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Mineralization of phenol by ozone combined with activated carbon: Performance and mechanism under different pH levels

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ABSTRACT
The degradation of phenol using ozone with activated carbon (O3/AC system) was investigated in this study. The O3/AC system was also compared with the single O3 and AC systems. The total organic carbon (TOC) removal efficiency in the O3/AC system was roughly 26% and 30% higher than the single AC and O3 systems, respectively. It was demonstrated that the phenol degradation rate and TOC removal efficiency were significantly affected by the ozone concentration, AC dosage, and solution pH. The pseudo-first-order and pseudo-second-order kinetic models were fitted to identify the mechanisms of the phenol removal process. The results of Scanning Electron Microscopy, Brunauer-Emmett-Teller, and Fourier-transform infrared spectroscopy of raw and used AC indicated that the surface morphology, microstructure, and functional group properties had been changed during the reaction process. The possible O3/AC system mineralization mechanism for phenol removal was tentatively proposed using scavenging active species such as \( \cdot\)OH, O\(_2\)/C\(_1\)/C\(_0\), and H\(_2\)O\(_2\). The transformation byproducts generated during the application of the O3/AC system were identified by High Performance Liquid Chromatography and Gas Chromatography–Mass Spectrometry analyses. Therefore, the mineralization pathway of phenol in detail was proposed in acidic (pH 3.0) and alkaline (pH 11.0) conditions. This study provided a more systematic explanation of the mineralization mechanism for phenol in the O3/AC system.

1. Introduction
Phenolic compounds are generally considered as one of the most hazardous organic pollutants in refinery wastewater given they are highly toxic even at low concentrations [1]. Phenol, a common phenolic compound, could cause damage to the liver and kidney in humans [2]. Phenol poses serious problems to the environment due to its low biodegradability, high biotoxicity, and cumulative effects [3]. Therefore it has been registered as a priority pollutant by the US Environmental Protection Agency (USEPA) with a permissible limit of 0.1 mg/L in wastewater [4].

Several treatment methods have been proposed for purifying wastewater which contains phenol, including adsorption [5], biodegradation [6], photocatalytic degradation [7], Fenton’s reaction [8], electrochemical method [9], and ozonation process [10]. Among these treatment methods, ozonation is the most widely available treatment method because of its validity and availability [11]. Ozone can easily react with organic pollutants, but it has a low reaction rate with saturated organic compounds [12], which restricts its chemical oxidation efficiency. Additionally, a huge dosage of O\(_3\) should be employed in order to mineralize organic pollutants as much as possible, leading to a huge increase in treatment costs [11]. Currently, it was found that the simultaneous use of O\(_3\) with porous materials such as silica-gel [13], activated carbon [14], and zeolites [15], could enhance the mineralization rate and efficiency of phenol in wastewater and greatly reduce the processing costs.
Heterogeneous catalytic ozonation based on activated carbon (AC) can facilitate a cleaner process relative to other methods because of its low cost, no metal ions leaching, and various pore structures. This method also does not require intricate calculations nor the application of reagents. It was reported that the simultaneous use of an O₃ and activated carbon (O₃/AC) system could provide a better removal efficiency for chlorophyll, dissolved organic carbon, and antibiotics than the single O₃ oxidation process [11,16]. In fact, the presence of AC during the ozonation of organic pollutants can enhance the whole removal of total organic carbon (TOC) [17]. The synergistic effect of O₃ and AC was considered as a promising technology for removing organic pollutants from aqueous solutions.

In previous studies, the mechanisms of the O₃ reaction with phenol has been studied and the possible reaction pathways have been described [18]. Moreover, AC in the O₃/AC system can facilitate adsorption as well accelerate the degradation of O₃ [19]. However [19], only emphasized the enhancement effects of activated carbon and discussed the effects of operational factors but the mineralization pathway of phenol in the collaborative system was not clearly illustrated in detail [14,19]. It was reported that the hydroxide ion (OH⁻) can promote the decomposition of O₃ [20], and the decay of O₃ formed secondary oxidants such as hydroxyl radicals (⋅OH). This secondary oxidant can enhance the treatment efficiency in alkaline conditions [21]. Hence, the pH parameter may have the greatest influence on the mineralization pathway of phenol in the O₃/AC system. To further improve the removal efficiency and rate of removal of phenol as well as reduce the treatment costs, the mechanisms and pathways of the mineralization for phenol in the O₃/AC system needed a more detailed description and investigation.

The aim of this study was to determine the mineralization mechanisms and pathways of phenol by combining O₃ and AC from wastewater. The specific objectives of this study were: (1) to explore the effects of the reaction operating conditions of the O₃/AC system on treating phenol wastewater; (2) to clarify the mineralization pathways of phenol in acidic (pH 3.0) and alkaline (pH 10.0) conditions; (3) to identify and analyze the accumulation regularity of the intermediate products produced during the degradation process.

2. Materials and methods

2.1. Materials

Phenol (99.0%), ethylenediaminetetraacetic acid (EDTA; 99.5%), tert-butanol (99.5%), and ferric sulfate (Fe₂SO₄; 99.5%) used in experiment were supplied by Sinopharm (Sinopharm Chemical Reagent Co., Ltd., China). A phenol stock solution (200 mg/L) was prepared by adding tert-butanol (99.5%), and ferric sulfate (Fe₂SO₄; 99.5%) used in experiments. The raw AC (852.1 m²/g) were purchased from Sigma Aldrich (Sigma Aldrich Co. Ltd., USA). The surface morphologies of the AC were visualized using a Scanning Electron Microscopy (SEM) analyzer (SXE-550, Shimadzu, Japan). Table 1 Characteristics of the activated carbon samples.

| Samples     | S_BET (m²/g) | S_text (m²/g) | S_micro (m²/g) | Micropore volume (cm³/g) |
|-------------|--------------|---------------|---------------|--------------------------|
| Raw AC      | 852.1        | 130.8         | 721.3         | 0.349                    |
| Used AC     | 865.4        | 135.0         | 730.4         | 0.354                    |

AC was washed with ultrapure water, and then freeze-dried at −55 °C for 12 h under a vacuum to obtain adsorption saturated AC. These samples were named after the saturation treatment (AC-AS). All chemicals used in this study were analytical grade.

2.2. Degradation experiment

The schematic diagram of the experimental setup is shown in Fig. 1. Ozone was generated from dried oxygen gas with a laboratory O₃ generator (CF-G-3-10 g, QingDao Guolin, China). The working volume of the reactor was 2.0 L and tetrafluoroethylene tubing was used for all connections between the generator and reactor. Ozone gas was continuously bubbled into the reactor by a titanium alloy porous diffuser, and the O₃ concentration in the gaseous form was determined with the iodometric method as described in Standard Method [22]. Samples were taken at consistent time intervals and filtered through a 0.22 μm membrane to determine the phenol concentration, total organic carbon (TOC), and oxidation by-products. The ozonation experiments were stopped by bubbling a stream of nitrogen (N₂) for 5 min. Each experiment was conducted in triplicate and only the average data were recorded and reported.

2.3. Adsorptive dynamic experiment

The adsorption phenol tests for different AC dosages were run under the same conditions in the reactor. In addition, the adsorption experiment was performed to determine the kinetics of phenol removal by AC adsorption. Approximately 0.6 g of AC was added to 200 mL of a phenol (100, 200, 300, and 400 mg/L) solution in the reactor under continuously stirred conditions for 40 h at 150 r/min. In order to investigate the adsorption process of phenol onto AC, the pseudo-first-order and pseudo-second-order kinetic models were given in Eqs. (1) and (2) to determine the mechanisms of the adsorption process [23].

\( Q_e = Q_0 - \frac{Q_0}{k_f t} \)  
\( Q_0 = \frac{k_s Q_{et}}{1 + k_s Q_{et}} \)

where, \( Q_0 \) and \( Q_e \) are the amount of phenol adsorbed (mg/g) at equilibrium and at time (h); \( k_f \) is the pseudo-first-order equilibrium rate constant (h⁻¹); \( k_s \) is the pseudo-second-order rate constant (g/mg h⁻¹).

2.4. Analytical methods

The concentration of phenol and the intermediate products were measured by high-performance liquid chromatography (HPLC) (1260 Series, Agilent, USA), using a mixture of acetonitrile and ultrapure water (7:3, by volume) as the mobile phase. The injection volume was 20 μL. The identification of aromatic intermediate products was carried out by a Gas Chromatography–Mass Spectrometry (GC-MS) (7890A/5975C Series, Agilent, USA) equipped with HPS-MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) using helium as the carrier gas. The injector temperature was held constant at 275 °C, whereas the temperature of the column oven was initially set at 60 °C for 5 min, and then ramped up to 275 °C at 5 °C/min. The TOC was measured using a Multi TOC/TN Analyzer (2100, Analytik Jena, Germany). The surface area of the AC was obtained according to the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption at liquid nitrogen temperature using a BET Analyzer (AUTOSORBQ2, Quantachrome, USA). The Fourier-transform infrared spectroscopy (FTIR) spectra were determined with a Fourier transformation infrared spectrometer (Nexus, Nicolet, USA). The surface morphologies of the AC were visualized using a Scanning Electron Microscopy (SEM) analyzer (SSX-550, Shimadzu, Japan).

To rapidly quench the reaction, Tempol, tert-butanol, and Fe²⁺-EDTA
were employed since they are effective scavengers for superoxide radicals (O$_2^-$) [24,25], hydroxyl radicals (·OH) [26], and hydrogen peroxide (H$_2$O$_2$) [27,28]. In order to determine the roles of O$_3^-$, ·OH, and H$_2$O$_2$ in the O$_3$/AC system, the discrepancy of TOC removal with the addition of 160 μM Tempol, 100 μM tert-butanol, and 0.2 μM Fe$^{2+}$-EDTA scavengers within 90 min was compared.

3. Results and discussion

3.1. Comparison of phenol removal performance

In order to investigate the influence of AC on phenol removal in the aqueous phase, the single adsorption of phenol, ozonation by single O$_3$, and ozonation in the presence of AC were carried out. Fig. 2 shows the temporal phenol (Fig. 2a) and TOC (Fig. 2b) removal profiles during the operation of the AC, O$_3$, and O$_3$/AC systems. Whenever O$_3$ was used, complete removal was achieved after approximately 40 min. The phenolic hydroxyl (·OH) was an electron donor and resulted in the activation of the aromatic ring by increasing its electronic density. The aromatic compounds had a higher delocalization of electrons and exhibited higher reactivity towards O$_3$ [29]. Consequently, phenol was likely to suffer electronic attack by O$_3$, and approximately 42.6% of phenol was removed via the AC system at a contact time of 90 min. The removal of phenol in the O$_3$/AC and O$_3$ systems was more efficient relative to the AC system, suggesting that O$_3$ was able to quickly react with phenol in the ozonation process. The addition of AC with both adsorptive and catalytic ability made the phenol removal efficiency in the O$_3$/AC system quicker relative to the single O$_3$ system. The graphs in Fig. 2b show the removal efficiency of TOC after 90 min. It was observed that the removal efficiency was around 70.2% in the O$_3$/AC system, 39.8% in the AC system, but only 44.1% in the O$_3$ system. Although the sum of the degree of mineralization of the O$_3$ system and AC system exceeded the combined O$_3$/AC system, it was unreasonable to judge whether or not the O$_3$/AC system had a synergistic effect on phenol and AC due to the complete degradation of the easily adsorbed phenol during the first 25 min. As shown in Table 2, the removal efficiency of TOC in the O$_3$ and O$_3$/AC-AS systems was 44.3% and 51.5%, respectively, which indicated that AC had certain catalytic ability to degrade phenol. Consistent with the above results [30], proved that AC (or carbon black) can accelerate the degradation of organic compounds by catalyzing O$_3$ to generate hydroxyl radicals (·OH).

The combined O$_3$/AC system can enhance the degree of mineralization of phenol due to the addition of AC. Moreover, the removal of phenol and TOC in O$_3$ and the O$_3$/AC system had significant discrepancies. Since O$_3$ attacked the aromatic ring or double bonds selectively, phenol was quickly decomposed into intermediate products with small molecular weights. Therefore, a large amount of O$_3$ was used to mineralize the released intermediate products, which was also the reason for the low mineralization efficiency in the single O$_3$ system. The addition of AC compensated for this shortcoming in the single O$_3$ system, which made the increase in the degree of mineralization of phenol. Compared to the O$_3$ system, the adsorption of intermediates and small-molecule acids on the AC had a significant effect on TOC removal in combined the O$_3$/AC system. Therefore, the O$_3$/AC system was more efficient in the degree of mineralization of phenol relative to the O$_3$ system, as well as improving the TOC removal efficiency. This observation was explained by a sum of contributions of the adsorption onto the AC and O$_3$ oxidation and catalytic ozonation.
Fig. 2. Evolution of phenol (a) and TOC (b) removal efficiency with time during the course of the AC, O₃, O₃/AC experiments (AC dosage = 1.00 g/L; ozone dosage = 22.00 mg/L; pH = 7.0). The effect of the ozone concentration on phenol (c) and TOC (d) removal (AC dosage = 1.00 g/L; pH = 7.0). The effect of the AC dosage on phenol (e) and TOC (f) removal (ozone dosage = 22.00 mg/L; pH = 7.0). The effect of pH on phenol (g) and TOC (h) removals (ozone dosage = 22.00 mg/L; AC amount = 1.00 g/L).
from 0 to 1.0 g/L. This trend could be related to the increase in the 
surface adsorption sites for organic compounds with the increased AC
dosage, which accounted for the significant enhancement in both 
the phenol and TOC removals. Additionally, the AC can also accelerate 
O₃ decomposition which might result in the formation of hydroxyl radicals 
in an aqueous solution [33]. The addition of more AC will also lead to 
more active sites for oxidation reactions and facilitate the production of 
more hydroxyl radicals [34,35]. The adsorbed O₃ and organic com-
ounds on the surface of AC played a predominant role in the ozonation 
system, which can improve the mass transfer efficiency [36]. However,
the trend in TOC removal did not increase significantly relative to the 
additional dosage of AC from 1.0 to 5.0 g/L. Moreover, the maximum 
removal capacity of AC was 46.92 mg/g at a dosage of 1.0 g/L whereas 
the increase of the AC dosage to 5.0 g/L resulted in the removal capacity 
of AC decreasing to 12.76 mg/g. Previous studies showed that an opti-
imum amount of AC would be favorable to catalyze the oxidation of or-
ganics by creating oxidative radical species but if the amount exceeded a 
certain quantity, then its role might be inhibited [37]. Moreover, taking 
into account the constant concentration of pollutants and O₃ per 
unit area, which would weaken the catalytic efficiency [38].

### 3.3. Kinetics study of phenol removal

In order to validate the mechanisms of phenol adsorption on the AC, 
the pseudo-first-order and pseudo-second-order models were used to fit 
the dynamic processes in the O₃/AC system. The adsorption kinetics of 
phenol was conducted at 25 °C with an initial phenol concentration range 
of 100–400 mg/L. The fitted curve rose quickly during the initial stage 
and stabilized near equilibrium after 5 h. These results showed that many 
vacant adsorption sites were available for adsorption during the initial 
stage. During the latter contact times, the remaining vacant adsorption 
sites were more difficult to occupy due to the reduced amounts of va-
cancies available [42]. The Qₜₐₙketic constants and the coefficient of 
determination (R²) values were shown in Table S1. It was found that 
the correlation coefficients for the pseudo-second-order model were signifi-
cantly higher than those of the pseudo-first-order model, indicating that 
the mechanisms of adsorption involved a chemical reaction process be-
tween functional groups present on the adsorbent surface and organic 
compounds.

It was found that the removal process of phenol and TOC were fitted 
to the first-order kinetic model in the O₃ and O₃/AC systems. The 
oxidation rate constants of phenol and TOC in the O₃/AC system were 
approximately 1 and 2 times higher than that in O₃ system, respectively 
(shown in Table S2). These results indicate that the O₃/AC system 
showed a better oxidation ability for phenol compared to the O₃ system. 
The O₃/AC system can significantly enhance the phenol removal rate due 
to the addition of AC. Therefore, a high phenol removal performance of a 
wastewater treatment system could be developed by the simultaneous 
usage of AC with O₃.

### 3.4. Characterization of AC

SEM images of raw and used AC are shown in Fig. 3 and it could be 
seen that the raw AC had a relatively rough surface, while the surface of 
the AC was rough after the reaction. This change can be attributed to the 
elimination of ash in acidic environment. Fig. 3c showed the BJH (Bar-
rett-Joyner-Halenda) pore size distribution of the AC and the inset 
figure in Fig. 3c illustrated the N₂ adsorption-desorption isotherm curves. 
In accordance with the classification approach of Brunauer, Deming, 
Deming, and Teller (BDTD) [43], the adsorption isotherms can be cate-
gorized into type I isotherms, which are used to describe mesoporous 
adsorbents. There was a characteristic hysteresis loop in the desorption 
isotherm at relative pressure (P/P₀) in the range from 0.45 to 0.95. The 
shape of hysteresis loop may help to access the pore shape of the ad-
sorbents [44]. As shown in Table 1, the BET surface area of the used AC 
(865.4 m²/g) was larger than the raw AC (852.1 m²/g). The Sₜₐₚ, Sₘₐₜro, 
and micropore volumes also had a corresponding increase. Previous 
studies showed that acid treatment can increase the specific surface area 
of carbon materials [45,46].

FTIR spectra of the AC with the range of 700–3800 cm⁻¹ were shown 
in Fig. 3d. The basic characteristic bands of the raw AC were as follows: 
3500-3200 cm⁻¹ (O–H stretching vibrations), 2924 cm⁻¹ and 2847 cm⁻¹ 
(asymmetric and symmetric C–H stretching vibration of –CH₂, respec-
tively) [47,48], 1627 cm⁻¹ (C≡C stretching vibration), and 1044-1049 cm⁻¹ 
(O–H stretching vibration) [49]. Compared to the raw AC, the FTIR 
analysis of AC at pH 3.0 and 11.0 revealed a new band of 1400–1450 cm⁻¹ 
(OH stretching vibration) [50], as well as an increased in most of the 
peak intensities of the bands. These observations are consistent with 
previous studies [46]. The above phenomenon could be attributed to the 
fact that the AC adsorbed a certain amount of phenol and intermediate 
products (e.g., oxalic acid, maleic acid, fulvic acid) during the reaction 
process. Additionally, the peak intensity in acidic conditions (pH 3.0) 
was stronger than alkaline conditions (pH 11.0), which was attributed to
the improved adsorption ability for intermediate products under acidic conditions (pH 3.0). However, compared to the raw AC, the peak intensity of O\text{–}H at alkaline condition was slightly decreased. The bond (O\text{–}H) might be partially consumed in combination with O3 during the reaction process [31] and O3 molecules can form a five-membered ring with oxygen-containing groups on the surface of a catalyst via hydrogen bonds and electrostatic forces. This bond was then decomposed to form free radicals by means of electron transfer [51–53].

3.5. Mineralization mechanism

3.5.1. Mechanism exploration of the O3/AC system

Active substances, O2\textsuperscript{–}, H2O2, and \cdot OH, were detected in the O3/AC oxidation reaction system [54,55]. In this study, Tempol, Fe\textsuperscript{2+}-EDTA, and tert-butanal were used as scavengers of O2\textsuperscript{–}, H2O2, and \cdot OH, respectively, to explore the species of the active substances. As shown in Fig. 4, in acidic conditions (pH 3.0), the TOC removal efficiencies in the three reaction systems decreased minimally, indicating that O2\textsuperscript{–}, H2O2, and \cdot OH hardly contributed to the removal of TOC. However, in alkaline conditions (pH 11.0), Tempol, Fe\textsuperscript{2+}-EDTA, and tert-butanal led to a TOC removal efficiency decrease of 3.5%, 6.3%, and 16.7%, respectively. These results suggest that the removal of organic compounds by \cdot OH was relatively dominant in the O3/AC system. Consistent with the above results [56], also found that partial amount of \cdot OH was generated in the O3/AC system under acidic and neutral conditions. The mechanisms of O3 decomposition and radical chain reactions were as follows (Eqs. (3)–(9)) [56–58]:

Acidic conditions

\[
O_3 + AC \rightarrow AC-O_3
\]  

(3)

\[
AC-O_3 \rightarrow AC-O + O_2
\]  

(4)

Alkaline conditions

\[
O_3 + AC \rightarrow \cdot OH + AC_{\text{oxid}}
\]  

(5)
Reactions (3) and (4) were the steps of the surface action which involve the adsorption and degradation processes. At acidic condition (pH 3.0), O₃ was firstly adsorbed on the surface of the AC, then it was decomposed to oxygen rather than active substances (OH or O₂⁻) [59]. Therefore, the O₃/AC system had a relatively weak removal performance for organic compounds at acidic condition. Consistent with the above results [60], also found that the O₃/H₂O₂ system also suffer greatly from an extremely limited reaction rate constant under acidic conditions (pH 3.0). However, as presented in Eqs. (5)-(9), O₃ could be degraded by hydroxide ions (OH⁻) rapidly to generate free radicals such as O₂⁻ and HO₂ at alkaline conditions. FTIR analysis also indicated that the surface hydroxyl groups on the AC were involved in the catalytic ozonation process, and the O₃ adsorbed on the AC surface also could be catalyzed by –OH groups on the AC to form –OH at a pH between 6.0 and 9.0 [61]. [62] reported that the radical chain reactions of O₃ decomposition might be induced by HO₂⁻ formed by a –OH chain reaction. In conclusion, in acidic condition, organic compounds were mainly attacked by O₃ molecules via the Criegee mechanism [63], while in alkaline condition, the active substances had a relatively greater contribution to the mineralization of phenol process.

Based on the above analyses, the possible mechanisms for phenol removal in the O₃/AC system and the intermediate products removal process was tentatively proposed and depicted in Fig. 5. In the O₃/AC reaction system, organic compounds were partially removed by adsorption on the AC, and the rest of organic compounds were mineralized. At acidic conditions (pH 3.0), organic compounds were mainly mineralized by O₃ molecules to form small molecule organic acids, whereas at alkaline condition (pH 11.0), O₃ can react with OH⁻ and oxygen-containing functional groups (O–H from FTIR analysis) on the surface of the AC to generate active species. These active species (OH, H₂O₂, O₂⁻) were then used to degrade the organic compounds [51-53] and these redox reactions (Eqs. (5)-(9)) could enhance the decomposition of O₃, which was efficient for promoting the generation of active species. Finally, the small molecule organic acids were completely mineralized to CO₂ and H₂O.

3.5.2. Degradation pathway of phenol

In order to deeply understand the phenol degradation process, the intermediate products were identified by HPLC and GC-MS, and the results are shown in Table S3. Firstly, phenol was attacked by the active species (O₃, OH⁻) to form hydroquinone and catechol [18]. Afterwards, the aromatic rings of these compounds were disconnected via the Criegee mechanism to form muconic acid at acidic condition (pH 3.0) [63]. However, benzoquinones were only detected at alkaline condition (pH 11.0), therefore, ortho- and para-hydroxylated byproducts, formed by the oxidation of phenol, would lose hydrogen ions and electrons to form quinone compounds [64]. Additionally, the reaction solution was found to be red-brown in the early stage of the reaction at alkaline condition, which was probably due to the generation of complex chromogenic compounds formed by benzoquinones. Consequently, two different pathways have been considered based on the different phenomena in the above reaction system. At acidic condition, muconic acid was degraded to small carboxylic acid molecules such as maleic, fumaric, oxalic and acetic acids [18], while at alkaline condition, quinone compounds were transformed to be maleic and fumaric acids, then turned to be oxalic and acetic acids [18, 64]. Finally, the small carboxylic acid molecules were mineralized to CO₂ and H₂O by active species (O₂, OH⁻). Based on the above analyses, the possible reaction pathways for phenol degradation in O₃/AC system were proposed in Fig. 6.

The above results indicated that some small molecular acids were generated during the ozonation of phenol. However, the accumulation of the small molecular acids had an effect on the ozonation efficiency of the AC/O₃ system. Therefore, it was necessary to study the accumulation regularity of small molecule organic acids. In order to determine the accumulation regularity of small molecule organic acids during the reaction process, organic compounds at different reaction times were determined by HPLC. As shown in Fig. 7, the peak areas of maleic, fumaric, and acetic acids gradually decreased with the reaction time, while increases in oxalic acid were observed. These results show that oxalic acid was mainly attacked by free radicals [56]. The lower production of free radicals caused by the acidification of the reaction solution (around pH 3.1) in the phenol removal process, had an adverse impact on the degradation of oxalic acid which caused this compound to accumulate.

4. Conclusions

The performance and mechanisms of phenol removal in the O₃/AC system were systematically studied in the present study. The kinetics of phenol adsorption were well fitted with the pseudo-second-order kinetic equation, and the reaction rate constants of phenol and TOC were approximately 1 and 2 times higher than in the O₃ system alone. Free radicals were more easily generated under alkaline conditions by
scavenging active species such as $\cdot$OH and $O_2^\cdot$. During the ozonation process, the accumulation of small-molecule acids (e.g., maleic, fumaric, oxalic and acetic acids) decreased the solution pH, and the intermediate product oxalic acid was formed and was difficult to be completely eliminated. Hydroquinone and catechol were converted to muconic acid under acidic conditions, whereas they were degraded to quinone compounds under alkaline conditions.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.esse.2019.100005.

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