Activated carbon enhanced ozonation of oxalate attributed to HO• oxidation in bulk solution and surface oxidation: effect of activated carbon dosage and pH

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Received 09 December 2013; revised 27 January 2014; accepted 11 February 2014

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Abstract

Ozonation of oxalate in aqueous phase was performed with a commercial activated carbon (AC) in this work. The effect of AC dosage and solution pH on the contribution of hydroxyl radicals (HO•) in bulk solution and oxidation on the AC surface to the removal of oxalate was studied. We found that the removal of oxalate was reduced by tert-butyl alcohol (tBA) with low dosages of AC, while it was hardly affected by tBA when the AC dosage was greater than 0.3 g/L. tBA also inhibited ozone decomposition when the AC dosage was no more than 0.05 g/L, but it did not work when the AC dosage was no less than 0.1 g/L. These observations indicate that HO• in bulk solution and oxidation on the AC surface both contribute to the removal of oxalate. HO• oxidation in bulk solution is significant when the dosage of AC is low, whereas surface oxidation is dominant when the dosage of AC is high. The oxalate removal decreased with increasing pH of the solution with an AC dosage of 0.5 g/L. The degradation of oxalate occurs mainly through surface oxidation in acid and neutral solution, but through HO• oxidation in basic bulk solution. A mechanism involving both HO• oxidation in bulk solution and surface oxidation was proposed for AC enhanced ozonation of oxalate.

Key words: activated carbon, oxalate, ozonation, hydroxyl radicals, surface oxidation, catalytic ozonation

Introduction

Nowadays, water pollution is still an important issue especially in developing countries although the wastewater discharge standards are becoming more stringent in the past decades (Li et al., 2012). One of the main problems is the refractory organic contaminants which cannot be degraded efficiently by the traditional biological treatment and thus discharge into the natural water matrixes (Yang et al., 2013). Therefore, it is greatly urgent to develop efficient treatment technologies for the removal of refractory organic contaminants. Advanced oxidation processes (AOPs) that produce highly reactive hydroxyl radicals (HO•) are promising to promote the degradation of refractory organics in water (Li and Qu, 2009; Liu et al., 2013; Yu et al., 2006). Among them, activated carbon (AC) enhanced ozonation is considered as a promising one because it is efficient and environmentally friendly (Li et al., 2009; Wang et al., 2009).

AC has been reported to enhance the removal of organics through two ways: AC enhancing the generation of HO• in bulk solution and providing reaction sites for organics oxidation on
AC acts as an initiator or promoter in the radical chain decomposition of ozone that proceed in bulk solution, and thus enhances the generation of HO• (Beltrán et al., 2002b; Jans and Hoigné, 1998). The hydroxide ion (OH⁻) and hydrogen peroxide (H₂O₂) are generated from reactions of ozone with basal plane electrons and basic surface groups, respectively. They are believed to enhance ozone decomposition and improve HO• generation in bulk solution (Alvárez et al., 2006; Rivera-Utrilla and Sánchez-Polo, 2002). Acidic surface groups are also reported to enhance the reaction rate of ozone because of the nucleophilic character (Dehouli et al., 2010; Valdés and Zaror, 2006).

In the past decade, many studies have focused on AC enhanced HO• generation in bulk solution; only a few discoveries have been made with respect to surface oxidation which is hardly affect by HO• scavenger. Faria et al. (Faria et al., 2008a) observed ozonation of oxalic acid in the presence of AC was not affected by the HO• scavenger, tert-butyl alcohol (tBA), at pH 3 and it was partially inhibited by tBA at pH 7. Therefore they proposed a mechanism involving the surface reactions besides bulk reactions between the organic solute and HO•, and the surface reactions is important at a low initial pH. Similar results were obtained for ozonation of oxalic acid in the presence of carbon nanotube (Liu et al., 2009; Liu et al., 2011). HO• is very important in the degradation of refractory organics, but surface oxidation may play a key role in the treatment of water or wastewater containing high concentration of HO• scavengers. Consequently, study on the factors that affect the contributions of these two kinds of oxidation behaviors and the mechanism involved in AC enhanced ozonation is of great importance for the practical application of this process. The above studies show that pH is an important factor that influences the contribution of surface reactions or HO• reactions in solution to the removal of target compounds. However, only acid and neutral solution was studied, and a wider pH range including basic solution needs to be studied systematically. Other important factors that influence the contribution of these two kinds of oxidation behaviors and ozone decomposition should also be studied in order to reveal the mechanism involved in AC enhanced ozonation process.

The object of this study is to investigate the quantitative contribution of surface oxidation and HO• oxidation in bulk solution to the removal of a target compound and ozone consumption during ozonation with AC. The influence of AC dosage and pH were systematically studied and the reaction mechanism was proposed. We chose oxalic acid as the target compound because it is normal oxidation product of many organics (Faria et al., 2008b).
and its degradation products are carbon dioxide and water (Beltrán et al., 2002a). Oxalic acid hardly react with ozone \((k < 0.04 \text{ mol/L·s})\) (Hoigné and Bader, 1983), and it reacts slowly with HO• \((k = 1.4 \times 10^6 \text{ mol/L·s})\) (Getoff et al., 1971). These properties make it a suitable model compound to study both the HO• oxidation in bulk solution and the surface oxidation in AC enhanced ozonation.

1 Materials and methods

1.1 Materials and reagents

All chemicals were analytical reagent grade. Solutions were prepared with ultrapure water (resistivity greater than 18 MΩ·cm), which was produced by a Millipore-Q® Direct 8 System (Millipore, USA). A commercial AC (analytical-reagent grade, Xilong Chemical, China) with particle size of approximately 75 μm was used. The specific surface area and the pH of the point of zero charge (pH_{PZC}) of this AC was 896.4 m²/g and 9.33, respectively.

1.2 Ozonation procedure

Ozonation experiments were conducted in a semi-batch system. Figure 1 shows the schematic diagram of experimental apparatus. Ozone was generated from pure oxygen by an ozone generator (COM-AD-01, Anseros, Germany). The gaseous mixture of ozone and oxygen was bubbled through a porous plate into the reactor with a flow rate of 116 mL/min and an ozone concentration of 65±0.25 mg/L. A thermostatic magnetic agitator held the temperature constant at 25℃ during experiments. The reactor was loaded with 1 L of phosphate-buffered oxalate solution. The concentrations of oxalate and phosphate were 0.5 and 5 mmol/L, respectively. Gaseous ozone mixture was fed into the reactor immediately after the AC sample was added. The total reaction time was 15 min. The concentrations of ozone and oxalate were analyzed at different time intervals. The initial solution pH was 7 for the experiments with various AC dosages. The PAC dosage was 0.5 g/L for the experiments with various solution pH values. The experiments were performed in duplicate to check the reproducibility of the results. The standard deviation for the concentrations of oxalate, gaseous ozone, aqueous ozone and H₂O₂ were within 0.9 mg/L, 0.6 mg/L, 0.4 mg/L and 0.5 μmol/L, respectively.
1.3 Analytical methods

The concentration of gaseous ozone was determined with an ozone analyzer (Ozomat GM6000PRO, Anseros, Germany), and that of aqueous ozone was analyzed by the indigo method (Bader and Hoigné, 1981). The concentration of oxalate was measured by ion chromatography (DX500, Dionex, USA) with an AS11 analytical column and a suppressed conductivity detector. The H$_2$O$_2$ concentration was determined by the peroxidase-DPD method (Bader et al., 1988). The specific surface area of AC was obtained by physisorption of nitrogen at 77 K (Autosorb-1, Quantachrome, USA) using the BET isotherm method. The pH of the point of zero charge (pH$_{PZC}$) of AC was determined by the mass titration method (Noh and Schwarz, 1990).

1.4 Parameters calculation

The ozone consumption (mg) in the ozonation systems was calculated according to equation (1):

$$
\text{Ozone consumption} = C_{O_3, \text{in}} dt - Q \int_{t_0}^{t} (C_{O_3, \text{out}} dt - C_{O_3, \text{in}}) V
$$

where, $C_{O_3, \text{in}}$ (mg/L) and $C_{O_3, \text{out}}$ (mg/L) are the inlet and outlet concentrations of gaseous ozone, respectively; $C_{O_3}$ (mg/L) is the concentration of aqueous ozone at time $t$; $Q$ (L/min) is the flow rate of the gaseous ozone mixture; $V$ (L) is the volume of the solution; and $t$ (min) is the reaction time.

The contribution of HO• oxidation in bulk solution to the removal of oxalate can be quantitatively determined using tBA to quench the reaction. It was designate $\eta$ and calculated as follows:

$$
\eta = \left(1 - \frac{\text{oxalate removal with tBA}}{\text{oxalate removal without tBA}}\right) \times 100\%
$$

where, oxalate removal was determined by $(1 - \frac{C_{\text{ox}, \text{t}}}{C_{\text{ox}, 0}}) \times 100\%$, and $C_{\text{ox}, 0}$ (mmol/L) and $C_{\text{ox}, t}$ (mmol/L) are the concentrations of oxalate, at time 0 and $t$, respectively.

The molar ratio of oxalate removed to ozone consumed ($R_{\Delta O\Delta O_3}$) was used to describe the ozone efficiency, and it was calculated via equation (3):

$$
R_{\Delta O\Delta O_3} = \frac{(C_{\text{ox}, 0} - C_{\text{ox}, t})V}{\text{Ozone consumption}} \times 48
$$
2 Results and discussion

2.1 Effect of AC dosage

2.1.1 Ozonation of oxalate with various AC dosage

The effect of AC dosage on the ozonation of oxalate was firstly evaluated and the results were shown in Fig. 2 and Table 1. Firstly the adsorption of oxalate on AC was carried out, and it was found that approximately 0.03 mmol of oxalate was absorbed on one gram of AC in 15 min (data not shown). Table 1 shows that the oxalate removal increased from 8.4% to 99.2% as the AC dosage increased from 0 to 2 g/L. This indicates that AC can enhance the removal of oxalate during the ozonation. The ozone consumption also increased with increasing dosage of AC. AC was reported to initiate or promote the radical-type chain reaction of ozone decomposition to generate HO• in bulk solution, and a higher concentration of AC generated more HO• (Sánchez-Polo et al., 2005). Accordingly, the higher oxalate removal and ozone consumption resulting from higher AC dosage in this study indicate that HO• may contribute to oxalate oxidation. However, Fig. 2 shows the degradation rate of oxalate was not elevated with PAC dosage in the early stage of reaction when the PAC dosage was higher than 0.5 g/L. This observation may imply other reaction influences the oxalate degradation when a higher dosage of PAC is used which we will discuss later.

2.1.2 Effect of tBA

To certificate the role of HO• in the ozonation process, further experiments were performed in the presence of an HO• scavenger, tBA. tBA was founded to inhibit the oxidation of organics by HO• in bulk solution as it adsorbed poorly on AC (Beltrán et al., 2002a). Figure 3a shows that oxalate removal decreased when 1 to 100 mmol of tBA was added, which indicates that HO• oxidation is involved in oxalate removal. Oxalate removal was not completely inhibited by tBA, this indicates that surface reactions among oxalate, ozone and AC are also responsible for oxalate removal. Oxalate removal curves were almost the same when 1 or 10 mmol of tBA were added regardless of AC dosage (an example with 0.5 g/L AC is shown in Fig. 3b). This indicates that 1 mmol of tBA is sufficient to inhibit HO• oxidation in bulk solution, and the surface oxidation of oxalate was not influenced when 10 mmol of tBA was added. However, the presence of 100 mmol tBA did suppress the surface oxidation. This can be explained that tBA occupied active sites for catalytic reactions on the AC surface and/or
scavenged surface radicals, because the amount of tBA adsorbed on AC was relatively high when its concentration was 100 mmol (Fig. 4). Consequently, 1 mmol of tBA was added as the scavenger of HO• in bulk solution in the following experiments.

The effect of tBA on the ozonation of oxalate with varying AC dosage was studied (Fig. 5 and Table 1). We found that oxalate removal by HO• oxidation in bulk solution, calculated as the difference in oxalate removal without and with tBA, exhibited an increasing trend as the AC dosage increased to 0.2 g/L (Table 1). It indicates that AC at these low dosages can enhance the generation of HO• in bulk solution. This is consistent with the widely accepted HO• related mechanism for ozonation with AC (Sánchez-Polo et al., 2005). Oxalate removal by HO• oxidation in bulk solution gradually decreased when more than 0.2 g/L of AC was added, which may be due to HO• scavenging by AC. Furthermore, oxalate removal in the presence of tBA increased with AC dosage (Table 1). As HO• oxidation in bulk solution was completely hindered, this indicates oxalate removal through surface oxidation increases with AC dosage. The contribution of HO• oxidation in bulk solution to the removal of oxalate (η) was calculated and shown in Table 1. It decreased as AC dosage increases from 0 to 2.0 g/L. η was larger than 50% when the AC dosage was less than 0.05 g/L, which indicates that HO• oxidation in bulk solution is significant in this case. tBA did not significantly affect oxalate removal when the AC dosage was greater than 0.3 g/L (i.e., η < 7.4%). Therefore, the rapid removal of oxalate was attributed mainly to the oxidation occurring on the AC surface.

The ozone consumption in ozonation systems with and without tBA were also compared (Table 1). Ozone consumption with various dosages of AC was correlated with oxalate degradation. We found that tBA reduced ozone consumption when the AC dosage was less than 0.05 g/L, which meant that ozone decomposition through the radical chain reaction in bulk solution is inhibited. Ozone consumption got higher with tBA when the AC dosage was greater than 0.1 g/L, which indicates that the radical chain decomposition of ozone in bulk solution is not significant. Accordingly, ozone was consumed mainly through surface reaction on AC, as its reaction with oxalate and tBA in bulk solution is negligible. The inhibition of radical chain reaction on AC surface by tBA will also decrease ozone consumption although it may be negligible because tBA was poorly adsorbed on AC surface as we mentioned previously. Consequently, the increased ozone consumption should be attributed to the surface catalytic oxidation of tBA.
2.1.3 Ozone efficiency

The ozone efficiency ($R_{\text{OA}/\text{O3}}$) for oxalate removal was examined with various AC dosages (Table 1). For the ozonation systems with or without tBA, the $R_{\text{OA}/\text{O3}}$ value gradually increased as the AC dosage increased to 1 g/L, but then slightly decreased with 2 g/L of AC. The $R_{\text{OA}/\text{O3}}$ value increased with AC dosage in the presence of tBA as surface reaction efficiently oxidized oxalate and increasing the AC dosage promoted oxalate removal. Ozone consumption also affects ozone efficiency. Aqueous ozone decomposes through several pathways, such as: (a) radical chain reaction (b) surface catalytic reaction with oxalate, and (c) direct reaction with AC which does not contribute to the oxalate oxidation or radical chain reaction. The presence of tBA inhibited radical-type chain decomposition of ozone proceeding in bulk solution. When excess AC was used, ozone decomposition through pathway (c) increased, which may lead to a deficiency of oxalate ozonation. Consequently, the rate of increase in $R_{\text{OA}/\text{O3}}$ slowed down, and then it became slightly negative with higher dosages of AC (i.e., $R_{\text{OA}/\text{O3}} = 0.202$ with 1.0 g/L of AC and 0.200 with 2.0 g/L of AC, respectively). In the systems without tBA, the AC dosage also affects ozone decomposition through pathway (a). Ozone is a significant competitor of oxalate because it reacts with HO• more rapidly ($k = 3 \times 10^9$ mol/L·s (Staehelin and Hoigné, 1985) than bivalent oxalate ($k = 7.7 \times 10^6$ mol/L·s ) (Getoff et al., 1971), the main form of oxalate at pH 7. The decreased concentration of ozone with increased AC dosage (Fig. 2c) leads to less competition for HO•, which contributes to an elevated $R_{\text{OA}/\text{O3}}$ value. However, the scavenging of HO• by AC may slow down the increasing rate of $R_{\text{OA}/\text{O3}}$. The $R_{\text{OA}/\text{O3}}$ values for systems with tBA were lower than for those without tBA, which could be explained by the ozone consumption during surface catalytic oxidation of tBA and the inhibition of HO• oxidization of oxalate by tBA.

2.1.4 H$_2$O$_2$ concentration

The concentrations of H$_2$O$_2$ during oxalate ozonation are shown in Fig. 6. In the system without AC, the H$_2$O$_2$ concentration was much higher in the presence of tBA. This could be explained by: (a) the generation of HO$_2^-$ through the reaction between OH$^-$ and ozone increases because the concentration of ozone in solution rises when tBA is present (Fig. 2c and Fig. 5c), and (b) less H$_2$O$_2$/HO$_2^-$ reacts with HO• as tBA scavenges HO•. Similar phenomena were observed during ozonation with AC. In addition to the above reasons, the higher ozone concentration in the system with tBA (Fig. 5c) may also enhance the reaction between AC and ozone to generate H$_2$O$_2$. For example, the cycloaddition of ozone to the unsaturated aromatic C=C bonds on the surface of AC releases H$_2$O$_2$ as a by-product.
according to the Criegee mechanism (Alvárez et al., 2006). Fig. 6 also shows that the H\textsubscript{2}O\textsubscript{2} concentrations decreased as the AC dosage increased no matter tBA was added or not, which occurs because the higher AC dosage increases H\textsubscript{2}O\textsubscript{2} decomposition as H\textsubscript{2}O\textsubscript{2} was reported to react with AC to generate HO• (Serp and Figueiredo, 2009). The reaction of H\textsubscript{2}O\textsubscript{2} and AC could also be illustrated by the observation that the H\textsubscript{2}O\textsubscript{2} concentration reached a peak and then decreased when the AC dosage was larger than 0.5 g/L and 0.2 g/L for the systems without and with tBA, respectively. This corroborates that the accumulation of ozone in water (Fig. 2c and Fig. 5c) leads to more H\textsubscript{2}O\textsubscript{2} through the reactions of ozone with OH\textsuperscript{-} and AC. The reaction rates of H\textsubscript{2}O\textsubscript{2} with ozone and AC increase with increasing H\textsubscript{2}O\textsubscript{2} concentration, which tends to stabilize the H\textsubscript{2}O\textsubscript{2} concentration. A higher AC dosage consumes more H\textsubscript{2}O\textsubscript{2} and thus reduces the H\textsubscript{2}O\textsubscript{2} concentration.

2.2 Effect of pH

The effect of pH on the ozonation of oxalate was examined with 0.5g/L of AC and the results were shown in Fig. 7 and Table 2. The oxalate removal decreased when the pH increased from 3 to 11. tBA test shows that the oxalate removal by HO• oxidation in bulk solution increased as pH increased up to 9, but then decreased as pH became higher. This indicates that the basicity of solution enhances the generation of HO• for the higher concentration of OH\textsuperscript{-}. The lower values at pH 11 could be attributed to the HO• scavenging by AC, which will be discussed in detail later in this section. The contribution of HO• oxidation in bulk solution to the removal of oxalate (\(\eta\)) increased as the solution became more alkaline. The values of \(\eta\) indicate that surface oxidation dominates in acidic and neutral solution but HO• oxidation in bulk solution dominates in basic solution. Fig. 8 shows that more oxalate was adsorbed on AC in the acid solution. As the pH\textsubscript{PZC} of AC was 9.33, AC was positively charged when the pH of the solution was 9 or lower, and vice versa. The negatively charged oxalate showed no adsorption on AC at pH 11 as AC was also negatively charged. The adsorption of oxalate was found positively related with the removal of oxalate through surface oxidation, which indicates that the adsorption of oxalate is important for surface reaction. Besides, the constitution of oxalate solution at varying pH may also contribute to the increase of oxalate removal rate with the decrease of pH (according to calculation result in Table 3) if surface HO• participate in the surface oxidation of oxalate.

Table 2 also shows that the ozone consumption slowly increased when pH increased from 3 to 11 in the ozonation systems with AC no matter tBA was added or not. This is because ozone decomposition through pathway (b) decreases, but that through pathways (a) and (c)
increase with increasing pH as ozone reaction is electrophilic in the solution (Beltrán, 2003). The addition of tBA did not decrease the ozone consumption, although HO• oxidation dominated in basic solution. This could also be attributed to the ozone consumed by the catalytic oxidation of tBA. tBA has a relatively high pKa of about 17, thus it hardly dissociates even at pH 11. Accordingly, the solution pH will not significantly affect the adsorption and catalytic oxidation of tBA on AC. The values of \( R_{\Delta O3/\Delta O3} \) in Table 2 show that ozone efficiency was higher at lower pH, where surface oxidation of oxalate dominates.

The experimental results with 0.5 g/L of AC were compared to those with 0.1 g/L AC and without AC at varying pH (Fig. 9). The oxalate removal rates at both pH 3 and 7 increased with the increasing AC dosage, but the result was opposite at pH 11. Previously, HO• in bulk solution was shown to oxidize oxalate in the AC enhanced ozonation system at pH 11. As HO• is strongly electrophilic (Minakata et al., 2009), the reaction between HO• and AC will be enhanced when AC is negatively charged. As a result, AC scavenges more HO• at pH 11, and thus the oxalate removal decreased as AC dosage increased at pH 11. Fig. 9 also shows that ozone consumption was greatly enhanced when the AC dosage increased from 0 to 0.5 g/L at both pH 3 and 7. However, no significant increase in ozone consumption was observed at pH 11. This indicates the accelerated HO• scavenging reactions at pH 11 also show an inhibiting effect to the radical chain decomposition of ozone. The inhibiting reactions could slow down the increase rate of ozone decomposition with increasing AC dosage. Otherwise, AC would greatly enhance ozone decomposition at pH 11 because ozone is an electrophile in the aqueous solution (Beltrán, 2003).

### 2.3 Considerations of the reaction mechanism

The above experimental results indicate that both HO• oxidation in bulk solution and oxidation on the AC surface contribute to the removal of oxalate in the ozonation system with AC. We found that AC could enhance ozone decomposition and HO• generation in bulk solution, which indicates that AC initiates or promotes the radical chain decomposition of ozone in aqueous solution (Jans and Hoigné, 1998). AC was observed to scavenge HO•, and it could also inhibit the ozone decomposition, as mentioned previously. Consequently, AC acts not only as an initiator or promoter but also as an inhibitor for the decomposition of ozone. The surface oxygenated functional groups on AC include acidic groups (e.g., carboxylic, phenolic, carbonyl lactone, and lactol anhydride groups) and basic groups (e.g., pyrone-type groups and benzopyrylium derivatives). The \( \pi \) basicity of the exposed graphene layer also contributes to the basic behavior of AC (Boehm, 2002). Consequently, AC could participate
in the radical chain reaction of ozone decomposition through the reactions among the acidic/basic groups, π electrons on the surface of AC, and the main reagents, such as ozone, HO•, and H2O. The reactions that potentially initiate, promote, or inhibit the radical chain decomposition of ozone are listed in Table 4 and illustrated in Fig. 10. AC could initiate the radical chain reaction directly or indirectly through Reactions (4) to (11). As hydroxyl ion (OH⁻) is an initiator of ozone decomposition, the OH⁻-generating reactions, including the dissociation of basic surface groups (Reaction (4)), the reaction between the π electrons of the basal planes and H₂O (Reaction (5)), and the reduction of ozone by the delocalized π electrons of basic carbons (Reaction (6)), indirectly initiate ozone decomposition. As the surface groups of AC contain phenolic and other groups similar to those of natural organic matter (NOM), reactions similar to those between ozone and phenol or NOM, which generate ozonide ion radicals (O₃²⁻), perhydroxyl radical (HO₂•), and superoxide anion radicals (O₂⁻), may also occur during the ozonation of AC (equation (7) and (8)). These are considered the initiation reactions because they generate chain carriers such as O₃²⁻, HO₂• / O₂⁻. As discussed previously, the observed generation of H₂O₂ may occur through cycloaddition of ozone to the unsaturated aromatic C=C double bonds on the surface of AC, according to the Criegee mechanism (reaction (9)). H₂O₂ further dissociates to form HO₂⁻, which initiates the chain reaction of ozone decomposition. H₂O₂ may also react with AC to generate HO• (reaction (10)). In addition, H₂O₂ and HO₂⁻ react with HO• to form HO₂•, which can promote the chain reaction, and therefore reaction (9) is also considered a promoting reaction. On one hand, AC could react with HO• through a pathway similar to that of HO• reacting with phenol to generate ozone-selective HO₂•, and thus promote the radical chain reaction (reaction (11)). On the other hand, HO• reacts with AC to form species other than HO₂• / O₂⁻ or H₂O₂/HO₂⁻, and thus inhibit the decomposition of ozone (Reaction (12)).

OH⁻, H₂O₂ and radicals with longer lifetime generated on the surface of AC can diffuse to bulk solution and initiate radical chain reaction of ozone decomposition, which enhance the HO• generation and oxalate oxidation by HO• in bulk solution. However, the diffusion of radicals from the surface of AC to bulk solution may be less efficient because of their high reactivity with the surface of AC and other reagents such as oxalate and ozone. Accordingly, the radicals on the AC surface and their derivation reactions may contribute to oxalate removal on the surface of AC. Besides, the scavenging of HO• by AC through the inhibiting reactions will lower the HO• concentration in bulk solution and thus reduce the oxalate removal. We should also pay attention to the reaction of AC and ozone through pathway (c) as we mentioned previously. It consumes ozone but does not contribute to the removal of
oxalate. Consequently, we should try to reducing these influences to increase the efficiency of this process.

We also proposed that surface catalytic ozonation exist and the adsorption of oxalate critically affects the surface oxidization of oxalate. On the one hand, the increase in the adsorption of oxalate leads to higher surface concentration of oxalate and further the higher oxalate reaction rate with surface radicals. On the other hand, it may also improve the surface catalytic oxidation of oxalate. The formation of a surface metal-oxalate complex was involved in heterogeneous catalytic ozonation of oxalic acid with metals or metal oxides (Andreozzi et al., 1996; Zhang et al., 2011). AC is positively charged when the pH is lower than the pH_PZC of AC, and thus the adsorbed oxalate on the AC surface could form surface complexes which may act as metal-oxalate complexes in catalytic reaction. Consequently, AC could catalyze the reaction between oxalate and free or adsorbed ozone through the formation of surface oxalate complexes (Fig. 10).

3 Conclusions
This study shows AC significantly enhanced the ozonation of oxalate. Both HO• oxidation in bulk solution and surface reaction contribute to the removal of oxalate. HO• oxidation in bulk solution dominates with lower AC dosage, but the surface oxidation of oxalate dominates with higher AC dosages. Within our experimental scope, the oxalate removal decreased as the pH of solution increased. Surface oxidation of oxalate is dominant in acidic and neutral solution and HO• oxidation in bulk solution is dominant in basic solution. The scavenging of HO• and the inhibition of ozone decomposition by AC were observed in basic solution. The ozone efficiency was higher with larger AC dosage and lower pH, and surface oxidation was dominant for oxalate removal in these cases.

A mechanism involving both HO• oxidation in bulk solution and surface oxidation was proposed for AC enhanced ozonation of oxalate. AC could affect the generation of HO• and oxalate removal through initiating, promoting and inhibiting the radical chain decomposition of ozone. AC could also catalyze the surface ozonation of oxalate through formation of surface oxalate complexes. This study provides theoretical support for the regulation of the HO• oxidation in bulk solution and surface reaction in AC enhanced ozonation to obtain higher pollutants removal and ozone efficiency in treatment of different kinds of water or wastewater.
Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21177130), the National Key Technology R&D Program (No. 2011BAC06B09) and the Chinese Academy of Sciences Visiting Professorships for Senior International Scientists (No. 2009G2-28). Daisuke Minakata and John Crittenden appreciate support from the Brook Byers Institute for Sustainable Systems, Hightower Chair, and the Georgia Research Alliance at the Georgia Institute of Technology

References


**Table 1** Calculated parameters in oxalate ozonation with varying AC dosage

<table>
<thead>
<tr>
<th>AC dosage (g/L)</th>
<th>Oxalate removal without tBA (%)</th>
<th>Oxalate removal with tBA (%)</th>
<th>Oxalate removal by HO• oxidation in bulk solution (%)</th>
<th>η (%)</th>
<th>Oxalate consumption without tBA (mg)</th>
<th>Oxalate consumption with tBA (mg)</th>
<th>R_{\Delta OA/\Delta O3} without tBA</th>
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<td>0.105</td>
</tr>
<tr>
<td>0.3</td>
<td>75.8</td>
<td>70.2</td>
<td>5.6</td>
<td>7.4</td>
<td>85.1</td>
<td>103.0</td>
<td>0.196</td>
<td>0.145</td>
</tr>
<tr>
<td>0.5</td>
<td>92.6</td>
<td>89.3</td>
<td>3.3</td>
<td>3.6</td>
<td>88.0</td>
<td>105.3</td>
<td>0.237</td>
<td>0.191</td>
</tr>
<tr>
<td>1.0</td>
<td>98.8</td>
<td>98.1</td>
<td>0.8</td>
<td>0.8</td>
<td>89.0</td>
<td>108.8</td>
<td>0.247</td>
<td>0.202</td>
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<tr>
<td>2.0</td>
<td>99.2</td>
<td>98.4</td>
<td>0.8</td>
<td>0.8</td>
<td>91.4</td>
<td>110.8</td>
<td>0.240</td>
<td>0.200</td>
</tr>
</tbody>
</table>

**Table 2** Calculated parameters in AC enhanced ozonation of oxalate with varying solution pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Oxalate removal without tBA (%)</th>
<th>Oxalate removal with tBA (%)</th>
<th>Oxalate removal by HO• oxidation in bulk solution (%)</th>
<th>η (%)</th>
<th>Oxalate consumption without tBA (mg)</th>
<th>Oxalate consumption with tBA (mg)</th>
<th>R_{\Delta OA/\Delta O3} without tBA</th>
<th>R_{\Delta OA/\Delta O3} with tBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>99.1</td>
<td>100.0</td>
<td>0</td>
<td>0</td>
<td>86.4</td>
<td>101.0</td>
<td>0.771^a</td>
<td>0.692^a</td>
</tr>
<tr>
<td>5</td>
<td>97.8</td>
<td>99.7</td>
<td>0</td>
<td>0</td>
<td>86.8</td>
<td>102.5</td>
<td>0.385^b</td>
<td>0.335^b</td>
</tr>
<tr>
<td>7</td>
<td>92.6</td>
<td>89.3</td>
<td>3.3</td>
<td>3.6</td>
<td>88.0</td>
<td>105.3</td>
<td>0.237</td>
<td>0.191</td>
</tr>
</tbody>
</table>
### Table 3: Constitution of oxalate solution and the relative reaction rate with HO• with varying pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Proportion of HOOCCOOH, $\alpha_0$</th>
<th>Proportion of HOOCCOO$^-$, $\alpha_1$</th>
<th>Proportion of OOCOO$^-$, $\alpha_2$</th>
<th>$k_{\text{HOOCCOOH}$, $\alpha_0$ (mol/L·s)}</th>
<th>$k_{\text{HOOCCOO}$, $\alpha_1$ (mol/L·s)}</th>
<th>$k_{\text{OOCOO}$, $\alpha_2$ (mol/L·s)}</th>
<th>Total$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.01736</td>
<td>0.93255</td>
<td>0.05008</td>
<td>24311.0</td>
<td>43830034.4</td>
<td>385624.6</td>
<td>44239969.9</td>
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<tr>
<td>5</td>
<td>0.00003</td>
<td>0.15697</td>
<td>0.84300</td>
<td>40.9</td>
<td>7377752.0</td>
<td>6491079.4</td>
<td>13868872.3</td>
</tr>
<tr>
<td>7</td>
<td>0.00000</td>
<td>0.00186</td>
<td>0.99814</td>
<td>0.0</td>
<td>87355.4</td>
<td>7685688.6</td>
<td>7773044.0</td>
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<tr>
<td>9</td>
<td>0.00000</td>
<td>0.00002</td>
<td>0.99998</td>
<td>0.0</td>
<td>875.2</td>
<td>7699856.6</td>
<td>7700731.8</td>
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<tr>
<td>11</td>
<td>0.00000</td>
<td>0.00000</td>
<td>1.00000</td>
<td>0.0</td>
<td>8.8</td>
<td>7699998.6</td>
<td>7700007.3</td>
</tr>
</tbody>
</table>

$^a$ Total = $k_{\text{HOOCCOOH}} + k_{\text{HOOCCOO}^-} + k_{\text{OOCOO}^-}$.

Where $k_{\text{HOOCCOOH}} = 1.4 \times 10^6$ mol/L·s, $k_{\text{HOOCCOO}^-} = 4.7 \times 10^7$ mol/L·s, and $k_{\text{OOCOO}^-} = 7.7 \times 10^6$ mol/L·s (Getoff et al., 1971)

### Table 4: AC-relevant initiating, promoting and inhibiting reactions

<table>
<thead>
<tr>
<th>Category</th>
<th>Reaction</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiating reactions</td>
<td>$\text{AC} + \text{H}_2\text{O} \rightarrow \text{AC}^- + \text{H}^- + \text{O}^- + \text{OH}^-$</td>
<td>(4) (Rivera-Utrilla and Sánchez-Polo, 2004)</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2\text{O}^- + \text{OH}^-$</td>
<td>(5) (Rivera-Utrilla and Sánchez-Polo, 2002)</td>
</tr>
<tr>
<td></td>
<td>$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{O}_2^- + 2\text{OH}^-$</td>
<td>(6) (Buffle and von Gunten, 2006; von Gunten, 2003)</td>
</tr>
<tr>
<td></td>
<td>$\text{AC} + \text{O}_1 \rightarrow \text{AC}^- + \text{O}_2^-$</td>
<td>(7) (Mvula and von Sonntag, 2003; Sánchez-Polo et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>$\text{AC} + \text{O}_1 \rightarrow \text{AC}^- + \text{H}_2\text{O}_2$</td>
<td>(8) (Alvárez et al., 2006)</td>
</tr>
<tr>
<td></td>
<td>$\text{AC} + \text{H}_2\text{O}_2 \rightarrow \cdots \rightarrow \text{AC}^- + \text{HO}_2^- + \text{H}_2\text{O}_2$</td>
<td>(9) (Serp and Figueiredo, 2009)</td>
</tr>
<tr>
<td>Promoting reactions</td>
<td>$\text{AC} + \text{HO}_2 \rightarrow \text{AC}^- + \text{O}_2^-$ or $\text{H}_2\text{O}_2$</td>
<td>(11) (Mvula and von Sonntag, 2003)</td>
</tr>
</tbody>
</table>
Inhibiting reactions: \[ AC + HO \rightarrow AC^- + \text{others (not } O_2/\text{HO}_2^\cdot \text{or } H_2O_2/\text{HO}_2^- \) \] (12)

AC* is the AC after reaction.
List of Figure Captions

Fig. 1 Schematic diagram of experimental apparatus

Fig. 2 Effect of AC dosage on oxalate removal (a), ozone concentration in the outlet gas (b) and solution (c).

Fig. 3 Effect of tBA dosage on ozonation of oxalate with 0.1 g/L (a) and 0.5 g/L (b) of AC.

Fig. 4 Adsorption isotherm of tBA on AC at 25°C.

Fig. 5 Effect of tBA on oxalate removal (a), ozone concentration in the outlet gas (b) and solution (c) with varying AC dosage.

Fig. 6 H$_2$O$_2$ concentration profiles in the ozonation systems without tBA (a) and with tBA (b)

Fig. 7 Effect of pH on oxalate removal (a), ozone concentration in the outlet gas (b) and solution (c).

Fig. 8 Effect of pH on oxalate adsorption onto AC. Experimental conditions: oxygen flow rate = 116 mL/min, AC dosage = 0.5 g/L, temperature = 25°C.

Fig. 9 Effect of pH on oxalate removal (a) and ozone concentration in the outlet gas (b) and in the aqueous phase (c) with varying AC dosage.

Fig. 10 The role of AC in ozonation of oxalate.
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Fig. 9 Effect of pH on oxalate removal (a) and ozone concentration in the outlet gas (b) and in the aqueous phase (c) with varying AC dosage. The aqueous ozone concentrations in the systems with 0, 0.1, and 0.5 g/L AC at pH 11 and with 0.5 g/L AC at pH 7 were too low to be measured accurately.
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