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Study on US/O₃ mechanism in *p*-chlorophenol decomposition

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Abstract: Study on the effects of sonolysis, ozonolysis and US/O₃ system on the decomposition of *p*-chlorophenol in aqueous solutions indicated that in the cases of US/O₃ 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 COD_{cr} (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/O₃ 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/O₃, *p*-chlorophenol, Synergetic effect, Decomposition mechanism

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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 combining ozonolysis technique with other methods, including advanced oxidation processes (AOPs) such as UV/O₃, H₂O₂/O₃, H₂O₂/UV/O₃, US/O₃ (Stachelin 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/O₃ has been proved to be an effective one. According to Destailats *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 O₃. 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/O₃ 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 $4.1 \times 10^{-4} \text{ s}^{-1}$ to $8.5 \times 10^{-4} \text{ s}^{-1}$, 1.5~3.9 times more than the original rate. However, the degradation of contaminants by US/O₃ 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/O₃ on its decomposition showed that there was a synergetic effect of US/O₃ system on the decomposition of *p*-chlorophenol. The *p*-chlorophenol decomposition mechanism under US/O₃ 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), Na₂S₂O₃, NaOH, H₃PO₄ 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 O₃ concentration, we maintained the gross amount of O₃ 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, O₂ was instilled till saturation in the solution, then ultrasonic irradiation was introduced. Fixed amounts of Na₂S₂O₃ were added into the samples to remove the remnant O₃. 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, O₃/O₂ 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:

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

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 ozonolysis and US/O₃. It was evident that US/O₃ 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/O₃, 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, CO₂ and H₂O.

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.

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

Fig.2 First-order degradation of *p*-chlorophenol (a) and COD_{cr} (b) due to sonication with O₂, ozonation, and sonolytic ozonation

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

Processes	<i>k</i> for <i>p</i> -chlorophenol (10 ² min ⁻¹)	<i>k</i> 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 O₃, US and US/O₃ systems were similar to those in the references (Destailats *et al.*, 2000; Kang and Hoffmann, 1998; Olson and Baraier, 1994) and that US/O₃ 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:

In the bulk aqueous phase, ozone could be decomposed by OH⁻, or the conjugate base of H₂O₂ (HO₂⁻) to yield HO₂⁻ and ·OH as shown below:

The coupling of sonolysis with ozonolysis augments ·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):

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

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 ·OH are formed per O₃ molecule consumed. Therefore, the coupling of sonolysis with ozonolysis provides more ·OH due to the decomposition of ozone which partly accounts for the synergetic effects. *p*-chlorophenol and its by-products 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/O₃ 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 produced, 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 $\cdot\text{OH}$, 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 $\cdot\text{OH}$. 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 $\cdot\text{OH}$; 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/O₃ 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/O₃, individual ozonolysis and individual sonolysis, the pseudo-first-order reaction rate constant for *p*-chlorophenol removal was $0.1225 \pm 0.00519 \text{ min}^{-1}$, $0.07291 \pm 0.00353 \text{ min}^{-1}$, $0.00231 \pm 0.00002 \text{ min}^{-1}$ while its COD_{cr} pseudo-first-order reaction rate constant was $0.02799 \pm 0.00234 \text{ min}^{-1}$, $0.00800 \pm 0.00007 \text{ min}^{-1}$, $0.000299 \pm 0.00001 \text{ min}^{-1}$. The enhancement factors of *p*-chlorophenol and its COD_{cr} under US/O₃ system reach 61% and 237% respectively.

Under US/O₃ 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 CO₂ and H₂O.

References

- Adams, C.D., Scanlan, P.A., Secrist, N.S., 1994. Oxidation and biodegradability enhancement of 1,4-dioxane using hydrogen peroxide and ozone. *Environ. Sci. Technol.*, **28**:1812-1818.
- Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. *Wat. Res.*, **15**:449-456.
- Dahi, E., 1976. Physicochemical aspects of disinfection of water by means of ultrasound and ozone. *Wat. Res.*, **10**:677-684.
- Destailats, H., Colussi, A.J., Joseph, J.M., Hoffmann, M.R., 2000. Synergistic effects of sonolysis combined with ozonolysis for the oxidation of azobenzene and methyl orange. *J. Phys. Chem. A.*, **104**:8930-8935.
- EPA (Environment Protection Bureau), 1989. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington DC, p.4-162.
- Guittoneau, S., Duguet, J.P., Bonnel, C., Dore, M., 1990. Oxidation of parachloronitrobenzene in dilute aqueous solution by O₃+UV and H₂O₂+UV: A comparative study. *Ozone. Sci. Eng.*, **12**:73-94.
- Hart, E.J., Henglein, A., 1986. Sonolysis of ozone in aqueous solution. *J. Phys. Chem.*, **90**:3061-3062.
- Kang, J.W., Hoffmann, M.R., 1998. Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone. *Environ. Sci. Technol.*, **32**:3194-3199.
- Mokrini, A., Oussi, D., Esplugas, S., 1997. Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water. Sci. Technol.*, **35**(4):95-102.
- Olson, T.M., Baraier, P.F., 1994. Oxidation kinetics of natural organic matter by sonolysis and ozone. *Wat. Res.*, **28**(6):1383-1391.
- Peyton, G.R., Glaze, W.H., 1988. Destruction of pollutants in water with oxone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone. *Environ. Sci. Technol.*, **22**:761-767.
- Sierka, R.A., Amy, G.L., 1985. Catalytic effects of ultraviolet light and/or ultrasound on the ozone oxidation of humic acid and trihalomethane precursors. *Ozone. Sci. Eng.*, **7**:47-62.
- Stachelin, J., Hoigné, J., 1982. Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.*, **16**:676-681.
- Xi, D.L., Shun, Y.S., Liu, X.Y., 1989. Environmental Monitoring. China Publishing Company of Higher Education, Beijing (in Chinese).

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