Mineralization of Recalcitrant Organic Pollutants in Pulp and Paper Mill Wastewaters through Ozonation Catalyzed by Cu-Ce Supported on Al_2O_3

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There has been great interest in developing cost-effective and high-performance catalysts for the ozonation treatment of biologically refractory wastewaters. This study developed a novel copper-cerium oxide supported alumina (Cu-Ce/Al_2O_3) catalyst for the catalytic ozonation of pulp and paper mill wastewater. The evenly distributed composite metal oxides on the surface of catalysts evidently improved the catalytic degradation efficiency. The Cu-Ce/Al_2O_3/O_3 process increased the total organic carbon (TOC) removal by 6.5%, 9.5%, 24.5%, and 35.5%, compared with Ce/Al_2O_3/O_3, Cu/Al_2O_3/O_3, Al_2O_3/O_3, and ozone alone processes, respectively. The enhanced catalytic ozonation efficiency was mainly ascribed to an increased hydroxyl radical (·OH)-mediated ozonation, both in the bulk solution and on the surface of catalysts. The surface hydroxyl groups (-OHs) of Al_2O_3 along with the deposited Cu-Ce oxides greatly enhanced the catalytic performance. This work illustrated potential applications of Cu-Ce/Al_2O_3 catalyzed ozonation for the advanced treatment of biologically recalcitrant wastewaters.

Keywords: Catalytic ozonation; γ-Al_2O_3; CeO_2; *CuO; Papermaking wastewater; TOC*

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INTRODUCTION

Effluents of the pulp and paper industry contain many recalcitrant organic pollutants, such as carboxylic acids, phenolic compounds, saccharides, and surfactants. These pollutants are either formed during lignin decomposition or introduced by adding needed chemicals during pulping and paper-making processes (Thompson *et al.* 2001; Malaviya and Rathore 2007; Kamali and Khodaparast 2015; Song *et al.* 2017; Jia *et al.* 2018). These toxic compounds may cause deleterious ecological and environmental impacts upon direct discharge to receiving waters (Wu *et al.* 2005; Hubbe *et al.* 2016; Sun *et al.* 2017). Recently, great efforts have been made to remove these recalcitrant organic pollutants (Jaafarzadeh *et al.* 2017; Marques *et al.* 2017; Yadav and Garg 2018). However, conventional physico-chemical and biological treatments are not sufficient for the complete degradation of these recalcitrant organic pollutants (Rintala and Puhakka 1994; Liu *et al.* 2011; Krishna *et al.* 2014). Heterogeneous catalytic ozonation is one of the most promising treatment methods for the removal of recalcitrant organic pollutants due to its ease of operation and high efficiency (Roncero *et al.* 2003; Chen *et al.* 2017b). The catalysts adopted in the process of catalytic ozonation can facilitate the generation of the strong oxidant •OH. The •OH-mediated oxidation can effectively oxidize these recalcitrant organic pollutants.

A variety of support materials, such as carbon nanofibers (Restivo *et al.* 2012; Restivo *et al.* 2013; Yang *et al.* 2017), activated carbon (Faria *et al.* 2008; He *et al.* 2016; Gümüş and Akbal 2017; He *et al.* 2017), graphene (Wang *et al.* 2016b; Yin *et al.* 2017), carbon nanotube (Fan *et al.* 2014; Wang *et al.* 2016b), silica (Afzal *et al.* 2016), resins (Liotta *et al.* 2009), zeolites (Ikhlaq and Kasprzyk-Hordern 2017), and alumina (Al_2O_3) (Ikhlaq *et al.* 2013; He *et al.* 2017a; Ziylan-Yavaş and Ince 2017), have been widely investigated for catalytic applications. Among these, Al_2O_3 has been extensively studied as a catalyst or a catalyst support material due to its excellent catalytic performance and low cost. The surface basic sites (Al-OH) of Al_2O_3 can promote the generation of •OH, and the relatively high surface area of Al_2O_3 benefits the adsorption of recalcitrant organic pollutants (Ernst *et al.* 2004; Trueba and Trasatti 2005). Vittenet *et al.* (2014) reported that in comparison to the ozone alone process, the ozonation process catalyzed by Al_2O_3 enhances total organic carbon (TOC) removal of the 2,4-dimethylphenol solution by two-fold due to the interactions between the aqueous ozone and the surface basic sites (Al-OH) of Al_2O_3. Active components, such as metal oxides loaded on Al_2O_3, can further increase the catalytic degradation efficiency of recalcitrant organic pollutants. Metal oxides, including copper (Cu) (Qu *et al.* 2004), manganese (Mn) (Roshani *et al.* 2014), iron (Fe) (Nie *et al.* 2014), cerium (Ce) (Nie *et al.* 2014), and ruthenium (Ru) (Wang *et al.* 2013), were found to greatly increase the degradation efficiency of recalcitrant organic pollutants in effluents when they were deposited onto Al_2O_3. In comparison to single metal oxides, composite metal oxides loaded on Al_2O_3 can increase the efficiency of ozonation for the treatment of organic pollutants (Tong *et al.* 2011). Copper oxide (CuO) particles have rich surface basic sites, where the ozonation process catalyzed by CuO mainly follows OH-mediated oxidation causing the high mineralization of recalcitrant organic pollutants, such as alachlor (Qu *et al.* 2004) and substituted phenols (Udrea and Bradu 2003), to occur. By doping into or loading on activated carbon (Qin *et al.* 2014), SBA-15 (Yan *et al.* 2013), and zeolites (Lan *et al.* 2013), the surface of cerium oxides form abundant Lewis acid sites as well as –OH groups that can promote the transformation of aqueous ozone into •OH. Hence, ozonation systems catalyzed by cerium oxides show high degradation efficiency of recalcitrant organic pollutants such as fulvic acids (Qin *et al.* 2014), dimethyl phthalate (Yan *et al.* 2013), and p-chlorobenzoic acid (Lan *et al.* 2013). In the past, studies of catalytic ozonation have been focused on model compounds. Only a few studies have used actual papermaking wastewater.

In this study, the composite Cu-Ce/Al_2O_3 catalysts were prepared and characterized. The catalytic degradation efficiency, mechanism, and potential of the prepared catalysts for catalytic ozonation of recalcitrant and complex organic pollutants in papermaking wastewater were investigated.

EXPERIMENTAL

Materials

Copper (II) nitratetrihydrate [$Cu(NO_3)_2 \cdot 3H_2O$], Cerium (III) nitrate hexahydrate [$Ce(NO_3) \cdot 6H_2O$], tert-butanol (TBA), and phosphate were purchased from Fuchen Chemical Reagent Co., Ltd. (Tianjin, China). The commercial γ-Al_2O_3, with a diameter range of 3 mm to 5 mm, was obtained from Jiangsu Jingjing New Material Co., Ltd.

(Jiangsu, China). The ozone generator was supplied by Guangzhou Weigu Equipment Co., Ltd. (Guangdong, China).

Pulp-making wastewater after secondary biological treatment was collected at an integrated pulp and paper mill in Guangdong Province, China. The main properties of the effluent are as follows: 152 mg/L TOC, 206 mg/L chemical oxygen demand (COD), 35 mg/L biochemical oxygen demand (BOD_5), 438 Color Unit (C.U.) color, and pH 7.9.

Preparation of catalysts

The Cu-Ce/γ-Al_2O_3 catalyst was prepared *via* an incipient wetness impregnation method. The $Cu(NO_3)_2 \cdot 3H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were used as precursors, and the γ-Al_2O_3 (φ = 3 mm to 5 mm) was used as catalyst support. Commercial γ-Al_2O_3 was ground and passed through an 80-mesh sieve, then 4 g γ-Al_2O_3 powder was dispersed in a mixture solution of 30 mL (0.3 g $Cu(NO_3)_2 \cdot 3H_2O$ and 0.28 g $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in DI water) for 12 h at room temperature. The samples then underwent filtration and drying at 105 °C for 12 h. Finally, the dried samples were heated to 550 °C for 4 h in air to obtain Cu-Ce/γ-Al_2O_3 catalysts. The Cu/γ-Al_2O_3 and Ce/γ-Al_2O_3 catalysts were prepared according to a similar method.

Methods

Characterization of catalysts

X-ray diffraction (XRD) was performed using a Bruker D8 advance X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) with a scanning range of 10° to 80° and a Cu Kα radiation source at 40 kV and 40 mA.

The Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes of the catalysts were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 BET surface area analyzer (Norcross, Georgia, USA). First, the porous catalysts samples were degassed at 110 to 115 °C on the instrument, then they were transferred into the PCT Pro 2000 sample holder (Hy-Energy, Newark, CA, USA) in a glove box. Measurements were conducted with the pressure up to 3.0 MPa in a microdoser with the sample holder placed in a Dewar containing liquid nitrogen. The Brunauer-Emmett-Teller (BET) equation was adopted to compute specific surface areas based on nitrogen adsorption isotherms obtained at 77 K and relative pressures approaching 1.0.

The surface morphologies of the as-prepared catalysts were observed by a scanning electron microscope (EVO18, Zeiss Corporation, Oberkochen, Germany). The chemical composition concentrations of the catalysts were determined by X-ray fluorescence (XRF) with a PW 4000 X-ray spectrometer (Axios, Groningen, Holland). The pH of point of zero charge (pH_{pzc}) of catalysts was measured according to the pH-drift method (Newcombe *et al.* 1993; Bessekhouad *et al.* 2004).

Ozonation reaction and analytical methods

The schematic of experimental apparatus for ozonation and catalytic ozonation of the effluent has been reported in the authors' former work (He *et al*. 2016). All catalytic ozonation experiments were performed in a 1-L glass column reactor at room temperature. First, 500 mL papermaking wastewater and 1 g catalyst were added in the column reactor. Then, 0.3 g/h O_3 was introduced into the reactor through a porous diffuser at the bottom of the glass reactor. The operation was performed using the effect of different catalyst types, doses, and initial pH (adjusted with 1 N NaOH or 1 N HCl). Wastewater samples were withdrawn at regular intervals and centrifuged for 5 min to separate solid catalysts before further analyses. Radical quenching experiments were conducted to investigate the mechanism of catalytic ozonation. As usually done, 1 g/L hydroxyl radical scavenger tert-butanol (TBA) and phosphate were added to the effluent before the catalytic ozonation reaction. The excess ozone in the off-gas stream was immediately quenched with a 5% potassium iodide (KI) solution. The stability of the as-prepared catalyst was investigated by reusing it up to 10 times.

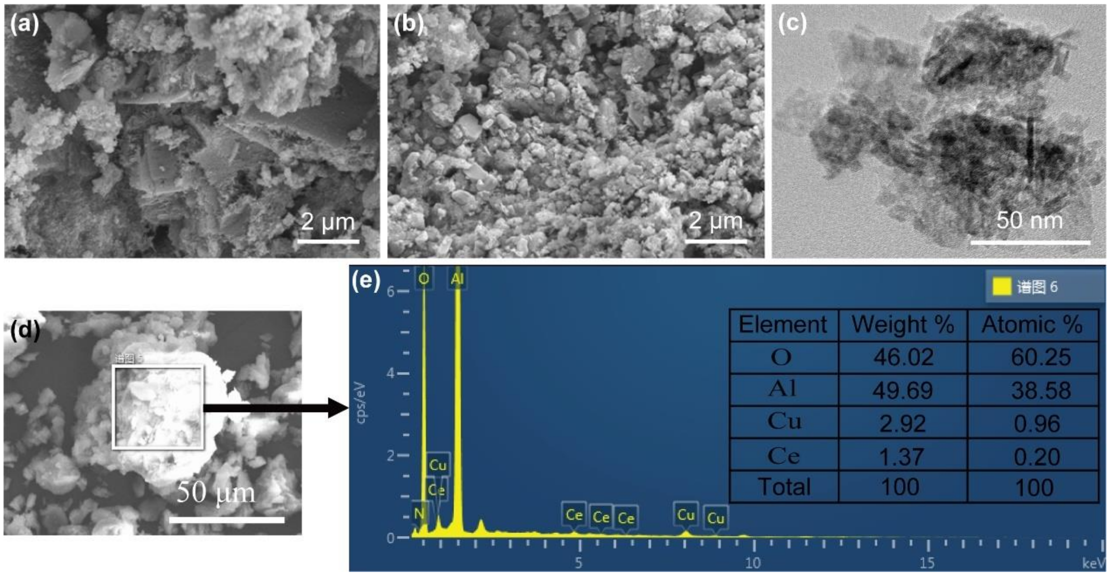
Analyses of papermaking wastewater

The TOC of the effluent was determined *via* Hach® TOC Method 10173 Direct (Mid-Range TOC 15-150 $mg \cdot L^{-1}$). The COD was tested by the dichromate closed reflux colorimetric method using a Hach DR2800 model spectrophotometer (Hach, Loveland, CO, USA) and the BOD_5 was determined on a BOD Trak II meter (Hach, Loveland, CO, USA). The ratio of BOD_5/COD represented the biodegradability of the effluent. The color of the wastewater before and after treatment was measured according to the Platinum-Cobalt method using a HACH DR2800 model UV-Vis spectrophotometer (Hach, Loveland, CO, USA). The leaching of metal ions from the solid catalysts into the effluent after treatment was determined through inductively coupled plasma mass spectroscopy (ICP/MS 7500a, Agilent, Salt Lake City, UT, USA).

RESULTS AND DISCUSSION

Characterization of Catalysts

To confirm the effective loading of Cu and Ce on the Al_2O_3 catalyst carriers and to characterize the morphologies and physical properties of the as-prepared catalyst, XRF, SEM, BET, and XRD analyses were conducted. As shown in Fig. 1a, the surface of Al_2O_3 was very rough. Copper oxides and cerium oxides were deposited on the surface of Al_2O_3 creating micro-agglomerates in irregular sizes and shapes (Fig. 1b). The micro-agglomerates of copper oxides and cerium oxides in irregular shapes and sizes can be observed on the surface of γ-Al_2O_3 by transmission electron micrographs (TEM) analyses (Fig. 1c). These micro-agglomerates may facilitate the interaction between the recalcitrant organic pollutants and catalysts.



Element	Weight %	Atomic %
O	46.02	60.25
Al	49.69	38.58
Cu	2.92	0.96
Ce	1.37	0.20
Total	100	100

Fig. 1. SEM images of (a) γ-Al_2O_3; (b) Cu-Ce/γ-Al_2O_3; (c) transmission electron micrographs (TEM) of Cu-Ce/γ-Al_2O_3 catalysts; SEM-EDX spectrum (e) of the area indicated in (d). Inset: the table shows the weight percentage and atomic ratio of elements in the Cu-Ce/γ-Al_2O_3 catalysts

Selected area SEM images and energy dispersive X-ray (EDX) patterns of the Cu-Ce/Al_2O_3 catalysts are illustrated in Figs. 1d and e. Note that Cu, Ce, and O elements can be found on the catalysts surfaces. The elemental contents of Cu, Ce, and O were further obtained *via* the EDX patterns analyses. As can be seen from the inset of Fig. 1e, the weight percentages of Cu and Ce in the Cu-Ce/Al_2O_3 catalyst were 2.92% and 1.37%, respectively.

The XRD diffraction patterns of γ-Al_2O_3 and Cu-Ce/γ-Al_2O_3 catalysts are 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 (Liu *et al.* 2015) (Fig. 2a). In comparison to the XRD pattern of γ-Al_2O_3, newly emerged diffraction peaks at $2\theta = 28.6°$, 33.1°, 47.6°, and 56.5° in the patterns of Cu-Ce/γ-Al_2O_3 catalysts were due to the presence of CeO_2 (JCPDS File No. 81-0792). Other newly emerged diffraction peaks at $2\theta = 35°$, 38°, and 50° were attributed to the presence of CuO (JCPDS File No. 48-1548). The binding energies of $Cu2p_{3/2}$ of Cu-Ce/Al_2O_3 were centered at 932.5, 932.6, and 933.4 eV, respectively (Fig. 2b) (Biesinger *et al.* 2010). The binding energies at 882.1 eV, 888.1 eV, 898 eV, 900.9 eV, 906.4 eV, and 916.4 eV correspond to Ce^{4+} oxide (CeO_2) (Fig. 2c) (Nikolaev *et al.* 2015). The adsorption-deadsorption isotherms varied among different kinds of catalysts (Fig. 2d). These isotherms indicate the existence of representative type IV mesoporous structures within catalysts (Chen *et al.* 2017a).

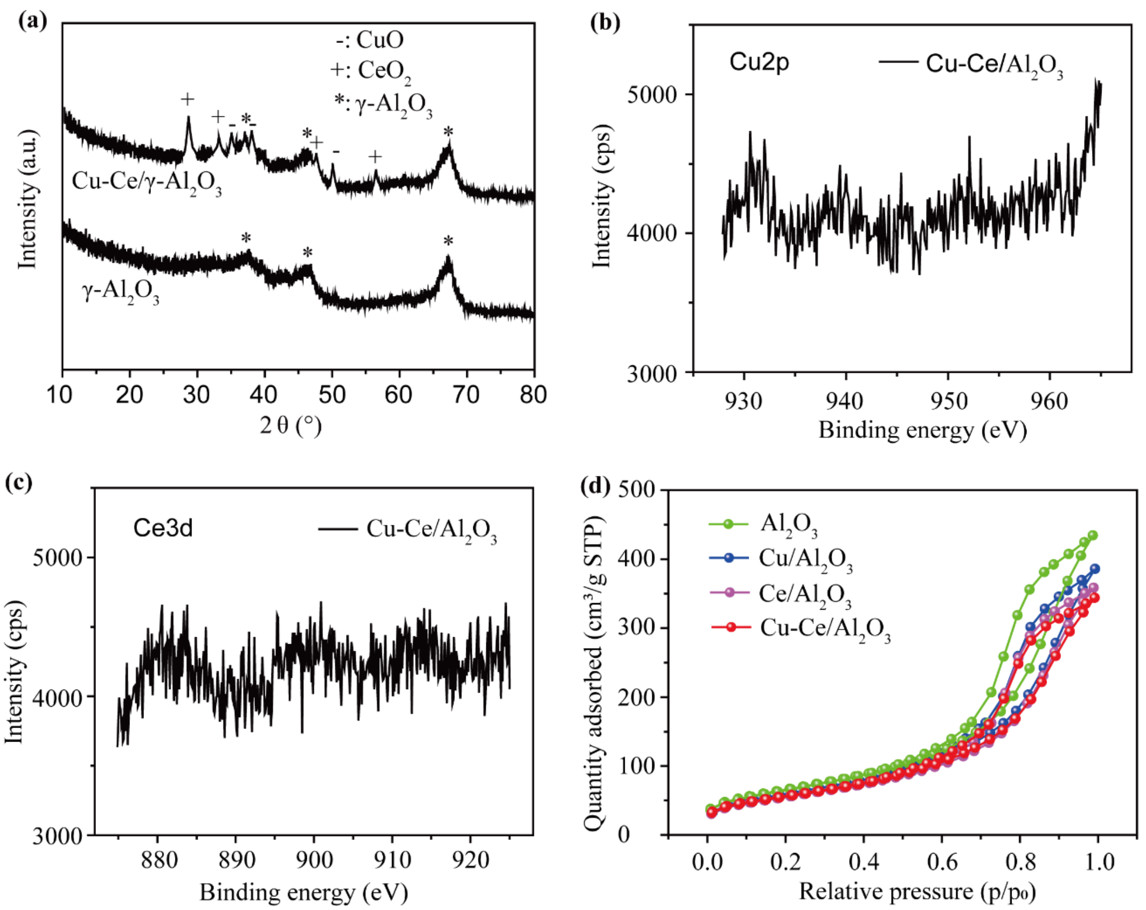


Fig. 2. (a) XRD patterns of γ-Al_2O_3 and Cu-Ce/γ-Al_2O_3; X-ray photoelectron spectroscopy (XPS) spectra of Cu2p (b) and Ce3d (c); (d) N_2 adsorption-desorption isotherm curves of γ-Al_2O_3, Cu/γ-Al_2O_3, Ce/γ-Al_2O_3, and Cu-Ce/γ-Al_2O_3 catalysts

As shown in Table 1, the loadings of CuO and CeO_2 on γ-Al_2O_3 reduced the BET surface area, average pore diameter, and pore volume. The decrease of BET surface area and pore volume may be due to the partial capping of the pores on the γ-Al_2O_3 catalyst after loading metal oxides. The weight contents of CuO and CeO_2 in Cu-Ce /γ-Al_2O_3 catalysts were 3.7% and 1.7%, respectively, and the pH_{pzc} of γ-Al_2O_3, Cu/Al_2O_3, Ce/Al_2O_3, and Cu-Ce/Al_2O_3 were 8.01, 8.06, 8.07, and 8.15, respectively.

Table 1. BET Analyses and Metal Oxide Contents of Catalysts

Catalysts	Surface Areas and Pore Structures			Metal Oxide Contents (wt. %)		pH_{pzc}
	BET Surface Area (m^2g^{-1})	Average Pore Diameter (nm)	Pore Volume (cm^3g^{-1})	CuO	CeO_2	
γ-Al_2O_3	249.7	10.4	0.677	-	-	8.01
Cu/γ-Al_2O_3	222.5	10.1	0.601	3.6	-	8.06
Ce/γ-Al_2O_3	221.2	10.0	0.600	-	1.7	8.07
Cu-Ce/γ-Al_2O_3	211.4	9.7	0.491	3.7	1.7	8.15

Enhanced Catalytic Performance

Figure 3 shows the treatment results of the effluent in O_3 alone, Cu-Al_2O_3/O_3, Ce-Al_2O_3/O_3, and Cu-Ce/Al_2O_3 processes. The effect of adsorption of the catalysts on the TOC removal of the effluent is depicted in Fig. 3a. Results indicated that the adsorption of Cu-Al_2O_3/O_3, Ce-Al_2O_3/O_3, and Cu-Ce/Al_2O_3 catalysts reached saturation in 60 min. The TOC removals of the effluent by adsorption after 60 min on Al_2O_3, Cu/Al_2O_3, Ce/Al_2O_3, and Cu-Ce/Al_2O_3 were 5.2%, 3.9%, 3.6%, and 2.8%, respectively (Fig. 3a). These catalysts showed weak adsorption capabilities toward the recalcitrant organic pollutants in the effluent.

Note that the adsorption capacity of Cu-Ce/Al_2O_3 was the lowest among these catalysts. This may have been due to the decreased surface area (Table 1). However, the TOC removal rates were all enhanced in the Cu/Al_2O_3/O_3, Ce/Al_2O_3/O_3, and Cu-Ce/Al_2O_3 processes. The Cu-Ce/Al_2O_3 process achieved the best performance in terms of TOC removal rate (Fig. 3b). The TOC removal rate was evidently enhanced by the introduction of the catalyst into the ozonation system. For example, after a reaction time of 60 min, the TOC removal rate remained at 26% in the ozone alone process. After adding Al_2O_3, Cu/Al_2O_3, Ce/Al_2O_3/O_3, and Cu-Ce/Al_2O_3 catalysts to the ozonation system, the TOC removal rates were enhanced 11% (37%), 26% (52%), 29% (55%), and 35.5% (61.5%), respectively.

The enhancement of the TOC removal rate was mainly due to the generation of strong oxidant radical species (such as •OH) induced by these catalysts (Zhao *et al.* 2009; Rosal *et al.* 2010; Tong *et al.* 2010, Thibault-Starzyk *et al*. 2014; Bing *et al.* 2015; Chen *et al.* 2017b). It is worth noting that the TOC removal rate was much faster in the first 30 min of the degradation reaction compared to the second 30 min of the reaction. This may have been due to the fast oxidation of easily degraded organic pollutants in the initial 30 min of treatment and the slow degradation of the refractory organic pollutants remaining after 30 min of treatment. The results of the analyses showed that the effect of adsorption of the catalysts on TOC removal of the effluent was negligible when compared to catalytic ozonation during these processes.

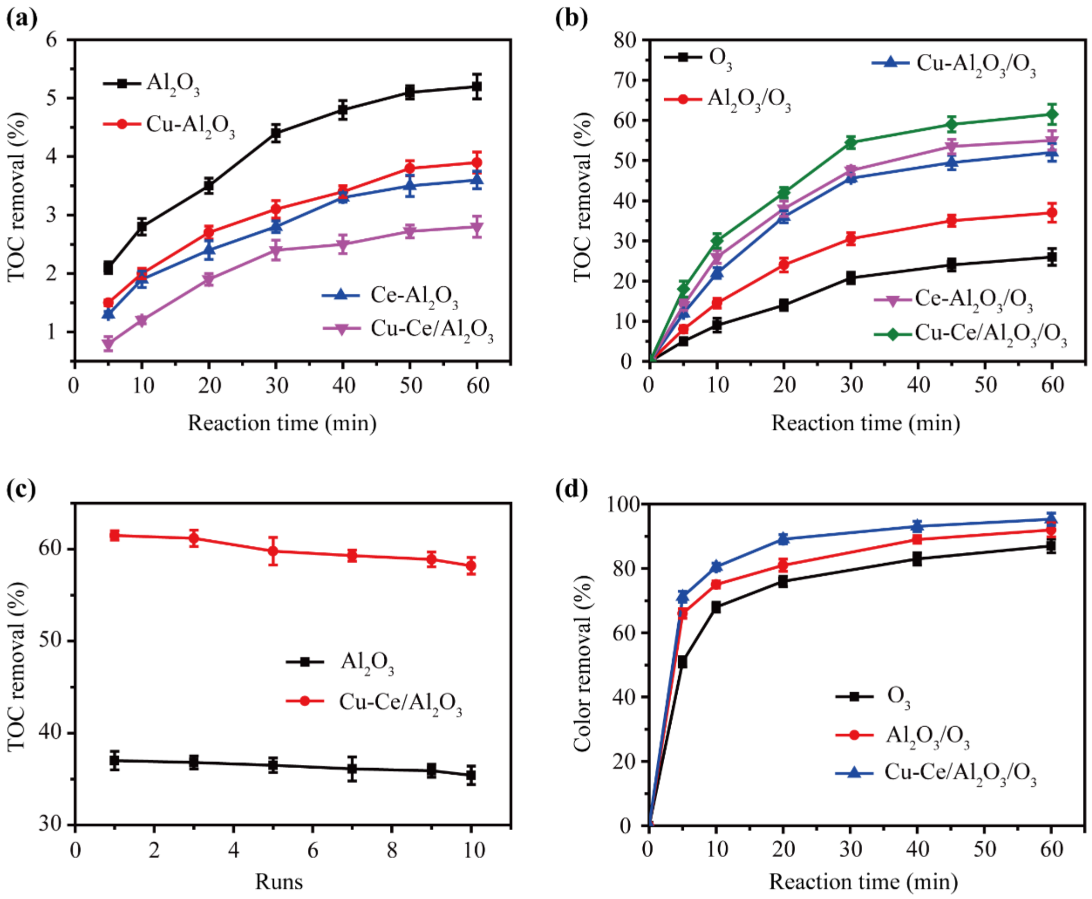


Fig. 3. TOC removals of the effluent by adsorption (a), by ozone alone and catalytic ozonation processes (b), and by 10 repeated uses of the catalyst (c); color removal during catalytic ozonation (d) (note: 5 g/L catalyst, initial pH 7.9, 0.3 g/h ozone, and 25 °C)

No evident leaching of Cu and Ce elements was measured in the Cu-Ce/Al_2O_3/O_3 process, indicating excellent stability of the catalysts. The TOC removals of the effluent after 10 repeated uses of Al_2O_3 and Cu-Ce/Al_2O_3 catalyzed ozonation were monitored (Fig. 3c). The TOC removal rates remained quite stable in the Al_2O_3/O_3 process (37% to 35.4%) and in the Cu-Ce/Al_2O_3/O_3 process (61.5% to 58.2%), indicating that the prepared catalysts were highly stable in the processes. Because ozone alone exhibited a high color removal rate (87%), the color removal rate was only increased approximately 8% (as high as 95.3%) in the Cu-Ce/Al_2O_3 process (Fig. 3d). Lignin compounds are responsible for the high color level of the effluent, and the ozone alone process can rapidly oxidize the lignin compounds by separating their double bonds and triple bonds (Bijan and Mohseni 2004; Hermosilla *et al*. 2015).

Effects of Experimental Conditions on TOC Removals

Effects of catalyst dosage

The effect of catalyst (Cu-Ce/Al_2O_3) dosage on the TOC removal efficiency is depicted in Fig. 4(a). The results indicate that the TOC removal efficiency was enhanced with the amount of catalyst used. The TOC removal efficiency increased from 26% for the ozone alone process to 48% with the addition of 2 g/L Cu-Ce/Al_2O_3 catalyst after 60 min of reaction time. The TOC removal efficiency increased from 48% to 61.5% with the increase in catalyst dosage from 2 g/L to 5 g/L after 60 min of treatment. This may have been due to the increased overall active surface area associated with higher catalyst dosages. Thus, the increased availability of active sites on the surface of the Cu-Ce/Al_2O_3 catalyst positively contribute to an enhanced •OH generation rate by transforming large amounts of aqueous ozone (Kasprzyk-Hordern *et al.* 2003). Previous studies (Chen *et al*. 2015a; Wang *et al.* 2016a; Ahmadi *et al*. 2017) have also reported that the degradation of organic pollutants in wastewater benefited from increased catalyst dosage. However, the TOC removal rate was enhanced slightly when the catalyst dosage was further increased from 5 g/L to 6 g/L, which is possibly due to the solutions undergoing self-quenching effects of aqueous hydroxyl radicals at high •OH concentrations or the existence of side reactions consuming the hydroxyl radicals (Basturk and Karatas 2015; Tabaï *et al.* 2017). Therefore, the optimal catalyst dosage should be 5 g/L considering the cost of wastewater treatment and TOC removal efficiency.

Effects of pH

Experimental pH values can greatly influence the degradation of organic compounds during ozonation and catalytic ozonation.

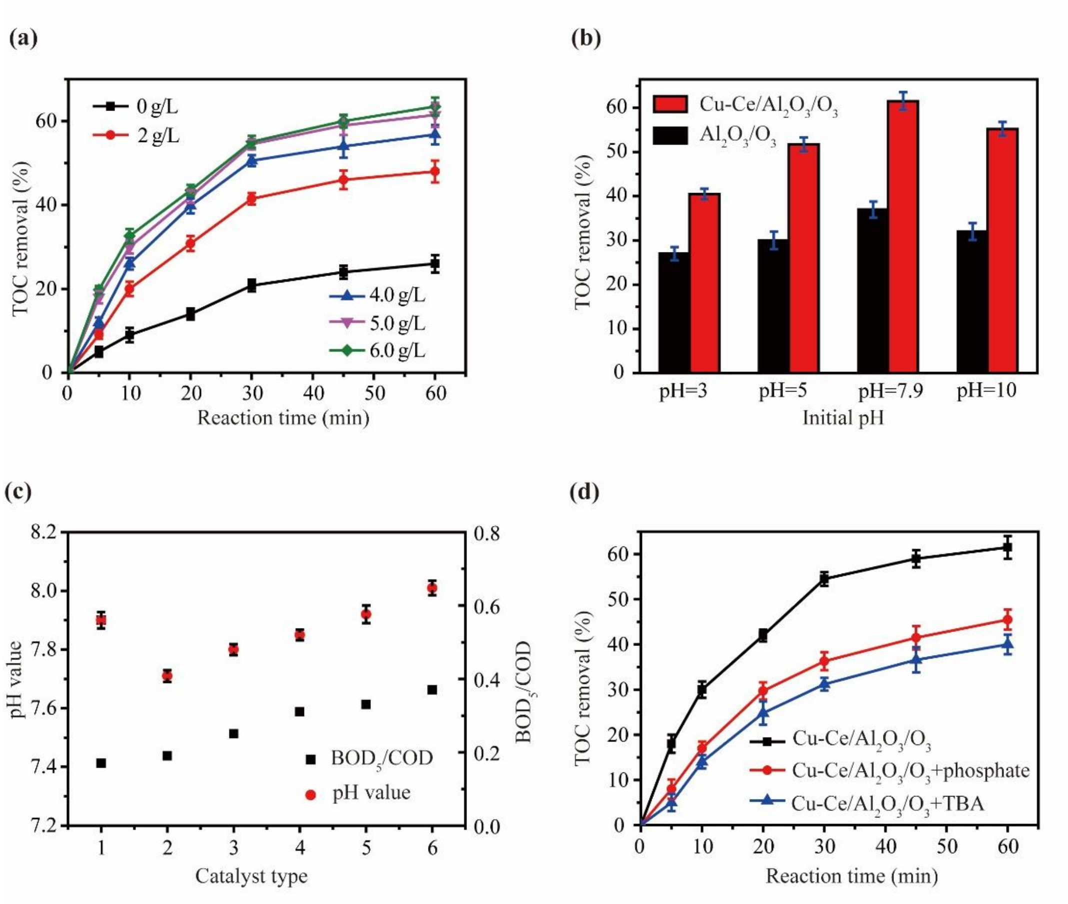


Fig. 4. Effect of: catalyst dosage (a), pH (b), and radical scavengers (d) on TOC removals; (c) changes of pH values and biodegradability of the effluent during ozone alone and catalytic ozonation processes (1: Initial wastewater; 2: Ozone alone process; 3: Al_2O_3/O_3 process; 4: Cu-Al_2O_3/O_3 process; 5: Ce-Al_2O_3/O_3 process; and 6:Cu-Ce-Al_2O_3/O_3 process); (note: 5 g/L catalyst, initial pH 7.9, 0.3 g/h ozone, and 25 °C)

The pH has a great impact on the surface properties of catalysts and the decomposition rate of ozone (Ikhlaq *et al.* 2015; Ikhlaq and Kasprzyk-Hordern 2017). Thus, the effect of initial pH on TOC removal was investigated (Fig. 4b). The results indicated that the TOC removal rate was increased in the Al_2O_3/O_3 and $Cu\text{-}Ce/Al_2O_3/O_3$ processes when the initial pH value increased from 3 to 7.9. However, the TOC removal rate suffered when the initial pH value was further increased from 7.9 to 10. The initial pH value of the effluent (7.9), which is close to the pH_{pzc} value of $Cu\text{-}Ce/Al_2O_3$ catalysts (8.15), promotes the generation of more surface •OH where the best TOC removal results are achieved. However, the degradation of the recalcitrant organic pollutants contained in the effluent was hindered at comparatively low or high pH values (Fig. 5b). The degradation of recalcitrant organic pollutants mainly relied on the direct oxidation of molecular ozone when the initial pH of the effluent was too low. However, the effect of the direct oxidation by ozone on the TOC removal was rather weak when compared with that of •OH. Furthermore, the as-prepared catalysts were potentially unstable under very low pH conditions. The decrease of the TOC removal rate at the higher pH value (10) may have been due to the fact that the prepared catalysts were negatively charged under alkaline conditions, leading to repulsive electrostatic interactions occurring between the catalyst and the organic pollutants contained in the effluent, which would hinder the degradation of organic pollutants (Martins and Quinta-Ferreira 2009; Huang *et al.* 2016; Gao *et al.* 2017). Furthermore, under strong alkaline conditions, the degradation of organic pollutants by catalytic ozonation generated CO_3^{2-} and HCO_3^-, which are both strong •OH scavengers.

The initial pH value of the effluent (7.9) decreased to 7.71 after 60 min of ozone alone treatment (Fig. 4c). This may be due to the formation of acidic intermediates during this process. The highest pH value (8.01) was determined in the effluent after 60 min of $Cu\text{-}Ce/Al_2O_3$ catalyzed ozonation, suggesting the degradation of the acidic intermediates. The biodegradability of the effluent improved after 60 min of catalytic ozonation treatment. The ratio of BOD_5/COD was enhanced from 0.17 to 0.37 after 60 min of reaction (Fig. 4c), indicating that the recalcitrant organic pollutants contained in the effluent became biodegradable after 60 min of the reaction (Ledezma Estrada *et al.* 2012; Jaafarzadeh *et al.* 2016).

Influence of •OH scavengers on TOC removals

Phosphate has a high affinity to Lewis acid sites on the surface of the catalyst, which can hinder the catalytic transformation of aqueous ozone into strong oxidant •OH on the surface (Lv *et al.* 2010; Zhao *et al.* 2014; Afzal *et al.* 2017; Zhu *et al.* 2017). In contrast, *tert*-butanol can rapidly quench •OH generation in bulk solution (Zhuang *et al.* 2014; Chen *et al.* 2015b; Zhao *et al.* 2015), producing inert intermediates that can inhibit aqueous ozone decomposition. The catalytic performance of the as-prepared catalyst was noticeably inhibited in the presence of tert-butanol and phosphate. As shown in Fig. 4d, the TOC removal rates of the effluent in the $Cu\text{-}Ce/Al_2O_3$ process were also dramatically reduced in the presence of tert-butanol and phosphate. These analyses indicated that the recalcitrant organic pollutants contained in the effluents were degraded mainly by an indirect •OH oxidation, both on the surface of the catalysts and in bulk solution. Note that the TOC removal rate remained at above 38% after the addition of •OH scavengers, which was probably due to direct oxidation degradation of organic pollutants by molecular ozone. Thus, indirect •OH oxidation dominated the degradation reactions of organic pollutants. At the same time, the effect of direct aqueous molecular ozone on TOC removal was noteworthy.

Reaction Pathways Involved in the Catalytic Ozonation System

The hydroxyl groups on the surface of γ-Al_2O_3 play an important role in the degradation of organic pollutants by catalytic ozonation (Ikhlaq *et al.* 2013, 2015). When the initial pH value of the effluent is close to the pH_{pzc} value of the as-prepared catalysts, the surface hydroxyl groups are in a neutral state, which is beneficial for the generation of more •OH (Wang and Xu 2012; Roshani *et al*. 2014; Wang *et al.* 2016c). It can be concluded from the effect of radical scavengers (TBA and phosphate) and initial pH value on TOC removal efficiency that the hydroxyl groups on the surface of Cu-Ce/γ-Al_2O_3 can also facilitate the generation of the strong oxidant •OH. Small amounts of organic pollutants in the effluent can be removed by the adsorption of the as-prepared catalyst (Fig. 5). The loading of Cu and Ce oxides onto γ-Al_2O_3 provided more active sites for the catalytic decomposition of ozone into •OH compared with loading single metal oxides. In the Cu-Ce/γ-Al_2O_3 process, the numerous surface hydroxyl groups of γ-Al_2O_3 initiated the decomposition of ozone to generate a lot of •OH on the surface of catalysts or in the bulk of the aqueous phase. Ozone can decompose into •OH in aqueous solution by itself, as well as oxidize the organic pollutants in the effluent directly to form intermediates. These intermediates can be further decomposed by strong oxidant •OH in bulk of the aqueous phase. Hence, the best treatment performance can be obtained in the Cu-Ce/γ-Al_2O_3 process.

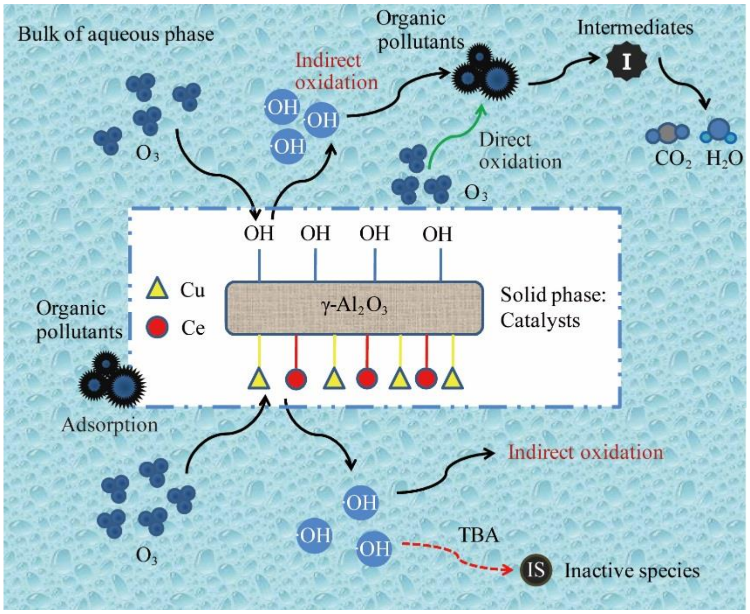


Fig. 5. Reaction pathways involved in ozonation catalyzed by Cu-Ce/Al_2O_3

CONCLUSIONS

1. The composited metal oxide loaded Al_2O_3 (Cu-Ce/Al_2O_3) catalysts were prepared, characterized, and applied to the tertiary treatment of pulp and paper mill effluents. The loaded metal oxides and surface OH groups on Al_2O_3 acted as highly active catalytic sites that facilitated the generation of more •OH.

2. In comparison to the ozone alone process, the catalytic ozonation processes showed higher TOC removal efficiencies. Within the processes, the prepared Cu-Ce/Al_2O_3 catalyst was more efficient than the Cu/Al_2O_3 and Ce/Al_2O_3 catalysts alone. The Cu-Ce/Al_2O_3 showed a higher catalytic degradation efficiency when compared with single metal oxides.
3. The Cu-Ce/Al_2O_3/O_3 process increased the TOC removal by 6.5%, 9.5%, 24.5%, and 35.5%, compared with the Ce/Al_2O_3/O_3, Cu/Al_2O_3/O_3, Al_2O_3/O_3, and ozone alone processes, respectively.
4. Ozone alone exhibited a high color removal rate (87%). The color removal rate was increased by only approximately 8% (as high as 95.3%) with the Cu-Ce/Al_2O_3 process.
5. The enhanced catalytic ozonation efficiency was mainly ascribed to an increased •OH-mediated ozonation, both in the bulk solution and on the surface of the catalysts.
6. The results indicate that the prepared Cu-Ce/Al_2O_3 catalyst is commercially feasible due to its high efficiency, high stability, ease of preparation, and low cost.

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