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Degradation of high concentration phenol by ozonation in combination with ultrasonic irradiation

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ABSTRACT

The combination of 50 kHz ultrasound and ozone for the degradation of phenol was studied. The effect of temperature, ozone gas flow rate, initial pH, hydroxyl radical scavenger, and initial phenol concentration on the degradation was investigated. Of the pseudo-first-order degradation rate constants of COD reduction, 4.8×10^{-3} and 5.4×10^{-3} min^{-1} were observed with O_3 and a combination of US and O_3, respectively. The COD reduction by single US was negligible. The degradation rate increased with the increase of temperature and gas flow rate, but decreased with the increasing initial phenol concentration. The optimal pH was 11.0 but it had no much effect on the COD removal efficiency, indicating that the low frequency ultrasound enhanced ozonation process for the degradation of phenol is mainly a direct reaction rather than radical reaction. The synergistic effect of phenol degradation by ultrasound enhanced ozonation was not significant in this system. The variation of the concentrations of related ions (oxalate, formate, acetate) during the reaction process was monitored by ion chromatography. Other organic intermediates detected by GC/MS were hydroquinone and catechol. Based on these findings, a tentative degradation pathway was proposed.

Keywords: Ozone; Ultrasound; Advanced oxidation; Phenol; Synergistic effect

1. Introduction

Phenol is one of the most common compound found in the effluents of many industries such as petroleum refining and petrochemicals, pharmaceuticals, pesticides, paint and dye industries, organic chemicals manufacturing etc. Minute quantities of phenol or derivatives of phenol (of the order of a few ppm) result in high levels of toxicity in the effluent stream and also give foul odor to the water [1]. It has been classified as a priority pollutant in the United States Environmental Protection Agency (USEPA) list for its toxic, carcinogenic, mutagenic, teratogenic and non-biodegradable properties [2]. Therefore, the removal of phenol from industrial effluents and other environments is an important problem. Recently, considerable attention has been paid to chemical degradation of phenol.

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There has been tremendous interest in the use of AOPs (advanced oxidation processes) such as treatment with high energy radiation, ozone, or ultraviolet radiation for degradation of toxic components. Among them, using strong but environmentally friendly oxidants such as ozone in combination with additional physicochemical processes is considered to be promising [3–6].

Combined sonolysis and ozonation (US/O_3) is one of the most effective methods of producing free radicals in AOPs. Combining O_3 with US leads to better utilization of the oxidant and hence higher degradation rate due to the dissociation of ozone under the action of ultrasound. The mass transfer resistance, which is a major limiting factor for the application of ozone alone, is also eliminated due to the enhanced turbulence generated by ultrasound [1]. Therefore, US/O_3 process has become a hot investigation area and was extensive studied due to its advantages of being non-selective, leading to no secondary pollution and being particularly effective in removing persistent and biorefractory pollutants such as aniline [7], pentachlorophenol [8], reactive dye [9], dinitrobenzene [10] and *p*-chloronitrobenzene [11].

Up to now, the great majority of researchers employed ultrasonic with a probe directly immersing in the solution to intensify ozonization to degrade pollutions. However, very few used the ultrasonic cleaner (or bath) which emitting ultrasonic from its bottom to enhance ozonization to degrade high concentration wastewater. The range of the pollutant concentration is often between 10^{-9} and 10^{-3} M [12]. However, in practice, the concentration of some natural industrial wastewaters often is very high and beyond this range. Therefore, to determine the practicability of the process, high concentration of phenol (from 1679 to 5037 mg/L) was adopted in this study. At the same time, the effects of important variables, such as pH, dosages of ozone, temperature, and initial phenol concentration, on the COD reduction of phenol were examined in order to get the optimum process conditions. The intermediates of degradation were detected and a possible degradation pathway of phenol was also proposed.

2. Experimental set up and procedure

2.1. Reagents

Phenol (molecular mass is 94.11g/mol) is obtained from Chengdu Chemical Reagent Company, China. It is over 99% pure and was used without further purification. *n*-Butanol was chosen as a ·OH radical scavenger. $K_2Cr_2O_7$ and $(NH_4)_2Fe(SO_4)_2$ were of analytical grade and were used without further purification. The water used throughout was distilled water.

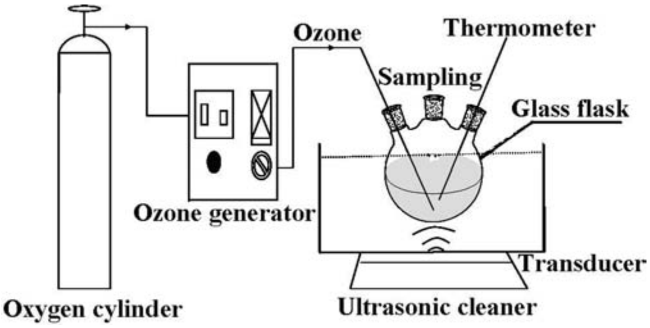


Fig. 1. The experimental set up.

2.2. Apparatus

The experimental apparatus employed in this work (Fig. 1) consisted of a three necked round flask reactor (1000 ml) coupled with an ultrasonic cleaner (SB3200T, Shanghai Binengxing Ultrasonic Equipment Co. Ltd., China), an ozone generator (OGA, variable flow control, Shenyang Dongyu Ozone Equipment Co. Ltd., China). The ultrasonic cleaner output is 120 W and the frequency is 50 kHz fixed. The round flask reactor was plugged with a polyethylene cap during operation. The ozone generator used pure oxygen as original gas and the production rate was 0–0.8 m^3/h, determined by iodometric method, which correspond to 0–3.65 g O_3/L on supplied gas. The oxygen/ozone flow-rate to the generator was monitored with a rotameter incorporated in the ozone generator. Except the single ozonation experiment of effect of temperature was carried out in a temperature controlled bath, all the other experiments were conducted in closed atmosphere at room temperature (299 ± 2 K) and no reactor cooling was provided.

A solution (800 ml) of phenol was degraded with the chosen O_3 and/or US. Samples were withdrawn by a glass suction pipette at various reaction time points and analyzed for solutes.

2.3. Analytical methods

The organic intermediates in the water samples were extracted out with ethyl acetate (or chloroform). Organic compounds were detected by gas chromatography coupled with mass spectrometry (GC/MS) (TraceMS, Thermo Finnigan). Detection of the compounds was achieved by using a HP-5MSi capillary column (30 m × 0.25 mm, 0.25 μm film thickness). Helium (purity 99.9999%) was used as carrier gas and maintained at a constant flow rate of 1.0 mL/min. The ion source temperature and the quadrupole temperature were kept at 220 and 150°C, respectively. A sample volume of 1 μL was injected in splitless mode at an inlet temperature of 280°C. The column temperature was programmed as follows: initial temperature set at

60°C for 2 min, then it was increased to 160°C at 20°C/min (hold 5 min), then ramped at 2°C/min to 200°C, then ramped at 4°C/min to 240°C (hold 3 min) and finally at 290°C (hold 5 min) at 5°C/min. The MS interface temperature was maintained at 270°C.

Acetic acid and oxalic acid were determined by ion chromatography (761 compact IC, Metrohm, Switzerland) with a separating column (Metrosep A supp5) and electrical conductivity detector, using the mixture of Na_2CO_3 (3.2 mmol/L) and $NaHCO_3$ (0.8 mmol/L) and CH_3OH (3%, V/V) eluent, and a total flow-rate was 0.8 ml/min. The samples (20 uL) were injected manually through an injection port.

The concentration of phenol was determined by a high performance liquid chromatography (HPLC, Agilent 1200 series) equipped with DAD and Zorbax Eclipse XDB-C18 (4.6 × 150 mm, 5 μm). The mobile phase was methanol-water (60:40, v:v) containing 1% acetic acid. The detection wavelength was set at 270 nm. The flow rate of the mobile phase was 0.8 mL/min and the injection volume was 20 μL.

The samples were putted aside for about 30 min to cool to room temperature, while most of ozone and other active substances were eliminated or auto-decomposed. The values of chemical oxygen demand (COD) were obtained through oxidation with $K_2Cr_2O_7$ under acidic conditions and titrate analysis with $(NH_4)_2Fe(SO_4)_2$ aqueous solution according to the national criterion of PR China(GB11914-89,1989)[13]. The pH value was measured by PH-3C instrument (Rex Analytical Instrument Co. Ltd., Shanghai, China).

The definition of COD removal efficiency (R) is as follows:

$$R = \frac{COD_0 - COD_t}{COD_0} \times 100,$$

where COD_0 is the initial COD (mg/L) of phenol wastewater and COD_t is the COD (mg/L) after reaction for t min.

3. Results and discussion

3.1. Comparison of three processes for degradation and mineralization of phenol (US, O_3, and US/O_3)

The degradation efficiencies of phenol at an initial concentration of 1679 mg/L (COD is 4000 mg/L) by treatment with US and O_3 singly and in combinations were presented in Fig. 2. The single US almost had no effect on COD removal. The poor effects of US alone on the COD removal may be attributed to the fact that low-frequency ultrasound cannot promote the production of ·OH [14]. In addition, US treatment generally demands a long time of contact for significant degradation efficiency [15]. Furthermore, the ultrasonic did not contact with the wastewater directly but must penetrate a wall of the glass flask in this system. Therefore the energy must decrease and the amount of ·OH produced by US was very few. These facts may partially explain the very low efficiency of COD removal found for the US system [16].

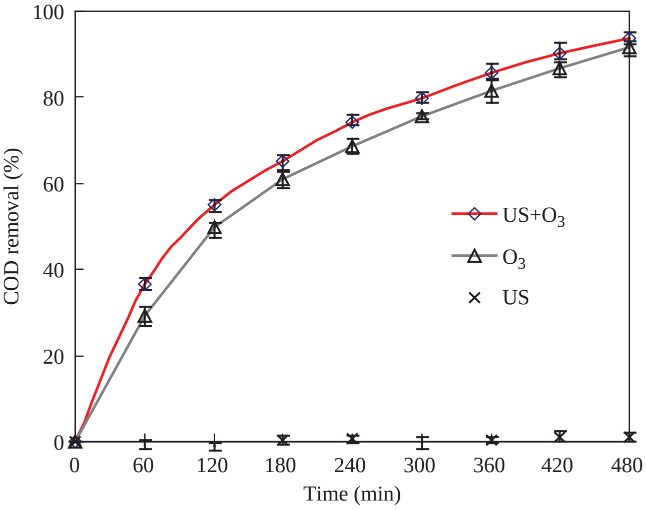


Fig. 2. The comparison of COD removal by ultrasonic, ozonation and ozonation/ultrasonic (Q_{ozone}= 0.1 m^3/ h, room temperature, no pH adjustment).

Using O_3 alone (29.2% and 75.7% efficiency of COD at 60 min and at 300 min, respectively) was much more effective than using US alone. However, the efficiency of the combination of US and O_3 (36.5% and 79.8% at 60 min and 300 min, respectively) exceeded the sum of those using O_3 and US alone.

During ozonalysis without sonication, ozone moves from the gas phase into solution and then reacts in bulk solution either directly with the substrate or indirectly via reactions with radicals generated by O_3 autodecomposition. In sonolysis alone, the substrate can undergo direct pyrolysis, and/or secondary reactions take place between the substrate and reactive radicals from the pyrolysis of H_2O in a cavitation bubble. However, in the combined system, the above pathways may be altered by the addition of other pathways that only occur by the direct interaction of sonolysis and ozonation. For example, sonolysis could enhance the decomposition of O_3, resulting in the generation of additional ·OH to react with the substrate. Additionally, US could enhance the mass transfer of O_3, which may result in additional O_3 being transferred to the solution.

The errors of the data mostly come from titration process, hydroxyl radical and ozone. But all the errors did not exceed three percent. Therefore in the following experiments the errors analysis was omitted.

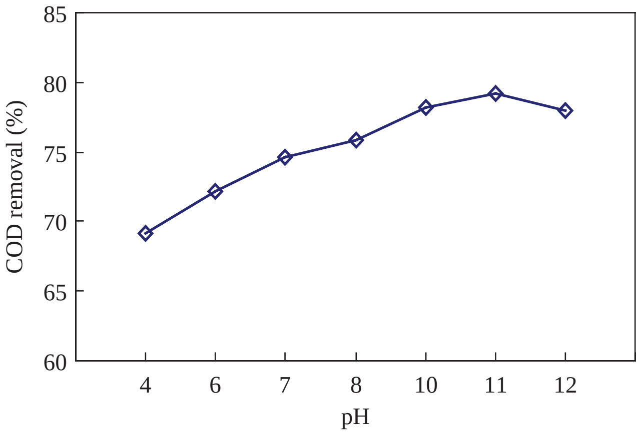


Fig. 3. The effect of initial pH on the COD removal (COD_0 = 4000 mg/L, ozone flow rate = 0.1 m^3/ h, reaction time = 240 min, room temperature).

3.2. *Effect of pH*

Fig. 3 showed the effect of the initial pH on the COD removal as the pH changed from 4.0 to 12.0. All phenol solutions with different initial pH values were adjusted by phosphate buffer containing sodium hydroxide and phosphoric acid. At the 240 min reaction time-point, removal efficiency of COD was 69.2%, 75.9%, 79.2%, and 78.0% at pH 4.0, 8.0, 11.0, and 12.0, respectively. The most effective removal of COD was obtained at pH 11.0.

At higher pH value, hydroxyl radical would be generated from ozone decomposition in the presence of hydroxide ion. Therefore, ozonation process may proceed via free radical pathway [9]. Furthermore, the stability of O_3 was decreased when the pH was increased, which resulted in the generation of more free radicals. In addition, the reaction of ·OH with phenol might be more efficient at high pH rather than at low pH. These facts can partially explained the high removal efficiency of COD at high pH.

However, the COD removal was decreased when the pH above 11.0. Two factors likely interpreted it. First, phosphate species, added to the solution as pH buffers in our experiments, were radical scavengers and reacted with ·OH at different rates, depending on the particular species present. The reaction of ·OH with various phosphate species would be expected to be least in the pH region from 2.8 to 4.5. When the pH was above 11, the predominant species of phosphate was PO_4^{3-} which reacted with ·OH at a high rate. Second, the phenol was oxidized and at last mineralized to carbon dioxide which keep in the solution as CO_3^{2-} at high pH, and CO_3^{2-} is a strong radical scavenger. Therefore, at high pH beyond 11.0 the concentration of free radicals could be lowered in the presence of radical scavengers such as CO_3^{2-} and PO_4^{3-} [17].

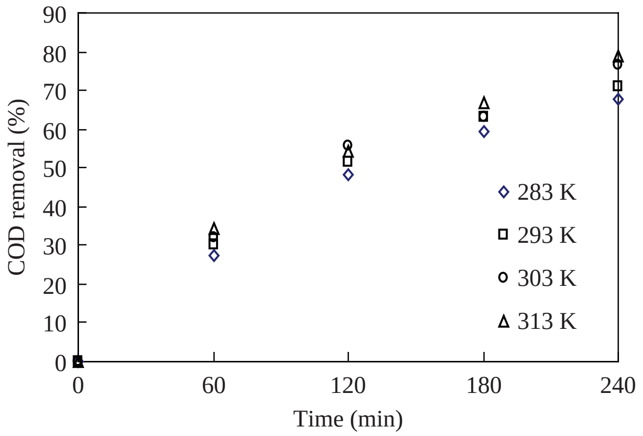


Fig. 4. The effect of temperature on the COD removal (COD_0 = 4000 mg/L, ozone flow rate = 0.1 m^3/h, no pH adjustment).

The figure also indicated that the effect of pH to COD removal was not pronounced. Therefore, taking the economic and practical factors into considered, it was not necessary to adjust the initial pH of the wastewater in practice.

3.3. *Effect of temperature*

The influence of reaction temperature on single ozonation of phenol was investigated (because the system cannot control temperature with the ultrasonic cleaner). The reaction temperature was controlled at 283, 293, 303 and 313 K, respectively. Fig. 4 illustrated the COD removal efficiency at different temperatures and indicates that the COD removal efficiency was accelerated with the increase of reaction temperature. It may be explained that, although the concentration of ozone in water decreases with the rising of temperature, the generation rate of hydroxyl radical from ozone molecule was faster at higher temperature. Therefore, hydroxyl radicals may play an important role in the degradation of phenol, because the degradation of phenol by hydroxyl radical is much faster than that by ozone [2]. However, without the ultrasonic irradiation, the hydroxyl radical come from the ozone autodecomposition was few and the dominant pathway was directly ozonization. Therefore, the effect of temperature on COD removal was unremarkable. So in the following experiments the temperature was not controlled.

3.4. *Effect of O_3 flow rate*

Proper selection of the ozone flow rate for the destruction of a target pollutant is crucial for process

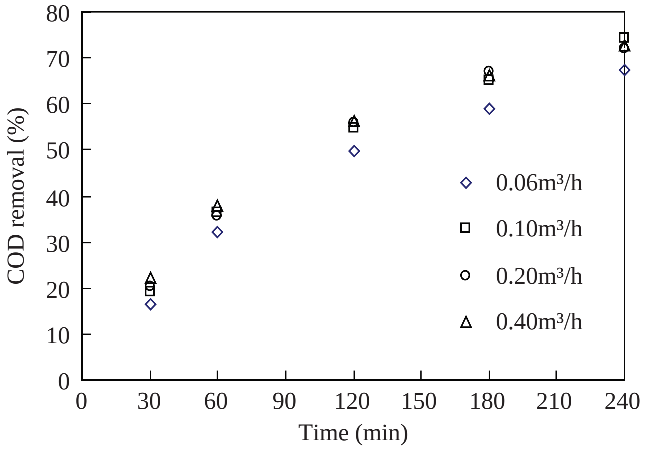


Fig. 5. The effect of ozone flow on the removal of COD by 240 min US/O_3 (COD_0 = 4000 mg/L, room temperature, no pH adjustment).

optimization. Fig. 5 showed the COD removal efficiency in the combined US/O_3 system at different ozone flow rate. It illustrated that the removal efficiency of COD increased with the increase of gas flow rate when the flow rate below 0.2 m^3/ h. Removal efficiency varied from 32.2% to 36.5% and from 58.9% to 65.1% when the ozone flow rate ranged from 0.06 to 0.10 m^3/h for 60 and 180 min, respectively.

This finding indicated that increasing the flow rate corresponds to a larger net surface area for mass transfer of ozone to the aqueous phase, and hence increases the volumetric mass transfer coefficient of ozone. This resulted in the increase of mass transfer rate of ozone from gas phase to liquid phase and hence the COD removal due to the mass transfer controlled characteristics in the coupled US/O_3 system.

Nevertheless, the solubility of ozone was limited at a certain temperature; thus, with the increase of ozone flow rate the COD removal efficiency would approach a maximum value. Furthermore, an ozone flow rate higher than the optimum value could result in unreacted O_3 being released from the system. The actual optimum ozone flow rate should be determined by experiments for individual treatment systems. Therefore, optimization of the ozone flow rate is necessary to minimize energy consumption and the amount of O_3 gas exhaust. With the economic factor into considering, 0.1 m^3/ h is the optimum ozone flow rate in this system.

3.5. Effect of the initial concentration of phenol

Fig. 6a and b showed that percentage removal of phenol and the reduction of COD in the combined US/O_3 system at different initial phenol concentration, respectively. The phenol removal after 240 min reaction was 99.1%, 90.5%, and 86.2% when initial phenol concentration was 1679, 3358 and 5037 mg/L, respectively. However, the removal efficiency of COD after 480min reaction was 93.8%, 82.5%, and 74.3% when initial COD was 4000, 8000 and 12,000 mg/L, respectively. Phenol degradation produced organic intermediates that were still measured as COD compounds, which lead to the phenol conversion rate was much higher than that of COD reduction.

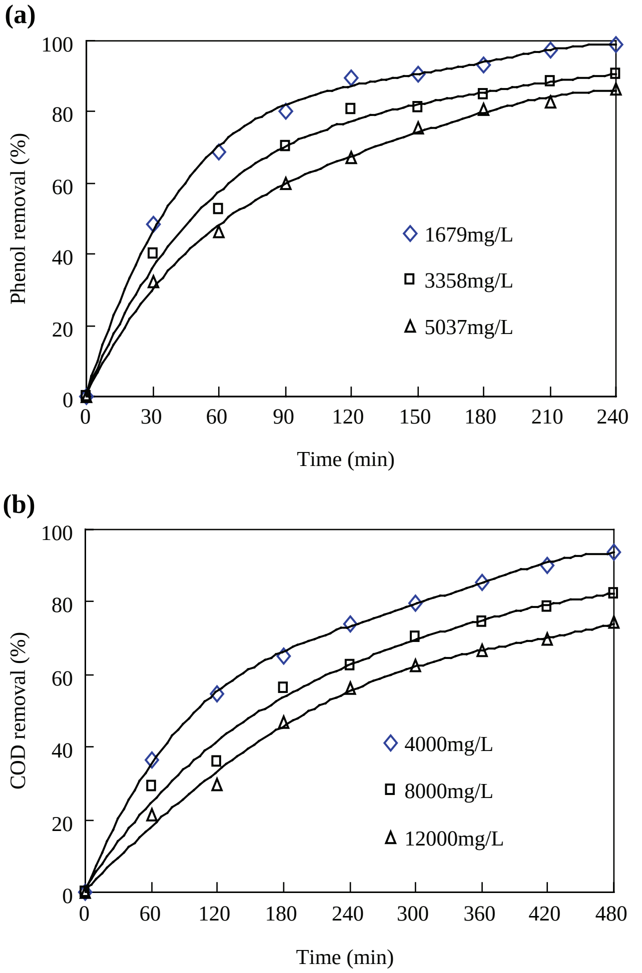


Fig. 6. (a) Percentage removal of phenol with reaction time at different initial phenol concentrations (the ozone flow = 0.1 m^3/h, room temperature, no pH adjustment). (b) The effect of initial concentration of phenol on the COD removal (the ozone flow = 0.1 m^3/h, room temperature, no pH adjustment).

Fig. 6b also showed that higher initial concentration corresponded to lower COD reduction. As the concentration of phenol increased, the cavities and ·OH radicals approached saturation. In addition, more free radical scavengers, such as CO_3^{2-}, might be generated when the initial concentration was high. The

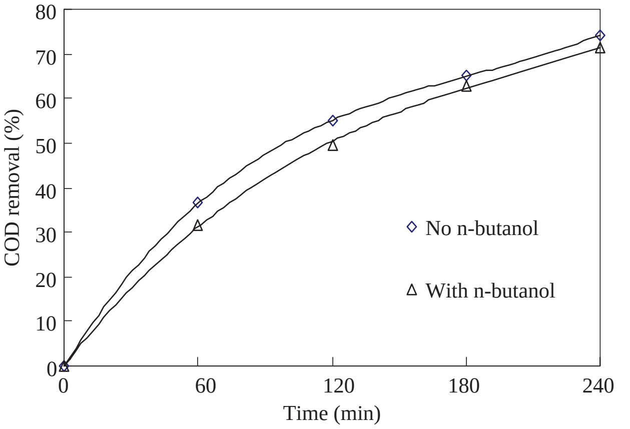


Fig. 7. The effect of hydroxyl radical scavenger (*n*-butanol) on the COD removal (COD_0= 4000 mg/L, ozone flow rate = 0.10 m^3/ h, room temperature, no pH adjustment).

competition between the free radical scavengers and carbonaceous substances for ·OH would become intense because of the nonselective reactivity of ·OH.

3.6. Effect of n-butanol

According to traditional catalytic ozonation theory, molecular ozone can oxidize organic substances via a direct route or can undergo decomposition via a chain reaction mechanism to produce free hydroxyl radicals. In order to demonstrate the role of hydroxyl radical in the degradation of phenol, the influence of hydroxyl radical scavenger was investigated. Because n-butanol was easy to react with hydroxyl radical and difficult to react with molecular ozone, it has been widely used as a probe to determine the role of hydroxyl radicals in degradation of pollutants [2]. Therefore, *n*-butanol was introduced here. In this experiment, 200 mg of *n*-butanol was added to 800 mL of reaction system with other reaction conditions kept constant.

Fig. 7 showed the results obtained when US/O_3 was carried out in the presence of n-butanol. After adding 250 mg/L of *n*-butanol, the COD removal efficiency decreased to 71.3%. Compared to the effect of US/O_3 without the addition of the radical scavenger, the decrease of the COD removal efficiency was not very obvious after adding *n*-butanol. The decrease extent was only 2.9% after 240 min reaction. Thus, it could be concluded that the phenol degradation by US/O_3 was mainly through directly ozonization, although free radicals such as ·OH play a role in the oxidation of phenol.

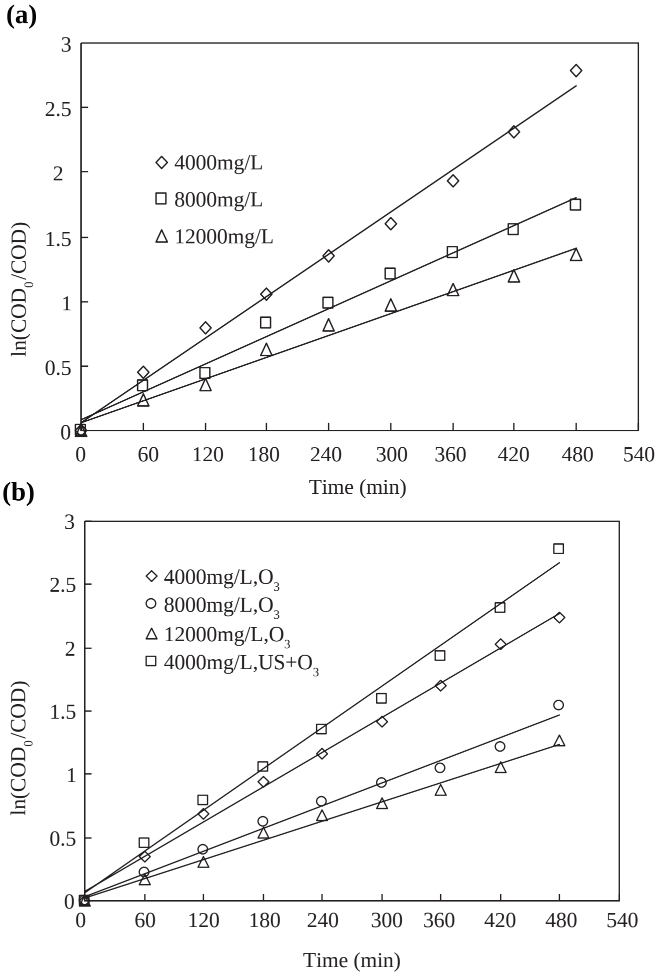
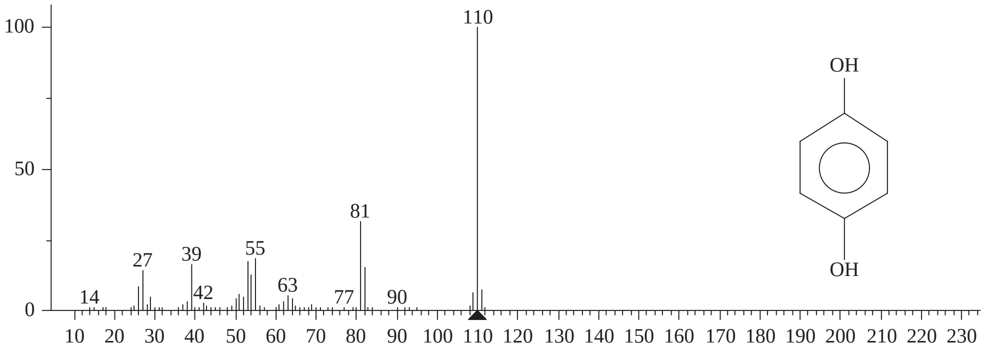


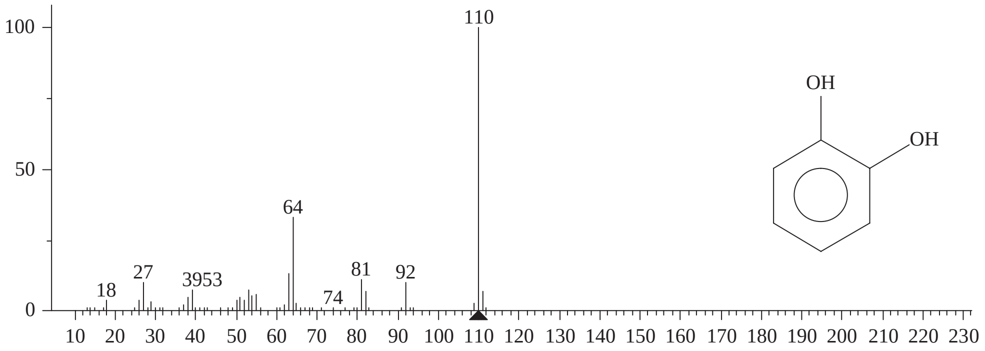
Fig. 8. (a) The kinetic of degradation of phenol by US/ ozonization. (b) The comparison of kinetic of phenol degradation by ozonization and US/O_3.

Table 1
Pseudo-first-order rate constants and rate equations of chemical reaction obtained as the function of initial COD.

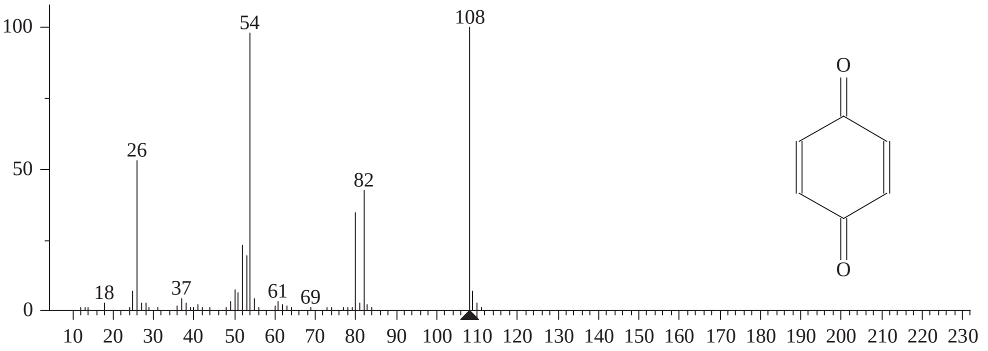
COD_0(mg/L)	Process mode	Reaction time (min)	Pseudo-first-order rate constant ($\times10^{-3}min^{-1}$)	Rate equation of chemical reaction
4000	O_3	480	4.8	$C = 3866.3e^{-0.0048t}$
8000	O_3	480	3.0	$C = 7701.7e^{-0.0030t}$
12,000	O_3	480	2.5	$C = 11737.7e^{-0.0025t}$
4000	O_3+US	480	5.4	$C = 3755.4e^{-0.0054t}$
8000	O_3+US	480	3.6	$C = 7339.3e^{-0.0036t}$
12,000	O_3+US	480	2.8	$C = 11244.8e^{-0.0028t}$



(mainlib) Hydroquinone



(mainlib) 1,2-Benzenediol



(mainlib) p-Benzoquinone

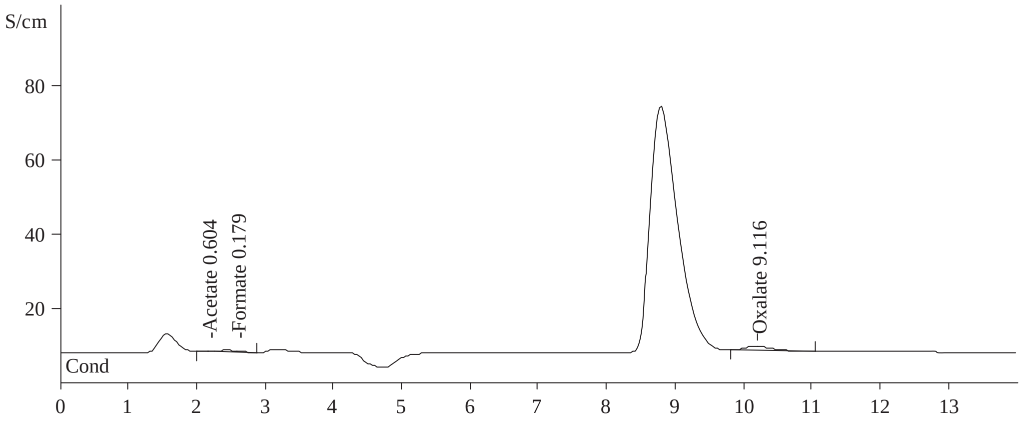


Fig. 9. Intermediates pictures of GC/MS and IC.

3.7. Kinetic study

From the COD data, a plot of $\ln(COD_0/COD)$ as a function reaction time led to a straight line from which the rate constant (k) was determined (Fig. 8a and Fig. 8b). The calculated pseudo-first-order rate constants are shown in Table 1. For all concentrations of phenol, the first order rate constants were calculated with correlation coefficient values of greater than 0.98.

For the purpose of discussion, k_{US}, k_{O3} and $k_{US/O3}$ define as the overall pseudo-first-order degradation rate constants for sonolysis, ozonalysis, and US/O_3, respectively. Both k_{O3} and $k_{US/O3}$ significantly decreased when the initial COD concentration increased from 4000 to 12,000 mg/L. To the same initial concentration, $k_{US/O3}$ was greater than the addition of k_{O3} and $k_{US}(=0)$. It indicatesd that there exist synergistic effect between ozonization and ultrasonic radiations.

Three factors likely explained the synergistic effect of O_3/US. First, the mechanical action of US enhances the dissolution of O_3 and the generation of additional ·OH, leading to a faster reaction rate with the organic substrate. Second, US improved the mass transfer of O_3, which resulted in more O_3 entering the liquid phase or reacting on the liquid–gas interface. Third, aeration of ozone might increase the turbulence of the aqueous solution and enable more related substances to migrate from the collapsing cavities into the bulk of the solution.

However, the synergistic effect was not pronounced. Maybe two factors can interpret it. First, the ultrasonic frequency was too low. Second, the ultrasonic does not directly contact with the wastewater but must penetrate a glass wall of the flask which could attenuate some of the ultrasonic radiations.

3.8. Reaction mechanism investigation

Hydroquinone, catechol, *o*-quinone, and *p*-benzoquinone was detected when these samples were injected into the GC/MS. Using the IC, some organic acid, such as formate, acetate, and oxalate was detected. The corresponding pictures of the intermediates are shown in Fig. 9. Based on the GC/MS and IC data, a tentative reaction mechanism was proposed. The possible degradation pathway for phenol is illustrated in Fig. 10.

The phenol was first oxidized to hydroquinone and catechol, and then the hydroquinone was oxidized to *p*-benzoquinone and catechol was oxidated to *o*-quinone quickly. Under the influence of ·OH and O_3, the aromatic rings may be opened to yield organic acid, such as formate, acetate, and oxalate. These organic acids were oxidized to carbon dioxide and water finally.

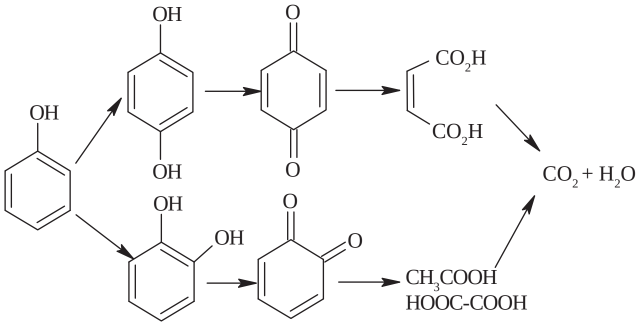


Fig. 10. Reaction pathway in the phenol degradation by US/O_3.

4. Conclusions

The US/O_3 process was an effective way to degrade high concentration phenol under such mild conditions as no adjustment the pH of phenol wastewater, normal pressure and room temperature (299 ± 2 K). After 480 min US/O_3 treatment, to the initial concentration of 1679 and 5037 mg/L phenol, the COD removal efficiency can reach 93.8% and 74.3%, respectively. This study showed ozonation in combination with 50 kHz ultrasound irradiation had synergistic effect on the COD removal of phenol. The COD removal efficiency of phenol fitted the pseudo-first-order rate kinetic model for both the US/O_3 and single ozonization process. The presence of hydroxyl radical had some influence on the degradation rate but the effect was not significant, which indicated that the primary mechanism of degradation was direct decomposition by ozone instead of the reaction involved in radicals formed in the US/O_3 process. Intermediates such as hydroquinone, catechol, and benzoquinone were detected and measure by GC/MS. A possible reaction to explain the degradation process was suggested.

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