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Catalytic degradation of phenol in sonolysis by coal ash and H_2O_2/O_3

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ABSTRACT

This study demonstrated that coal ash, as widely distributed solid waste disposal, would function as a media for organic pollutants removal in the presence or absence of H_2O_2/O_3 under ultrasonic radiation. Coal ash could act as a catalyst to generate $^{\bullet}OH$ radicals with the presence of H_2O_2/O_3 and consequently enhance the phenol degradation. Experimental results showed that when using coal ash as a catalyst under ultrasonic irradiation, 83.4% and 88.8% of phenol was degraded in the presence of H_2O_2 or O_3, respectively. The degradation rate of phenol would increase with increasing amount of O_3, while there was an optimal concentration of H_2O_2 (1.5 mM) for phenol degradation. Higher dosage of coal ash could result in higher phenol degradation rates. H_2O_2/coal ash/ultrasonic system could achieve better performance for phenol degradation under more acidic conditions, while more alkaline condition in O_3/coal ash/ultrasonic system favored phenol degradation. This study provides a new approach for wastewater treatment especially when contaminated with phenolic pollutants.

1. Introduction

Among the various wastes, phenolic compounds constitute a family of pollutants particularly toxic to the aquatic fauna and flora [1]. Phenol, the most common phenolic compound, is generally produced in the petrochemical, chemical and pharmaceutical industries [2]. Due to its toxic, carcinogenic, mutagenic, teratogenic and non-biodegradable properties [3], phenol has been classified as a priority pollutant in the list of United States Environmental Protection Agency (USEPA). Therefore, intensive attention has been paid to explore the degradation pathways to remove phenolic compounds from wastewater, especially with chemical methods [4–8].

Recently, using industrial solid wastes from another industry to treat wastewater is highly favored, and also helpful to reduce the solid waste disposal in the environment [9]. Coal ash is the fine powder formed from the mineral matter and power generation in coal, consisting of the noncombustible matter in coal and a small amount of carbon remaining from incomplete combustion. It is usually discarded as industrial wastes [10,11] and the annual production of coal ash is about 200 millions tonnes in China. In the past years, the physical applications of coal ash have been well explored [12], in which it was used for cement production and/or concrete products, structural fills or embankments, stabilization of waste materials, road base or subbase materials, flowable fill and grouting mixes, and mineral filler in asphalt paving. But still 70–75% leave unused, which was disposed in landfills or storage lagoons. Thus exploring the new application methods appears to be quite urgent for coal ash [13].

Previous studies reported that coal ash can be used as low-cost sorbents for removing heavy metals, organics and dyes from waters, and the research efforts are mostly focused on their adsorption property [13–15]. On the other hand, coal ash contains some metal oxides, such as Fe_2O_3, Al_2O_3 and MgO, and various amounts of silica, carbon, calcium and sulfur. The empirical formula for coal ash basing on the dominance of key elements is generally proposed as: $Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}$ [16]. The active elements, such as Fe, Mg, Al and Ti, present the coal ash a potential application as catalysts and accelerating materials for organic pollutants removal in wastewater treatment process in the presence of active reagents such as ozone and hydrogen peroxides [17].

Sonochemistry is an example of advanced oxidation processes (AOPs) [18,19], in which the destruction or mineralization of organic compounds by ultrasonic is depended on the oxidative degradation by free radical attack, particularly by hydroxyl radical, which is a far more powerful oxidizing agent than all commonly known oxidants [20]. Lately, ultrasonic was reported to be the energy source for organic pollutants degradation in the wastewater treatment process [7,20–26], and also for the degradation of phenol [27]. Hydrogen peroxide and ozone are two active materials that have been widely used in organic pollutants degradation in AOPs.

The application of using coal ash with the presence of H_2O_2 or O_3 under ultrasonic irradiation in the processes of phenol degradation was rarely studied, and neither for the optimal conducting parameters and mechanisms, which are important and

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interesting for wastewater treatment. Therefore, the aim of this study was to investigate the role of coal ash in phenol degradation under ultrasonic irradiation in the presence of H_2O_2 or O_3. We in particular made efforts for the adsorption and degradation of phenol by coal ash at aqueous suspension under different conditions. More importantly, the reaction conditions, including the concentrations of H_2O_2/O_3, ash dosages, and pH values, were systematically investigated. Results from this study may propose a new approach for the application of coal ash in wastewater treatment process for organic pollutants removal, and also present an economical way for their disposal.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical reagent grade except acetonitrile, which was HPLC grade and used as the component of mobile phase for phenol analyses. All of them were used without further purification. Phenol was purchased from Sigma–Aldrich Co., and the rest were obtained from Guangzhou Chemical Inc., China. All solutions were prepared using 18 MΩ Milli-A water from a Millipore system.

2.2. Characterization of coal ash

The coal ash used in this study was a clinker ash produced from the thermal power station in Hunan, China. The coal ash was sieved to collect the small particles in the sizes range of 100–200 μm. The microstructures of the samples were characterized using a LEO scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX) as well as a computer controlled image analyzer. The specific surface area of the coal ash was measured by the Brunauer–Emmett–Teller (BET) method in which the N_2 adsorption at 77 K was applied and Carlo Erba Sorptometer (1800) was used.

2.3. Experimental setup and procedure

All the ultrasonic degradation experiments were performed in an ultrasound cleaning bath KQ-500DB (Ultrasound Instrument Co., Ltd., Kunshan, China) under the constant temperature of $25 \pm 1\,^{\circ}C$ and ambient air pressure. The working frequency and power were 40 kHz and 500 W, respectively. The internal dimension of the ultrasonic cleaning bath was 50 cm × 30 cm × 15 cm with a volume of 22.5 L.

Adsorption of phenol on coal ash was determined by the batch experiment. A fixed amount of ash (0.1 g) was added into 10 mL of phenol solution at varying concentrations in glass tubes with an initial pH 6 adjusted with 1N of HCl or 1N of NaOH. Then the tubes were agitated for 24 h at 200 rpm in a thermostatic shaker bath and maintained at the temperature of $25 \pm 1\,^{\circ}C$. The concentrations of phenol after 24 h were measured with high performance liquid chromatography (HPLC) and the adsorbed amount of phenol was determined according to the mass balance.

All the degradation experiments by coal ash were conducted in 250 mL Pyrex vials at room temperature ($25 \pm 1\,^{\circ}C$) and the reaction suspension were placed into the ultrasonic generator. 1N of HCl or 1N of NaOH was used to adjust the initial pH values of the reaction suspension. To investigate the effect of H_2O_2 or O_3 on phenol degradation by coal ash under ultrasonic condition, the reaction suspension was prepared by adding given dosage of coal ash (1.0 g/L) into 100 mL of phenol solution with a concentration of 10 mg/L. After stirred for 30 min to establish an adsorption/desorption equilibrium status, H_2O_2 was added with the desired concentrations (0.5, 1.0, 1.5, 2.0, and 2.5 mM, respectively) or different flow rate of ozone/oxygen gas stream (0.2, 0.5, 1.0, and 2.5 dm^3/min) was pumped at the initial pH 6. Ozone was generated from dried pure oxygen by corona discharge using an ozone generator (Ozonair RXO-5), which can produce 12% ozone concentration (w/w) in the oxygen enriched gas stream. To test the effect of ash dosage on phenol degradation, 0.2, 0.6, 1.0, 2.0, and 3.0 g/L ash was added respectively to conduct the experiments at the initial pH 6 with 1.5 mM H_2O_2 or 1.0 dm^3/min O_3. For studying the effects of initial pH values, 10 mg/L phenol degradation by 1.0 g/L coal ash with 1.5 mM H_2O_2 or 1.0 dm^3/min O_3 was tested under different pH conditions adjusted with 1N of HCl or 1N of NaOH.

2.4. Analytical methods

At given intervals, the samples were withdrawn by using a 5 mL glass syringe and immediately filtered through a 0.2 μm syringe filter (Millipore, cellulose acetate membrane) to remove particles before analysis. Phenol in the solution was analyzed by high performance liquid chromatogram (HPLC, Agilent 1100 LC). The column used in HPLC was a Merck LichroCART 250-4 (250 mm length, 4 mm diameter), packed with LiChrospher 100 RP-18e. A mixture of acetonitrile and deionized water (70:30, v/v) was used as the mobile phase at a flow rate of 1.0 mL/min. An aliquot of 50 μL sample was injected using Rheodyne valve and analyzed at a wavelength of 270 nm with an UV detector (Perkin Elmer, Series 200). The detection limit for phenol was 0.05 mg/L and the retention time of phenol was 6.8 min with this analysis method. The generated $^{\bullet}OH$ radicals were determined with the method of indirect capture by 2-propanol, which was previously described in detail in Ref. [28]. The pH values were monitored with a pH meter (pHs-3B, Cany, Shanghai, China).

3. Results and discussion

3.1. Properties of the coal ash

The SEM image is shown in Fig. 1, from which it can be seen that the coal ash is surface roughness and porous. The surface elements composition of the coal ash was determined by EDX method, and the results are listed in Table 1. From Table 1, we can see that the highest contents in coal ash are O and Si, and followed by Al and Fe. The BET surface area of the coal ash was 25.8 m^2/g, determined by BET–BJH method.

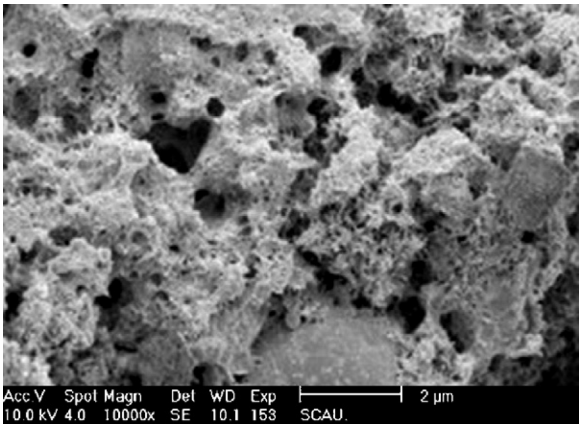

Fig. 1. The SEM micrograph of coal ash.

Table 1
Elements analysis of coal ash by EDX method.

Element	O	Si	Fe	Al	Mg	K	Ca	Ti	P	S	V
Conc. (g/kg)	383.7	222.8	73.5	81.3	44.5	9.3	79.3	25.1	9.8	2.5	1.6

3.2. The adsorption behavior of coal ash

The adsorption isotherm of phenol on coal ash is shown in Fig. 2, which was well fitted to the Langmuir adsorption model as Eq. (1)

$$\frac{C_e}{\Gamma} = \frac{1}{\Gamma_{\max}} \cdot C_e + \frac{1}{K_a \cdot \Gamma_{\max}} \tag{1}$$

where C_e is the equilibrium concentration in the solution in mM, K_a is the adsorption equilibrium constant in L/mol, and $\Gamma_{\max}$ is the saturated adsorption capacity in mol/g. The calculated saturated adsorption amount ($\Gamma_{\max}$) of phenol onto coal ash was 4.69×10^{-4} mol/g and the adsorption equilibrium constant (K_a) was 37.73 L/mol with the correlative coefficient R of 0.9962.

3.3. Degradation of phenol by coal ash under different conditions

Fig. 3A shows the degradation of phenol at an initial concentration of 10 mg/L by 1.0 g/L coal ash under different conditions, and Fig. 3B shows the corresponding concentrations of generated $^{\bullet}$OH radicals at the reaction time of 300 min. Data shows that the concentration of phenol remained constant (Fig. 3A, curve a) when phenol solutions were irradiated with ultrasonic without any addition, which indicates that the structure of phenol was fairly stable under ultrasonic conditions. Though Petrier et al. reported that $^{\bullet}$OH radicals and H_2O_2 can be sonochemically formed from water [29], no $^{\bullet}$OH radicals was detected in this test (column a in Fig. 3B). When coal ash was added in 10 mg/L of phenol solution in the case of stirring instead of ultrasonic, the concentration of phenol did not change (Fig. 3A, curve b) and none of $^{\bullet}$OH was generated (column b in Fig. 3B). When the same solution was radiated with ultrasonic, 18.1% of phenol was degraded by coal ash after 300 min (curve c, Fig. 3A). This may be the consequence of the presence of coal ash, which increased the nucleation sites for cavitation bubble and thus resulted in more $^{\bullet}$OH generation (5.67 μM at the reaction time of 300 min, column c, Fig. 3B) although coal ash itself has no catalytic property for $^{\bullet}$OH generation [30]. Previous studies [31–33] demonstrated that many organic pollutants could be degraded owing to $^{\bullet}$OH formation from the decomposition of O_3 or H_2O_2 by ultrasonic radiation. As shown in Fig. 3A, under ultrasonic radiation without coal ash, the removal of phenol achieved 25.8% and 35.7% in the presence of H_2O_2 or O_3, respectively (curves d and e, Fig. 3A). While in the presence of coal ash but absence of ultrasonic, using H_2O_2 or O_3 can result in 28.1% and 22.5% phenol degradation (curves f and g, Fig. 3A), due to the possible Fenton reaction by Fe in ash with H_2O_2 or O_3. In the above four reaction conditions, the generated $^{\bullet}$OH radicals were all about at a concentration of 10 μM (Fig. 3B).

However, phenol degradation could be significantly increased by the presence of H_2O_2 or O_3 with coal ash under ultrasonic radiation. The removal of phenol approached 83.4% and 88.8% when 2.0 mM H_2O_2 or 1.0 dm^3/min O_3 were respectively introduced into the reaction suspension added with 1.0 g/L coal ash under ultrasonic radiation (curves h and i, Fig. 3A). Clearly, under ultrasonic irradiation the coexistence of coal ash and H_2O_2/O_3 would lead to much higher phenol degradation rate than the either sole presence of coal ash or H_2O_2/O_3. This may be explained by the catalytic reaction induced by ultrasonic radiation as equations of (3) and (4). The presence of metal ions (M^{n+}) in the coal ash contributed to the catalytic properties, which was a consequence of more $^{\bullet}$OH generation

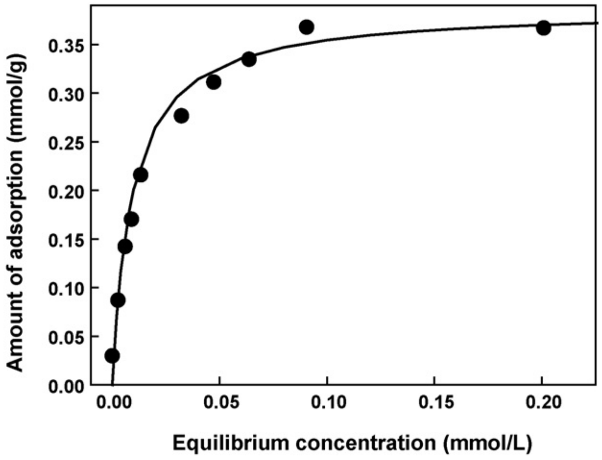

Fig. 2. The adsorption isotherm of phenol on coal ash obtained by plotting the equilibrium concentration (C_e) vs. the adsorbed amounts of phenol (Γ).

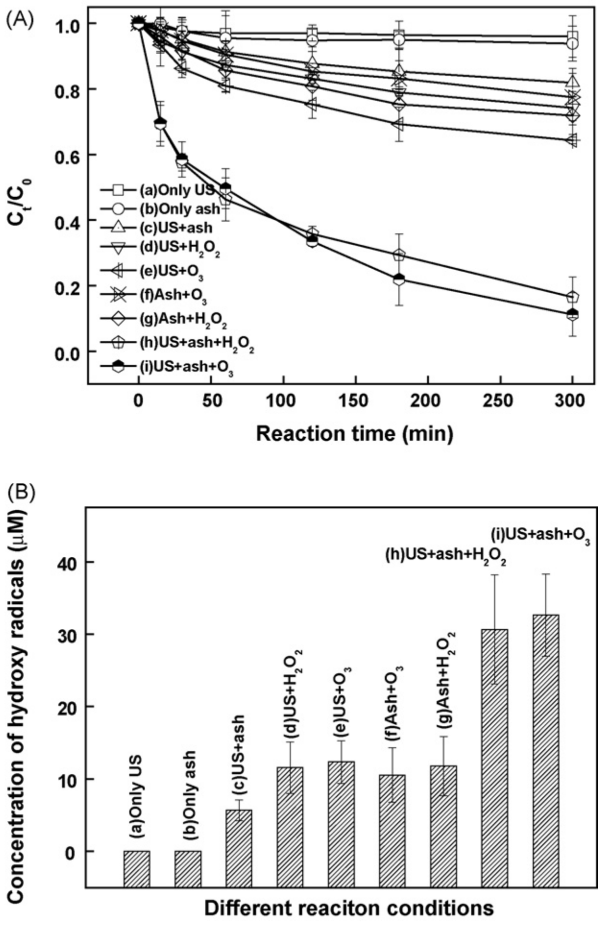

Fig. 3. Degradation of 10 mg/L phenol by 1.0 g/L coal ash at pH 6, 25 ± 1 °C and normal pressure under different conditions (A); and the concentration of generated $^{\bullet}$OH at reaction time of 300 min with the same reaction conditions (B).

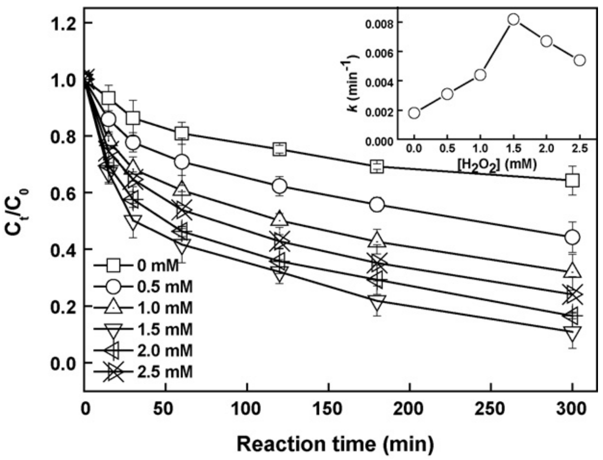

Fig. 4. The effect of H_2O_2 concentration (mM) on phenol (10 mg/L) degradation by 1.0 g/L coal ash at pH 6, 25 ± 1 °C and normal pressure. (The inset figure presents the relationship between kinetics constants of phenol degradation and H_2O_2 concentration.)

(30.6 and 32.6 μM respectively, columns h and i in Fig. 3B) and the producing processes followed Eqs. (2)–(11). As indicated by Eq. (12), the more $^\bullet$OH, the more phenol could be accordingly degraded.

For reaction with H_2O_2 [32–34]:

$$H_2O +))) \rightarrow {}^\bullet OH + H^+ \tag{2}$$

$$M^{n+} + 2H_2O_2 + H^+ +))) \rightarrow M^{(n-1)+} + {}^\bullet OOH + 2H_2O \tag{3}$$

$$M^{(n-1)+} + H_2O_2 + H^+ +))) \rightarrow M^{n+} + {}^\bullet OH + H_2O \tag{4}$$

$$M^{n+} + 2H_2O_2 \rightarrow M\text{-}O_2H^{2+} + {}^\bullet OOH \tag{5}$$

$$M\text{-}O_2H^{2+} +))) \rightarrow M^{(n-1)+} + {}^\bullet OOH \tag{6}$$

$$2{}^\bullet OOH +))) \rightarrow O_2 + 2{}^\bullet OH \tag{7}$$

For reaction with O_3 [32–34]:

$$O_3 + H_2O +))) \rightarrow O_2 + 2{}^\bullet OH \tag{8}$$

$$M^{n+} + O_3 + 2H_2O +))) \rightarrow M\text{-}O_2H^{2+} + 3{}^\bullet OOH + H^+ \tag{9}$$

$$M\text{-}O_2H^{2+} +))) \rightarrow M^{(n-1)+} + {}^\bullet OOH \tag{10}$$

$$2{}^\bullet OOH +))) \rightarrow O_2 + 2{}^\bullet OH \tag{11}$$

With the more production of $^\bullet$OH, phenol can be degraded at a much higher rate:

$$\cdot OH + \text{Phenol} \rightarrow \text{Degradation products} \tag{12}$$

Besides the catalytic function of coal ash for generating more $^\bullet$OH radicals that resulted in high degradation rate of phenol, the ultrasonic cavitation was another factor that accelerating the degradation process. As shown in Fig. 1, the surface of coal ash is of roughness, and the surface morphology was porous. Tuziuti et al. recently reported that the existence of particle in liquid could provide nucleation sites for cavitation bubble due to the surface roughness [35]. This phenomenon has also been qualitatively described in the previous study of sonochemistry [36]. Therefore, under ultrasonic irradiation, the coexistence of coal ash and H_2O_2/O_3 could form more nucleation sites for cavitation bubble when compared to the system without coal ash.

3.4. *Effect of H_2O_2 concentration on phenol degradation by H_2O_2/coal ash/ultrasonic*

Fig. 4 shows the dependence of phenol degradation on H_2O_2 concentration with 1.0 g/L coal ash under ultrasonic radiation at the initial pH 6. The degradation of phenol by coal ash/H_2O_2 fit the first-order kinetics pretty well. When H_2O_2 concentration was 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mM, the first-order kinetics constant (*k*) were 1.8×10^{-3} ($R = 0.863$), 3.3×10^{-3} ($R = 0.900$), 4.4×10^{-3} ($R = 0.874$), 8.2×10^{-3} ($R = 0.919$), 6.7×10^{-3} ($R = 0.896$), and $5.4 \times 10^{-3}\ \text{min}^{-1}$ ($R = 0.889$), respectively. Data obviously suggested that phenol degradation was significantly influenced by H_2O_2 concentration. The constant *k* for phenol degradation increased from 1.8×10^{-3} to $8.2 \times 10^{-3}\ \text{min}^{-1}$ as a consequence of increasing H_2O_2 concentration from 0 to 1.5 mM. The further increase of the H_2O_2 concentration from 1.5 to 2.5 mM slowed down the degradation rate of phenol. The initial increase in phenol degradation was due to the increased concentration of $^\bullet$OH formed by H_2O_2 and coal ash, while when H_2O_2 concentration was too high, the produced $^\bullet$OH may be consumed via other ways such as the scavenging effects of H_2O_2 and the recombination of $^\bullet$OH followed Eqs. (13)–(15) [37,38]. Moreover, the excess H_2O_2 could occupy the active sites of coal ash and inhibited the effect of cavitation bubble, which may also decrease the phenol degradation rate

$$H_2O_2 + {}^\bullet OH \rightarrow {}^\bullet OOH + H_2O \tag{13}$$

$${}^\bullet OOH + {}^\bullet OH \rightarrow H_2O + O_2 \tag{14}$$

$$2{}^\bullet OH \rightarrow H_2O_2 \tag{15}$$

3.5. *Effect of O_3 flux on phenol degradation by O_3/coal ash/ultrasonic*

The dosage of O_3 also had obvious effect on phenol degradation in the presence of coal ash under ultrasonic radiation. As shown in Fig. 5, the reaction constant *k* increased from 1.8×10^{-3} to 3.3×10^{-3}, 5.0×10^{-3}, 7.9×10^{-3}, and $9.9 \times 10^{-3}\ \text{min}^{-1}$ when O_3 flux increased from 0 to 0.2, 0.5, 1.0 and 2.5 dm^3/min, respectively. Results suggests that with increased flux of O_3, phenol can be more effectively degraded by coal ash. Different from the system of H_2O_2/coal ash/ultrasonic, no optimal flux of O_3 was observed for phenol degradation in the O_3/coal ash/ultrasonic system over the range we tested in this study. As discussed above, O_3 can participate in the reaction process of $^\bullet$OH generation, therefore, more O_3 was added, the more $^\bullet$OH radicals would be formed as Eqs. (8)–(11). Since O_3 would not consume the generated $^\bullet$OH, thus the more O_3 introduced in the reaction solutions, the more $^\bullet$OH radicals would be generated, resulting in higher *k* constant for phenol degradation. Data shows that the degradation rates of phenol at the O_3 flux of 1.0 and 2.5 dm^3/min were close to each other. This may be due to

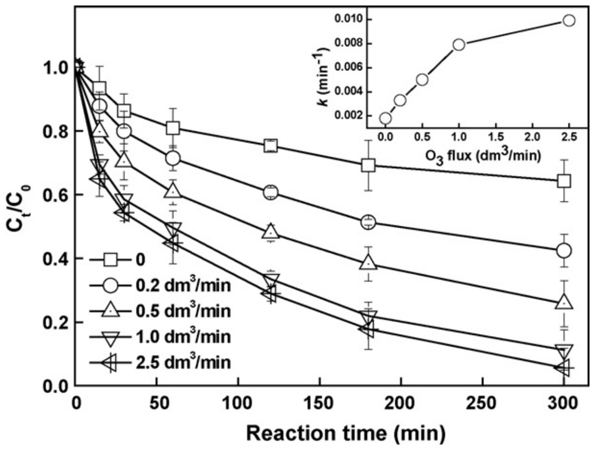

Fig. 5. The effect of O_3 flux on phenol (10 mg/L) degradation by 1.0 g/L coal ash at pH 6, 25 ± 1 °C and normal pressure. (The inset figure presents the relationship between kinetics constants of phenol degradation and O_3 flux.)

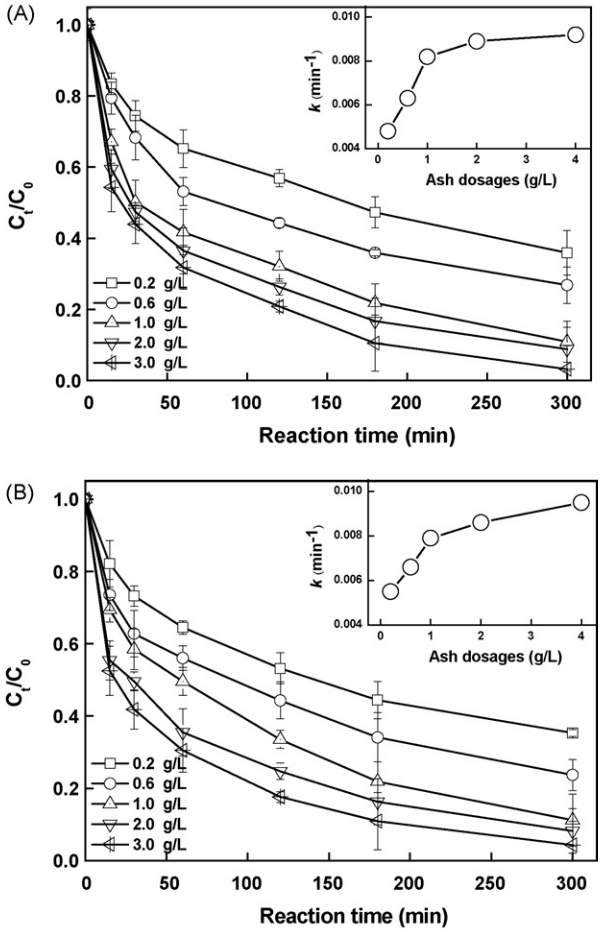

Fig. 6. The effect of ash dosage on 10 mg/L phenol degradation at pH 6, 25 ± 1 °C and normal pressure. (A: H_2O_2/coal ash/ultrasonic system; B: O_3/coal ash/ultrasonic system.)

the fact that 1.0 dm^3/min of O_3 was in excess for the reaction with 1.0 g/L coal ash used herein, and more O_3 flux than 1.0 dm^3/min cannot produce more $^{\bullet}OH$ radicals.

3.6. Effect of ash dosage on phenol degradation by H_2O_2 (or O_3)/coal ash/ultrasonic

Fig. 6 shows the results of phenol degradation in the system of H_2O_2 (or O_3)/coal ash/ultrasonic in the case of different dosages of coal ash. The degradation rate of phenol increased with increased dosage of coal ash for both H_2O_2 and O_3. As to H_2O_2/coal ash/ultrasonic (Fig. 6A), when the dosages increased from 0.2 to 0.6, 1.0, 2.0 and 3.0 g/L, the kinetics constant k increased from 4.8×10^{-3} to 6.3×10^{-3}, 8.2×10^{-3}, 8.9×10^{-3}, and 9.2×10^{-3} min^{-1}, respectively. For O_3/coal ash/ultrasonic with the same dosages (Fig. 6B), k increased from 5.5×10^{-3} to 6.6×10^{-3}, 7.9×10^{-3}, 8.6×10^{-3}, and 9.5×10^{-3} min^{-1}, respectively. As the system was added with more coal ash, the more active sites could be involved for the reaction of generating $^{\bullet}OH$ radicals. However, from the inset figures in Fig. 6, in the range of 0.2–1.0 g/L, the k values displayed a close linear correlation with the dosage of coal ash. While when the dosages were increased beyond 1.0 g/L, k values increased at a much slower rate. This may be due to the fact that 1.0 g/L ash was adequate for reacting with 1.5 mM H_2O_2 or 1.0 dm^3/min O_3, while the enhancement for phenol degradation at a coal ash concentration of higher than 1.0 g/L was likely a consequence of ash/ultrasonic effects rather than $^{\bullet}OH$ radicals.

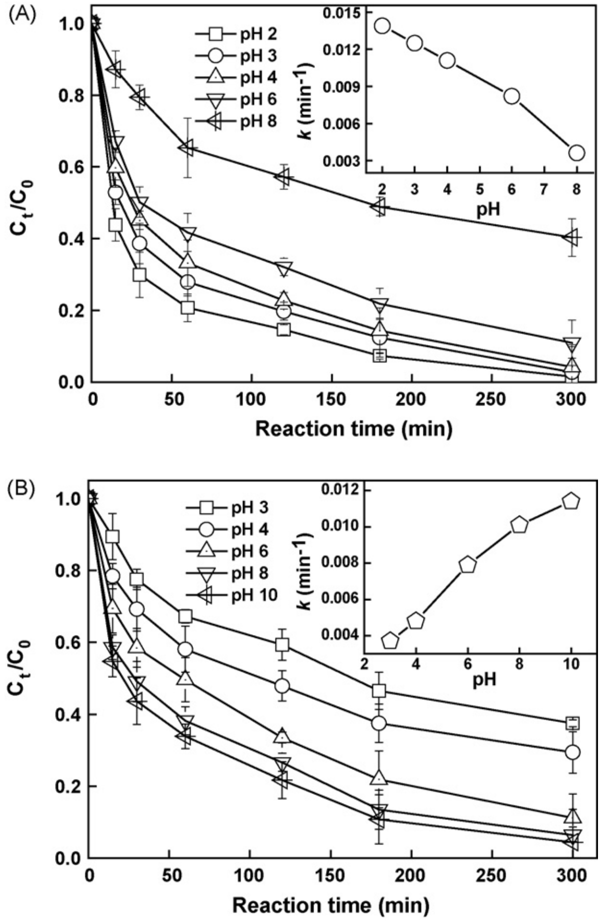

Fig. 7. The effect of initial pH values on phenol degradation in H_2O_2/coal ash/ultrasonic system (A), and O_3/coal ash/ultrasonic system (B). (Initial concentration of phenol: 10 mg/L; dosage of coal ash: 1.0 g/L; H_2O_2: 1.5 mM; O_3: 1.0 dm^3/min.)

3.7. Effect of pH values on phenol degradation by H_2O_2 (or O_3)/coal ash/ultrasonic

To investigate the effect of pH on phenol degradation by H_2O_2 (or O_3)/coal ash/ultrasonic, the pH of reaction solution was adjusted to the desired values by 1N of HCl or 1N of NaOH. Fig. 7A (with H_2O_2) and B (with O_3) show the degradation kinetics of phenol under different pH values and the inset figures plotted the relationship between pH and kinetics constant k. The changing pathway of pH values during the degradation processes in the two systems is presented in Fig. 8. In Fig. 7A, the reaction kinetics constant k increased with decreased pH values, i.e. the lower pH value of reaction solution may more favor phenol degradation in H_2O_2/coal ash/ultrasonic system. Previous literatures reported that the optimal initial pH was around 3 for organic pollutants degradation in Fenton-like reaction [39]. In this study, due to the existence of Fe(III) in coal ash, Fenton-like reaction may occur for generating $^{\bullet}OH$ radicals as discussed above. However, other $^{\bullet}OH$ generation mechanisms can also contribute to phenol degradation. When more H^+ presented in the reaction suspension (i.e., lower pH), more Fe(III) can be dissolved to take part in the Fenton-like reaction to form $^{\bullet}OH$ as Eqs. (3) and (4), consequently resulted in higher degradation rate of phenol. Because of the consumption of H^+ for generating $^{\bullet}OH$, the pH values in H_2O_2/coal ash/ultrasonic increased throughout the entire degradation process for all initial pH values (Fig. 8A).

As to O_3/coal ash/ultrasonic system for phenol degradation, Fig. 7B shows that with increasing initial pH values in the

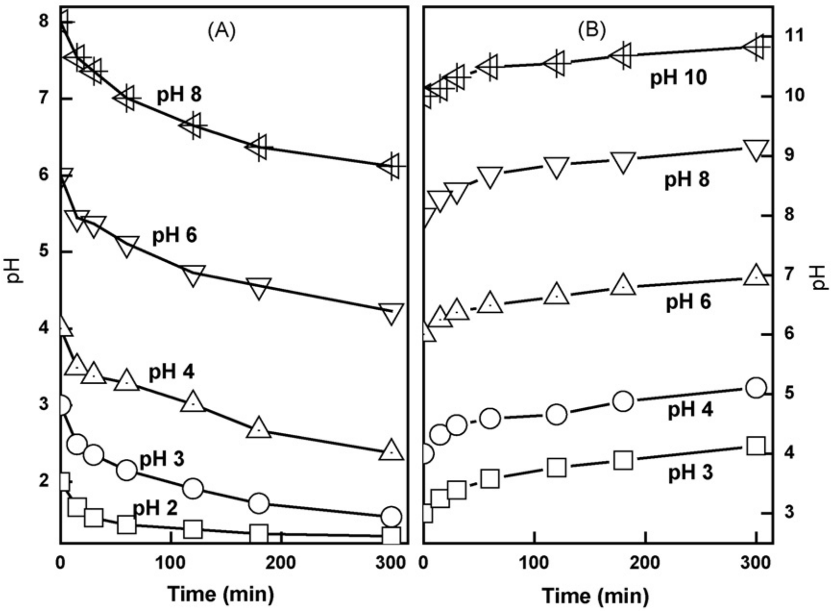

Fig. 8. The changing pathway of pH values during phenol degradation process in H_2O_2/coal ash/ultrasonic system (A), and O_3/coal ash/ultrasonic system (B) under the same reaction conditions as in Fig. 7.

range of this study, *k* values for phenol degradation increased accordingly. When the pH value increased to 10, the *k* value reached 11.4×10^{-3} min^{-1}, which was three times higher than that for pH 3 (3.7×10^{-3} min^{-1}). This indicates that the alkaline condition is more favorable for phenol degradation than acidic condition in O_3/coal ash/ultrasonic system. Indicated by Eq. (9), H^+ was produced accompanied $^{\bullet}OH$ generation at the consumption of O_3. The pH values of O_3/coal ash/ultrasonic system decreased throughout the degradation process as shown in Fig. 8B. The higher pH values, i.e. higher concentration of OH^- in solution, could favor the reaction of $^{\bullet}OH$ generation and thus can enhance the degradation rate of phenol. Furthermore, in the case of low pH, $^{\bullet}OH$ would be favorable to react with O_3. The recombination of $^{\bullet}OH$ radicals with O_3 would be significantly accelerated when great amount of H^+ presented in the reaction suspension, which might be a possible reason for the low decomposition rate of phenol in acidic solutions.

4. Conclusions

With ultrasonic radiation, phenol can be effectively degraded by coal ash with the presence of H_2O_2 or O_3. In the degradation processes, coal ash acted as a catalyst to accelerate the degradation of phenol with the presence of H_2O_2 (or O_3). Moreover, coal ash can provide active sites for phenol degradation. Higher flux of O_3 can increase phenol degradation rate in O_3/coal ash/ultrasonic system, however, too high concentration of H_2O_2 in H_2O_2/coal ash/ultrasonic system would reduce the degradation rate. Higher dosages of ash can increase phenol degradation rates. Increasing the initial pH values of the reaction suspension would increase phenol degradation rate in O_3/coal ash/ultrasonic system, whereas decrease phenol degradation rate in H_2O_2/coal ash/ultrasonic system.

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