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Ozonation with ultrasonic enhancement of *p*-nitrophenol wastewater

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Abstract: Synergetic effects for *p*-nitrophenol degradation were observed in the ozonation with ultrasonic enhancement. The enhancements of removal rate for *p*-nitrophenol and TOC were around 116% and 294% respectively in comparison with the individual ultrasound and ozonation systems. The synergetic phenomenon is attributed to two physicochemical mechanisms: (1) Ultrasound decomposes ozone causing augmentation of the activity of free radicals; (2) Ultrasonic wave increased the concentration of O_3 in solution because of ultrasonic dispersion.

Key words: Ozonolysis, Sonolysis, Synergetic effect, *p*-nitrophenol degradation
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INTRODUCTION

Advanced oxidation processes (AOPs), in which high reactive and non-selective hydroxyl radicals in aqueous solution are generated, have aroused among scientists great interest in destroying toxic and biorefractory organics of wastewater. AOPs such as photocatalyzation, electrocatalyzation, ozonolyzation, and wet air oxidation have been intensivels studied. There is a trend in recent years to develop processes combining two or more AOPs such as O_3/UV, O_3/H_2O_2, O_3/H_2O_2/UV, UV/H_2O_2 in which synergetic effects have been observed (Staehelin and Hoigne, 1982; Adams *et al*., 1994; Peyton and Glaze, 1988; Mokrini *et al*., 1997; Guittoneau *et al*., 1990).

The process combining ultrasonic irradiation with ozonation is a less developed AOP. Under-developed AOP ultrasonic irradiation has been studied in the purification of aqueous organic and inorganic pollutants (Bhatnagar and Cheung, 1994; Cheung *et al*., 1991; Hoffmann *et al*., 1992a; 1992b; Pétrier *et al*., 1992). Sound waves just above the audible level produce cavitation bubbles whose internal high temperatures and pressures lead to their collapse. The chemical destruction of compounds has been demonstrated either inside the cavitation bubble or on its interfacial sheath due to direct pyrolysis, hydroxylation, or radical reactions resulting from the gas-phase pyrolysis of H_2O. Radicals escaping the cavitation bubble diffuse into solution and react near the cavity boundary. Secondary reactions also occur in the bulk aqueous phase. It has been demonstrated that sonolytic systems with ozone added increase the net transformation rates of a wide range of chemical species (Sierka and Amy, 1985; Dahi, 1976; Olson and Baraier, 1994; Kang and Hoffmann, 1998; Destaillats *et al*., 2000).

With the aim of exploring whether synergetic effects exist in the combined ozonolysis and sonolysis process, and investigating the possible synergetic effects mechanism, we selected *p*-nitrophenol the model pollutant, as it is a main EPA (Environment Protection Bureau) toxic pollutants and widely exists in wastewater, and pesticides and dyes.

EXPERIMENT METHODS

Sonochemical experiments

The experiment was done with a 200 ml glass chamber reactor surrounded by a self-contained water jacket, constant gas flow, and a source of ultrasound

(Fig.1). The solution was kept constant at 25 °C with water bath flowing through the surrounding water jacket and O_3 or O_2 gas flowing out of a coarse fritted-glass diffuser at 40 ml/min. Before every experiment, a fixed amount of *p*-nitrophenol was dissolved in organic-free water and initial *p*-nitrophenol concentration was about 50 mg/L. pH was adjusted with phosphoric acid and sodium hydroxide. The ionic strength was stabilized at 0.1 mol/L. Aliquots (2.0 ml) were collected certain time. Thiosulfate (0.2 ml of 80 mmol/L) was used to eliminate residual ozone in solution in addition to determination of ozone and hydrogen peroxide concentration. All samples were filtered with 0.2 μm syringe filters before analysis. Total organic carbon (TOC) experiment was the only step not performed in triplicate, but TOC results were analyzed thrice. To analyze the possible stripping of *p*-nitrophenol in the oxidation, experiment without ultrasound was carried out. Measurements made before and after the experiment indicated there was no significant change in the concentration of *p*-nitrophenol.

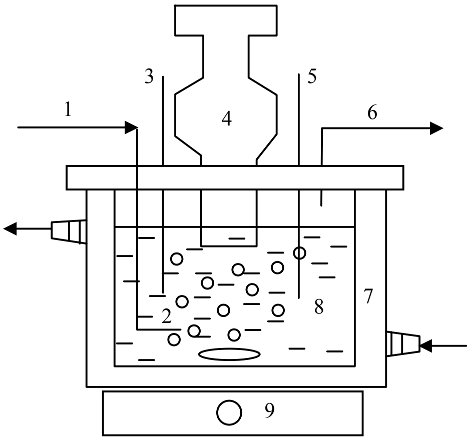


Fig.1 Schematic diagram of the sonozone reactor

1: O_3/O_2 inlet; 2: Coarse fritted-glass diffuser; 3: Thermometer; 4: Transducer; 5: Sample out; 6: Vent gas; 7: Cooling water jacket; 8: Reactor; 9: Magnetic agitator

Analysis

Concentration of *p*-nitrophenol and its degradation intermediates were determined through comparing the retention time of the standard compounds with a high-performance liquid chromatograph (HPLC, Gilson). Twenty-five μl aliquots of samples were injected into the HPLC running on mobile phase of phosphate buffer solution (pH 2)/methane alcohol at 70/30. The separation was performed using an ODS-18 reversed phase column at flow rate of 1.0 ml/min and temperature of 25 °C. An UV detector with the wavelength set at 280 nm was used. The ozone gas phase concentration was determined by standard methods (EPA, 1989). The concentrations of ozone and hydrogen peroxide in the solution were measured by the indigo method and spectrophotometric determination method (Bader and Hoigne, 1981; Sellers, 1980), respectively. TOC analysis was performed using an Apollo 9000 TOC Combustion Analyzer (USA) operating in the nonpurgable organic carbon (NPOC) mode.

RESULTS AND DISCUSSIONS

Synergetic effects

A systematic comparison of *p*-nitrophenol degradation and TOC removal was carried out by sonolysis and ozonolysis, with the combined process being shown in Fig.2. It was found that their removals in three processes fit the following pseudo-first-order kinetic equation:

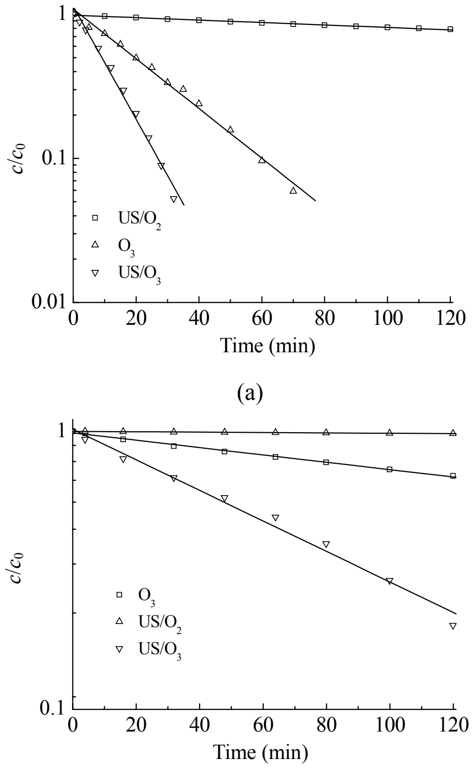
$$\ln(c_0/c)=kt$$

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

The combined process evidently had synergetic effect in enhancing the removal rate of both TOC and *p*-nitrophenol in comparison with sonolysis or ozonolysis alone. k for *p*-nitrophenol removal, for example, in the combined process (0.09012 ± 0.00321 min^{-1}) was much greater than its counterpart obtained either in the sonolysis process (0.00196 ± 0.00005 min^{-1}) or ozonolysis process (0.03978 ± 0.00107 min^{-1}). Factor (f) is put forward to evaluate the enhancement of the removal rate of around 116% obtained by using the following formula:

$$f=[k_{\text{US/O}_3}/(k_{\text{US/O}_2}+k_{\text{O}_3})-1]\times100\%$$

where $k_{\mathrm{US/O_3}}$ is the reaction rate constant in the sonolysis-ozonolysis process, $k_{\mathrm{US/O_2}}$ in sonolysis process and $k_{\mathrm{O_3}}$ in ozonolysis process. The enhancement factor of removal rate of TOC was up to 294%, which was much greater than that of *p*-nitrophenol. The experiments result indicated that the evolution of intermediates during *p*-nitrophenol degradation was significantly accelerated in the combined process.



(a)

(b)

Fig.2 First-order degradation of *p*-nitrophenol (a) and TOC (b) due to sonication with O_2, ozonation and sonolytic ozonation. The O_3 gas flow at 40 ml/min, pH=3, *T*=298 K. The initial *p*-nitrophenol concentration was 50 mg/L. The ultrasonic power generation of transducer was 125 W

Table 1 Reaction rate constant (*k*) for TOC and *p*-nitrophenol removal

Processes	*k* for *p*-nitrophenol (10^2 min^{-1})	*k* for TOC (10^2 min^{-1})
US/O_2	0.196±0.005	0.0161±0.001
O_3	3.978±0.107	0.305±0.008
US/O_3	9.012±0.321	1.264±0.052

Degradation intermediates

Benzoquinone is one of the rather consistent byproducts and indicates the difficulty of ring opening. It was identified by sonolysis, ozonolysis or the combined process. This speculation above was confirmed by taking benzoquinone as the intermediate product during *p*-nitrophenol degradation. As shown in Fig.3, benzoquinone increased slowly in sonolysis. In ozonolysis, it reached maximum 24 min later and then gradually decreased. In the combined process, however, both formation and disappearance of benzoquinone were greatly accelerated. It reached its peak of almost 3.9 mg/L 12 min later and died away in no more than 90 min.

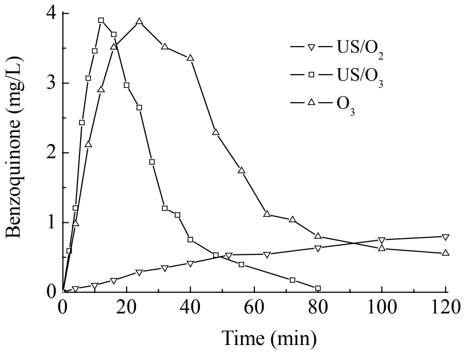


Fig.3 Formation of benzoquinone by sonication with O_2, ozonation and sonolytic ozonation. The O_3 gas flow rate was 40 ml/min, pH=3, *T*=298 K. The initial *p*-nitrophenol concentration was 50 mg/L. The ultrasonic power generation of transducer was 125 W

Synergetic mechanisms

The process combining sonolysis and ozonolysis shows higher degradation rates for *p*-nitrophenol and TOC than either system alone. And two physicochemical mechanisms account for the synergetic phenomenon: (1) Ultrasound decomposes ozone causing augmentation of the activity of free radicals; (2) Ultrasonic wave increased the concentration of O_3 in solution because of ultrasonic dispersion.

During acoustic cavitation, water is pyrolytically decomposed into 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 can be decomposed by hydroxide ion, OH^-, or the conjugate base of H_2O_2 (HO_2^-) to yield $HO_2\cdot$ and $\cdot OH$ as follows:

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

The coupling of sonolysis with ozonolysis increases ·OH because of thermolytical ozone decomposition which occur in the vapor phase of a cavitation bubble as follows (Hart and Henglein, 1986):

$$O_3 \rightarrow O_2 + O$$

The initiatal reaction yields atomic oxygen which reacts with water to form hydroxyl radical, and hydrogen peroxide are produced subsequently as described below:

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

The *p*-nitrophenol and its byproducts pyrolyses either directly inside the cavitation bubble or in its interfacial sheath and react with ozone and one of the active species generated by the combined sonolyzation of water and ozone. The combination of sonolysis and ozonolysis proved effective in oxidation since in this method, two ·OH molecules are produced by consuming per O_3 molecule. Hydrogen peroxide accumulation in the aqueous phase is an indirect indicator of ·OH production in the vapor phase and interface between bubbles and solution. Ozone's effect on the hydrogen peroxide formation was investigated. The [H_2O_2] vs time profiles (Fig.4) shows the combined O_3/US system produces more [H_2O_2] than the sonolysis system alone. H_2O_2 produced by sonication rapidly reacts with *p*-nitrophenol in the beginning, and increases gradually during the irradiation period with the decrease of *p*-nitrophenol. Similar results were observed by Kang and Hoffmann (1998).

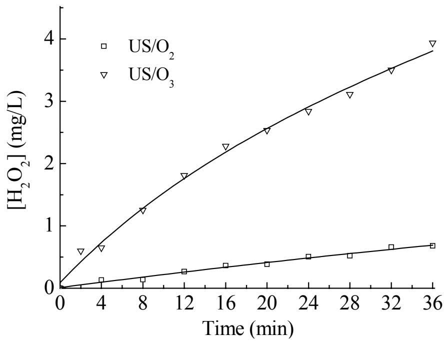


Fig.4 Formation of H_2O_2 by sonication with O_2 and sonolytic ozonation. The O_3 gas flow rate was 40 ml/min, pH=3, *T*=298 K. The initial *p*-nitrophenol concentration was 50 mg/L. The ultrasonic power generation of transducer was 125 W

In addition, ultrasonic irradiation enlarges the ozone effective surface area by higher blending and collapse of bubbles as they enter the reactor. In this way, more ozone is allowed to enter solution than that in a nonirradiated system. As shown in Fig.5, higher O_3 concentration in solution was obtained under sonolysis-ozonolysis than under ozonolysis alone, which further confirms the results of Dahi (1976), and Sierka and Amy (1985).

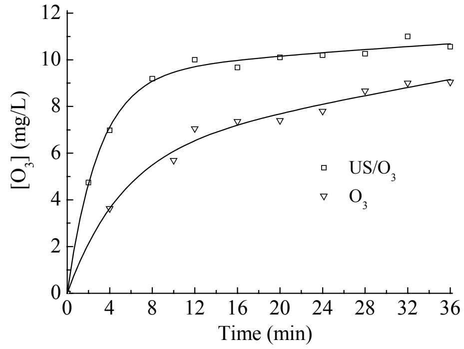


Fig.5 Effect of ozonation and sonolytic ozonation on the concentration of O_3 in the solution. The O_3 gas flow rate was 40 ml/min. The pH was 3. *T*=298 K. The initial *p*-nitrophenol concentration was 50 mg/L. The ultrasonic power generation of transducer was 125 W

CONCLUSION

Experiment on the process combining sonolysis and ozonolysis showed that degradation rates for *p*-nitrophenol and TOC were higher than those of ultrasound or ozone system alone. The enhancement of removal rate for *p*-nitrophenol and TOC were around 116% and 294%, respectively. In the ozonolysis system, ozone is decomposed by hydroxide ion, OH^-, or the conjugate base of H_2O_2 (HO_2^-) into $HO_2\cdot$ and $\cdot OH$ in the bulk aqueous phase. While in the sonolysis system, H_2O is pyrolytically decomposed into hydroxyl and hydroperoxyl radicals during acoustic cavitation. In the ozone-ultrasound process, however, the thermal decomposition of ozone in the cavitation bubbles leads to enhanced $\cdot OH$ radical and H_2O_2 yields, and the *p*-nitrophenol and its byproducts pyrolyze directly inside the cavitation bubble or in its interfacial sheath, reacting with ozone and one of the active species generated by the pyrolysis of water and ozone. At the same time, more ozone effective surface area was obtained by ultrasonic dispersion, allowing more ozone in the solution to react with *p*-nitrophenol and its byproducts.

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