Journal of Zhejiang University SCIENCE
ISSN 1009-3095
http://www.zju.edu.cn/jzus
E-mail: jzus@zju.edu.cn

Study on US/O_3 mechanism in *p*-chlorophenol decomposition

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Received Jan. 21, 2005; revision accepted Feb. 21, 2005

Abstract: Study on the effects of sonolysis, ozonolysis and US/O_3 system on the decomposition of *p*-chlorophenol in aqueous solutions indicated that in the cases of US/O_3 system, individual ozonolysis and sonolysis, the decomposition rate of *p*-chlorophenol reached 78.78%, 56.20%, 2.79% after a 16-min reaction while its CODcr (chemical oxygen demand) removal rate was 97.02%, 62.17%, 3.67% after a 120-min reaction. The decomposition reaction of *p*-chlorophenol follows pseudo-first-order kinetics. The enhancement factors of *p*-chlorophenol and its COD_{cr} under US/O_3 system reached 63% and 237% respectively. The main intermediates during the decomposition include catechol, hydroquinone, *p*-benzoquinone, phenol, fumaric acid, maleic acid, oxalic acid and formic acid. The decomposition mechanism of *p*-chlorophenol was also discussed.

Key words: US/O_3, *p*-chlorophenol, Synergetic effect, Decomposition mechanism
doi:10.1631/jzus.2005.B0553 **Document code:** A **CLC number:** TQ150.9; X783

INTRODUCTION

Due to its high oxidability, high reaction rate and absence of any secondary pollution, ozonolysis technique has increasingly been used in the sanitization of drinking water, treatment of industrial wastewater and especially in the treatment of pollutants which are difficult to get rid of in biological oxidation processes. Its low dispersion rate and high cost, however, impede it from wider applications. In recent years, in order to improve the utilization rate of ozone, several groups have made some advances in combing ozonolysis technique with other methods, including advanced oxidization processes (AOPs) such as UV/O_3, H_2O_2/O_3, H_2O_2/UV/O_3, US/O_3 (Staehelin and Hoigné, 1982; Adams *et al*., 1994; Peyton and Glaze, 1988; Mokrini *et al*., 1997; Guittoneau *et al*., 1990; Sierka and Amy, 1985), among which US/O_3 has been proved to be an effective one. According Destaillats *et al*.(2000), the removal rate of TOC (total organic carbon) in azobenzene solution, under 500 kHz, could be raised from 20% to 80% in the presence of O_3. According to Dahi (1976), sonolysis alone could not get rid of rhodamine B, while the combination of sonolysis and ozonolysis could raise its degradation rate to grade 0.5, 55% higher than that using ozonolysis alone. And according to Olson and Baraier (1994), the removal rate of fulvic acid in wastewater using US/O_3 was much higher than that using ozonolysis alone. Under the condition of 55 W, 20 kHz, sonolysis and continuous ozone instillation, after 10 min of reaction, 91% of TOC in 10 mg/L fulvic acid solution was removed in which 87% was completely mineralized. In comparison, with ozonolysis alone, TOC removal rate only reached 40% and only 28% was completely mineralized. And according to Kang and Hoffmann (1998), under the conditions of 205 kHz, 200 W/L, as the initial concentration of MTBE (methyl tert-butyl ether) dropped from 1.0 mmol/L to 0.01 mmol/L, its decomposition rate increased from 4.1×10^{-4} s^{-1} to 8.5×10^{-4} s^{-1}, 1.5~3.9 times more than the original rate. However, the degradation of contaminants by US/O_3 technique had mostly been carried out in laboratory settings so far, and its practical applications are far from being realized.

Because of its wide existence in wastewater from dyeing, paper-making, etc. and difficult decomposition by biological means, *p*-chlorophenol is one of

129 key pollutants which are under strict control by the American Environment Protection Bureau. In this paper, *p*-chlorophenol is used as the model pollutant, and study of the efficiency of different techniques such as sonolysis, ozonolysis and US/O_3 on its decomposition showed that there was a synergetic effect of US/O_3 system on the decomposition of *p*-chlorophenol. The *p*-chlorophenol decomposition mechanism under US/O_3 system was discussed.

EXPERIMENTAL METHODS

Chemicals

Potassium indigotrisulfonate (USA), *p*-chlorophenol (>99.0%, CP), hydroquinone (>98.0%, AR), *p*-benzoquinone (>98.5%, CP), catechol (>98.0%, CP), phenol (>99.9%, AR), fumaric acid (>99.0%, CP), maleic acid (>99%−101%, CP), oxalic acid (>99.5%, AR), $Na_2S_2O_3$, NaOH, H_3PO_4 and other reagents were analytical grade. These reagents except potassium indigotrisulfonate were purchased from Shanghai Chemical Reagents Company.

Sonochemical experiments

Experiments were carried out in a made by us 200 ml glass jacket reactor in the bottom of which was a glass gas diffuser. The top of the reactor had five openings providing connections to a thermometer, a pipette for sampling, an ultrasonic probe head, and a tube each for feeding and venting the gas. A horn type ultrasonic transducer (made by Acoustics Institute of the Chinese Academy of Sciences) at 22 kHz with an active acoustic vibration diameter of 20 mm generated ultrasonic irradiations. The ultrasonic probe head was positioned about 2−3 cm below the surface of the solution with temperature regulated through a jacket circulation of fixed-temperature water in the outside cistern, while ozone was produced through a 3A ozone producer (Product of Hangzhou Rongxin Electronic Equipment Co. Ltd.).

First, a certain amount of *p*-chlorophenol solution was injected into the reactor and the ozone producer was opened. Then, in order to stabilize the gaseous O_3 concentration, we maintained the gross amount of O_3 but diverted some outside and instilled the rest into the reaction solution through the gas diffuser. In the meantime, the ultrasonic transducer was turned on. In experiments on ozonolysis alone, this step was unnecessary and skipped. Samples were taken at regular intervals. Every time we took 2.0-ml samples except for measuring COD_{cr} alone, which was increased to 5 ml. The pH was adjusted with phosphoric acid and sodium hydroxide and the ionic strength was around 0.1 mol/L. In individual sonolysis experiments, O_2 was instilled till saturation in the solution, then ultrasonic irradiation was introduced. Fixed amounts of $Na_2S_2O_3$ were added into the samples to remove the remnant O_3. Unless discussed otherwise, the experiments were typically carried out under the following conditions: initial mass concentration of *p*-chlorophenol solution: 46.22 mg/L (COD_{cr} being around 74 mg/L), solution temperature: 25 °C, pH value of the solution: 3, ionic strength: 0.1 mol/L, O_3/O_2 flow rate: 40 ml/min, gaseous ozone mass concentration: 20.11 mg/L and ultrasonic power generation of transducer: 125 W.

To analyze the possible stripping of *p*-chlorophenol in the oxidation, a separate experiment of only oxygen without ultrasound was carried out. Measurements made before and after the experiment did not show significant change in the concentration of *p*-chlorophenol.

Analysis

High-performance liquid chromatograph (HPLC, Shimadzu) was employed to analyze *p*-chlorophenol and its intermediates. Twenty-five ml aliquots of samples were injected into the HPLC. A mobile phase of phosphate buffer solution (pH=2)/methanol at 70/30 (v/v) was used for determining *p*-chlorophenol and its intermediates. The separation was performed using an ODS−18 reversed phase column at a flow rate of 1.0 ml/min and a column temperature of 25 °C. A UV detector with the wavelength set at 280 nm was used. Organic acid and chloride produced was determined by ion chromatograph (Metrohm 792 Basic IC). The ozone gas phase concentration was determined by standard methods (EPA, 1989). The concentration of ozone in the solution was determined by the indigo method (Bader and Hoigné, 1981). Analysis of the COD_{cr} was carried out using a titrimetric method (Xi *et al.*, 1989).

The removal rate enhancement could be expressed by the promoting factor *f* defined as:

$$f = \left[k_{\text{US/O}_3} / \left(k_{\text{US/O}_2} + k_{\text{O}_3} \right) - 1 \right] \times 100\%$$

where, $k_{\text{US/O}_3}$, $k_{\text{US/O}_2}$, and k_{O_3} represent the reaction rate constant in the sonolysis-ozonolysis process, sonolysis process and ozonolysis process, respectively.

RESULTS AND DISCUSSIONS

Comparison of the decomposition effects under different systems

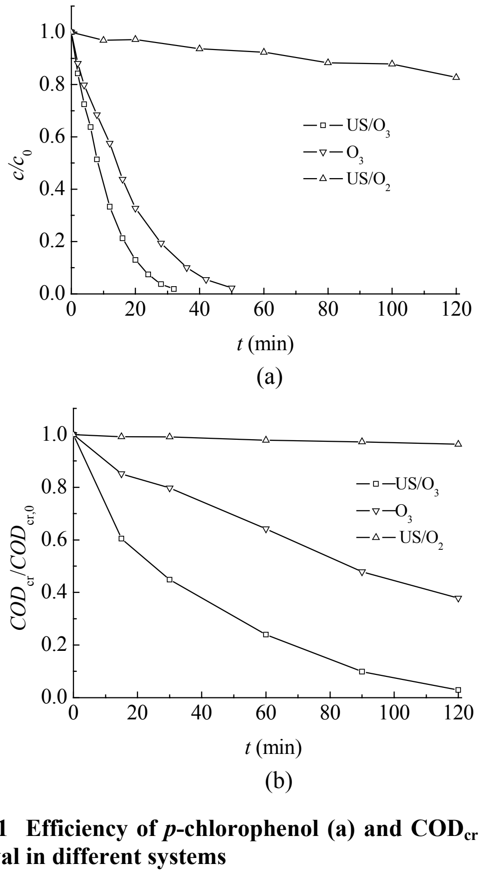
Fig.1 shows the decomposition of 46.22 mg/L *p*-chlorophenol and its COD_{cr} using different treatment systems, i.e., individual sonolysis, individual ozonlysis and US/O_3. It was evident that US/O_3 was the most effective system for decomposing *p*-chlorophenol, while individual sonolysis was the least effective one. The *p*-chlorophenol decomposition after 16-min reaction was determined to be 78.78%, 56.20% and 2.79% under US/O_3, individual ozonolysis and individual sonolysis respectively, COD_{cr} decomposition rate reached 97.02%, 62.17% and 3.67% after 120-min reaction. Since the COD_{cr} decomposition rate appeared to be distinctly lower than that of *p*-chlorophenol, it was possible that a series of intermediates were produced during the oxidization process of *p*-chlorophenol; these intermediates were later mineralized into organic acid, CO_2 and H_2O.

Decomposition kinetics

As shown in Fig.2, it was found that the decomposition using the above three approaches fit in the following pseudo-first-order kinetics:

$$\ln(c_0/c) = kt$$

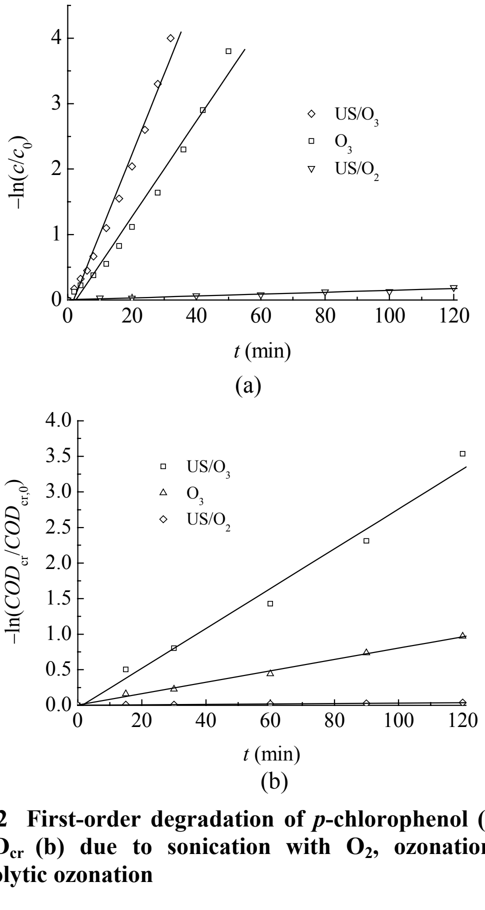
where, c_0 and c are the initial mass concentration of *p*-chlorophenol or COD_{cr} (mg/L) at the reaction time t, respectively; k is the pseudo-first-order reaction rate constant (min^{-1}) obtained by least square analysis, the linear regression equation is y=mx+b. The simulated reaction rate constants are listed in Table 1.



(a)

(b)

Fig.1 Efficiency of *p*-chlorophenol (a) and COD_{cr} (b) removal in different systems



(a)

(b)

Fig.2 First-order degradation of *p*-chlorophenol (a) and COD_{cr} (b) due to sonication with O_2, ozonation, and sonolytic ozonation

Table 1 Reaction rate constant (*k*) for *p*-chlorophenol and COD_{cr} removal

Processes	*k* for *p*-chlorophenol (10^2 min^{-1})	*k* for COD_{cr} (10^2 min^{-1})
US/O_2	0.231±0.002	0.0299±0.001
O_3	7.291±0.353	0.800±0.007
US/O_3	12.25±0.519	2.799±0.234

It was evident that in comparison with the individual sonolysis or ozonolysis, the combined process had synergetic effects in enhancing the removal rate of both *p*-chlorophenol and COD_{cr}. *k* for *p*-chlorophenol removal. For example, in the combined process (0.1225±0.00519 min^{-1}) the removal rate was much greater than that obtained by the addition of the value of *k* obtained in the individual sonolysis process (0.00231±0.00002 min^{-1}) and in the individual ozonolysis process (0.07291±0.00353 min^{-1}). The enhancement factor *f* was estimated to be about 63%. Similarly, the COD_{cr} removal rate enhancement factor was as high as 237%, much greater than that of the *p*-chlorophenol. The result indicated that the evolution of intermediates during *p*-chlorophenol decomposition was significantly accelerated in the combined process. It was concluded that the enhancement factors *f* we obtained under O_3, US and US/O_3 systems were similar to those in the references (Destaillats *et al*., 2000; Kang and Hoffmann, 1998; Olson and Baraier, 1994) and that US/O_3 is an efficient oxidation technology.

Decomposition mechanism

During acoustic cavitation, water is pyrolytically decomposed leading to the formation of hydroxyl and hydroperoxyl radicals as follows:

$$H_2O \rightarrow H\cdot + \cdot OH$$
$$H\cdot + O_2 \rightarrow HO_2\cdot$$

In the bulk aqueous phase, ozone could be decomposed by OH^-, or the conjugate base of H_2O_2 (HO_2^-) to yield $HO_2\cdot$ and $\cdot OH$ as shown below:

$$O_3 + OH^- \rightarrow HO_2^- + O_2$$
$$HO_2^- + H^+ \rightarrow H_2O_2$$
$$O_3 + HO_2^- \rightarrow O_2^- + \cdot OH + O_2$$
$$O_2^- + H^+ \rightarrow HO_2\cdot$$
$$O_3 + \cdot OH \rightarrow O_2 + HO_2\cdot$$
$$O_3 + O_2^- \rightarrow O_3^- + O_2$$
$$O_3^- + H_2O \rightarrow OH^- + \cdot OH + O_2$$

The coupling of sonolysis with ozonolysis augments $\cdot OH$ due to the decomposition of ozone. Ozone is decomposed thermolytically in the vapor phase of a cavitation bubble as follows (Hart and Henglein, 1986):

$$O_3 \rightarrow O + O_2$$

The initial reaction yields atomic oxygen which reacts with water to form hydroxyl radical and hydrogen peroxides are produced subsequently as follows:

$$O + H_2O \rightarrow 2\cdot OH$$
$$2\cdot OH \rightarrow H_2O_2$$

Based on the above analysis, it could be well established that the combination of sonolysis and ozonolysis is a much more effective oxidation system than either alone since two $\cdot OH$ are formed per O_3 molecule consumed. Therefore, the coupling of sonolysis with ozonolysis provides more $\cdot OH$ due to the decomposition of ozone which partly accounts for the synergetic effects. *p*-chlorophenol and its byproducts can be directly pyrolysed in the cavitation bubble itself or its interfacial sheath, react with ozone and one of the active species generated by the combined sonolysis of water and ozone.

Theoretically, in *p*-chlorophenol solution with initial concentration of 46.22 mg/L, the chlorine group is 12.78 mg/L. In order to explore the decomposition mechanism of *p*-chlorophenol using US/O_3 approach, the change of Cl^- mass concentration was measured. Fig.3 shows that after 6-min reaction, the removal rate of *p*-chlorophenol was 36.24%, which means that although in theory Cl^- mass concentration is 4.63 mg/L, it is actually 4.52 mg/L in practice or 97.62% of the former; while after 36 min, the removal rate of *p*-chlorophenol reaches 99.68%, that is, in theory, Cl^- concentration is 12.73 mg/L, compared with 12.49 mg/L in practice or 98.11% of the former. In view of unavoidable experimental errors, it can be inferred that chlorine is the first group removed in the decomposition process of *p*-chlorophenol.

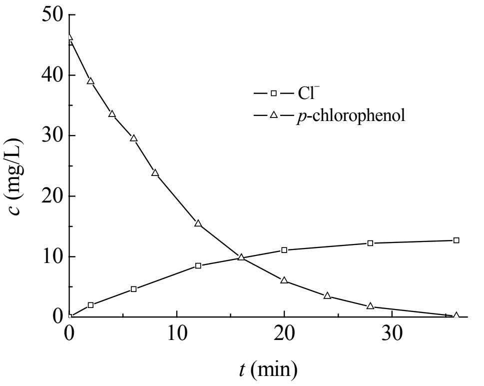


Fig.3 Mass concentration change of *p*-chlorophenol and Cl^-

Through HPLC and IC, catechol, hydroquinone, *p*-benzoquinone, phenol, fumaric acid, maleic acid, oxalic acid and formic acid were detected as the intermediates of *p*-chlorophenol decomposition (HPLC spectra shown in Fig.4) among which hydroquinone and *p*-benzoquinone were the most concentrated. Fig.5 indicates the mass concentration changes of hydroquinone, *p*-benzoquinone and catechol. At the initial stage, the mass concentration of hydroquinone increases quickly and after 8 min, reaches its maximum (2.49 mg/L), and finally decreases to 0 after 50 min. While *p*-benzoquinone reaches its maximum mass concentration (12.41 mg/L) and after 10 min, the reaction becomes much slower. As a result, little catechol is produce, and its maximum mass concentration reaches only 0.31 mg/L, stopped there after 25 min.

It can be derived from the experiments results that, *p*-chlorophenol decomposition can be divided into three stages: first, no matter whether it is in thermo-decomposition at cavitation bubble interfacial sheath or in reaction of O_3 and ·OH, it was the chlorine groups that were first removed, which resulted in phenol. Second, though the hydroxyl group is an electron density-enhancing substituent whose inductive effect and conjugative effect result in the *ortho* and/or *para* positions having higher electron density than the hydroxyl group; the electrophilic reaction favors a high electron density position with the phenol molecule being reactive substrate for electrophilic reaction and the *ortho* and/or *para* positions to the hydroxyl group being first attacked by O_3 and ·OH. Besides, as the steric effect of *para* position is not as obvious as that of *ortho* position, phenol was rapidly turned into hydroquinone and a small quantity of catechol with O_3 and ·OH; then hydroquinone turns into *p*-benzoquinone rapidly by dehydro reaction. Third, the above intermediates decrease and through ring opening, furtherly oxidized into fumaric acid, maleic acid, oxalic acid and formic acid which were finally turned into CO_2 and H_2O.

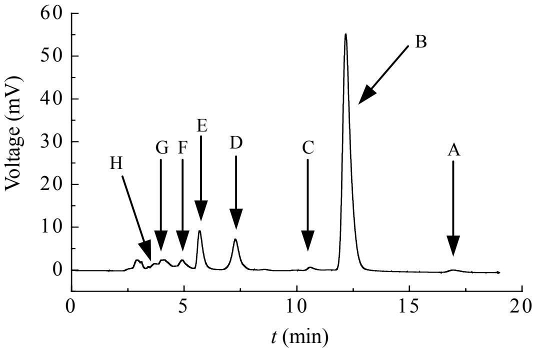


Fig.4 The HPLC spectra: intermediates in US/O_3 system after 10 min reaction

A: Phenol; B: *p*-chlorophenol; C: Catechol; D: *p*-benzoquinone; E: Hydroquinone; F: Fumaric acid; G: Maleic acid; H: Oxalic acid

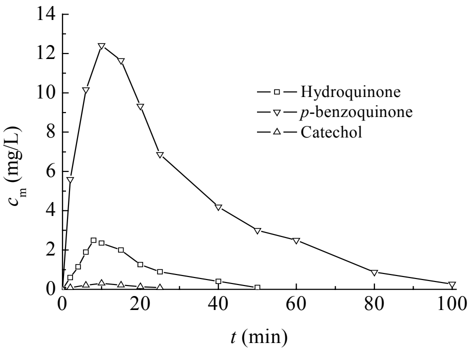
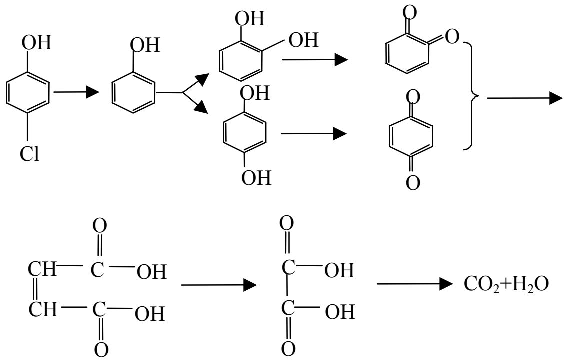


Fig.5 Intermediates mass concentrations

Over all, the whole reaction process of *p*-chlorophenol under US/O_3 could be described as follows:



CONCLUSION

US/O_3 was proven to be more effective than both individual sonolysis and ozonolysis in the decomposition of *p*-chlorophenol. The reaction follows apseudo-first-order kinetics. Under US/O_3, individual ozonolysis and individual sonolysis, the pseudo-first-order reaction rate constant for *p*-chlorophenol removal was 0.1225±0.00519 min^{-1}, 0.07291±0.00353 min^{-1}, 0.00231±0.00002 min^{-1} while its CODcr pseudo-first-order reaction rate constant was 0.02799±0.00234 min^{-1}, 0.00800±0.00007 min^{-1}, 0.000299±0.00001 min^{-1}. The enhancement factors of *p*-chlorophenol and its COD_{cr} under US/O_3 system reach 61% and 237% respectively.

Under US/O_3 system, chlorine groups were first removed, which resulted in phenol. Phenol was further decomposed to form hydroquinone and a small quantity of catechol by the electrophilic reaction with ozone and ·OH, and hydroquinone turned into *p*-benzoquinone rapidly. As the reaction proceeded, these intermediates were further oxidized and the several ring openings that occurred, resulted in the formation of fumaric acid, maleic acid, oxalic acid and formic acid, which finally led to the production of CO_2 and H_2O.

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