amplitude 120 μm, H_2O_2 concentration of 200 mg l^{-1}, pH 3, ionic strength 0.1 N, and temperature 25°C).

value was 2.5 to 8 times that of other reaction parameters. The proposed model can be used as a tool to calculate the effect of different reaction parameters on the decomposition of 2-cp. Furthermore, this model helps to adjust the reaction condition to get greater decomposition efficiency of the target compound.

5. Conclusions

Decomposition of *o*-chlorophenol (2-cp) using ultrasonic energy was studied in this work. The relationship between the reaction parameters and the ultrasonic process on the decomposition of 2-cp were explored. It was found that 2-cp decomposition fits well with a first-order kinetic equation. In addition, the magnitude of the effect of reaction parameters was investigated. The magnitude of the effect of each parameter is given below:

Parameter	Ultrasonic amplitude	H^+ concentration	Ionic strength	H_2O_2	2-cp initial concentration
Influence factor	0.60	0.48	0.19	0.09	−0.06

It is obvious from the above data that both ultrasonic amplitude and the pH value (H^+ concentration) significantly affect the decomposition of 2-cp. It has also been found that the first-order equation can be used for determining the rate constants of 2-cp decomposition. In addition, the magnitude of the effect of each reaction parameter is useful to help us to find a suitable condition for the decomposition of target compound.

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