Fe(III)-loaded activated carbon as catalyst to improve omethoate degradation by ozone in water

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ABSTRACT

Omethoate (OMT), a typical organophosphorus pesticide and also an oxidation byproduct of dimethoate, is very difficult to remove from water due to its hydrophilic nature and relatively low reactivity towards ozone. In this work, Fe(III)-loaded activated carbon (Fe@AC) was prepared and used as catalyst to promote OMT degradation by ozone. The catalytic activity of Fe@AC was investigated under various experiment conditions. Results indicate that the OMT removal was significantly enhanced in O_3/Fe@AC through effective generation of hydroxyl radicals ($\cdot$OH), as compared to ozonation alone and O_3/AC. The Fe(III) deposited on AC mainly existed in the form of ferrihydrite (FHD) particles which provided the main active sites promoting ozone decomposition. The optimal pH ranged from 7.0 to 8.0 for catalytic ozonation, which corresponded to a nearly neutral surface charge of the catalyst. The apparent rate constant of OMT degradation was almost linearly correlated with the aqueous ozone concentration. The acute toxicity of the reaction solution was substantially reduced by catalytic ozonation with Fe@AC.

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1. Introduction

Organophosphorus pesticides (OPPs) were extensively used for controlling plant diseases and insect pests in the last two decades [1]. However, the pesticides used in agriculture may seep into subterranean water and drain into surface water with storm-runoffs, and then cause micro-pollution of water sources [2,3]. OPPs of high water solubility and acute toxicity are generally hardly biodegradable in surface waters [4,5], and consequently, many OPPs have been detected in surface and ground waters [6,7]. The conventional water treatment processes, such as coagulation, sedimentation and filtration, are of low efficiency in removing OPPs from water [8]. Omethoate (OMT) is not only a typical OPP widely used in developing countries but also an oxidation byproduct of another pesticide, dimethoate [1]. Many OPPs could be removed from drinking water by chlorination and ozonation [1,9], whereas little is known about the degradation of OMT by these oxidants.

Ozone is a strong oxidant that can effectively degrade many organic pollutants, but its reactivity towards recalcitrant pollutants is quite low. Heterogeneous catalytic ozonation has attracted more and more interests in recent years because it can promote ozone oxidation of recalcitrant pollutants. Catalysts usually studied in this process include MnO_2, TiO_2, Al_2O_3, noble metals, and mixed metal oxides [10–14]. In combination with these catalysts, the removal of various organic compounds such as chlorobenzene, chlorophenols, dyes and natural organic matters by ozone was largely enhanced [14–16]. Among these catalysts, ferric oxides are more attractive due to their low cost and low solubility. In particular, ferrihydrite (FHD), which ubiquitously exists in nature and can be readily prepared in laboratory, has the distinguished characteristics of large surface area and high surface activity. It has high adsorption capacity for arsenic and phosphate in water [17,18]. However, its activity in catalytic ozonation is still unknown.

Activated carbon (AC) can promote the decomposition of aqueous ozone to generate more hydroxyl radicals ($\cdot$OH), thus enhancing the degradation of refractory pollutants. It was suggested that the electrons in the graphene planes, basic functional groups (e.g., chromene, pyrone and pyrrol) on the surface, and metals in the structure and/or on the surface of AC were possible active sites during ozonation [19,20]. Moreover, AC can also be used as an excellent catalyst carrier because of its high surface area and large porosity.

In this work, Fe(III) was deposited onto AC (designated as Fe@AC) with a simple impregnation method. The prepared Fe@AC catalysts were characterized and their activity was examined through catalytic ozonation of OMT. The effects of Fe(III) loading content, aqueous ozone concentration, water pH and catalyst reusing cycles on the removal rate of OMT were systematically investigated. Furthermore, the acute toxicity of the reaction solution was assessed during catalytic ozonation.

2. Experimental

2.1. Catalyst preparation

Fe@AC was prepared according to the method developed by Jiang et al. [17] with certain modifications. Granular activated carbon produced from coal was purchased from Xinhua Activated Carbon Company (Shanxi, China), which was grinded and the particles with diameters of 100–200 μm were sieved out. These particles were immersed in ferric nitrate solution with a desired concentration. The suspension was shaken at 20 °C for 24 h, and then cured in oven at 105 °C for 12 h. The prepared Fe@AC particles were sieved again and those of 100–200 μm were directly used in experiments. Our preliminary experiment showed that the rinsing of Fe@AC particles prior to use had negligible influence on the catalyst activity. The Fe@AC catalysts were designated as x%-Fe@AC, where x represents the Fe (III) loading content in weight percentage.

Ferrihydrite (FHD) was prepared by adding 1 mol L^{-1} NaOH solution dropwise into Fe(NO$_3$)$_3$ solution under magnetic stirring condition until the final pH reached 9.0. The precipitate was repeatedly rinsed with distilled water for 5–6 times, filtrated with 0.45 μm synthetic fiber membrane, and finally dried at 65 °C for 12 h. The FHD was used in control experiments.

2.2. Analysis

BET surface area and pore volume of the prepared catalysts were measured using a surface area and porosity analyzer (ASAP 2000, Micromeritics). The surface density of acidic and basic functional groups was determined according to Boehm [21]. To determine the surface density of acidic groups, NaOH solution (ca. 0.10 mol L^{-1}, 10 mL) was added to a test tube containing about 0.4 g of catalyst. The suspension was continuously shaken at 170 rpm and 25 °C for 24 h, and then 5 mL of supernatant was withdrawn, filtered with 0.45 μm syringe filter, and back titrated with HCl solution (ca. 0.10 mol L^{-1}). The surface density of acidic groups was thus calculated on the basis of the consumed NaOH. Likewise, to determine the surface density of basic groups, HCl solution was used to soak the catalyst and NaOH solution was used for back titration. The surface density experiments were conducted in triplicate.

The pH$_{pzc}$ (a pH value corresponding to zero-charged surface) was measured with a powder addition method [22]. Crystallite structures were analyzed on a Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα radiations ($\lambda = 0.15406$ nm). Morphologies were visualized by a transmission electron microscope (TEM) system (H-7500, Hitachi). The total ash content of AC was determined to be 13.5% through incineration, of which the relative atomic percentages of Si, Fe, Al and Ca were determined by X-ray photoelectron spectroscopy (XPS) with an Escalab 250 spectrometer (Thermofisher).

Aqueous ozone concentration was measured with the indigo method [23]. OMT concentration was determined with a high-performance liquid chromatograph (HPLC, Agilent 1200) equipped with a DPD detector (monitored at 210 nm) and an Atlantis dC18 column (4.6 mm × 250 mm, Waters). The eluent consisted of an isocratic mixture of Milli-Q water (mobile phase A) and acetonitrile (mobile phase B) at a volume ratio of 8:2. An inductively coupled plasma mass spectrometer (ICP/MS, 7500a, Agilent) was used to determine the concentration of ferric ion in water, which may leach from the Fe@AC catalyst during catalytic ozonation.

2.3. Experimental procedures

Experiments were carried out in a cylindrical glass reactor (inner diameter 12 cm, total volume 1.0 L) which was magnetically stirred and water-bathed. Ozone was produced from dried oxygen gas with an ozone generator (3S-A3G, Tonglin, Beijing). After the catalysts were added into 500 mL of OMT solution prepared at a desired concentration, the ozone gas was bubbled into the reaction solution through a silica dispenser. The aqueous ozone concentration could quickly reach a steady-state level within 3–5 min. Although in the initial period (i.e., 3–5 min), the aqueous ozone concentration increased from zero to a desired steady-state level, it had insignificant influence on the determination of OMT degradation rate considering that the whole reaction course was as long as 30 min. Different steady-state ozone concentrations could be readily achieved through adjusting the oxygen gas inflow rate and the electric current of the ozone generator. Water samples were withdrawn at specific time intervals, and the residual ozone was immediately quenched with dilute Na$_2$SO$_3$ solution [24]. The samples were thereafter filtered through 0.45 μm acetic acid fiber filters to separate the catalyst particles prior to HPLC analysis. The adsorption experiments of OMT on the catalyst were performed without ozone bubbling under otherwise identical conditions. Phosphate (10 mmol L^{-1}) was used as buffer in all reaction solutions.

2.4. Acute toxicity assessment

The acute toxicity of the reaction solution during catalytic ozonation with Fe@AC was assessed by *Daphnia magna* test following the National Standards of China (Water Quality-Determination of the Acute Toxicity of Substance to *Daphnia*, GB/T13266-91). *Daphnia* was cultured in laboratory for more than three generations. Reaction samples were immediately bubbled with nitrogen gas to blow off the residual ozone. An aliquot of reaction sample (0.5 mL) was added into each glass beaker containing 50 mL of synthetic natural water and 10 healthy *Daphnia* neonates. The test beakers were incubated for 48 h at 22 °C, and the toxicity was expressed by the immobilization percentage of neonates. The neonates were considered immobile if they remained at the bottom of the test beaker and did not resume swimming within the 15 s observation period. All toxicity tests were performed in triplicate.

3. Results and discussion

3.1. Improvement on OMT degradation

Since the dose of powdered activated carbon commonly adopted in drinking water treatment plants ranges from 1 to 100 mg L^{-1} [25,26], the catalyst was applied at a dose of 20 mg L^{-1} in this work. Fig. 1 compares the removal rates of OMT as a function of reaction time in oxidation by ozonation alone, O$_3$/AC, O$_3$/5%-Fe@AC and in adsorption by AC and 5%-Fe@AC. Results indicate that OMT exhibited a relatively low reactivity towards ozone, while the presence of either AC or 5%-Fe@AC could significantly promote the degradation of OMT. For example, at the reaction time of 30 min, the removal rates of OMT were about 37.6%, 58.0%, and 82.4% in ozonation alone, O$_3$/AC and O$_3$/5%-Fe@AC, respectively. In contrast, the adsorption by AC and 5%-Fe@AC only contributed to 6.5% and 5.7% removal of OMT, respectively. Therefore, it is seen that the enhanced removal of OMT in O$_3$/AC and O$_3$/5%-Fe@AC was mainly due to catalytic ozonation rather than adsorption by the catalysts.

Previous studies have shown that metals and surface basic groups on AC would act as active sites in catalytic ozonation [19,20]. The basic groups on the AC surface could promote aqueous ozone decomposition to generate ·OH, which is a stronger oxidant than ozone. As shown in Table 1, the surface densities of basic and acidic groups of AC were 1093 and 163 μeq g^{-1}, respectively. After 5% of Fe(III) was deposited onto AC, the surface densities of basic and acidic groups were remarkably changed to 192 and 1218 μeq g^{-1},

Table 1
Surface characteristics of the prepared catalysts.

Catalysts	BET surface area ($m^2 g^{-1}$)	Pore volume[a] ($cm^3 g^{-1}$)	Surface basic groups[d] ($\mu eq\, g^{-1}$)	Surface acidic groups[d] ($\mu eq\, g^{-1}$)
AC	862 ± 12	0.200	1093 ± 50	163 ± 9
0.2%-Fe@AC	842 ± 13	0.178	990 ± 14	308 ± 63
1%-Fe@AC	790 ± 12	0.174	699 ± 49	625 ± 47
5%-Fe@AC	747 ± 12	0.135	192 ± 67	1218 ± 79
10%-Fe@AC	647 ± 11	0.119	5 ± 9	1691 ± 61
5%-Fe@AC–1[b]	684 ± 11	0.133	360 ± 43	890 ± 19
5%-Fe@AC–2[c]	676 ± 11	0.122	310 ± 25	888 ± 10
FHD	171 ± 1	0.151	496 ± 9	496 ± 9

[a] Cumulative pore volume of the catalyst between 1.7 and 300 nm diameters.
[b] 5%-Fe@AC used once.
[c] 5%-Fe@AC used twice.
[d] Mean $\pm$ S.D. (triplicate experiments).

respectively. The high acidity of $Fe(NO_3)_3$ solution led to a decrease in the surface basic groups of Fe@AC, which would negatively impact the catalytic activity. Results indicate, however, the 5%-Fe@AC showed a much higher activity than AC in promoting OMT degradation by ozone (Fig. 1). It implies that the modification of AC with Fe(III) loading produced new active sites on the surface.

3.2. Surface changes of AC caused by Fe(III) loading

To evaluate the effect of Fe (III) loading content on AC, both AC and the prepared Fe@AC catalysts were characterized with XRD. Results indicate that the AC surface had many crystallized peaks (Fig. 2), which was mainly ascribed to the reflection of SiO_2, Fe_2O_3, Al_2O_3 and $CaCO_3$ crystals [17,27]. Further XPS analysis proves that the AC ash contained Si, Fe, Al and Ca elements with a relative atomic percentage of 9.3%, 0.7%, 7.9% and 7.0%, respectively. It is also noticed in Fig. 2 that the increase of Fe(III) loading content from 1% to 10% significantly weakened many XRD peaks of AC. In particular, with the increase of Fe(III) loading content, the two peaks of AC in the range of 34.3–37.7° gradually transformed into one broad peak, indicating the formation of FHD [28,29].

In general, the surface hydroxyl groups of metal oxides were important active sites in catalytic ozonation [30]. Their surface densities of acidic and basic hydroxyl groups should be quantitatively equal based on the principle of charge balance [31]. For FHD prepared in this study, the surface density of acidic

or basic hydroxyl groups was determined to be 496 $\mu eq\, g^{-1}$ (Table 1).

The TEM images of AC and prepared Fe@AC catalysts are shown in Fig. 3. It is observed that some black areas emerged on the AC after Fe(III) loading. These black areas were identified to be FHD particles by comparing with the structure of individually prepared FHD. In addition, the FHD particles in 10%-Fe@AC were considerably larger than those in 5%-Fe@AC, denoting the agglomeration of FHD particles at a high Fe(III) loading content that tended to decrease the activity of the prepared catalyst.

As shown in Table 1, the surface area of Fe@AC decreased with the increasing Fe(III) loading content. The FHD particles could penetrate into the pores of AC, as reflected by the notable decrease in the pore volume of Fe@AC. It is also noted that the negative impact on the catalytic activity from the decrease in the surface density of basic groups of Fe@AC, as compared to that of AC, was surpassed by the positive impact from the new active sites (i.e., surface hydroxyl groups) provided by FHD. As a result, the ozonation rate of OMT was significantly enhanced in the presence of 5%-Fe@AC (Fig. 1).
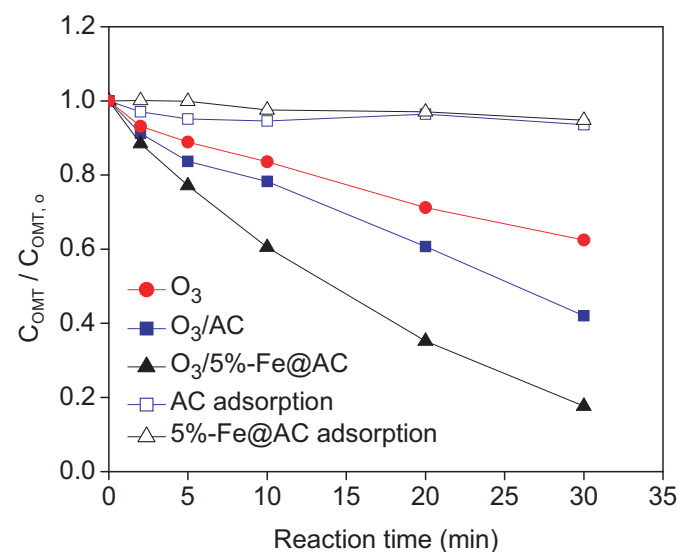

Fig. 1. Removal of OMT as a function of reaction time. Experimental conditions: pH = 7.5; $T = 20 \pm 2\,°C$; $[OMT]_o = 1.0\, mg\, L^{-1}$; catalyst dose = 20 mg L^{-1}; and $[O_3] = 1.0\, mg\, L^{-1}$.
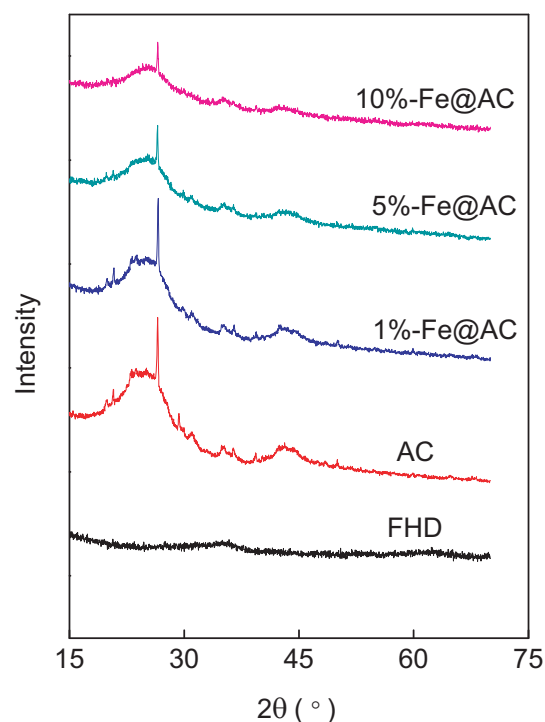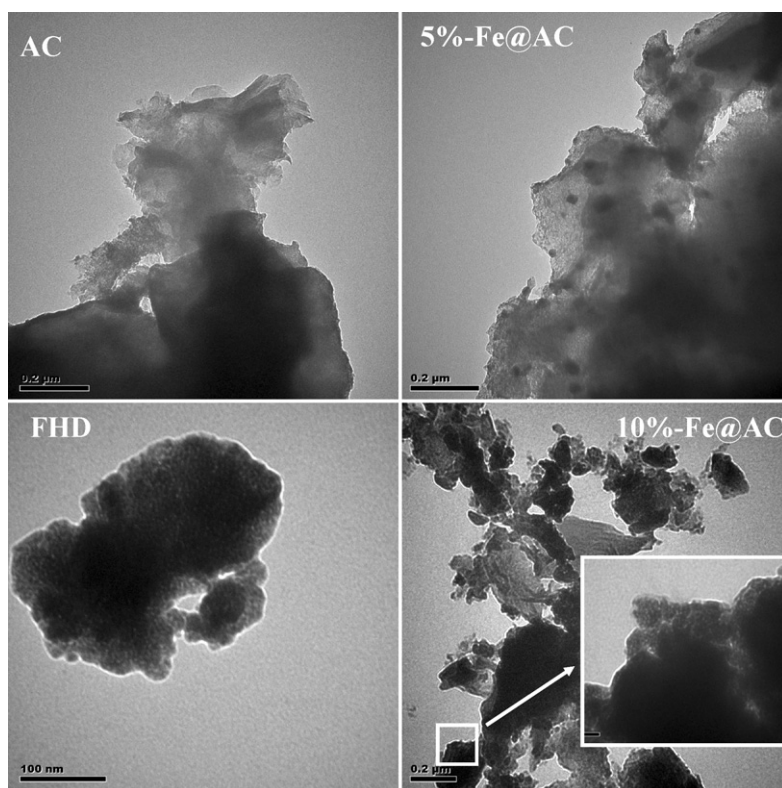

Fig. 2. XRD spectra of AC, Fe@AC and FHD.

Fig. 3. TEM images of AC and Fe@AC.

3.3. Enhanced hydroxyl radical generation

Tert-butanol (t-BuOH) is a commonly used scavenger for ·OH. In the presence of t-BuOH, the removal rates of OMT dramatically decreased to 4.6%, 9.8% and 4.3% at the reaction time of 30 min in ozonation alone, O_3/AC and O_3/5%-Fe@AC, respectively (Fig. 4a). This result shows that ·OH played a vital role in degrading OMT as compared to molecular ozone in either ozonation alone and catalytic ozonation. The enhanced generation of ·OH in the O_3/5%-Fe@AC process was mainly due to the FHD particles.

The decomposition of aqueous ozone in both ozonation alone and O_3/5%-Fe@AC could be well expressed by the first-order kinetics, and ozone decomposed more quickly in O_3/5%-Fe@AC than in ozonation alone (Fig. 4b). It is seen that the accelerated ·OH generation in O_3/5%-Fe@AC is pertinent to the promoted decomposition of aqueous ozone. It should be noted that the decomposition of aqueous ozone in the presence of AC was faster than that in the presence of 5%-Fe@AC (Fig. 4b), while the removal rate of OMT just reversed (Fig. 1). It is thus hypothesized that the oxidation of some surface reductive groups of AC consumed a significant portion of ozone, but did not lead to the generation of ·OH. In contrast, the loading of Fe(III) onto AC largely masked these reductive sites, and consequently reduced the inefficacious ozone consumption.

3.4. Influence of Fe(III) loading content

The effect of different Fe(III) loading contents on the removal rate of OMT in catalytic ozonation was examined, as shown in Fig. 5. Results indicate that as the Fe(III) loading content increased from 0.2% to 5%, the OMT removal rate was enhanced correspondingly; whereas further increasing the Fe(III) loading content to 10% retarded the removal of OMT.

As described above, the deposited FHD particles on AC were the major active species in catalytic ozonation. In general, increasing the Fe(III) loading content could provide more active sites for catalytic reactions. However, some adverse effects associated with Fe(III) loading may include: (a) the agglomeration of FHD particles at a high Fe(III) loading content, as revealed by the TEM image of 10%-Fe@AC (Fig. 3); (b) the decrease in surface area and pore volume of the catalyst (Table 1); and (c) the decrease in surface density of basic groups (Table 1). Therefore, the optimal Fe(III) loading content of 5% was actually a tradeoff between the positive and negative effects caused by the catalyst surface changes.

3.5. Influence of ozone concentration

In this work, oxidation experiments were carried out in the semi-continuous mode where aqueous ozone concentration was maintained constant during most of the reaction course. As shown in Table 2, the degradation of OMT could be well expressed by the pseudo-first-order kinetics in both ozonation alone and catalytic ozonation with AC or 5%-Fe@AC ($R^2 \geq 0.98$). At an aqueous ozone concentration of 1.0 mg L^{-1}, the apparent rate constants of OMT degradation (k_{app}) were 2.5×10^{-4}, 4.5×10^{-4} and 9.4×10^{-4} s^{-1} in ozonation alone, O_3/AC and O_3/5%-Fe@AC, respectively. The presence of AC and 5%-Fe@AC obviously accelerated the degradation of OMT by ozone. In addition, at a constant dose of 20 mg L^{-1} 5%-

Table 2
The apparent rate constant of OMT degradation (k_{app}) in ozonation alone and catalytic ozonation with AC or 5%-Fe@AC (pH = 7.5, $T = 20 \pm 2$ °C, [OMT]$_o$ = 1.0 mg L^{-1}, catalyst dose = 20 mg L^{-1}).

Reaction	[O_3] (mg L^{-1})	$k_{app} \times 10^4$ (s^{-1})	R^2
O_3	1.0	2.5	0.99
O_3/AC	1.0	4.5	0.98
O_3/5%-Fe@AC	0.4	2.3	0.99
O_3/5%-Fe@AC	1.0	9.4	0.99
O_3/5%-Fe@AC	2.4	18.7	0.98
O_3/5%-Fe@AC	4.3	28.4	0.98

Fig. 5. Influence of Fe(III) loading content of Fe@AC on OMT degradation in catalytic ozonation. Experimental conditions: $T = 20 \pm 2\,^\circ C$; $[OMT]_o = 1.0\,mg\,L^{-1}$; catalyst dose = 20 mg L^{-1}; and $[O_3] = 1.0\,mg\,L^{-1}$.

The removal rates of OMT in ozonation alone and O$_3$/5%-Fe@AC at a reaction time of 10 min were measured in the pH range of 6.1–8.5 (Fig. 7). Results indicate that the removal rate of OMT greatly increased as water pH increased, implying that OMT degradation was dominated by the indirect oxidation via ·OH radicals. In comparison to ozonation alone, 5%-Fe@AC exerted its catalytic effect mainly in the pH range of 7.0–8.0. When the pH was either below 6.1 or above 8.5, the catalyst could no longer promote OMT degradation. The pH$_{pzc}$ values of FHD and AC were measured to be about 7.6 ± 0.2 and 7.4 ± 0.1, thus the surface of Fe@AC was mainly zero-charged at pH 7.0–8.0. Similar to our previous study on catalytic ozonation with goethite (α-FeOOH) [24,33], the uncharged surface hydroxyl groups of FHD were the main active sites in promoting ozone decomposition to generate ·OH.

3.7. Reusability of 5%-Fe@AC

The reusability of Fe5%-@AC in catalytic ozonation of OMT was examined, as shown in Fig. 8. Results indicate that the removal

Fig. 4. Influence of t-BuOH on OMT degradation (a) and influences of AC and 5%-Fe@AC on ozone decomposition (b). Experimental conditions: pH = 7.5, $T = 20 \pm 2\,^\circ C$, catalyst dose = 20 mg L^{-1}; (a) $[OMT]_o = 1.0\,mg\,L^{-1}$, $[t\text{-BuOH}]_o = 74\,mg\,L^{-1}$, $[O_3] = 1.0\,mg\,L^{-1}$; (b) $[O_3]_o = 1.9 \pm 0.1\,mg\,L^{-1}$.

Fe@AC, the value of k_{app} increased with the increasing aqueous ozone concentration. A closely linear relationship was observed between k_{app} and the aqueous ozone concentration, as plotted in Fig. 6 ($R^2 = 0.99$).

3.6. Influence of water pH

In the normal pH range of drinking water treatment (i.e., 6.0–9.0), OMT predominantly exists in the neutral form. However, it is well known that pH significantly affects ozonation because hydroxyl ions can quickly initiate ozone decomposition to generate ·OH. Furthermore, pH is also an important factor governing the charge status at the FHD/water interface due to the protonation and deprotonation reactions of surface hydroxyl groups, which can be expressed by Eqs. (1) and (2) [32]:
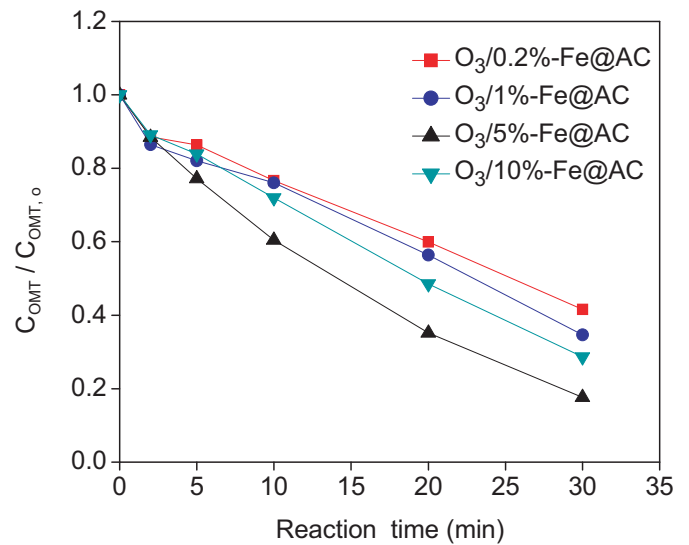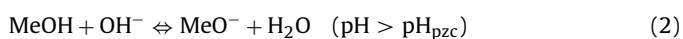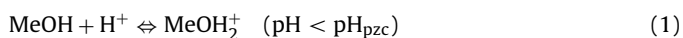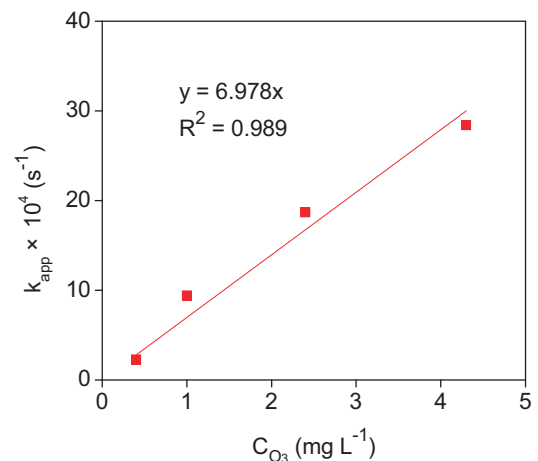
$$MeOH + H^+ \Leftrightarrow MeOH_2^+ \quad (pH < pH_{pzc}) \tag{1}$$

$$MeOH + OH^- \Leftrightarrow MeO^- + H_2O \quad (pH > pH_{pzc}) \tag{2}$$

Fig. 6. Linear relationship between the apparent rate constant of OMT degradation (k_{app}) and aqueous ozone concentration. Experimental conditions: pH = 7.5; $T = 20 \pm 2\,^\circ C$; $[OMT]_o = 1.0\,mg\,L^{-1}$; and catalyst dose = 20 mg L^{-1}.

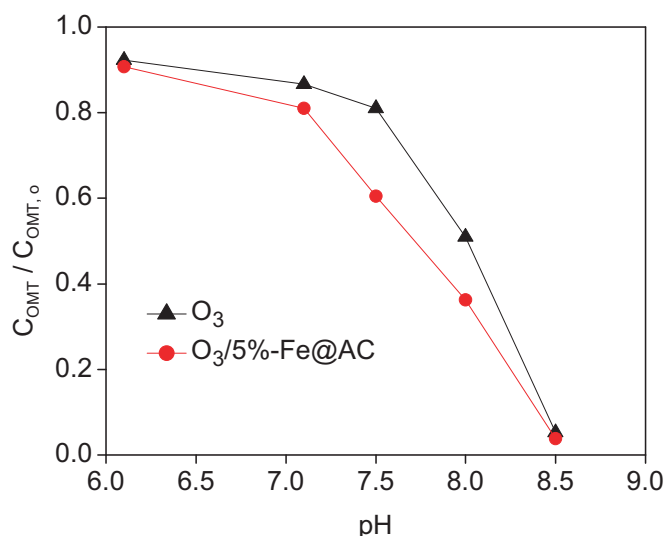**Fig. 7.** Influence of water pH on OMT degradation in catalytic ozonation with 5%-Fe@AC. Experimental conditions: $T = 20 \pm 2\,°C$; $[OMT]_o = 1.0\,mg\,L^{-1}$; catalyst dose $= 20\,mg\,L^{-1}$; $[O_3] = 1.0\,mg\,L^{-1}$; and reaction time $= 10\,min$.

rate of OMT gradually decreased as the reuse time of 5%-Fe@AC increased. At the reaction time of 30 min, the OMT removal rate was decreased only by about 12.5% when the catalyst was used for the fourth time as compared to that achieved by the fresh catalyst. The decrease in catalyst activity was probably attributed to the decrease of its surface area (Table 1), consumption of active sites, and leaching of Fe^{3+} ions (Fig. 8). At the dose of $20\,mg\,L^{-1}$ fresh catalyst, the concentration of leached Fe^{3+} ions was determined to be $36\,\mu g\,L^{-1}$ after 30 min of reaction, which accounted for about 4.0% of the total Fe(III) deposited on AC. It should be noted that this leaching level will not cause any problem to water treatment since the maximum contamination level is $0.3\,mg\,L^{-1}$ for iron as regulated by the National Standards for Drinking Water Quality of China (GB 5749–2006). AC is commonly used as adsorbent in drinking water plants and iron is a cheap material, so the Fe@AC catalyst is economically affordable. Therefore, the O_3/Fe@AC process may be applied as an effective pretreatment method for source water that is micro-polluted with recalcitrant pesticides. After catalytic ozonation, the Fe@AC particles can be easily removed in subse-
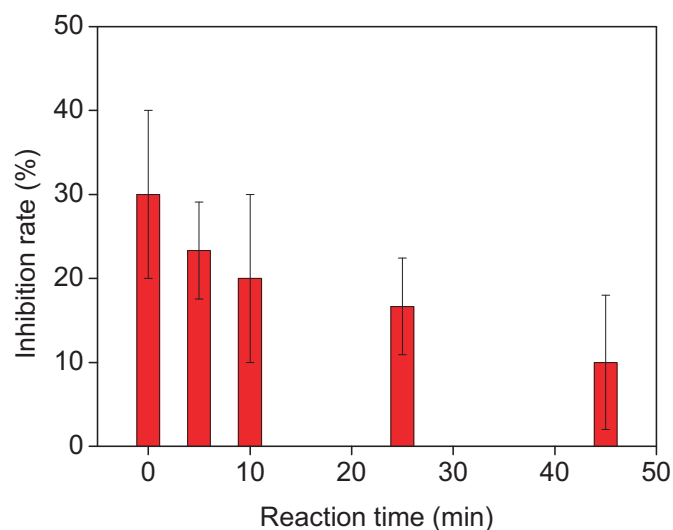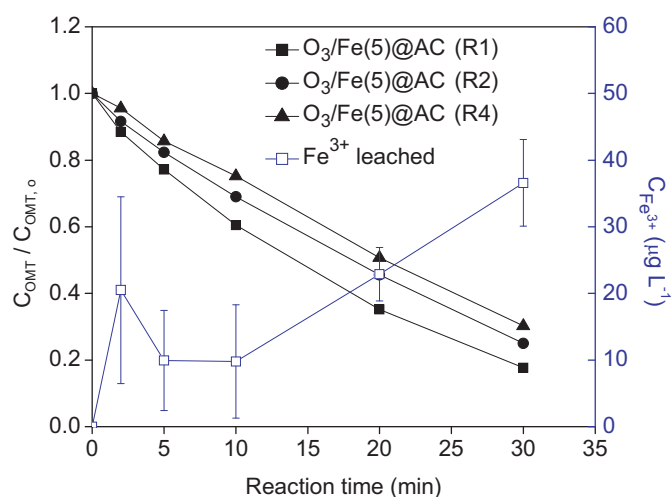

Fig. 8. Catalytic activity of 5%-Fe@AC in reusing cycles and leached concentrations of Fe^{3+} ions. Experimental conditions: pH = 7.5; $T = 20 \pm 2\,°C$; $[OMT]_o = 1.0\,mg\,L^{-1}$; catalyst dose $= 20\,mg\,L^{-1}$; and $[O_3] = 1.0\,mg\,L^{-1}$. R1, R2 and R4 denote the reusing cycles of catalyst. Error bars represent the standard deviation of duplicate experiments.

Fig. 9. Change of acute toxicity of OMT solution during catalytic ozonation with 5%-Fe@AC. Experimental conditions: pH = 7.5; $T = 20 \pm 2\,°C$; $[OMT]_o = 1.0\,mg\,L^{-1}$; catalyst dose $= 20\,mg\,L^{-1}$; and $[O_3] = 1.0\,mg\,L^{-1}$. The error bars represent the standard deviation of triplicate tests.

quent treatment processes such as coagulation, sedimentation and filtration.

3.8. Acute toxicity assessment

OMT has a high acute toxicity. The catalytic ozonation of OMT will produce a number of byproducts whose toxicity remains unknown up to date. The acute toxicity of the OMT solution throughout the catalytic ozonation with 5%-Fe@AC was assessed by the *Daphnia magna* test as mentioned above. Results indicate that the acute toxicity was notably reduced as the catalytic ozonation proceeded (Fig. 9). For example, the inhibition rate on *Daphnia* neonates approximately decreased from the initial 30 to 20% at 10 min, and further to 10% at 45 min. In other words, the acute toxicity was reduced by 33% and 67% after catalytic ozonation for 10 and 45 min, respectively. It is seen that the catalytic ozonation with 5%-Fe@AC can not only degrade the parent compound (i.e., OMT), but also produce the byproducts with less toxicity.

4. Conclusions

The heterogeneous catalytic ozonation with the prepared Fe@AC catalysts could significantly enhance the removal rate of OMT as compared to ozonation alone and O_3/AC. The Fe@AC catalysts promoted aqueous ozone decomposition to generate ·OH which was the dominant oxidant for OMT degradation. The FHD particles on AC acted as the major active sites to catalyze aqueous ozone decomposition. The optimal Fe(III) loading content was 5% which led to the most effective removal of OMT. Fe@AC exerted its catalytic effect mainly in the pH range of 7.0–8.0, which was ascribed to the nearly neutral surface charge state of the catalyst under this pH condition. The acute toxicity of the OMT solution was substantially reduced by catalytic ozonation with 5%-Fe@AC. The O_3/Fe@AC process may be applied as an effective pretreatment method for source water that is micro-polluted with recalcitrant pesticides.

References

[1] J. Wu, C. Lan, G.Y.S. Chan, Chemosphere 76 (2009) 1308–1314.
[2] R.H. Coupe, M.A. Manning, W.T. Foreman, D.A. Goolsby, M.S. Majewski, Sci. Total Environ. 248 (2000) 227–240.
[3] P.N. Schipper, M.J. Wissers, A.M. van der Linden, Water Sci. Technol. 57 (2008) 1277–1286.
[4] M.B. Abou-Donia, Arch. Environ. Health 58 (2003) 484–497.
[5] M.P. Mahadevaswami, B.B. Kaliwal, Environ. Toxicol. Pharm. 20 (2005) 251–257.
[6] R.J. Gilliom, J.E. Barbash, C.G. Crawford, P.A. Hamilton, J.D. Martin, N. Nakagaki, L.H. Nowell, J.C. Scott, P.E. Stackelberg, G.P. Thelin, D.M. Wolock, The Quality of Our Nation's Waters: Pesticides in the Nation's Streams and Ground Water, 1992–2001, US Geological Survey, Circular 1291 (2006), pp. 172.
[7] N. Sankararamakrishnan, A.K. Sharma, R. Sanghi, Environ. Int. 31 (2005) 113–120.
[8] M.P. Ormad, N. Miguel, A. Claver, J.M. Matesanz, J.L. Ovelleiro, Chemosphere 71 (2008) 97–106.
[9] D. Arapoglou, A. Vlyssides, C. Israilides, A. Zorpas, P. Karlis, J. Hazard. Mater. 98 (2003) 191–199.
[10] J. Ma, M. Sui, T. Zhang, C. Guan, X. Bao, Water Res. 39 (2005) 779–786.
[11] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, Appl. Catal. B: Environ. 39 (2002) 221–231.
[12] M. Ernst, F. Lurot, J.C. Schrotter, Appl. Catal. B: Environ. 47 (2004) 15–25.
[13] F. Delanöe, B. Acedo, N. Karpel Vel Leitner, B. Legube, Appl. Catal. B: Environ 29 (2001) 315–325.
[14] C. Cooper, R. Burch, Water Res. 33 (1999) 3695–3700.
[15] M.M. Hassan, C.J. Hawkyard, Catal. Commun. 3 (2002) 281–286.
[16] J.S. Park, H. Choi, J. Cho, Water Res. 38 (2004) 2284–2291.
[17] M. Jang, W. Chen, F.S. Cannon, Environ. Sci. Technol. 42 (2008) 3369–3374.
[18] B. Pan, J. Wu, B. Pan, L. Lv, W. Zhang, L. Xiao, X. Wang, X. Tao, S. Zheng, Water Res. 43 (2009) 4421–4429.
[19] M. Sánchez-Polo, J. Rivera-Utrilla, Carbon 41 (2003) 303–307.
[20] J. Rivera-Utrilla, M. Sánchez-Polo, Langmuir 20 (2004) 9217–9222.
[21] H.P. Boehm, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, Academic Press, New York, 1966, p. 179.
[22] G. Newcombe, R. Hayes, M. Drikas, Colloid Surf. A 78 (1993) 65–71.
[23] H. Bader, J. Hoigné, Ozone-Sci. Eng. 4 (1982) 169–176.
[24] T. Zhang, J. Ma, J Mol. Catal.: A: Chem. 279 (2008) 82–89.
[25] J.M. Laine, R. Glucina, L. Malleret, A. Bruchet, I. Baudin, J.G. Jacangelo, Water Sci. Technol. 1 (2001) 19–24.
[26] D. Cook, G. Newcombe, P. Sztajnbok, Water Res. 35 (2001) 1325–1333.
[27] J. Rivera-Utrilla, M. Sánchez-Polo, Appl. Catal. B: Environ. 39 (2002) 319–329.
[28] A. Hofmann, M. Pelletier, L. Michot, A. Stradner, P. Schurtenberger, R. Kretzschmar, J. Colloid Interf. Sci. 271 (2004) 163–173.
[29] A.A. Van der Giessen, J. Inorg. Nucl. Chem. 28 (1966) 2155–2159.
[30] J. Narcosis, B. Kasprzyk-Hordern, Appl. Catal. B: Environ. 99 (2010) 27–42.
[31] H. Tamura, A. Tanaka, J. Colloid Interface Sci. 209 (1999) 225–231.
[32] W. Stumm, Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems, Wiley-Interscience, New York, 1992.
[33] T. Zhang, C. Li, J. Ma, H. Tina, Z. Qiang, Appl. Catal. B: Environ. 82 (2008) 131–137.