



## The catalytic properties of manganese oxides supported on a novel type of copper-containing silica gel for tricyclazole degradation with ozone

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### ABSTRACT

An Mn oxide supported on a novel type of copper-containing silica gel (Mn-CuSG) has been fabricated by an impregnation-calcination method and tested in the catalytic ozonation of tricyclazole (TC). An inductively coupled plasma optical emission spectrometer and scanning electron microscopy equipped with an energy dispersive spectrometer were used to reveal that the Mn element was successfully loaded and uniformly distributed on the CuSG. The catalytic activity was systematically assessed by monitoring the TC and total organic carbon (TOC) removal efficiencies at different operational parameters including catalyst dosage, initial solution pH, and ozone concentration. The O<sub>3</sub>/Mn-CuSG system performed higher activity than ozone alone and O<sub>3</sub>/Mn-γ-Al<sub>2</sub>O<sub>3</sub> system, improving the TC removal efficiencies by 28% and 9%, respectively and TOC removal efficiencies by 24% and 6%, respectively. The Mn-CuSG catalytic activity was only a slight loss after five consecutive cyclic treatments, showing good stability. The addition of *t*-butanol as hydroxyl radicals scavengers proved that the catalytic ozonation mechanism was the enhancement of molecular ozone attacks and •OH generation by the Mn-CuSG. TC degradation pathway in the O<sub>3</sub>/Mn-CuSG system was that the attacks of the 1,2,4-triazole ring resulting in the formation of N-oxides and hydroxylated intermediates. The above results render the Mn-CuSG an industrially promising candidate for catalytic ozonation of TC containing wastewater.

**Keywords:** Catalytic ozonation; Manganese oxide; Copper oxide; Copper-containing silica gel; Tricyclazole

### 1. Introduction

Heterocyclic compounds are often present in the production wastewater of pharmaceuticals, dyes, herbicides, insecticides, etc. [1]. Their cyclic structure consists of carbon atoms with nitrogen, oxygen, or sulfur atoms, and a closed conjugate system is constructed with different degrees of

aromaticity [2]. Most heterocyclic compounds are toxic, mutagenic and carcinogenic, and can be stably present in soils and water bodies for a long time [3]. Therefore, they are difficult to completely biodegrade in the environment, which poses a great threat to the ecological environment and human health. tricyclazole (5-methyl-1,2,4-triazole-(3,4-beta)-benzothiazole, TC in short), an N, S-heterocyclic compound, is mainly used

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for controlling rice blast disease caused by *Pyricularia oryzae* [4]. TC becomes commonly detected in soil and water due to its wide application and strong persistence in the environment [3,5]. Because of the high toxicity and refractory of TC, the low cost and environmentally friendly biological wastewater treatment are limited. Though the removal efficiency was significantly enhanced by bioaugmentation of specific microorganisms, the removal of 100 mg/L TC needed as long as 102 h [4]. As a consequence, robust and environmentally friendly technologies are needed to deal with the sites contaminated by TC.

Presently, treatment methods for TC contaminated sites are mainly focused on adsorption and extraction methods. Azarkan et al. [6] investigated TC removal from the soil slurry through adsorption by natural clay, with TC removal efficiency as high as 96% achieved. Krieger et al. [7] used the subcritical water to extract TC from soils and sediments. The extraction of TC could be essentially completed within 20 min at 150°C, with TC removal efficiency as high as 96% achieved. However, the used adsorbents and extractants still need further treatment, causing serious secondary pollution to the environment.

Nowadays, advanced oxidation processes (AOPs) are widely used for the treatment of wastewater containing various toxic and refractory pollutants [8]. Hydroxyl radical ( $\cdot\text{OH}$ ) generated in AOPs can non-selectively mineralize most organics into carbon dioxide, water, and inorganic ions, due to its standard electrode potentials as high as 2.8 eV. Xu et al. [9] studied the electrochemical oxidation of TC in a tubular membrane electrode reactor, and TC removal efficiency as high as 79% could be achieved within 20 min. Zhong et al. [10] investigated the electrochemical degradation of TC in wastewater using Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> anode. TC removal efficiency as high as 93% could be achieved within 150 min at an initial pH of 5.0 and a current density of 25 mA cm<sup>-2</sup> [10]. The electrochemical degradation of TC using TiO<sub>2</sub>-NTs/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> anode was investigated by Han et al. [11], where the acute toxicity of TC could be significantly decreased after treatment by electrochemical oxidation. However, electricity consumption was estimated to be higher than 250 kWh for each ton of wastewater, which was unacceptable for actual engineering applications [10]. When TC subjected to sunlight irradiation, 95% of TC in the influent could be removed through photodegradation, however, the reaction time required was as long as 14 d [12].

Recently, heterogeneous catalytic ozonation, a type of promising AOPs, has received increasing attention in toxic and refractory pollutants removal due to its merits such as environmental friendliness and high oxidation efficiency [13,14]. Application of different heterogeneous catalysts such as metal oxides (e.g. MnO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and FeOOH) and metals (Cu, Ru, Pt, Co) on various supports (e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and activated carbon) for the enhancement of ozone reaction rate has been widely studied [15]. Among the catalysts, the supported oxide of transition metals such as MnO<sub>2</sub> is the most widely studied as a catalyst of the ozonation process. The mechanism of MnO<sub>2</sub> is still controversial, depending on the different preparation methods, target organic pollutants, and experimental conditions. Generally, it is believed that the organic molecules were first adsorbed on the surface of MnO<sub>2</sub> and subsequently attacked by the ozone molecule [16,17].

To increase the catalytic activity of MnO<sub>2</sub>, other metal oxides were incorporated as a promoter. Recently, evidence had been obtained that the dispersed active species on the surface of the support could have a synergistic catalytic effect with ozone [18]. Mixed oxides containing Cu and Mn as the main metal element have been reported to be very active for the mineralization of benzotriazole, as compared to Cu or Mn alone [19]. Different from MnO<sub>2</sub>, the process of ozonation catalyzed by copper oxide was proposed as followed: firstly, the simultaneous adsorption of ozone and organic molecules on copper oxide surface, then the decomposition of ozone on the metallic sites and production of surface-bound hydroxyl radicals, and lastly the oxidation of adsorbed organic molecules by the adjacent hydroxyl radicals [20]. Though the copper-manganese mixed metal oxides as efficient catalysts in the air pollutant control have been studied by some investigators, the effectiveness and mechanism of the bimetallic catalyst in heterogeneous catalytic ozonation have not been explored adequately.

Therefore, manganese oxide was loaded on a novel type of Cu-containing silica gel (CuSG) to confirm whether the synergistic catalytic effects happen. Compared with the widely used carriers, e.g. Al<sub>2</sub>O<sub>3</sub> [21] and activated carbon [22], CuSG has a higher specific surface. Taken TC as a model toxic and refractory organic matter, the effects of key operating parameters such as initial pH, amount of catalyst, the applied ozone dose on the degradation efficiency and mineralization degree were studied. To the best of our knowledge, there is no study on the catalytic ozonation of TC previously. The oxidation intermediates were identified and followed by mass spectrometry (MS). Finally, the TC mineralization pathway in the bimetallic catalytic ozonation system was proposed.

## 2. Materials and methods

### 2.1. Materials and reagents

The CuSG was manufactured by Jiangxi Jiujiang Huaxing Chemical Co. Ltd., China, with a diameter of 0.2–0.5 mm, the pore volume of 1.0 mL/g, and specific surface 400–500 m<sup>2</sup>/g. The copper was added during the synthesis of silica gel, significantly increasing the pore diameters and the loading amount of active metal. The model wastewater was prepared by dissolving TC (Adamas Reagent Co. Ltd., Switzerland) into ultra-pure water containing 10 mM phosphate buffer.

### 2.2. Catalyst preparation

The catalyst of MnOx loaded on CuSG (Mn-CuSG) was prepared using an impregnation-calcination method, according to Zhang et al. [23]. Briefly, 10 g CuSG was immersed in a 400 mL solution containing 6.97 g manganese acetate. The mixture was stirred on a shaker at room temperature for 30 min and then ultrasonic vibrated for 3 h. After rinsing three times by deionized water, the composite was dried at 328 K in the air for 6 h, and calcined in a tube furnace in the air from room temperature to 723 K at a ramping rate of 283 K/min and finally kept at 723 K for 10 h. The commercial catalyst support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was selected for comparison and MnOx loaded on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Mn- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was prepared likewise except for the carrier namely used.

### 2.3. Catalytic oxidation with ozone

The experimental setup is shown in Fig. 1. Ozone was generated from pure oxygen using an ozone generator (CF-G-3-10g, Qingdao Guolin Environmental Technology Co. Ltd., China). The generated ozone was injected into a 2.5 L batch reactor containing 2 L TC containing model wastewater through a sintered porous diffuser fixed at the bottom of the reactor. The experiments were performed at a constant gas flow rate of 0.5 L/min and  $O_3$  concentration in inlet gas was controlled through an online  $O_3$  concentration monitor. The solution was mixed by a mechanical stirrer at 500 rpm during the reaction, which was placed at the bottom of the reactor to ensure an adequate mixture between contaminants, catalysts, and ozone. The remaining ozone after the reaction was ejected by another silicone tube and absorbed by the KI solution.

To investigate the effect of  $O_3$  concentration on TC removal, the experiments were performed at initial TC concentration of 100 mg/L, initial pH of 7.0 and catalyst dosage of 13 g/L, with  $O_3$  concentration varied from 5 to 20 mg/L. To reveal the effect of catalyst dosage on TC removal, 7–16 g of Mn- $\gamma$ - $Al_2O_3$  or Mn-CuSG were dosed but with initial TC concentration, initial pH and  $O_3$  concentration controlled at 100, 7.0, and 15 mg/L. To study the effect of initial pH on TC removal, the initial pH was varied from 6.0 to 9.0 through adjusting the proportion of  $Na_2HPO_4$  and  $KH_2PO_4$ , but with initial TC concentration, initial catalyst dosage and  $O_3$  concentration controlled at 100, 13, and 15 mg/L, respectively. The reuse experiment was conducted five times to evaluate the catalytic activity and stability of Mn-CuSG. The catalyst was regenerated by rinsing thoroughly using ultra-pure water. The initial TC concentration, the ozone dose, and the catalyst dose were 100, 15, and 13 g/L, respectively. The initial pH of the solution was 7.0.

### 2.4. Analytical methods

The specific surface and pore volume of the catalyst were measured using a micromeritics instrument (ASAP 3020, USA). Scanning electron microscopy (SEM, JFC-1600, JEOL, Japan) equipped with an energy dispersive spectrometer

(EDS) was used to characterize the surface morphology of the catalyst. The actual metal loading was determined by using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 7000DV, PerkinElmer, USA). Before ICP analysis, Mn- $\gamma$ - $Al_2O_3$  and Mn-CuSG catalysts before and after use were solubilized using HCl/HNO<sub>3</sub>/HF mixed acid (8:4:3, v:v:v) in a microwave digester. The leaching of Cu and Mn ions into the TC wastewater during catalytic ozonation was also assessed by ICP-OES.

The ozone concentration in the gas phase was analyzed using an ozone monitor (LT-200B, Lontec, China). TC was quantified by high-performance liquid chromatography (HPLC, 20AT, Shimadzu, Japan) equipped with an ODS-SP C18 column (5  $\mu$ m, 4.6 mm  $\times$  250 mm) and a 2998 PDA detector. 10  $\mu$ L water samples were injected after filtering by a 0.22  $\mu$ m syringe filter. The mobile phase consisted of methanol/water (50/50, v/v) at a flow rate of 1.0 mL/min. Total organic carbon (TOC) concentration was determined on a TOC analyzer (VARIO TOC, Elementar, German). To elucidate TC biodegradation pathways, the samples were analyzed through HPLC-MS. HPLC-MS analysis was performed on the HPLC system (U3000, Dionex, USA) coupled with an ion trap mass spectrometer (maXis 4G, Bruker, USA) and an electrospray ionization source. The mobile phase consisted of methanol/water (30/70, v/v) pumped at a flow rate of 0.3 mL/min. The operation condition was as follows: ion source temperature, 250°C; collision energy, 10.0 eV; in-source collision-induced dissociation energy and ion energy, 5.0 eV; dry gas, 7 L/min; dry temperature, 250°C; gas pressure, 1.5 bar; positive capillary voltage, 4.0 kV; negative capillary voltage, 3.5 kV.

## 3. Result and discussion

### 3.1. Catalyst properties

Figs. 2a and b show SEM images of the CuSG before and after MnO<sub>x</sub> loading. The morphology of the CuSG were regular spherical particles while most of the particles of Mn-CuSG were irregular. SEM-EDS data showed the presence of Mn and Cu in the catalysts of Mn-CuSG on the surface of the supports (Figs. 2c and d). The Cu element was

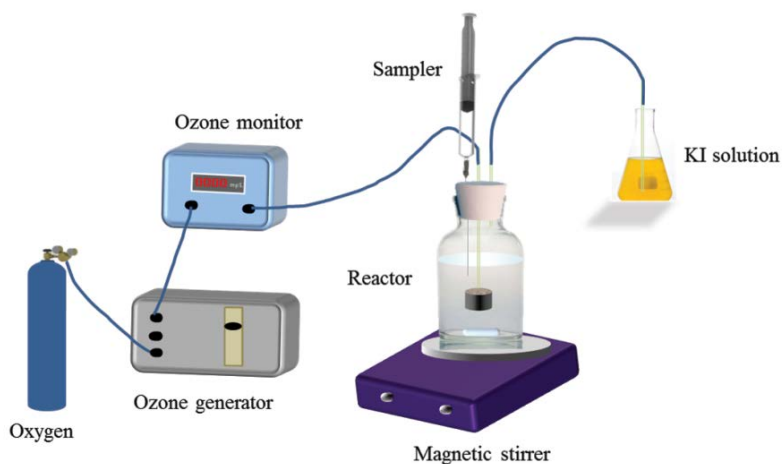


Fig. 1. Schematic representation of ozonation experimental setup in this study.

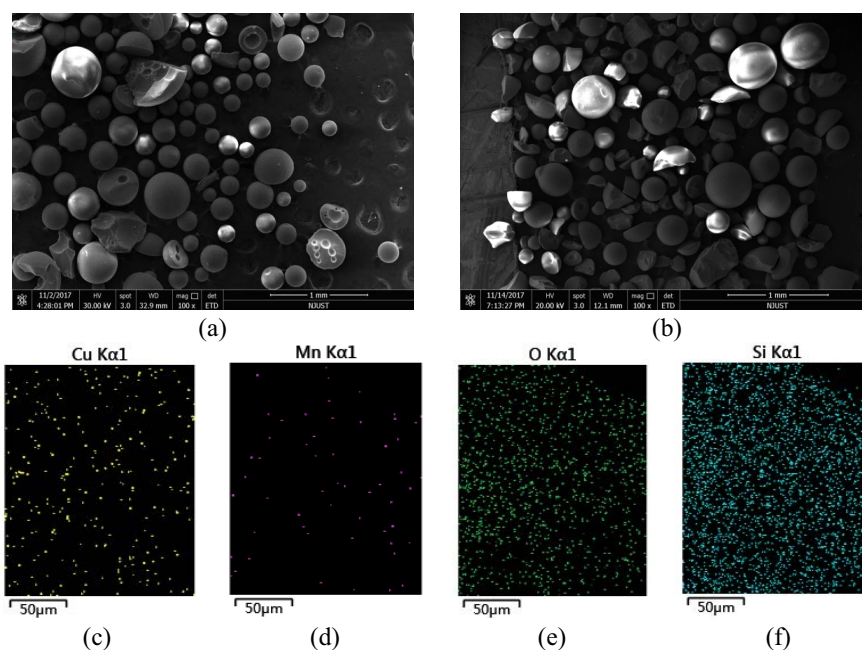


Fig. 2. SEM images of CuSG (a), Mn-CuSG (b) and EDS elemental maps of Mn-CuSG (c) Cu, (d) Mn, (e) O, and (f) Si.

derived from the Cu metal mixed in the preparation process of the catalyst carrier. It could be inferred from Fig. 2d that  $\text{MnO}_x$  was well distributed on the surface of the CuSG. The  $\text{N}_2$  adsorption-desorption curves and the pore sizes distribution of Mn-CuSG are shown in Fig. 3. As shown in Table 1, the surface area of CuSG is  $478 \text{ m}^2/\text{g}$ , and the pore volume is  $0.8 \text{ cm}^3/\text{g}$ , which is much larger than that of commercial  $\gamma\text{-Al}_2\text{O}_3$ . Due to the uniform large pore diameter and high specific surface area of the CuSG, the active metal Mn loading on the CuSG was 3.7%, about 3.5 times higher than on  $\gamma\text{-Al}_2\text{O}_3$ . The amount of Cu in the prepared Mn-CuSG catalyst was about 12.6%, which was also significantly higher than that of  $\gamma\text{-Al}_2\text{O}_3$  (shown in Table 2).

### 3.2. Degradation efficiency of TC in different processes

The experiments were performed in different processes to investigate the degradation efficiency of TC, including  $\text{O}_3$  alone,  $\text{O}_3/\text{CuSG}$ ,  $\text{O}_3/\text{Mn-CuSG}$ , and  $\text{O}_3/\text{Mn-}\gamma\text{-Al}_2\text{O}_3$  under

the condition of the ozone dose of  $15 \text{ mg/L}$ ,  $\text{pH} = 7.0$ , and TC concentration of  $100 \text{ mg/L}$ . As represented in Fig. 4, the concentration of TC decreased with the increasing reaction time in all the mentioned processes. Comparing  $\text{O}_3/\text{CuSG}$  with the  $\text{O}_3$  alone, an increment of approximately 7% of TC degradation at the same applied ozone dose was observed. It might be caused by the existence of  $\text{CuO}_x$  in the silica gel catalyzing the decay of ozone to form reactive species of radicals, which were able to react with TC faster than ozone molecule [15]. The  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{MnO}_x$  had shown good catalytic activity on the ozonation of TC. The existence of active material  $\text{MnO}_x$  and  $\text{Al}_2\text{O}_3$  might be both responsible for catalytic activity [24]. The highest degradation efficiency of TC was observed for the  $\text{O}_3/\text{Mn-CuSG}$  system. Under the same experimental conditions, the  $\text{O}_3/\text{Mn-CuSG}$  system led to about 96% TC degradation after 60 min treatment and the adsorption contributed less than 5%. There was an increment of 28% comparing  $\text{O}_3/\text{Mn-CuSG}$  with the cumulative effect of  $\text{O}_3$  alone. For one reason, due to the porous structure

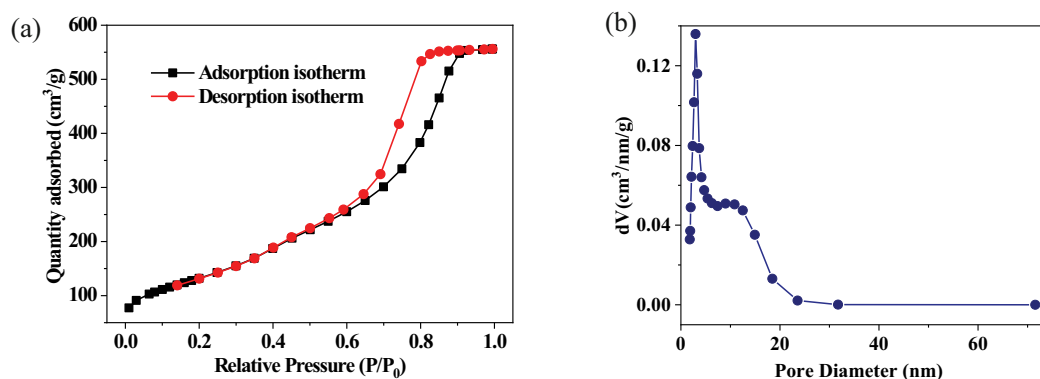


Fig. 3.  $\text{N}_2$  adsorption-desorption isotherms and pore size distribution profiles of the Mn-CuSG catalyst.

Table 1  
Structure parameters of catalyst carriers

Catalyst carriers	Pore volume (cm <sup>3</sup> /g)	Specific surface area (m <sup>2</sup> /g)	Pore diameter (nm)
CuSG	0.8	478	7.2
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.4	262	5.7

Table 2  
Active component content of catalysts

Catalysts	Concentration (mg/L)		Percentage (%)	
	Mn	Cu	Mn	Cu
Mn- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	21.1	0.06	1.1	0.003
Mn-CuSG (Before)	75.3	251.2	3.7	12.6
Mn-CuSG (After)	74.9	249.0	3.7	12.5

and high specific surface of CuSG, the loading amount of Mn is significantly higher than commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Besides, the catalytic activity of the Mn-CuSG catalyst might result from the synergistic catalytic action of manganese oxides and copper oxides existed [25].

As can be seen from Fig. 4, comparing O<sub>3</sub>/Mn-CuSG with the O<sub>3</sub> alone, the TOC removal efficiencies increased from 50% to 74% within 60 min. The TOC removal efficiency was lower than that of TC at the same ozonation time, which could be explained by that part of TC was degraded to other organic intermediates.

### 3.3. Effect of operating conditions on Mn-CuSG performance in batch reactor

#### 3.3.1. Effect of pH on Mn-CuSG performance

The effect of pH on the degradation of TC in the O<sub>3</sub>/Mn-CuSG system was investigated by conducting experiments at different pH depicted in Fig. 5.

The removal efficiency of TC in the O<sub>3</sub>/Mn-CuSG system increased with pH range from 6.0 to 9.0. As presented, 91% of TC degradation was obtained after 60 min's reaction at pH 6.0, and the TC degradation efficiency was up to 95% when the initial pH increased to 7.0. However, only a slight improvement in TC degradation was achieved when the initial pH further increased to 9.0. It has been reported that the catalytic activity of MnO<sub>2</sub> in the aqueous medium increases with a decrease of pH [17,26]. However, Udrea et al. [27] reported that the increase of pH from 6.97 to 9.27 caused a rise of 2-nitrophenol removal efficiency by ozone over a CuO-Al<sub>2</sub>O<sub>3</sub> catalyst. The different effects of pH on manganese oxides and copper oxides might be caused by their different point of zero charge (pHpzc). The highest activity of the many metal oxides catalyst was observed at pH of the solution close to pHpzc. Since the pHpzc of MnO<sub>2</sub> and CuO was around 2.25 [28] and 9.5 [29], respectively, they might show contradictory pH response in the range of pH 6.0–9.0. Simultaneously, the result also showed that

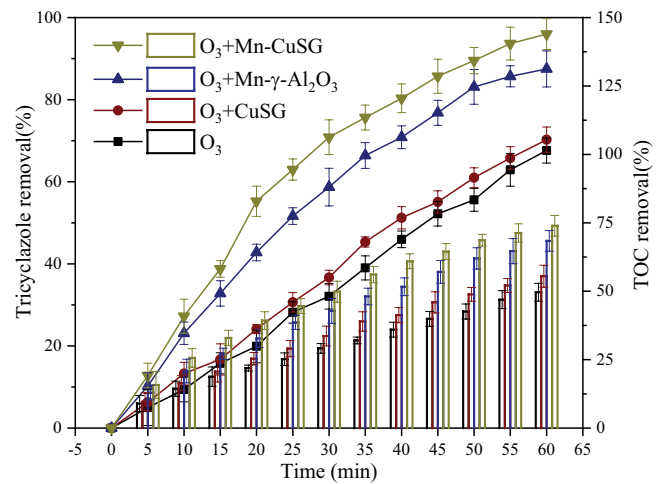


Fig. 4. Comparison of removal efficiency on TC and TOC in the different processes.

the catalyst has good catalytic performance in the pH range from 6.0 to 9.0 due to the combined effect of active material MnO<sub>2</sub> and CuO. Therefore, the Mn-CuSG catalyst has a strong adaptability to pH and can be applied to pH from 6.0–9.0.

As can be seen from Fig. 5, the mineralization rate of TC under acidic conditions was slightly lower than that of alkaline reaction conditions; however, there was no significant difference for TOC removal at different pH values from 6.0 to 9.0.

#### 3.3.2. Effect of ozone dose on Mn-CuSG performance

As the source of oxidant in the catalytic ozonation system, the concentration of ozone affects the decomposition of ozone and the amount of •OH produced, which results in differences in the effectiveness of degrading TC. The degradation performance of the O<sub>3</sub>/Mn-CuSG system on TC at different ozone concentrations (5, 10, 15, and 20 mg/L) as shown in Fig. 6.

It was noted that in Fig. 6, as the ozone concentration increased from 5 to 20 mg/L, the degradation efficiencies of TC after 60 min catalytic ozonation were 84%, 89%, 95%, and 97%, respectively. Corresponding TOC removal efficiencies were 66%, 71%, 73%, and 76%, respectively. It indicated that with the increase of ozone concentration in gas, the removal effect of TC gradually increased. It was induced that the increasing ozone dosage increased the equilibrium ozone concentration in the aqueous phase and improved the mass transfer driving force accordingly. The attack of TC adsorbed on manganese oxides by adjacent molecular ozone was thereupon increased. Besides, the increased molecular ozone adsorbed on the CuO<sub>x</sub> surface resulted in the increase of •OH generated and the probability of contact with TC per unit volume [30]. Therefore, the degradation and mineralization efficiencies of TC increased.

#### 3.3.3. Effect of catalyst dose on Mn-CuSG performance

Heterogeneous catalytic ozonation of TC in aqueous solution is a reaction system of gas-liquid-solid three phases,

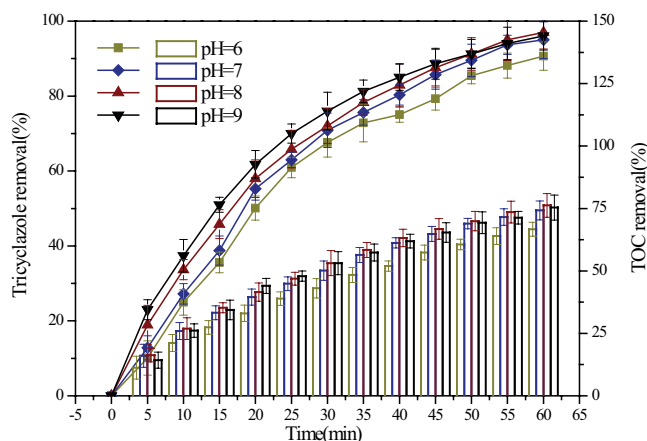


Fig. 5. Comparison of removal efficiency on TC and TOC in the different pH.

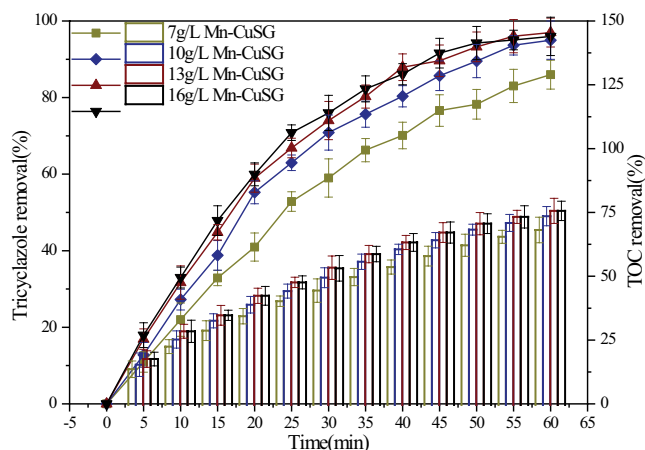


Fig. 7. Comparison of removal efficiency on TC and TOC in the different catalyst dosages.

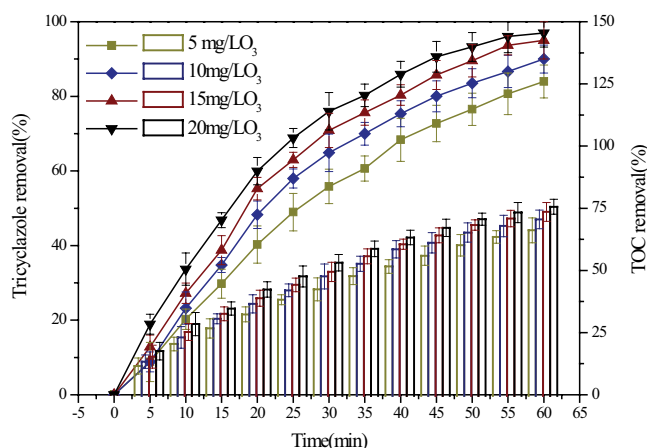


Fig. 6. Comparison of removal efficiency on TC and TOC in the different ozone concentration.

in which the solid catalyst is a crucial factor affecting the degradation efficiency. Therefore, it is necessary to assess the influence of catalyst dose.

The effects of catalyst dose on the TC degradation were investigated during ozonation with Mn-CuSG. As observed in Fig. 7, the removal efficiency of TC increased gradually by 23%, positively, with the increasing amount of catalysts from 7 to 16 g/L after 60 min catalytic ozonation. The ultimate TOC removal values were 69%, 74%, 76% and 76% at Mn-CuSG dosage of 7, 10, 13, and 16 g/L, respectively. It was on a rise of TC degradation efficiency, which was possible that the increase of catalyst amount enhanced the heterogeneous catalytic surface and effective active sites. As illuminated by the results, the increase of the catalyst amount from 7 to 13 g/L yielded a further increase of the removal efficiency of TC in the process. However, the TC removal efficiencies were almost the same when the catalyst dose increased from 13 to 16 g/L.

Therefore, taking the cost and disposal of used catalyst into consideration, it was suggested that the suitable catalyst dose was 13 g/L according to this experiment.

### 3.3.4. Catalyst stability

The stability of the catalyst was investigated by reusing it in five successive catalytic ozonation experiments. Fig. 8 showed the TC degradation decreased gradually with the increase of using times, but the declining trend was becoming less pronounced with the prolonging of Mn-CuSG reuse during ozonation. The TC removal efficiency at 60 min decreased from 95% to 90% after the fifth run. In comparison to the treatment effect of the first run, the TC removal levels decreased only by 4%, 5%, 6%, and 8%, respectively. A similar phenomenon was observed for the TOC removal, and the TOC removal efficiencies were 76%, 74%, 72%, 71%, and 71% for the first, second, third, fourth and fifth using time of Mn-CuSG catalyst, respectively. It was found that after five times reuse, the Mn-CuSG catalyst still had good catalytic activity on TC degradation. It was consistent with that the active ingredient Mn and Cu supported remained almost unchanged after repeated use for five times as shown in Table 2. Also, the concentrations of Mn and Cu ions in the ozonated tricyclazole wastewater were 0.001 and 0.02 mg/L, respectively, after catalytic ozonation for five cycles, which

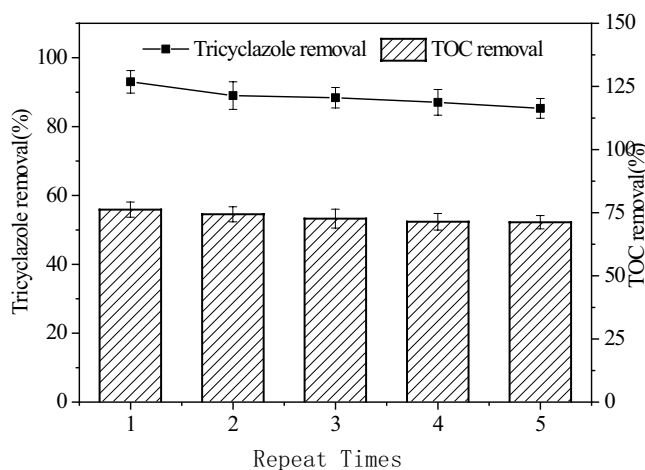


Fig. 8. Effect of repeated use of catalyst on the degradation efficiency of TC.

was safe for the ecosystem. Compared with the excellent ozone catalyst, the Mn-CuSG catalyst had high stability and remarkable reusability [31]. Moreover, the Mn-CuSG catalyst can be easily separated from the treated effluent, so they are suitable for both the successive batch process and continuous process.

### 3.4. Reaction mechanism

#### 3.4.1. Influence of the presence of free radical scavengers

To preliminarily reveal the reaction mechanism of TC degradation in the process of  $O_3$ /Mn-CuSG, the experiments were carried out to compare the degradation efficiency of TC obtained in the presence of *t*-butanol (TBA) with that in the case of its absence. Being a stronger radical scavenger, TBA reacts with  $\cdot OH$  and generates inert intermediates, which do not predominantly produce the  $HO_2\cdot$  and  $O_2\cdot$  radicals, thus causing the termination of the radical chain reaction. Therefore, TBA is believed to be a relatively suitable indicator for radical type reaction produced in the present oxidative systems. As indicated in Fig. 9, the presence of TBA in aqueous solution had a remarkable influence on the degradation efficiency of TC in the processes of  $O_3$  alone and  $O_3$ /Mn-CuSG, leading to a significant reduction of degradation efficiency. With the increasing additional concentration of TBA from 0 to 0.1 M, the degradation efficiency of TC after 60 min ozonation decreased by 24% in the process of  $O_3$ /Mn-CuSG, but still 13% higher than the process of  $O_3$  alone with 0.1 M TBA. Therefore, both of the molecular ozone and free radicals, e.g.  $\cdot OH$  were responsible for the degradation of TC in the  $O_3$ /Mn-CuSG system. As mentioned before, the catalytic mechanism of manganese oxides was increasing the attack of the molecular ozone by the formation of surface  $MnO_x$ /organic complex. The generated free radicals were mainly catalyzed by the decomposition of ozone on the active sites of CuO. Therefore, the higher degradation efficiency of TC in the  $O_3$ /Mn-CuSG adding TBA system than that in  $O_3$  alone adding the TBA system was mainly contributed by  $MnO_x$  loaded. Besides, the degradation of TC was only enhanced by 1%–6% in the process of  $O_3$ /CuSG catalyzed only by CuSG compared with  $O_3$  alone as shown in Fig. 4. As a consequence, the

significant decrease of TC removal efficiency, about 2%–29%, caused by adding TBA into the  $O_3$ /Mn-CuSG system was not only catalyzed by  $CuO_x$  but also by the synergistic effect of the two active species.

#### 3.4.2. Infer the degradation pathway by HPLC-MS analysis of intermediate products

As shown in Table 3, the intermediates in the catalytic ozonation of TC were identified by LC/MS analysis. There were obvious protonated molecular ion peaks at  $m/z = 228$   $[M + Na^+]$ , and the intermediate could be identified as 5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4] triazole 2-oxide (intermediate I). A relatively protonated molecular ion peak was present at  $m/z = 244$   $[M + Na^+]$ , and the intermediate 5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4] triazole 1,2-dioxide (intermediate II) could be determined. Based on the molecular ion peak at  $m/z = 206$   $[M-H^+]$ , another intermediate, 5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4] triazole-2(3H)-ol (III), could also be detected.

Up to now, only a few mechanistic studies evaluated the reaction of ozone with nitrogen-containing heterocyclic compounds. Molecular ozone reacts with amines by adduct formation at the lone electron pair and the ozone adducts then lose  $^1O_2$  to form N-oxides [32]. Based on the identified intermediates, a possible route to degrade TC in the  $O_3$ /Mn-CuSG system is therefore proposed and summarized in Fig. 10. The molecular ozone attacks the tertiary amine groups in 1,2,4-triazole ring of tricyclazole to form the N-oxides (intermediate I and II). The attacks of hydroxyl radicals with the electron-rich 1,2,4-triazole ring of TC result in the hydroxylation of TC and the intermediate III is formed. The continuous degradation pathway ultimately results in the direct conversion of these intermediates to small molecular compounds such as oxalic acid, formic acid, and acetic acid according to a previous study [10]. The final small molecular compounds are converted to carbon dioxide and water during mineralization inferred from the removal of TOC.

## 4. Conclusions

Mn-CuSG, a novel type of ozonation catalyst was successfully synthesized and applied to remove the heterocyclic compound, tricyclazole. It appeared clearly that the bimetallic catalyst allowed increasing the removal efficiency of TC in comparison to single ozonation and  $MnO_x$  supported on commercial carrier  $\gamma-Al_2O_3$ . The significant positive influences of catalyst dosage, initial solution pH, and ozone concentration on TC removal efficiencies were observed, showing that the Mn-CuSG had strong adaptability to pH. After five reused times of the Mn-CuSG, a minor decrease in catalyst activity was found, indicating that the catalyst exhibited good catalytic activity and stability. Both of the molecular ozone and  $\cdot OH$  were responsible for the degradation of TC in the  $O_3$ /Mn-CuSG system demonstrated by the experiments adding free radical scavengers. The synergistic effect of manganese oxides and copper oxides significantly increased the TC removal efficiency besides the catalytic effect of manganese oxides and copper oxides alone. The possible mechanism to degrade TC in the  $O_3$ /Mn-CuSG system is that the molecular ozone attacks the tertiary amine to form N-oxides

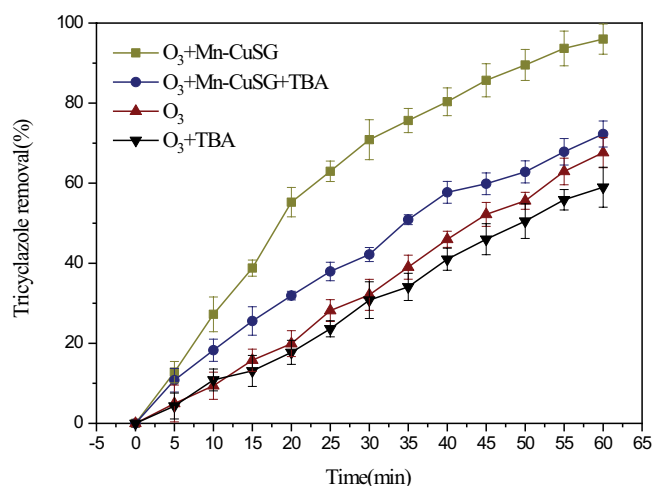
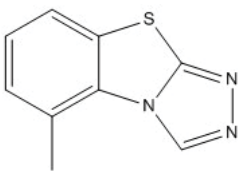
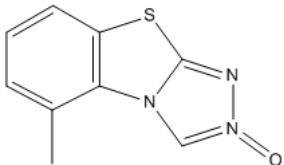
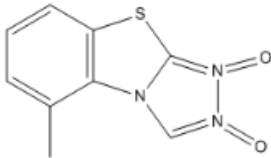
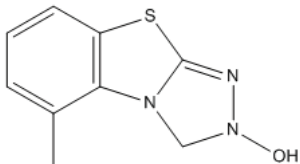


Fig. 9. Effect of TBA on the TC removal efficiency.

Table 3  
Intermediates during tricyclazole degradation identified by HPLC-MS

Compound	Chemical structure	Molecular formula	Retention time (min)	MW
Tricyclazole		$C_9H_7N_3S$	1.79 min	189
5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4]triazole 2-oxide (intermediate I)		$C_9H_7N_3SO$	2.58 min	205
5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4]triazole 1,2-dioxide (intermediate II)		$C_9H_7N_3SO_2$	5.49 min	221
5-methylbenzo[4,5]thiazolo[2,3-c][1,2,4]triazole-2(3H)-ol (intermediate III)		$C_9H_9N_3SO$	4.88 min	207

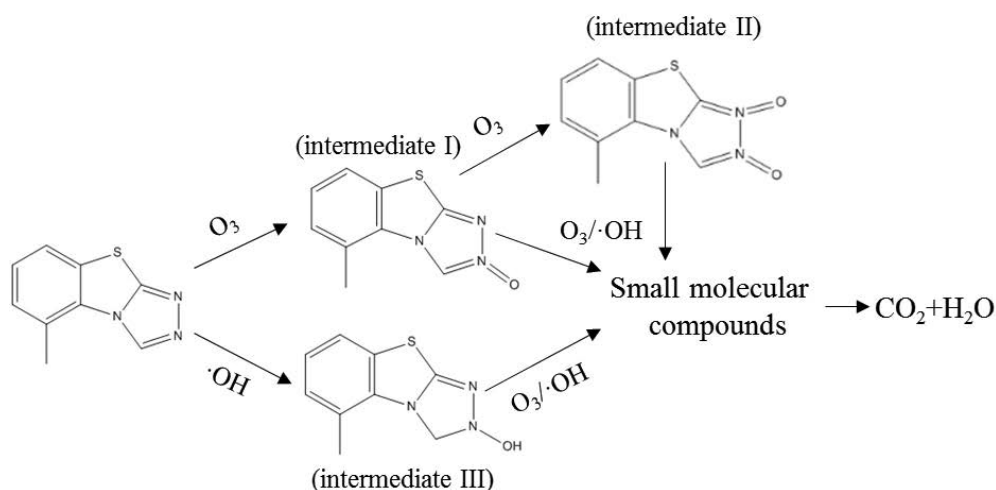


Fig. 10. Degradation pathway of tricyclazole during the ozonation catalyzed by Mn-CuSG.

and hydroxyl radicals attacks the electron-rich 1,2,4-triazole ring to achieve hydroxylation. The catalytic ozonation of the Mn-CuSG reported herein is a hopeful technology for the removal of TC.

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## References

- [1] A. Rubio-Clemente, R.A. Torres-Palma, G.A. Peñuela, Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review, *Sci. Total Environ.*, 478 (2014) 201–225.
- [2] M.A. Engwall, J.J. Pignatello, D. Grasso, Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo-Fenton reaction, *Water Res.*, 33 (1999) 1151–1158.
- [3] L. Padovani, E. Capri, C. Padovani, E. Puglisi, M. Trevisan, Monitoring tricyclazole residues in rice paddy watersheds, *Chemosphere*, 62 (2006) 303–314.
- [4] H.B. Wu, J.Y. Shen, X.B. Jiang, X.D. Liu, X.Y. Sun, J.S. Li, W.Q. Han, Y. Mu, L.J. Wang, Bioaugmentation potential of a newly isolated strain *Sphingomonas* sp. NJUST37 for the treatment of wastewater containing highly toxic and recalcitrant tricyclazole, *Bioresour. Technol.*, 264 (2018) 98–105.
- [5] L. Pareja, M.J. Martinez-Bueno, V. Cesio, H. Heinzen, A.R. Fernandez-Alba, Trace analysis of pesticides in paddy field water by direct injection using liquid chromatography-quadrupole-linear ion trap-mass spectrometry, *J. Chromatogr. A*, 1218 (2011) 4790–4798.
- [6] S. Azarkan, A. Pena, K. Draoui, C.I. Sainz-Diaz, Adsorption of two fungicides on natural clays of Morocco, *Appl. Clay Sci.*, 123 (2016) 37–46.
- [7] M.S. Krieger, W.L. Cook, L.M. Kennard, Extraction of tricyclazole from soil and sediment with subcritical water, *J. Agric. Food Chem.*, 48 (2000) 2178–2183.
- [8] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, *Crit. Rev. Env. Sci. Technol.*, 42 (2012) 251–325.
- [9] A.L. Xu, W.Q. Han, J.S. Li, X.Y. Sun, J.Y. Shen, L.J. Wang, Electrogeneration of hydrogen peroxide using Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> anode in dual tubular membranes electro-Fenton reactor for the degradation of tricyclazole without aeration, *Chem. Eng. J.*, 295 (2016) 152–159.
- [10] C.Q. Zhong, K.J. Wei, W.Q. Han, L.J. Wang, X.Y. Sun, J.S. Li, Electrochemical degradation of tricyclazole in aqueous solution using Ti/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> anode, *J. Electroanal. Chem.*, 705 (2013) 68–74.
- [11] W.Q. Han, C.Q. Zhong, L.Y. Liang, Y.L. Sun, Y. Guan, L.J. Wang, X.Y. Sun, J.S. Li, Electrochemical degradation of triazole fungicides in aqueous solution using TiO<sub>2</sub>-NTs/SnO<sub>2</sub>-Sb/PbO<sub>2</sub> anode: experimental and DEF studies, *Electrochim. Acta*, 130 (2014) 179–186.
- [12] F. Gosetti, U. Chiominatto, E. Mazzucco, R. Mastroianni, B. Bolfi, E. Marengo, Ultra-high performance liquid chromatography tandem high-resolution mass spectrometry study of tricyclazole photodegradation products in water, *Environ. Sci. Pollut. Res.*, 22 (2015) 8288–8295.
- [13] A. Carusi, M.R. Davies, G. De Grandis, B.I. Escher, G. Hodges, K.M.Y. Leung, M. Whelan, C. Willett, G.T. Ankley, Harvesting the promise of AOPs: an assessment and recommendations, *Sci. Total Environ.*, 628–629 (2018) 1542–1556.
- [14] N. Karami, A. Mohagheghian, M. Shirzad-Siboni, K. Godini, Degradation of bentazon herbicide by heterogeneous catalytic ozonation with ZnO-scallop shell nanocomposite: kinetic, reaction pathways and mineralization, *Desal. Wat. Treat.*, 138 (2019) 237–247.
- [15] J. Nawrocki, B. Kasprzyk-Hordern, The efficiency and mechanisms of catalytic ozonation, *Appl. Catal., B*, 99 (2010) 27–42.
- [16] R. Andreozzi, A. Insola, V. Caprio, R. Marotta, V. Tufano, The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution, *Appl. Catal., A*, 138 (1996) 75–81.
- [17] S.P. Tong, W.P. Liu, W.H. Leng, Q.Q. Zhang, Characteristics of MnO<sub>2</sub> catalytic ozonation of sulfosalicylic acid and propionic acid in water, *Chemosphere*, 50 (2003) 1359–1364.
- [18] Y.L. Nie, S.T. Xing, C. Hu, J.H. Qu, Efficient removal of toxic pollutants over Fe-Co/ZrO<sub>2</sub> bimetallic catalyst with ozone, *Catal. Lett.*, 142 (2012) 1026–1032.
- [19] B. Roshani, I. McMaster, E. Rezaei, J. Soltan, Catalytic ozonation of benzotriazole over alumina supported transition metal oxide catalysts in water, *Sep. Purif. Technol.*, 135 (2014) 158–164.
- [20] J.H. Qu, H.Y. Li, H.J. Liu, H. He, Ozonation ofalachlor catalyzed by Cu/Al<sub>2</sub>O<sub>3</sub> in water, *Catal. Today*, 90 (2004) 291–296.
- [21] Y. Wang, W. Yang, X. Yin, Y. Liu, The role of Mn-doping for catalytic ozonation of phenol using Mn/γ-Al<sub>2</sub>O<sub>3</sub> nanocatalyst: performance and mechanism, *J. Environ. Chem. Eng.*, 4 (2016) 3415–3425.
- [22] J. Ma, M.H. Sui, Z.L. Chen, L.N. Wang, Degradation of refractory organic pollutants by catalytic ozonation – activated carbon and Mn-loaded activated carbon as catalysts, *Ozone Sci. Eng.*, 26 (2004) 3–10.
- [23] X.J. Zhang, Y. Liu, G.Q. Liu, K. Tao, F.Z. Meng, Q.A. Jin, T. Kawabata, K. Matsuda, S. Ikeno, R.G. Fan, Y. Kurokawa, N. Tsubaki, One-step preparation of bimodal Fe-Mn-K/SiO<sub>2</sub> catalyst and its catalytic performance of slurry phase Fischer-Tropsch synthesis, *Catal. Lett.*, 139 (2010) 7–16.
- [24] D. Wang, H.D. Xu, J. Ma, X.H. Lu, J.Y. Qi, S. Song, Strong promoted catalytic ozonation of atrazine at low temperature using tourmaline as catalyst: influencing factors, reaction mechanisms and pathways, *Chem. Eng. J.*, 354 (2018) 113–125.
- [25] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal., B*, 47 (2004) 219–256.
- [26] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, V. Tufano, The ozonation of pyruvic acid in aqueous solutions catalyzed by suspended and dissolved manganese, *Water Res.*, 32 (1998) 1492–1496.
- [27] I. Udrea, C. Bradu, Ozonation of substituted phenols in aqueous solutions over CuO-Al<sub>2</sub>O<sub>3</sub> catalyst, *Ozone Sci. Eng.*, 25 (2003) 335–343.
- [28] J.W. Murray, The surface chemistry of hydrous manganese dioxide, *J. Colloid Interface Sci.*, 46 (1974) 357–371.
- [29] W. Peng, J. Liu, C.X. Li, F.X. Zong, W.S. Xu, X. Zhang, Z.D. Fang, A multipath peroxy monosulfate activation process over supported by magnetic CuO-Fe<sub>3</sub>O<sub>4</sub> nanoparticles for efficient degradation of 4-chlorophenol, *Korean J. Chem. Eng.*, 35 (2018) 1662–1672.
- [30] L. Zhao, J. Ma, Z.Z. Sun, H.L. Liu, Mechanism of heterogeneous catalytic ozonation of nitrobenzene in aqueous solution with modified ceramic honeycomb, *Appl. Catal., B*, 89 (2009) 326–334.
- [31] Z.Q. Liu, J.L. Tu, Q. Wang, Y.H. Cui, L.H. Zhang, X.H. Wu, B.P. Zhang, J. Ma, Catalytic ozonation of diethyl phthalate in aqueous solution using graphite supported zinc oxide, *Sep. Purif. Technol.*, 200 (2018) 51–58.
- [32] C. Von Sonntag, U. Von Gunten, *Chemistry of Ozone in Water and Wastewater Treatment*, IWA Publishing, London SW1H 0QS, UK, 2012.