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Enhanced mineralization of aqueous Reactive Black 5 by catalytic ozonation in the presence of modified GAC

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ABSTRACT

A modification of granular activated carbon (GAC) by Fe–Mn–O was proposed to improve the catalytic activity of GAC for the enhanced mineralization of aqueous RB5. The efficiency, kinetics, and possible mechanism of ozonation of aqueous RB5 catalyzed by GAC and mGAC have been investigated. mGAC exerted enhanced catalytic activity in the mineralization of aqueous RB5 and a slight promotion in decoloration. An additional 18% TOC removal efficiency was observed in the degradation of RB5 by O_3/mGAC compared with O_3/GAC under identical experimental conditions within 1 h. The pH exerted an evident impact on the degradation of RB5, with maximal mineralization achieved at pH 7. mGAC showed stable catalytic activity in the ozonation of aqueous RB5. Reaction kinetics showed that the TOC removal rate constant of RB5 degradation by O_3/mGAC was 5.4 times higher than that by O_3 alone. The reaction mechanism involved the enhanced mineralization of aqueous RB5 at the catalyst–solution interface via hydroxyl radicals produced by the reaction between O_3 and the surface of mGAC.

Keywords: Catalytic ozonation; GAC; Modification; Fe–Mn–O; Aqueous RB5; Mineralization

1. Introduction

Dye is a type of compound with a synthetic origin and complex aromatic molecular structure that make it stable [1]. Currently, dyeing wastewater has the characteristics of not only large volume and varying pH, but also complex composition [2]. Dye wastewaters may overload the self-purification mechanism, prevent or reduce photosynthetic processes, and can have toxic or carcinogenic effects on the environment [3]. A conventional biological wastewater treatment process is not effective in treating dye wastewater, because the presence of some reactive colorants can inhibit microorganism activity in such treatment systems, thus reducing their depurative capacity [4].

Among all the oxidation methods, ozonation emerges as the most promising one for color removal in textile wastewater. It presents rapid color removal efficiency because ozone molecules attack unsaturated bonds of chromophores rapidly and selectively [5]. However, ozonation by-products, which cannot be oxidized by ozone molecules easily, such as organic acids, aldehydes, and ketones, produced due to the oxidation of dye molecules. Catalytic ozonation is one of the

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advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals that exerts high effectiveness in degrading of organic pollutants [6]. Compared with homogeneous catalytic ozonation, heterogeneous catalytic ozonation has received more attention in recent years. In the ozonation of atrazine, it was found that hydrous MnO_2 was active in catalyzing the destruction of atrazine, while commercial MnO_2 did not show any catalytic activity [7]. CuS enhanced decolorization of aqueous reactive dye, and higher efficacy of decolorization at a lower pH was observed [8]. In the degradation of 2,4,6-trichloroanisole by iron and manganese-modified bauxite, Qi et al. found that surface property was the key factor that influenced the activity of the catalyst and a low zeta potential for modified bauxite-enhanced catalytic activity [9]. In addition to high efficiency in decomposing O_3 into $HO^{\cdot}$, heterogeneous catalytic ozonation excluded metal ion pollution and the catalysts could not be recycled. Granular activated carbon (GAC) has drawn great interest because it is practical and economical as a catalyst in the treatment of industrial wastewater by ozone [10]. In addition to its excellent adsorption capacity, GAC also exhibits catalytic activity due to its high surface area and surface chemical properties [11]. Recently, it was found that GAC exhibited activity in catalytic ozonation [12]. For example, in ozonation of aniline promoted by activated carbon, the increase in TOC removal was of 19% at a pH of 7 and 27% at a pH of 3, relative to ozonation alone [13]. To provide active sites on the catalyst and improve ozone decomposition, different metal oxides (such as CeO_2, MnO_x) supported by GAC were investigated [14,15]. Synergistic catalytic activity between metal oxides and GAC has been confirmed. A remarkable enhancement in the degree of mineralization was obtained during the ozonation catalyzed by the composite AC–Ce–O compared with that by AC, in which less than 14% of the initial TOC remained in solution and completely mineralization was achieved in less than 2 h [14]. Catalytic ozonation emerges as the most promising alternative in industrial wastewater treatment, but relatively low ozone utilization efficiency limited its application. To the best of our knowledge, active carbon-supported metal oxides was worthy of investigation in the improvement of ozone utilization. Various metal oxides were proved to have a stable structure, great oxygen vacancies, and high density of surface hydroxyl groups, such as Fe–Cu–O [5] and Fe–Ni–O [16] and they exerted high catalytic activity in the ozonation. However, little information about GAC-deposited multiple metal oxides has been reported [17]. Therefore, the effectiveness and mechanism of multiple metal oxides in the promotion of GAC catalytic activity remains unclear.

In this work, GAC-deposited Fe–Mn–O (mGAC) were employed to improve ozonation. The SEM–EDS (Energy Dispersive Spectrometer) analysis of GAC and mGAC was performed. The degradation of RB5 by ozonation in the presence and absence of mGAC and GAC was investigated. The objective is to reveal the effectiveness of mGAC in improving the ozonation of RB5 and the possible catalytic ozonation mechanism at the solid–liquid interface. In addition, the catalytic stability of mGAC was also discussed. Our work may be a motivation for promoting the application of ozonation in the advanced treatment of industrial wastewater.

2. Methods

2.1. Materials

Simulated wastewater was prepared by spiking RB5 (Shanghai Chem. Ltd.) in distilled water. All of the reagents, such as NaOH, KI, $Na_2S_2O_3$, $FeSO_4{\cdot}7H_2O$, and $MnSO_4{\cdot}H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. They were all reagent grade and were used without further purification. Ultrapure water was used in preparing the solution for all the experiments. The pH was adjusted with HCl and NaOH.

2.2. Catalyst preparation and characterization

The catalyst was prepared following an incipient wetness impregnation method. First, the raw GAC was washed with ultrapure water several times to remove surface dust and then sieved to obtain 8–30 mesh particles. Second, the sieved GAC was impregnated with an aqueous solution containing 0.1 mol L^{-1} $MnSO_4$ and 0.5 mol L^{-1} $FeSO_4$ followed by an adjustment of the pH to 10. Then, after 30 min vigorous stirring, this solid–liquid system was placed in boiling water for 2 h. Before centrifugation and washing of the solid, the pH of the system was adjusted to 7. Finally, we obtained the optimal catalyst (mGAC) after calcinating the solid at 300 °C for 2 h. The granule was the catalyst prepared. In addition, the Mn–GAC and Fe–GAC mentioned below were prepared similarly, except that aqueous solutions contained only 0.1 mol L^{-1} $MnSO_4$ and 0.5 mol L^{-1} $FeSO_4$, respectively.

The chemical composition of the catalysts was analyzed by a D8 Advance X-ray Spectrometer (Bruker, D8). The specific surface area was obtained by the Bunauer–Emmet–Teller (BET) method (Micromeritics, Tristar 3000). The pH at the point of zero charge (pH_{pzc}) was measured by a mass titration method (Zatesizer, Nauo Z). A XL30 scanning electron microscope (Philips, Holland) was used to create an SEM image of the samples.

2.3. Catalytic ozonation runs

The removal of Reactive Black 5 from aqueous solutions at different pH levels was investigated at room temperature in semi-batch mode in a column glass reactor equipped with agitation. The catalyst and Reactive Black 5 (2 L) were added into the reactor and were followed by the input of a steady ozone flow, which was generated by an ozone generator (CF-3–10 g, Qingdao Guolin CO., Ltd.). For comparative purposes, adsorption and single ozonation experiments were also performed under identical experimental conditions. In particular, the same flow rate of oxygen was input into the reactor with other reaction conditions kept identical with the catalytic process in the adsorption experiment. The addition of the gaseous flow was made through an aerator placed at the bottom of the reactor. The withdrawn samples were centrifuged immediately at the speed of 2000 rpm for 5 min. In the experiments carried out in the presence of radical scavenger *tert*-butanol (TBA), a concentration of 5 mM was used. In cyclic experiments, the same procedure was followed except that the catalyst used was dried at 100℃ for another use.

2.4. Analytical method

The concentration of RB5 was analyzed by the three wavelength methods using a TU-1810 UV–vis spectrophotometer (PERSEE, China), as American Dye Manufacturers Institute (ADMI) method [10]. TOC was measured in a Shimadzu TOC-L CPHCN200 analyzer. The ozone concentration in the reactor gas feed was determined by the standard iodometric method, and the dissolved ozone was determined by indigo method.

3. Results and discussion

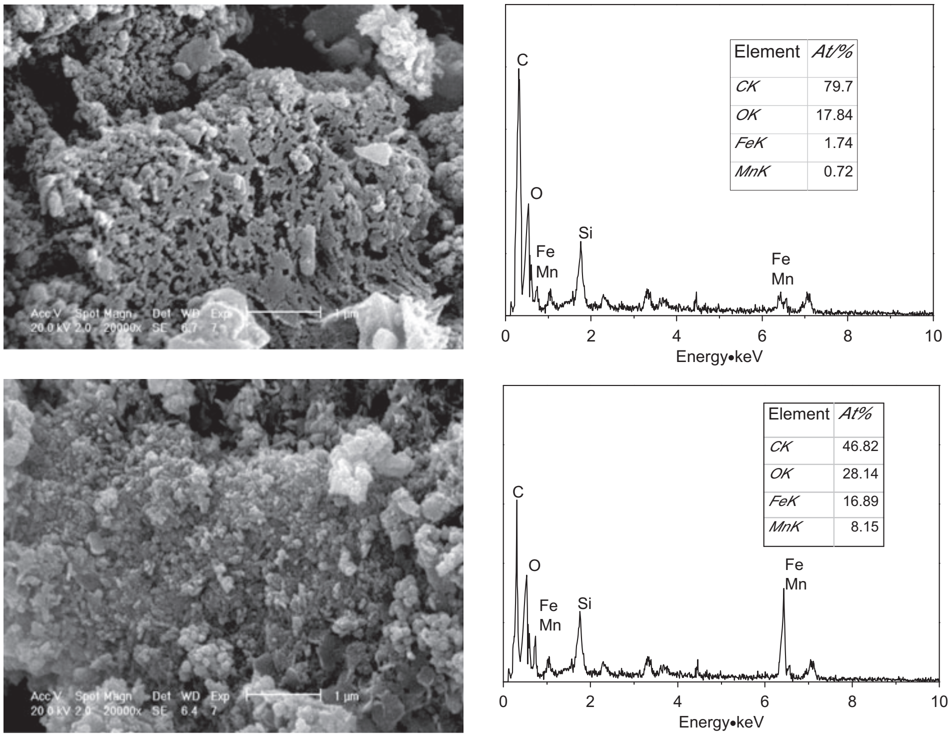
3.1. Characterization of the catalyst

Fig. 1 shows the SEM images of GAC and mGAC. Significant differences were found between GAC and mGAC. GAC had the characteristics of a porous structure, while mGAC contained various particles with different shapes (almost spherical) and sizes. After modification, the SEM showed that the metal oxides caused GAC surface to erode and collapse. Additionally, in the EDS analysis of the catalysts shown in Fig. 1, mGAC had a homogeneous distribution of Fe and Mn and no major composition differences were detected within the catalyst particles. In addition, a new surface area and pore volume appeared after the modification. The surface area and pore volume of the GAC and mGAC were investigated using nitrogen adsorption and desorption isotherms, as listed in Table 1. As seen, major differences were observed in the textural property of materials, particularly, in the case of BET surface area and total pore volume. The fact that BET surface area of the mGAC was approximately 20% smaller than that of the GAC revealed effective modification of GAC by Fe–Mn–O, because higher surface area can facilitate the development of higher metal dispersions. However, modification exerted no effect in the microvolume. Higher surface area means higher contact area, namely more active sites on the catalyst. A novel ceria-activated carbon was prepared, but the BET surface area decreased from 909 to 583 $m^2\ g^{-1}$ after the modification [18].

3.2. Catalytic activity of mGAC

Degradation of aqueous RB5 at the initial concentration of 200 mg L^{-1} was carried out by adsorption and ozonation in the presence and absence of GAC or mGAC. Fig. 2 shows the kinetic data corresponding to both color and TOC removal. As shown in Fig. 2(a), adsorption by both GAC and mGAC showed limited effect on the removal of RB5 in a reasonable time. On the other hand, total decolorization was easily achieved by ozonation in the presence and absence of GAC or mGAC. Adsorption showed limited effect on mineralization, which agreed well with the case in decolorization, as showed in Fig. 2(b). The TOC removal efficiency achieved by O_3/mGAC and O_3/GAC was 74.7 and 56.7%, respectively, compared with 32.6% achieved by O_3 in 1 h. GAC exerted effective catalytic activity in the mineralization of aqueous RB5 and its catalytic activity was greatly enhanced after the modification by Fe–Mn–O. Therefore, the synergistic effect of mineralization was evidently strengthened by the simultaneous use of O_3 and mGAC.

The mechanism of generation of hydroxyl radicals was one of the most acceptable proposals referred to GAC and metal oxides in the catalytic ozonation. Dye oxidation by-products that resistant to an ozone attack accounted for the high efficiency of decolorization but a considerably lower efficiency for mineralization during ozonation. The catalyst modification may result in the conversion of surface characteristics and improvement in the density of surface hydroxyl groups [19], thus accelerating the catalytic activity of the catalyst in decomposing O_3 into $HO^{\bullet}$. The mineralization was



Element	At/%
CK	79.7
OK	17.84
FeK	1.74
MnK	0.72

Element	At%
CK	46.82
OK	28.14
FeK	16.89
MnK	8.15

Fig. 1. SEM images and EDS analysis of GAC and mGAC.

Table 1
Characteristics of GAC and mGAC

Catalyst	A_{BET}[a] ($m^2 g^{-1}$)	V_{tot}[b] ($cm^3 g^{-1}$)	V_{micro}[c] ($cm^3 g^{-1}$)	D_{BJH}[d] (nm)	pH_{pzc}
GAC	931	0.56	0.24	2.90	8.6
mGAC	779	0.45	0.24	2.38	7.1

[a] BET surface area.
[b] Total pore volume of the surface of catalyst.
[c] Micropore volume of the surface of catalyst.
[d] BJH Adsorption average pore diameter.

evidently enhanced because generated $HO^{\bullet}$ can react with dye oxidation by-products quickly.

3.3. The influence of initial pH

In addition to initiating the decomposition of O_3 into $HO^{\bullet}$, pH was also an important factor to determine the charge properties of surface hydroxyl groups at the catalyst/water interface [20]:

$$MOH + H^+ \leftrightarrow MOH_2^+\left(pH < pH_{pzc}\right) \tag{1}$$

$$MOH + OH^- \leftrightarrow MO^- + H_2O\left(pH > pH_{pzc}\right) \tag{2}$$

The effect of the initial solution pH on the degradation of RB5 was studied at pH values ranging from 3 to 10 in O_3/GAC and O_3/mGAC. As seen in Fig. 3(a), the color removal efficiency of O_3/mGAC was slightly higher than that of O_3/GAC in the degradation of RB5 at neutral and acidic conditions. However, the enhancement was not obvious under alkaline conditions, which may be due to the differences in surface characteristic between GAC and mGAC. Fig. 3(b) shows the TOC removal efficiency after 1 h. It was found that the TOC removal efficiency increased with the increase in pH in the degradation of RB5 by O_3/GAC. Moreover, it revealed a regular pattern that O_3/mGAC could enhance mineralization compared with O_3/GAC in the degradation of RB5. For example,

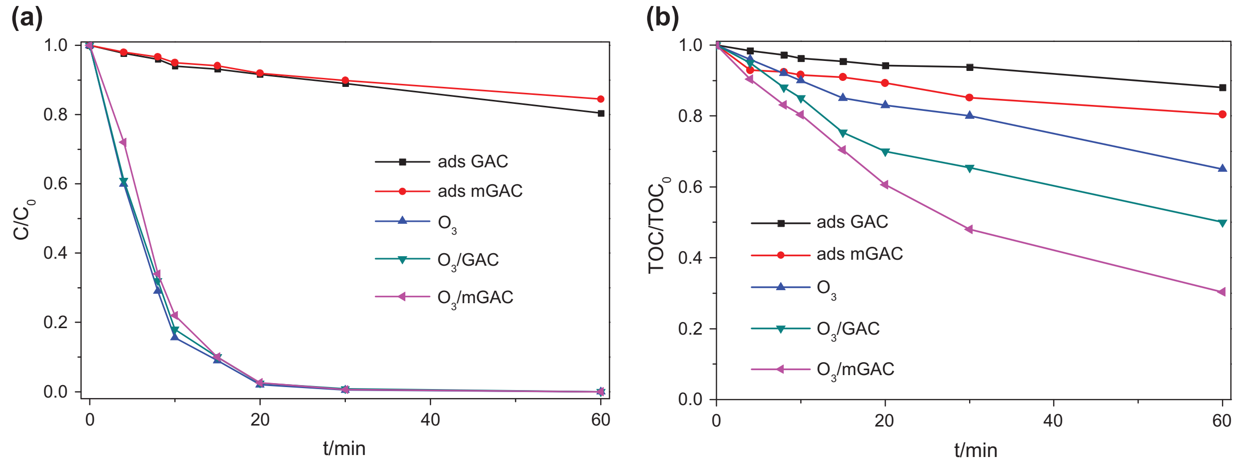


Fig. 2. Variations of aqueous RB5 decolorization and mineralization in selected processes, (a) Decolorization and (b) mineralization (T = 298 K; initial pH 7.0; C_0 = 200 mg L^{-1}; Q_{O3} = 100 mg L^{-1}; m$_{GAC}$ and m$_{mGAC}$ (if use) = 5 g L^{-1}).

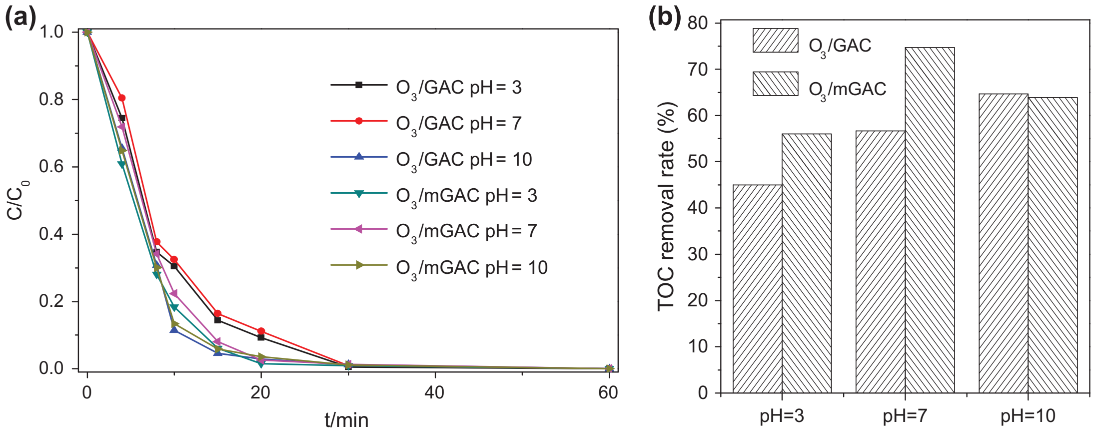


Fig. 3. The catalytic effect of GAC and mGAC in the degradation of aqueous RB5, under different pH levels (RB5 removal in curve and TOC removal in column, T = 298 K; C_0 = 200 mg L^{-1}; t = 60 min; Q_{O3} = 100 mg L^{-1}; m$_{GAC}$ and m$_{mGAC}$ = 5 g L^{-1}).

an additional 18% TOC removal efficiency was noticed in the O_3/mGAC within 1 h. What should be mentioned was that TOC removal efficiency decreased with the increase in pH from 7 to 10 in the degradation of RB5 by O_3/mGAC. At high pH, ozone decomposition produced hydroxyl radicals, which were highly oxidizing species that would react with organic compounds in a non-selective way [21]. However, it can be inferred that ozone decomposition was much easier at pH 7 than that at pH 10 in O_3/mGAC. Table 1 shows the pH$_{pzc}$ of GAC and mGAC as 8.6 and 7.1, respectively. Such a result suggested that the zero-charged surfaces were more active than the protonated or deprotonated in promoting hydroxyl radical generation, and this was consistent with the results drawn from Zhang [22] and Ren [16]. Under pH 3 and 10, the surface hydroxyl groups became protonated or deprotonated, and consequently, the catalytic activity decreased.

In addition, the pH value of the solution was measured during the reaction, as showed in Fig. 4. It can be found that pH decreased rapidly in first 10 min and then a slight pH decrease as reaction time for both O_3 alone and catalytic ozonation. Rapid pH decrease in first 10 min was ascribed to the generation of some intermediates, such as small molecular carboxylic acids and alcohols. The increase in pH later may be due to the acids further decomposed into CO_2 and H_2O. Moreover, pH value in catalytic ozonation system was higher than that in O_3 alone system due to the higher mineralization of RB5 by hydroxyl radicals during catalytic ozonation. The fact that pH value

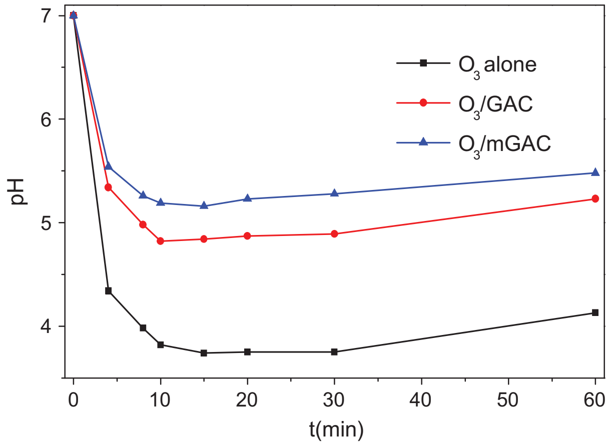


Fig. 4. The change of pH over reaction process ($T = 298$ K; initial pH 7.0; $C_0 = 200$ mg L^{-1}; $Q_{O3} = 100$ mg L^{-1}; m_{GAC} and $m_{mGAC} = 5$ g L^{-1}).

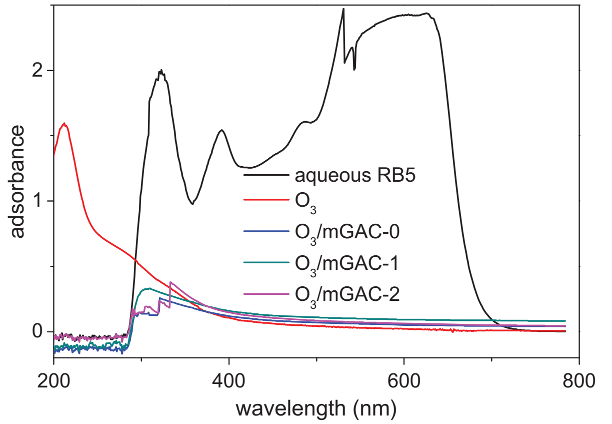


Fig. 5. Spectrum scanning of raw aqueous RB5 and effluents with mGAC reused three times ($T = 298$ K; initial pH 7.0; $t = 60$ min; $C_0 = 200$ mg L^{-1}; $Q_{O3} = 100$ mg L^{-1}; $m_{mGAC} = 5$ g L^{-1}).

in O_3/mGAC was slightly higher than that in O_3/GAC might indicate mGAC has higher catalytic activity than GAC in the mineralization of intermediates. This has been demonstrated by the fact that the TOC removal efficiency by O_3/mGAC was higher than that by O_3/GAC in the degradation of RB5. Similar results have already been reported in the ozonation of ARB catalyzed by Fe–Cu–O in aqueous phase [5].

3.4. Catalytic stability of mGAC

To evaluate the catalytic stability of mGAC, the catalyst was reused three times (namely mGAC-0, mGAC-1, and mGAC-2) under the same conditions, as seen in Fig. 5. It was noticed that both O_3/mGAC and O_3 showed a significant effect on the degradation of RB5. Nevertheless, O_3 showed much higher adsorbance than catalytic ozonation under short wavelengths (approximately 200–300 nm). This was due to the high efficiency of O_3/mGAC in the mineralization of small carboxylic acids, such as formic acid, oxalic acid, and aldehydes. Fig. 5 witnessed that the adsorbance of aqueous RB5 effluents by O_3/mGAC-1 and O_3/mGAC-2 almost coincided with that by O_3/mGAC-0. TOC analysis (not showed) indicated TOC decreased 3.4 and 4.1% by O_3/mGAC-1 and O_3/mGAC-2, respectively, compared with O_3/mGAC-0 in the degradation of RB5.

The N_2 adsorption–desorption isotherms of both mGAC-0 and mGAC-2 are shown in Fig. 6. The fact that the BET surface area of mGAC-2 was 749 m^2 g^{-1} showed a slight decreasing tendency compared with that of mGAC-0, which may be due to the structural collapse induced by vigorous stirring in the experiment. Other characteristics, such as pore diameter and pore volume, remained almost the same. Therefore, mGAC exerted stable catalytic activity in the ozonation of aqueous RB5.

3.5. The kinetics and possible mechanism of RB5 degradation

3.5.1. Possible mechanism of RB5 degradation by catalytic ozonation

TBA that reacts rapidly with $HO^{\bullet}$ ($k = 6 \times 10^8$ M^{-1} s^{-1}) [23] and slowly with O_3 ($k = 3 \times 10^{-3}$ M^{-1} s^{-1}) [24] was used as a hydroxyl radical scavenger to evaluate if the O_3/mGAC (GAC) follows the hydroxyl radical reaction mechanism. As shown in

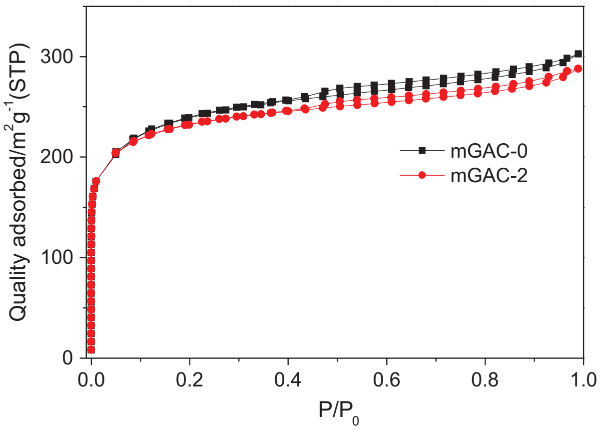


Fig. 6. N_2 adsorption–desorption isotherms of mGAC-0 and mGAC-2.

Fig. 7, the presence of TBA result in an obvious decrease in the mineralization of aqueous RB5, indicating that O_3/GAC and O_3/mGAC were radical generation mechanism in the degradation of RB5.

In a heterogeneous catalytic ozonation system, the mechanism of aqueous O_3 decomposition was complicated by the presence of solid catalyst. Firstly, it was well known that ozone decomposition has a high dependency on pH. Aqueous ozone can decompose into active species such as $HO^{\cdot}$ in the presence of HO^{-}. In addition, ozone decomposition was affected by the dissociated forms of inorganic carbons in the aqueous matrix.

$$HCO_3^- + HO^{\cdot} \rightarrow H_2O + CO_3^{-\cdot}, \quad k = 1.5 \times 10^7\ \mathrm{LM^{-1}s^{-1}} \tag{3}$$

[25]

$$CO_3^{2-} + HO^{\cdot} \rightarrow OH^- + CO_3^{-\cdot}, \quad k = 4.2 \times 10^8\ \mathrm{LM^{-1}s^{-1}} \tag{4}$$

[26]

In a heterogeneous system, there exists proton transference on the surface of metal oxides [20]. Thereby, the pH of the solution is altered more or less and the finally ozone decomposition was different. In addition, the decomposition of aqueous ozone can also be initiated by a solid catalyst.

The decomposition of O_3 under O_3 and O_3/mGAC in pure water at pH 7 was investigated. As shown in Fig. 8, both GAC and mGAC were effective in O_3 decomposition. Moreover, mGAC showed enhanced catalytic activity in O_3 decomposition compared with GAC. Previous investigations have confirmed that O_3 decomposition took place in the catalytic–solution interface and in the bulk [27]. The catalyst surface can absorb oxidants and modify oxidation intensity, and the solid surface–solution interface can catalyze oxidation reactions [28]. Therefore, a plausible reaction mechanism involved the enhanced mineralization of aqueous RB5 at the catalyst–solution interface via the hydroxyl radicals produced by the reaction between O_3 and the surface of the mGAC.

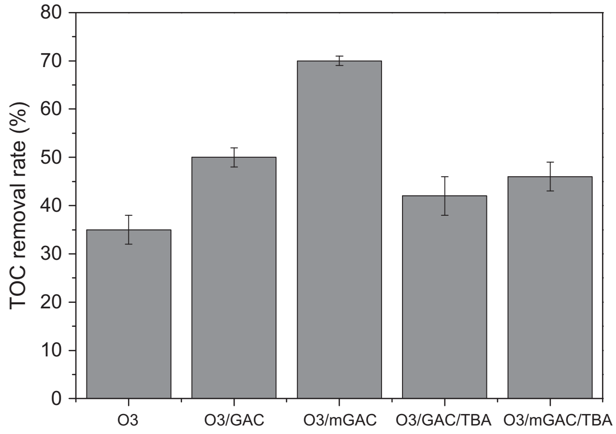


Fig. 7 Effect of TBA on heterogeneous catalytic ozonation at pH 7 (T = 298 K; initial pH 7.0; t = 60 min; C_0 = 200 mg L^{-1}; C_{TBA} = 5 mM; Q_{O3} = 100 mg L^{-1}; m_{mGAC} and m_{GAC} = 5 g L^{-1}).

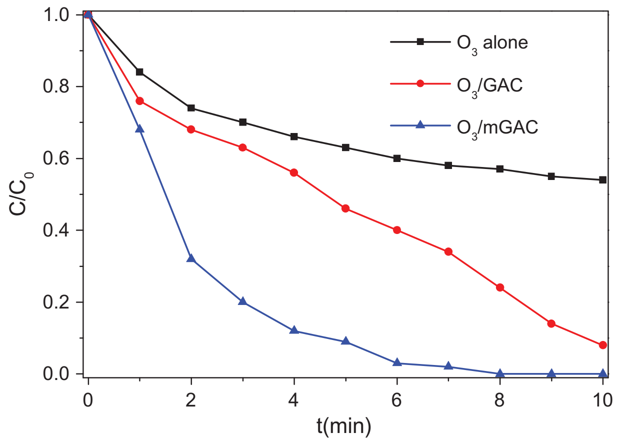


Fig. 8. Decomposition of O_3 under O_3 alone and catalytic ozonation at pH 7.

3.5.2. *The kinetics of RB5 mineralization: heterogeneous catalytic ozonation*

From the above analysis, it can be deduced that the possible mechanism of catalytic ozonation included an indirect oxidative reaction by hydroxyl radicals and a direct oxidative reaction by the ozone molecule. Thus, the decoloration of RB5 can be represented by the following equation [29]:

$$RB5 + O_3 \xrightarrow{k_1} P^* \tag{5}$$

$$RB5 + HO^{\cdot} \xrightarrow{k_2} P^* \tag{6}$$

The overall removal of RB5 can be described by the pseudo-first-order equation:

$$\begin{aligned} -\frac{dc_{RB5}}{dt} &= k_1 c_{O_3} c_{RB5} + k_2 c_{HO^{\cdot}} c_{RB5} \\ &= (k_1 c_{O_3} + k_2 c_{HO^{\cdot}}) c_{RB5} \end{aligned} \tag{7}$$

where k_1 and k_2 are the apparent reaction rate constants of the reaction of RB5 with molecular ozone and $HO^{\cdot}$, respectively.

Table 2
Pseudo-first-order apparent rate constants of RB5 degradation by O_3 and catalytic ozonation at a pH of 7

	O_3		O_3/GAC		O_3/mGAC	
Factor	k_{obs} (min^{-1})	R^2	k_{obs} (min^{-1})	R^2	k_{obs} (min^{-1})	R^2
C	0.072	0.96	0.069	0.98	0.076	0.96
TOC	0.0018	0.91	0.0062	0.99	0.0098	0.98

The impact of external mass transfer resistances (gas to liquid and liquid to solid mass transfer) was eliminated due to high stirring speed [5]. Therefore, the reactor was in perfect mixing condition. Besides, aqueous O_3 concentration was regarded to be a constant due to sufficient amount of gaseous O_3 pumped into the reactor continuously. What's more, excessive amount of gaseous O_3 can keep a relative steady generation of HO$^\bullet$. Then, owing to perfect mixing condition and rapid generation of hydroxyl radical, degradation of RB5 was the rate-limiting step. Besides,

$$k_1' \approx k_1 c_{O_3}, \quad k_2' \approx k_2 c_{O_3}$$

Then,

$$k_{obs} = k_1' + k_2'$$

Therefore, Eq. (7) can be simplified as the following equation:

$$-\frac{dc_{RB5}}{dt} = k_{obs} c_{RB5} \tag{8}$$

Or,

$$\ln\frac{C_0}{c_{RB5}} = -k_{obs} t \tag{9}$$

where C_0 represents the initial concentration of RB5.

The overall removal of TOC was represented similarly to the following equation:

$$\ln\frac{T_0}{T_{RB5}} = -k_{obs} t \tag{10}$$

where T_0 represents the TOC of the initial aqueous RB5 and k_{obs} represents $k_1[O_3] + k_2[HO^\bullet]$.

The values of the rate constants (Table 2) were obtained from the linear plot of ln (C_0/C) and ln (T_0/T_{RB5}) vs. time. As can be seen, decolorization and TOC removal by O_3 alone and catalytic ozonation were well fitted to the pseudo-first-order kinetic. The color removal rate constant of RB5 degradation showed indistinctive differences between ozonation and catalytic ozonation, whereas the rate constant of O_3/mGAC was slightly higher than that of O_3/GAC. The TOC removal rate constants of RB5 degradation by O_3/GAC and O_3/mGAC were 3.4 and 5.4 times higher, respectively, than that of O_3 alone under the same conditions. Thus, the TOC removal rate constant by O_3/mGAC was 1.58 times higher than that by O_3/GAC. The results suggested that mGAC is a promising catalyst for efficient RB5 degradation.

3.5.3. The role Fe and Mn played in the RB5 degradation

Enhanced mineralization efficiency was proved in O_3/mGAC in the degradation of aqueous RB5. However, the specific catalytic mechanism of Fe and Mn remained unclear. Fig. 9 showed the TOC removal rate of several processes in the degradation of RB5,

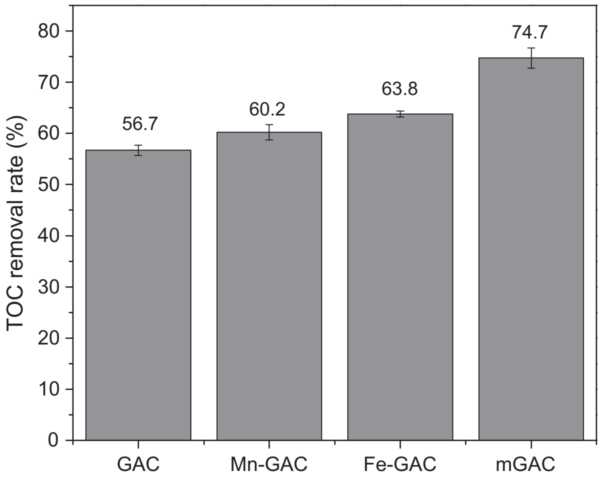


Fig. 9. TOC removal rate of RB5 degradation by O_3/GAC, O_3/Fe–GAC, O_3/Mn–GAC and O_3/mGAC (T = 298 K; initial pH 7.0; t = 60 min; C_0 = 200 mg L^{-1}; Q_{O3} = 100 mg L^{-1}; m$_{catalyst}$ = 5 g L^{-1}).

including O_3/GAC, O_3/Fe–GAC, O_3/Mn–GAC, and O_3/mGAC. O_3/Mn–GAC and O_3/Fe–GAC had an additional 3.5 and 7.1% TOC removal efficiency, respectively, compared with O_3/GAC in the degradation of RB5. However, the sum of both increments was lower than the increased TOC removal rate acquired by O_3/mGAC (18%). Therefore, the synergetic effect between Mn and Fe in the enhancement of catalytic activity was proposed. Section 3.5.1 has confirmed O_3/mGAC followed hydroxyl radical reaction mechanism. Based on the preparation and SEM analysis of mGAC, the Fe–Mn–O existed as a community on the surface of GAC. The introduction of Fe–Mn–O enhanced the formation and activation of surface hydroxyl groups, resulting in higher catalytic reactivity. New surface hydroxyl groups might be produced by the interaction of Fe–Mn–O and ozone and there are more active sites in the presence of MnO_x [30].

4. Conclusion

GAC-deposited Fe–Mn–O remarkably enhanced its catalytic activity, with an additional 18% TOC removal efficiency observed in the degradation of RB5 by O_3/mGAC compared with degradation by O_3/GAC under identical experimental conditions within 1 h. mGAC was more effective at a pH of 7 than at a pH of 3 or 10 in the decolorization and mineralization of aqueous RB5 by ozone. It was proposed that zero-charged surfaces facilitated the generation of hydroxyl radicals decomposed by ozone. Kinetics analysis showed the TOC removal rate constant of O_3/mGAC was 5.4 times higher than that of O_3. In addition, mGAC exerted stable catalytic activity; only a 5% TOC removal efficiency decrement was noticed in the reuse of mGAC. According to the catalytic ozone decomposition experiment, mGAC was much more effective in O_3 decomposition. By enhancing O_3 decomposition, more hydroxyl radicals can be formed. In addition, the synergetic catalytic activity between Mn and Fe was proposed.

Therefore, GAC-deposited Fe–Mn–O was an appropriate alternative as the catalyst in ozonation. By promoting the decomposition of O_3 into hydroxyl radicals, the overall cost decreased markedly as the ozone utilization efficiency increased.

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