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Heterogeneous catalytic ozonation of paper-making wastewater with α-Fe_2O_3/γ-Al_2O_3 as a catalyst for increased TOC and color removals

Shuaiming He[a], Jun Li[a,*], Jun Xu[a], Lihuan Mo[a,*], Liqi Zhu[b], Pengcheng Luan[a], Jinsong Zeng[a]

[a]*State Key Laboratory of Pulp and Paper-Making Engineering, South China University of Technology, Guangzhou City, Guangdong Province 510640, China, Tel./Fax: +86 2087110084;emails: ppjunli@scut.edu.cn (J. Li), lhmo@scut.edu.cn (L. Mo), he.shuaiming@163.com(S. He), xujun@scut.edu.cn (J. Xu)*

[b]*Department of Materials Science and Engineering, University of Maryland College Park, College Park, MD 20742, USA, email: lrz001@terpmail.umd.edu*

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ABSTRACT

There exists great passion to develop an economical and high-efficient catalyst for the catalytic ozonation treatment of biologically recalcitrant wastewater. The present work utilized a Fe/γ-Al_2O_3 catalytic ozonation process for tertiary treatment of actual paper-making wastewater. Results indicated that in comparison with ozone alone, the addition of a Fe/γ-Al_2O_3 catalyst enhanced the removal efficiency of total organic carbon (TOC) during ozonation after 60 min of treatment, which initiated a 25% enhancement for TOC removal. After 60 min of treatment, TOC removal rates reached 51% using Fe/γ-Al_2O_3 as a catalyst, 37% in the presence of γ-Al_2O_3 and only 26% with ozonation alone, which already showed excellent color removal results. The presence of *tert*-butanol (a well-known hydroxyl radical scavenger) had a negative effect on the TOC removal rate of the Fe/γ-Al_2O_3/O_3 process, indicating that the Fe/γ-Al_2O_3/O_3 process follows a hydroxyl radical ($^{\bullet}OH$) reaction mechanism. Finally, the prepared Fe/γ-Al_2O_3 catalyst exhibited good stability and recyclability. These results illustrate that there are potential applications of ozonation catalyzed by Fe/Al_2O_3 for the tertiary treatment of biologically recalcitrant wastewater.

Keywords: Catalytic ozonation; γ-Al_2O_3; α-Fe_2O_3; Paper-making wastewater; TOC

1. Introduction

The pulp and paper industry is one of the most important industrial sectors in the world due to its huge economic benefits. However, the industry is the world's third largest industrial consumer of freshwater and sixth largest source of industrial pollution [1,2]. The effluents of pulp and paper industry usually contain a variety of organic contaminants such as saccharides, carboxylic acids, phenolic compounds and surfactants [3]. These organic contaminants may cause severe ecological and environmental damage upon direct discharge to receiving waters without appropriate treatment. In order to remove these organic contaminants to minimize ecological and environmental damage, effluents from pulp and paper mills need to be effectively treated [4]. Primary wastewater treatment aims to remove suspended solids, colloid and grease using physical methods [5]. Secondary treatment usually involves an activated sludge process to degrade the dissolved organic pollutants retained after primary wastewater treatment owing to the action of microorganisms [6,7]. Because some of the organic contaminants are non-biodegradable, the effluents have difficulty in meeting discharge standards after secondary treatment. In order to meet progressively strict discharge limits, the pulp and paper industry is forced to employ more powerful and advanced oxidation processes (AOPs) as tertiary treatment.

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* Corresponding author.

AOPs have been shown to be capable of degrading refractory organic pollutants effectively by the generation of powerful and non-selective oxidizing species such as hydroxyl radicals ($OH^\bullet$), which were considered as the main oxidizing species [8]. Catalytic ozonation, as one of the most promising AOPs, has attracted significant interest due to its high efficiency in refractory organic pollutants removal and ease of operation [9–13]. In comparison with single ozonation process, catalytic ozonation process is more efficient owing to the catalysts used in the process promoting the generation of free radicals with much higher oxidation potential than ozone [14–18]. The combination of catalyst supports and active components is very critical for preparing highly efficient catalysts for the practical application of catalytic ozonation process. Different kinds of catalyst supports such as activated carbon [12,17], zeolites [19], silica [10], ceramic [20] and alumina (Al_2O_3) [19,21–25] have been formerly investigated. Among these, Al_2O_3 is the most intensively studied because of its good catalytic performance and low-cost. The addition of Al_2O_3 catalysts has greatly enhanced the efficiency of ozonation for the degradation of recalcitrant chemicals such as 2-methylisoborneol [26–28], 2,4,6-trichloroanisole [28–30] and 2-isopropyl-3-methoxypyrazine [31]. It has been reported that the enhanced removal of recalcitrant contaminants from aqueous solution in Al_2O_3-catalyzed ozonation processes is attributed to the interaction between the hydroxyl group on the surface of Al_2O_3 and ozone [32,33].

A lot of ozone applications for degradation of paper-making wastewaters highlight that ozone oxidation can reduce toxicity and color, targeting organic contaminants such as extractive, lignin, organochlorines (AOX), fatty acid and resins [34–38]. However, only a part of organic pollutants can be oxidized by ozone. Some recalcitrant organic contaminants such as oxalic or acetic or formic acids are very resistant to ozone oxidation. Ozonation catalyzed by powdered Mn/sepiolite [39] and TOCCATA® metal oxides [40] greatly enhanced the degradation efficiency of organic pollutants in pulp and paper mill effluents. To the best of our knowledge, Fe-loaded γ-Al_2O_3 has not been developed for catalytic ozonation of paper-making wastewater. In a former study on catalytic ozonation [41], Fe_2O_3/Al_2O_3 has functioned as a highly efficient catalyst in the mineralization of recalcitrant compound oxalic acid, which is a kind of intermediate formed during the degradation of pulp and paper mill effluents [42]. Iron type catalysts can be suggested for catalytic ozonation process due to its abundance in earth. Al-Hayek et al. [43] have shown that in comparison with single ozonation, a significant increase of the total organic carbon (TOC) removal can be obtained in the ozonation of recalcitrant organic pollutants phenol catalyzed by $Fe(III)/Al_2O_3$. The authors proposed that the enhanced TOC removal maybe due to the formation of free radicals. These cited works primarily focused on the catalytic activity of Fe/Al_2O_3 in ozonation of a given recalcitrant organic pollutant, and few studies were performed on ozonation of real industrial wastewater by the catalysts.

In this work, pulp and paper mill effluent after biological treatment was chosen as a research subject, and Fe was chosen as an active catalyst component because of its abundance in earth and low solubility in water. Fe oxide loaded onto γ-Al_2O_3 (Fe/γ-Al_2O_3) catalyst was prepared and characterized, then used as catalysts for the catalytic ozonation of biologically treated pulp and paper mill effluent. The objective of the present study was to assess the influence of the prepared catalysts on color removal and, primarily, on the removal efficiency of TOC in ozonation system. Meanwhile, the possible reaction pathways of catalytic ozonation are proposed.

2. Materials and methods

2.1. Materials

Iron nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] and *tert*-butanol (TBA) were purchased from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). The commercial γ-Al_2O_3 used in this study was supplied by Jiangsu Jingjing New Material Co., Ltd. (Jiangsu, China). Ozone generator was obtained from Guangzhou Weigu Equipment Co., Ltd. (Guangdong, China).

Pulp and paper mill wastewater after secondary biological treatment was collected from an integrated paper mill in Guangxi Province, China. The main properties of the effluent are as follows: the TOC is 128 mg/L, the color is 418 C.U. and the pH is 7.6.

2.2. Preparation of the Fe/γ-Al_2O_3 catalysts

The Fe/γ-Al_2O_3 catalysts were prepared by a wet impregnation method. $Fe(NO_3)_3 \cdot 9H_2O$ was used as precursor and γ-Al_2O_3 (ϕ = 3–5 mm) was used as a carrier. Commercial γ-Al_2O_3 was first crushed and passed through an 80-mesh sieve, then dispersed in a certain concentration of $Fe(NO_3)_3 \cdot 9H_2O$ solution for 12 h at room temperature. After impregnation, the samples were dried for 12 h at 60°C and then dried at 105°C for 3 h. The dried samples were calcined at 350°C in a muffle furnace for 3 h to obtain Fe/γ-Al_2O_3 catalysts.

2.3. Characterization of catalysts

X-ray diffraction (XRD) analysis was conducted using a Bruker D8 advance X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) with a scanning range of 10°–80° and a Cu Kα radiation source at 40 kV and 40 mA, and a scanning speed of 4°/min.

The Brunauer–Emmett–Teller (BET) specific surface area, pore volume and average pore size of the catalysts were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 BET surface area analyzer (Norcross, USA). The surface morphology of the samples was investigated by a scanning electron microscope (EVO18, Zeiss Corporation, Oberkochen, Germany).

The pH of point of zero charge (pH_{pzc}) of the Fe/Al_2O_3 catalyst was tested according to the pH-drift method [44,45].

2.4. Ozonation reactions and analytical methods

Experiments were conducted in a 1 L cylindrical glass reactor at room temperature (Fig. 1). First, the glass reactor was loaded with 2.5 g Fe/γ-Al_2O_3 and 500 mL pulp and paper mill effluent. Then, 0.3 g/h O_3 produced by ozone generator continuously bubbled into the reactor through a porous

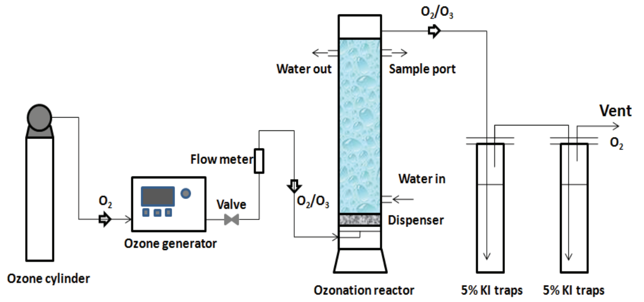


Fig. 1. Schematic of the experimental setup.

ceramic plate situated at the bottom of the glass reactor. Wastewater samples were periodically withdrawn and filtered with 0.45 μm synthetic fiber membrane to determine the TOC and color of the effluent. The excess ozone in the off-gas steam of the reactor was immediately dispatched in a 5% potassium iodide (KI) solution.

The TOC of the effluent was determined via Hach® TOC Method 10173 Direct (mid-range TOC 15–150 mg/L).

The color of the wastewater before and after treatment was measured according to the platinum–cobalt method using a UV–Vis spectrophotometer (HACH DR2800, Hach Company, Colorado, USA).

The leached out concentration of ferric ion in treated wastewater from the solid catalysts during catalytic ozonation process was measured by an inductively coupled plasma mass spectroscopy (ICP/MS, 7500a, Agilent, USA).

3. Results and discussion

3.1. Catalyst characterization

The X-ray powder diffraction patterns of γ-Al_2O_3 and Fe/γ-Al_2O_3 catalysts were shown in Fig. 2. Three typical diffraction peaks at $2\theta = 38.7°$, 46.2° and 67.3° corresponding to γ-Al_2O_3 were observed [46]. In comparison with the XRD pattern of γ-Al_2O_3, newly emerged diffraction peaks at $2\theta = 33.2°$, 35.7°, 49.5° and 54.2° in the patterns of Fe/γ-Al_2O_3 catalysts were attributed to the existence of α-Fe_2O_3 (JCPDS File No. 33-0664).

The BET surface area, average pore diameter and pore volume of γ-Al_2O_3 and Fe/γ-Al_2O_3 catalysts are listed in Table 1. It can be seen from Table 1 that in comparison with the γ-Al_2O_3 support, the BET surface area and pore volume of Fe/γ-Al_2O_3 catalysts were reduced after the introduction of Fe into γ-Al_2O_3. This might be due to the partial capping of the pores in γ-Al_2O_3 catalyst after loading Fe. The average pore diameter of the Fe/γ-Al_2O_3 catalysts also decreased compared with the γ-Al_2O_3 support.

The morphologies of γ-Al_2O_3 and Fe/γ-Al_2O_3 catalysts were characterized by scanning electron microscopy (SEM) (Fig. 3). It can be seen from Fig. 3 that γ-Al_2O_3 and Fe/γ-Al_2O_3 catalysts exhibit very different morphologies. The surface of γ-Al_2O_3 catalyst was very rough instead of smooth as shown in Fig. 3(a), and particles with different dimensions can be found on the surface of Fe/γ-Al_2O_3 catalyst as shown in Fig. 3(b). These particles were most likely α-Fe_2O_3 deposited on γ-Al_2O_3. The α-Fe_2O_3 was deposited on the surface of γ-Al_2O_3 to form microagglomerates in irregular shapes and sizes (Fig. 3(c)). Figs. 3(d) and (e) show the selected area SEM images and energy dispersive X-ray (EDX) patterns of the catalysts. The results indicated that Fe and O elements were observed on the catalysts surfaces. The element contents of Fe, Al and O were further confirmed from the results of the EDS patterns. As shown in the inset of Fig. 3(e), the weight and atomic percentages of Fe and O in the catalyst were 6.53% and 2.52%, respectively.

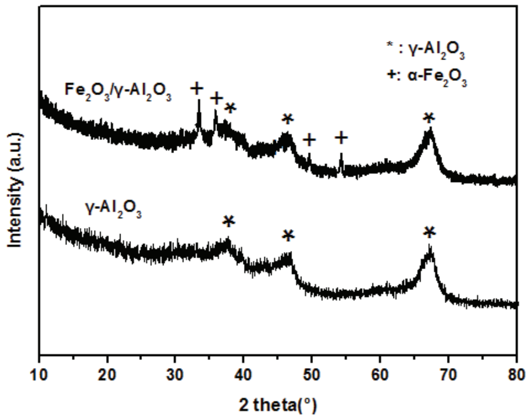


Fig. 2. XRD spectra of γ-Al_2O_3 and Fe/γ-Al_2O_3.

Table 1
The results of BET analysis

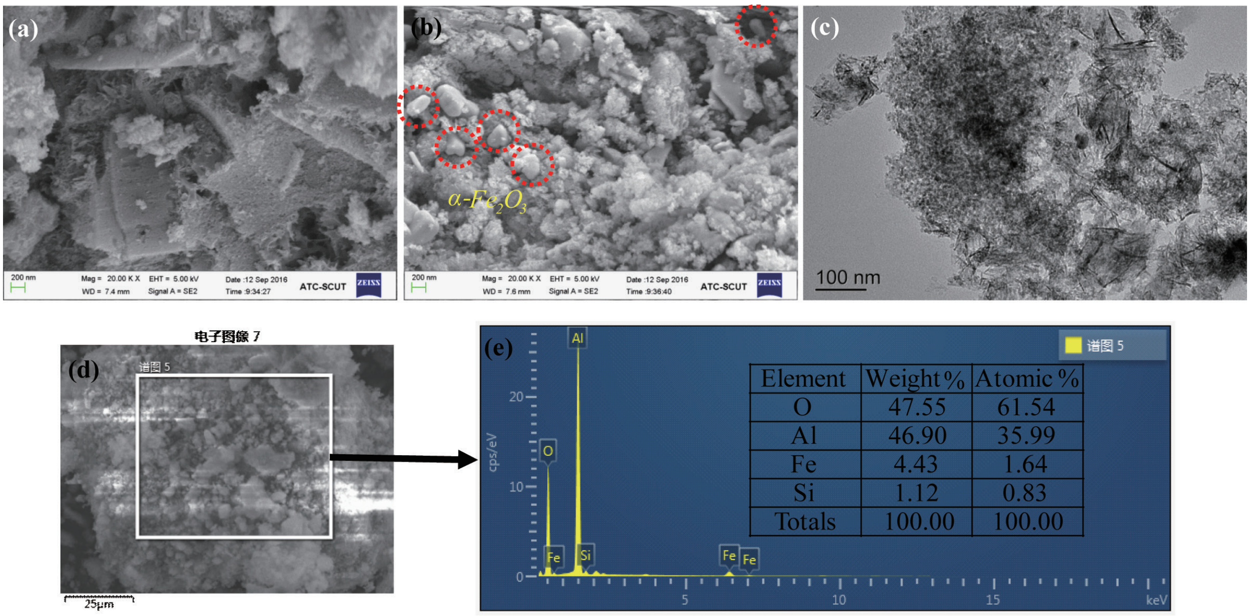
Samples	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
γ-Al_2O_3	249.7	10.4	0.677
Fe/γ-Al_2O_3	225.8	10.0	0.604
Fe/γ-Al_2O_3-5	202.3	10.2	0.558

Fe/γ-Al_2O_3-5 denotes the catalyst was reused for the fifth time.

3.2. Catalytic performances of catalysts

Results showed that the adsorption of γ-Al_2O_3 and Fe/γ-Al_2O_3 became saturated after 60 min. The TOC removals of the effluent by adsorption after 60 min on γ-Al_2O_3 and Fe/γ-Al_2O_3 were 5.2% and 3.9%, respectively (Fig. 4(a)). These catalysts exhibit weak adsorption capability toward refractory chemicals in the effluent. Note that the adsorption capacity of Fe/γ-Al_2O_3 was lower than γ-Al_2O_3. This may be due to the decreased surface areas (Table 1). However, the TOC removal rates were all increased in Al_2O_3/O_3 and Fe/γ-Al_2O_3 processes.

The removal rate of TOC and color of the effluent in ozone alone, γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes is shown in Figs. 4(b) and (c). Results indicated that in comparison with ozone alone, the TOC and color removal rates of the effluent were increased in catalytic ozonation processes. Among the three processes, the Fe/γ-Al_2O_3/O_3 process achieved the best TOC and color removal performance. The TOC removal rates of the effluent after 60 min of reaction in ozone alone, γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes, reached 26%, 37% and 51%, respectively. It is worth noting that the color removal rates remained relatively stable after 20 min of



Element	Weight%	Atomic%
O	47.55	61.54
Al	46.90	35.99
Fe	4.43	1.64
Si	1.12	0.83
Totals	100.00	100.00

Fig. 3. SEM images of (a) γ-Al_2O_3 and (b) Fe/γ-Al_2O_3, (c) transmission electron micrographs of Fe/γ-Al_2O_3 catalysts, energy dispersive X-ray (EDX) spectrum (e) of the area indicated in (d). Inset: the table presents the atomic ratio, percentage of the components in the catalysts.

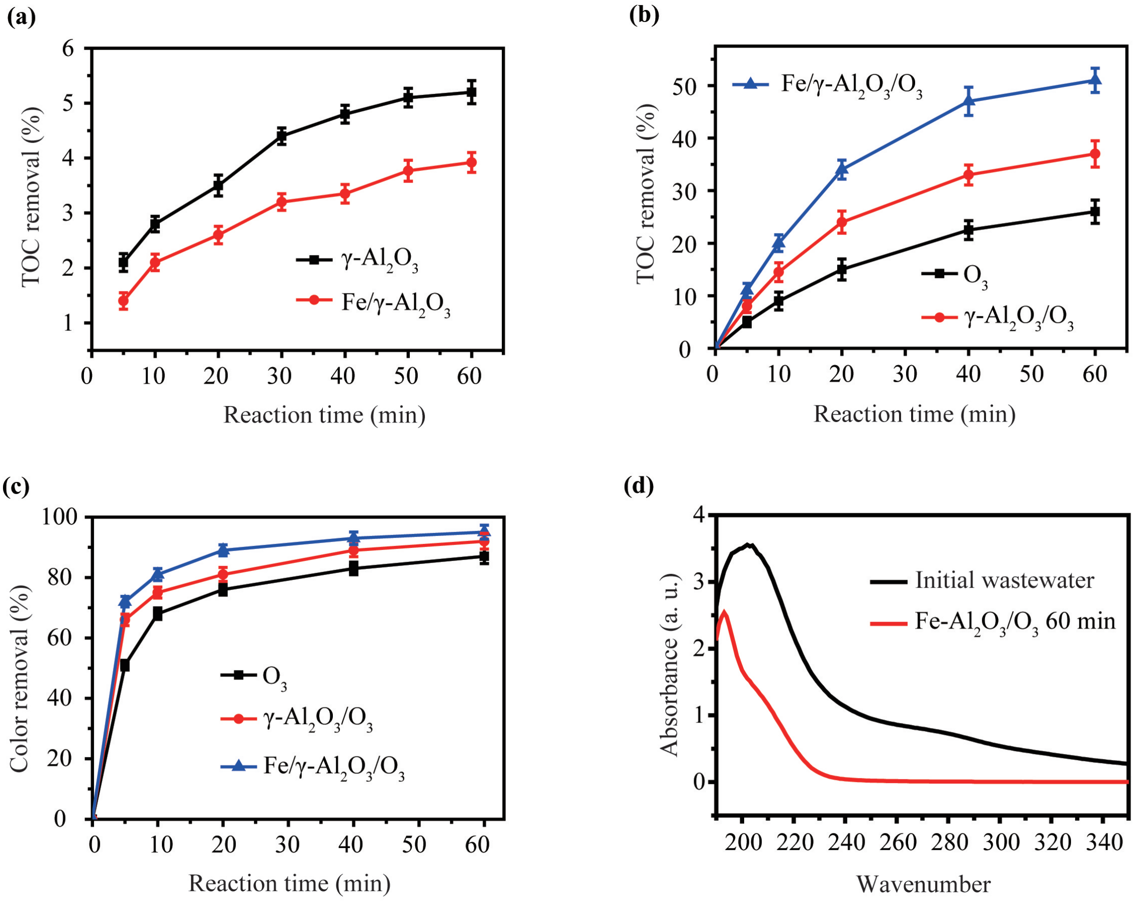


Fig. 4. TOC removal by adsorption (a) and catalytic ozonation processes (b), color removal by ozonation and catalytic ozonation processes (c), UV–visible analysis of the effluent before and after treatment (d). Note: 5 g/L catalyst, 5 mg/min ozone, 30°C and 60 min.

reaction in these three processes and the removal efficiency of color was much higher than that of TOC. Also note that the degree of enhanced color removal rate of the effluent in catalytic ozonation processes (γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes) was not as obvious as that of enhanced TOC removal rate compared with ozone process. Catalytic ozonation processes do not usually show superiority in terms of color removal. Ozone alone can achieve comparatively good color removal rate (as high as 87%). Because lignin compounds contained in the effluent caused the high value of color of the effluent and ozone can effectively decompose these lignin compounds by oxidizing the double bonds and triple bonds of them, the color of the effluent can be easily removed by ozone alone [47,48]

Because both γ-Al_2O_3 and Fe/γ-Al_2O_3 can accelerate the decomposition of aqueous ozone to form strong oxidant and non-selective radical ($^{\bullet}OH$) in both processes, the TOC removal rate was significantly enhanced in the two processes [49,50]. The active component Fe contained in Fe/γ-Al_2O_3 catalysts can provide more active sites than γ-Al_2O_3 catalyst [41,51], thus Fe/γ-Al_2O_3 catalyst showed better catalytic performance than γ-Al_2O_3 catalyst (Figs. 4(b) and (c)). Some intermediate compounds, such as carboxylic acid, oxalic acid and formic acid, can be accumulated during the degradation of aromatics contained in the effluent, and these intermediate compounds are very hard to degrade by ozone oxidation but could be mineralized by radical $^{\bullet}OH$ [52,53].

Since pulp and paper mill effluents usually contain large amounts of organic pollutants, and these organic pollutants have strong absorption in ultraviolet spectral region, the changes of contents of organic pollutants can be reflected by UV analyses results of the initial wastewater and treated wastewater [54]. The changes of the UV–visible light absorbance curves of the effluent before and after treatment are shown in Fig. 4(d). It can be seen from Fig. 4(d) that the UV absorbance of the effluent after treatment declined obviously, which indicated the organic pollutants had been removed significantly after 60 min of treatment. Specifically, the adsorption peak at around 204 nm was mainly attributed to the presence of aliphatic compounds in the initial wastewater [55]. This adsorption peak became much weaker after 60 min of treatment, indicating the degradation of these aliphatic compounds. Besides, a moderate intensity adsorption band was observed in the range of 230–310 nm, showing the existence of large amounts of aromatic contaminants in the initial wastewater [56–58]. However, this adsorption band was significantly decreased after treatment, indicating the effective destruction of aryl groups by the treatment.

3.3. The influence of pH and radical scavenger on TOC removal

Initial pH values can significantly impact the performance of catalytic ozonation. The surface properties of catalysts and decomposition rate of ozone can be different under different initial pH conditions [38,39]. Thus, the effect of initial pH on TOC removal was investigated (Fig. 4(d)). Results indicated that when the initial pH value increased from 3 to 7.9, the TOC removal rate was increased from 34% to 51% in Fe/γ-Al_2O_3/O_3 process. However, the TOC removal rate decreased to 45.6% when the initial pH value was further increased to 10. The initial pH (7.9) value of the effluent, close to the pH_{pzc} value (8.0) of Fe/Al_2O_3 catalysts, can facilitate the generation of more surface $OH^{\bullet}$, where the best TOC removal results were achieved. However, the degradation efficiency of refractory chemicals became lower at comparatively low or high pH values (Fig. 4(d)). And the degradation of refractory chemicals primarily depends on the direct oxidation of molecular ozone when the pH value of wastewater was too low. However, organic pollutants can only be partially degraded by direct oxidation by aqueous ozone molecules, and some refractory organic pollutants need to be degraded by strong oxidant $OH^{\bullet}$. Under a higher pH condition (10), Fe/γ-Al_2O_3 catalysts are negatively charged, thus a repulsive electrostatic interaction between the catalysts and organic pollutants occurs, which could impede the mineralization of organic pollutants [40–42]. Moreover, CO_3^{2-} and HCO_3^- can be easily formed under strong alkaline conditions, which are efficient $OH^{\bullet}$ scavengers.

The degradation pathways of organic pollutants contained in wastewater in a catalytic ozonation process usually contain two types: direct oxidation by aqueous ozone and indirect oxidation by radicals, mainly hydroxyl radicals [6,8]. In order to verify whether $^{\bullet}OH$ was involved in the three processes, experiments were carried out in the presence of 50 mg/L TBA, which is a very effective radical scavenger that has a scavenging reaction rate constant as high as 6.0×10^8 L/(mol·s) toward hydroxyl radicals and only 3.0×10^{-3} L/(mol·s) toward ozone [1,57,59,60]. The effect of TBA on the removal of TOC in the three processes is presented in Fig. 5. Results indicated that after 60 min of reaction, the removal rates of TOC in ozone alone, γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes were 23%, 25% and 37%, respectively. As mentioned above, in the absence of TBA, these values were 26%, 37% and 51%, respectively. Obviously, the catalytic activities of γ-Al_2O_3 and Fe/γ-Al_2O_3 were strongly inhibited by TBA in γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes. The increase in TOC removal efficiency was mainly due to the generation of more hydroxyl radicals in γ-Al_2O_3/O_3 and Fe/γ-Al_2O_3/O_3 processes. Because Fe can offer more active sites to promote the generation of more hydroxyl radicals in Fe/γ-Al_2O_3/O_3 process in comparison with γ-Al_2O_3/O_3 process, better catalytic performance can be obtained in Fe/γ-Al_2O_3/O_3 processes.

In order to investigate the stability of Fe/γ-Al_2O_3 catalysts, we collected the used Fe/γ-Al_2O_3 catalyst and washed them with distilled water, air dried them and heated them at 80°C for 12 h, then reused them under the same conditions as described above.

Results indicated that the TOC removal rate dropped slightly as the reused time was increased. The TOC removal rate decreased from 51% to 46.5% after catalytic ozonation of 60 min as the catalyst was reused for the fifth time. Two reasons probably caused the decrease of catalytic performance of the catalyst as the increase of reuse time: first, the surface area of Fe/γ-Al_2O_3 catalyst was reduced when the catalyst was reused for the fifth time (Table 1); second, the miniscule leaching of the active components Fe from the Fe/γ-Al_2O_3 catalyst during recycling led to the decrease of active sites of the catalyst. ICP/MS analysis was used to study the concentrations of Fe^{3+} leached from the catalyst. Results showed that the concentration of Fe^{3+} in the effluent after treatment were 64 μg/L, which did not cause secondary pollution. Overall, the prepared Fe/γ-Al_2O_3 remained a highly efficient and relatively stable catalyst for the ozonation of the effluent.

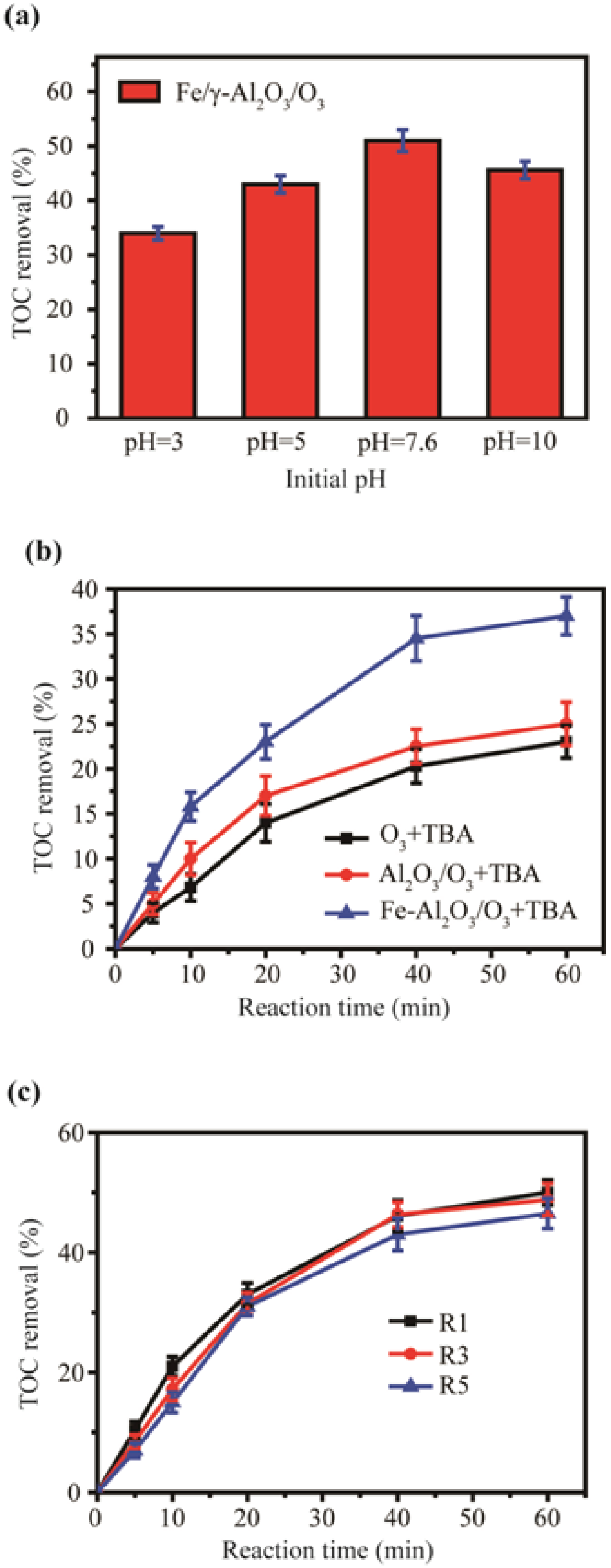


Fig. 5. The effect of pH (a) and *tert*-butanol (TBA) (b) on TOC removal. The stability of Fe/γ-Al_2O_3 catalysts (c), R1, R3 and R5 denote the catalyst was reused for the first, third and fifth time, respectively. Note: 5 g/L catalyst, 5 mg/min ozone, 1 g/L $^{\bullet}OH$ scavenger, 30°C and 60 min.

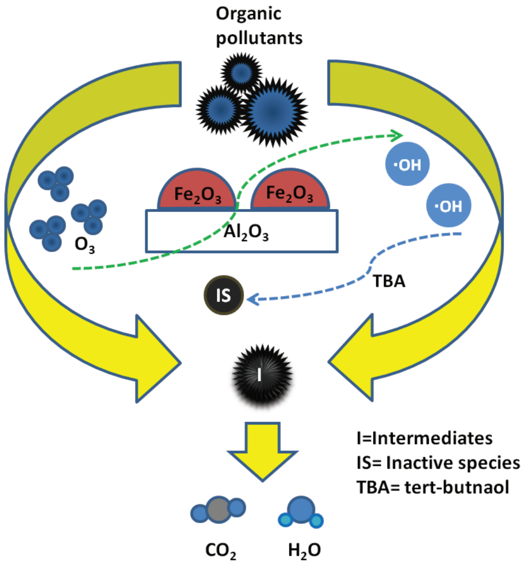


Fig. 6. Reaction pathways involved in catalytic ozonation of the effluent over Fe/γ-Al_2O_3.

3.4. Reaction pathways involved in the catalytic ozonation

The main reaction pathways occurring during the Fe/γ-Al_2O_3/O_3 process are shown in Fig. 6. On the one hand, ozone alone can degrade part of organic contaminants in the effluent. On the other hand, Fe/γ-Al_2O_3 can act as highly efficient catalyst to promote the decomposition rate of aqueous ozone to generate hydroxyl radicals ($^{\bullet}OH$) with a much higher oxidation capability, which can further degrade refractory organic contaminants in the effluent [41]. It is worth noting that highly efficient oxidant hydroxyl radicals ($^{\bullet}OH$) can be quenched quickly in the presence of radical scavenger TBA, thus the treatment efficiency of Fe/γ-Al_2O_3/O_3 process decreased quickly in the presence of TBA. Overall, the increased TOC and color removal rates were mainly attributed to the generation of more highly efficient oxidant $^{\bullet}OH$ catalyzed by Fe/γ-Al_2O_3 catalyst in the Fe/γ-Al_2O_3/O_3 process.

4. Conclusions

The presence of a Fe/γ-Al_2O_3 as a catalyst enhanced the removal rate of TOC by an additional 25% after 60 min of treatment in comparison with ozone alone. After 60 min of treatment, TOC removal rates reached 51% using Fe/γ-Al_2O_3 as catalyst, 37% in the presence of γ-Al_2O_3 and only 26% with ozonation alone. Because ozone alone can obtain a color removal rate as high as 87% after 60 min of treatment, catalytic ozonation processes did not show any significant superiority in terms of color removal. The TOC removal rate in the Fe/γ-Al_2O_3/O_3 process was strongly inhibited in the presence of TBA, indicating that Fe/γ-Al_2O_3/O_3 process follows a hydroxyl radical ($^{\bullet}OH$) reaction mechanism. The TOC removal rate of the effluent in the Fe/γ-Al_2O_3/O_3 process remained at 46.5% after catalytic ozonation of 60 min when the catalyst was reused for the fifth time. The prepared Fe/γ-Al_2O_3 catalyst is industrially feasible because of its high efficiency, ease of preparation and low-cost.

Acknowledgments

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References

[1] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: a review, Adv. Environ. Res., 5 (2001) 175–196.

[2] C.E. Blank, R.W. Parks, N.W. Hinman, Chitin: a potential new alternative nitrogen source for the tertiary, algal-based treatment of pulp and paper mill wastewater, J. Appl. Phycol., 28 (2016) 1–14.

[3] A.M. Amat, A. Arques, M.A. Miranda, F. López, Use of ozone and/or UV in the treatment of effluents from board paper industry, Chemosphere, 60 (2005) 1111–1117.

[4] D. Pokhrel, T. Viraraghavan, Treatment of pulp and paper mill wastewater – a review, Sci. Total Environ., 333 (2004) 37–58.

[5] H. Chu, Z. Wang, Y. Liu, Application of modified bentonite granulated electrodes for advanced treatment of pulp and paper mill wastewater in three-dimensional electrode system, J. Environ. Chem. Eng., 4 (2016) 1810–1817.

[6] M.A. Hubbe, J.R. Metts, D. Hermosilla, M.A. Blanco, L. Yerushalmi, F. Haghighat, P. Lindholm-Lehto, Z. Khodaparast, M. Kamali, A. Elliott, Wastewater treatment and reclamation: a review of pulp and paper industry practices and opportunities, Bioresources, 11 (2016) 7953–8091.

[7] K.P. Kringstad, K. Lindström, Spent liquors from pulp bleaching, Environ. Sci. Technol., 18 (1984) 236A–248A.

[8] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, Crit. Rev. Environ. Sci. Technol., 42 (2012) 251–325.

[9] B. Legube, N.K.V. Leitner, Catalytic ozonation: a promising advanced oxidation technology for water treatment, Catal. Today, 53 (1999) 61–72.

[10] Y. Wang, Y. Xie, H. Sun, J. Xiao, H. Cao, S. Wang, Efficient catalytic ozonation over reduced graphene oxide for *p*-hydroxylbenzoic acid (PHBA) destruction: active site and mechanism, ACS Appl. Mater. Interfaces, 8 (2016) 9710–9720.

[11] Y. Liu, Z. Chen, W. Gong, Y. Dou, S. Wang, W. Wang, Structural characterizations of zinc-copper silicate polymer (ZCSP) and its mechanisms of ozonation for removal of *p*-chloronitrobenzene in aqueous solution, Sep. Purif. Technol., 172 (2017) 251–257.

[12] S. He, J. Li, J. Xu, L. Mo, Enhanced removal of COD and color in paper-making wastewater by ozonation catalyzed by Fe supported on activated carbon, Bioresources, 11 (2016) 8396–8408.

[13] B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal., B, 46 (2003) 639–669.

[14] P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, The influence of various factors on aqueous ozone decomposition by granular activated carbons and the development of a mechanistic approach, Carbon, 44 (2006) 3102–3112.

[15] L. Zhao, J. Ma, Z.Z. Sun, X.D. Zhai, Catalytic ozonation for the degradation of nitrobenzene in aqueous solution by ceramic honeycomb-supported manganese, Appl. Catal., B, 83 (2008) 256–264.

[16] G. Gao, J. Kang, J. Shen, Z. Chen, W. Chu, Catalytic ozonation of sulfamethoxazole by composite iron-manganese silicate oxide: cooperation mechanism between adsorption and catalytic reaction, Environ. Sci. Pollut. Res., 23 (2016) 1–9.

[17] D. Gümüş, F. Akbal, A comparative study of ozonation, iron coated zeolite catalyzed ozonation and granular activated carbon catalyzed ozonation of humic acid, Chemosphere, 174 (2017) 218–231.

[18] A. Mashayekh-Salehi, G. Moussavi, K. Yaghmaeian, Preparation, characterization and catalytic activity of a novel mesoporous nanocrystalline MgO nanoparticle for ozonation of acetaminophen as an emerging water contaminant, Chem. Eng. J., 310 (2017) 157–169.

[19] A. Ikhlaq, B. Kasprzyk-Hordern, Catalytic ozonation of chlorinated VOCs on ZSM-5 zeolites and alumina: formation of chlorides, Appl. Catal., B, 200 (2017) 274–282.

[20] Y. Guo, B. Xu, F. Qi, A novel ceramic membrane coated with MnO_2-Co_3O_4 nanoparticles catalytic ozonation for benzophenone-3 degradation in aqueous solution: fabrication, characterization and performance, Chem. Eng. J., 287 (2016) 381–389.

[21] L. Yang, C. Hu, Y. Nie, J. Qu, Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide, Environ. Sci. Technol., 43 (2009) 2525–2529.

[22] A. Ziylan-Yavaş, N.H. Ince, Catalytic ozonation of paracetamol using commercial and Pt-supported nanocomposites of Al_2O_3: the impact of ultrasound, Ultrason. Sonochem., 18 (2017) 257–265.

[23] E. Rezaei, J. Soltan, EXAFS and kinetic study of MnO_x/γ-alumina in gas phase catalytic oxidation of toluene by ozone, Appl. Catal., B, 148 (2014) 70–79.

[24] E. Rezaei, J. Soltan, N. Chen, J. Lin, Effect of noble metals on activity of MnO_x/γ-alumina catalyst in catalytic ozonation of toluene, Chem. Eng. J., 214 (2013) 219–228.

[25] F.J. Beltrán, F.J. Rivas, R. Montero-De-Espinosa, A TiO_2/Al_2O_3 catalyst to improve the ozonation of oxalic acid in water, Appl. Catal., B, 47 (2004) 101–109.

[26] B. Xu, F. Qi, Reaction mechanism of 2-methylisoborneol and 2,4,6-trichloroanisole in catalytic ozonation by γ-AlOOH: role of adsorption, Clean-Soil Air Water, 44 (2016) 1099–1105.

[27] F. Qi, B. Xu, Z. Chen, L. Zhang, P. Zhang, D. Sun, Mechanism investigation of catalyzed ozonation of 2-methylisoborneol in drinking water over aluminum (hydroxyl) oxides: role of surface hydroxyl group, Chem. Eng. J., 165 (2010) 490–499.

[28] F. Qi, B. Xu, S. Li, Z. Chen, L. Zhang, D. Sun, Catalyzed ozonation decomposition of taste and odor-causing substances in water and simultaneous control of aldehyde generation, Environ. Eng. Sci., 29 (2012) 580–589.

[29] F. Qi, B. Xu, Z. Chen, J. Ma, D. Sun, L. Zhang, Influence of aluminum oxides surface properties on catalyzed ozonation of 2,4,6-trichloroanisole, Sep. Purif. Technol., 66 (2009) 405–410.

[30] F. Qi, B. Xu, Z. Chen, J. Ma, Catalytic ozonation for degradation of 2,4,6-trichloroanisole in drinking water in the presence of γ-AlOOH, Water Environ. Res., 81 (2009) 592–597.

[31] F. Qi, B. Xu, Z. Chen, L. Feng, L. Zhang, D. Sun, Catalytic ozonation of 2-isopropyl-3-methoxypyrazine in water by γ-AlOOH and γ-Al_2O_3: comparison of removal efficiency and mechanism, Chem. Eng. J., 219 (2013) 527–536.

[32] M. Ernst, F. Lurot, J.C. Schrotter, Catalytic ozonation of refractory organic model compounds in aqueous solution by aluminum oxide, Appl. Catal., B, 47 (2004) 15–25.

[33] F. Qi, Z. Chen, B. Xu, J. Shen, J. Ma, C. Joll, A. Heitz, Influence of surface texture and acid-base properties on ozone decomposition catalyzed by aluminum (hydroxyl) oxides, Appl. Catal., B, 84 (2008) 684–690.

[34] N. Merayo, D. Hermosilla, L. Blanco, L. Cortijo, Á. Blanco, Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry, J. Hazard. Mater., 262 (2013) 420–427.

[35] W. De los Santos Ramos, T. Poznyak, I. Chairez, Remediation of lignin and its derivatives from pulp and paper industry wastewater by the combination of chemical precipitation and ozonation, J. Hazard. Mater., 169 (2009) 428–434.

[36] M. Mohajerani, M. Mehrvar, F. Ein-Mozaffari, An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment, Int. J. Eng., 3 (2009) 120–146.

[37] J.-C. Hostachy, G. Lenon, J.-L. Pisicchio, C. Coste, C. Legay, Reduction of pulp and paper mill pollution by ozone treatment, Water Sci. Technol., 35 (1997) 261–268.

[38] L. Roy-Arcand, F. Archibald, Selective removal of resin and fatty acids from mechanical pulp effluents by ozone, Water Res., 30 (1996) 1269–1279.

[39] Z. Cheng, R. Yang, Y. Wang, Mn/sepiolite as the heterogeneous ozonation catalysts applied to the advanced treatment of regenerated-papermaking wastewater, Water Sci. Technol., 75 (2017) 1025–1033.

[40] V. Fontanier, V. Farines, J. Albet, S. Baig, J. Molinier, Study of catalyzed ozonation for advanced treatment of pulp and paper mill effluents, Water Res., 40 (2006) 303–310.

[41] F.J. Beltrán, F.J. Rivas, R. Monterodeespinosa, Iron type catalysts for the ozonation of oxalic acid in water, Water Res., 39 (2005) 3553–3564.

[42] A.M. Amat, A. Arques, F. López, M.A. Miranda, Solar photocatalysis to remove paper mill wastewater pollutants, Sol. Energy, 79 (2005) 393–401.

[43] N. Al-Hayek, B. Legube, M. Doré, Ozonation catalytique (Fe III/$A1_2O_3$) Du phénol et de ses produits d'ozonation, Environ. Technol., 10 (1989) 415–426.

[44] G. Newcombe, R. Hayes, M. Drikas, Granular activated carbon: importance of surface properties in the adsorption of naturally occurring organics, Colloids Surf., A, 78 (1993) 65–71.

[45] Y. Bessekhouad, D. Robert, J.-V. Weber, N. Chaoui, Effect of alkaline-doped TiO_2 on photocatalytic efficiency, J. Photochem. Photobiol., A, 167 (2004) 49–57.

[46] P. Liu, S. He, H. Wei, J. Wang, C. Sun, Characterization of α-Fe_2O_3/γ-Al_2O_3 catalysts for catalytic wet peroxide oxidation of M-cresol, Ind. Eng. Chem. Res., 54 (2015) 130–136.

[47] L. Bijan, M. Mohseni, Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents, Water Sci. Technol., 50 (2004) 173–182.

[48] D. Hermosilla, N. Merayo, A. Gascó, Á. Blanco, The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: a review, Environ. Sci. Pollut. Res. Int., 22 (2015) 168–191.

[49] J. Vittenet, W. Aboussaoud, J. Mendret, J.S. Pic, H. Debellefontaine, N. Lesage, K. Faucher, M.H. Manero, F. Thibault-Starzyk, H. Leclerc, Catalytic ozonation with γ-Al_2O_3 to enhance the degradation of refractory organics in water, Appl. Catal., A, 504 (2015) 519–532.

[50] Y. Nie, N. Li, C. Hu, Enhanced inhibition of bromate formation in catalytic ozonation of organic pollutants over Fe-Al LDH/Al_2O_3, Sep. Purif. Technol., 151 (2015) 256–261.

[51] H. Park, J. Kim, H. Jung, J. Seo, H. Choi, Iron oxide nanoparticle-impregnated alumina for catalytic ozonation of para-chlorobenzoic acid in aqueous solution, Water Air Soil Pollut., 225 (2014) 1–9.

[52] S.P. Tong, R. Shi, H. Zhang, C.A. Ma, Kinetics of Fe_3O_4–CoO/Al_2O_3 catalytic ozonation of the herbicide 2-(2,4-dichlorophenoxy) propionic acid, J. Hazard. Mater., 185 (2011) 162–167.

[53] A. Ikhlaq, D.R. Brown, B. Kasprzyk-Hordern, Mechanisms of catalytic ozonation on alumina and zeolites in water: formation of hydroxyl radicals, Appl. Catal., B, 123 (2012) 94–106.

[54] É.S. Souza, J.V. Souza, F.T. Silva, T.C. Paiva, Treatment of an ECF bleaching effluent with white-rot fungi in an air-lift bioreactor, Environ. Earth Sci., 72 (2014) 1289–1294.

[55] R. Maheshwari, B. Rani, A. Saxena, M. Prasad, U. Singh, Analysis of effluents released from recycled paper industry, J. Adv. Sci. Res., 3 (2012) 82–85.

[56] M. Boroski, A.C. Rodrigues, J.C. Garcia, A.P. Gerola, J. Nozaki, N. Hioka, The effect of operational parameters on electrocoagulation–flotation process followed by photocatalysis applied to the decontamination of water effluents from cellulose and paper factories, J. Hazard. Mater., 160 (2008) 135–141.

[57] C. Chen, B.A. Yoza, Y. Wang, P. Wang, Q.X. Li, S. Guo, G. Yan, Catalytic ozonation of petroleum refinery wastewater utilizing Mn-Fe-Cu/Al_2O_3 catalyst, Environ. Sci. Pollut. Res., 22 (2015) 5552–5562.

[58] M. Xu, Q. Wang, Y. Hao, Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process, J. Hazard. Mater., 148 (2007) 103–109.

[59] X. Lü, Q. Zhang, W. Yang, X. Li, L. Zeng, L. Li, Catalytic ozonation of 2,4-dichlorophenoxyacetic acid over novel Fe–Ni/AC, RSC Adv., 5 (2015) 10537–10545.

[60] F. Deng, S. Qiu, C. Chen, X. Ding, F. Ma, Heterogeneous catalytic ozonation of refinery wastewater over alumina-supported Mn and Cu oxides catalyst, Ozone Sci. Eng., 37 (2015) 546–555.