



Catalytic ozonation of dimethyl phthalate over cerium supported on activated carbon

Laisheng Li*, Weiyang Ye, Qiuyun Zhang, Fengqiang Sun, Ping Lu, Xukai Li

School of Chemistry & Environment, South China Normal University, Guangzhou 510006, China

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ABSTRACT

Cerium supported on activated carbon (Ce/AC), which was prepared by dipping method, was employed to degrade dimethyl phthalate (DMP) in water. The mineral matter present in the activated carbon positively contributes to its activity to enhance DMP ozonation process. A higher dipping $\text{Ce}(\text{NO}_3)_3$ concentration and calcination process increase its microporous volume and surface area, and decreases its exterior surface area. The catalytic activity reaches optimal when 0.2% (w/w) cerium is deposited on activated carbon. Ce/AC catalyst was characterized by XRD, SEM and BET. The presence of either activated carbon or Ce/AC catalyst considerably improves their degradation and mineralization in the ozonation of DMP. During the ozonation (50 mg/h ozone flow rate) of a 30 mg/L DMP (initial pH 5.0) with the presence of Ce/AC catalyst, TOC removal rate reaches 68% at 60 min oxidation time, 48% using activated carbon as catalyst, only 22% with ozonation alone. The presence of tert-butanol (a well known $\cdot\text{OH}$ radical scavenger) strongly inhibits DMP degradation by activated carbon or Ce/AC catalytic ozonation. TOC removal rate follows the second-order kinetics model well. In the ozonation of DMP with 50 mg/h ozone flow rate, its mineralization rate constant with the presence of Ce/AC catalyst is 2.5 times higher than that of activated carbon, 7.5 times higher than that of O_3 alone. Ce/AC catalyst shows the better catalytic activity and stability based on 780 min sequential reaction in the ozonation of DMP. Ce/AC was a promising catalyst for ozonizing organic pollutants in the aqueous solution.

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1. Introduction

Phthalate acid esters (PAEs) are a class of chemical compounds primarily used as plasticizers and additive in special paints and adhesives [1,2]. As a consequence, they are released into the natural environment during manufacture, use, disposal and leaching from plastic materials. PAEs are found in all water samples from Pear River, China [3]. They are found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base natural food chain in both marine and fresh environments [1]. Their toxic properties are even more important considering their high bioaccumulation rate (range from 100 to 3000) in different organisms [2]. And they are also endocrine disrupting chemicals [2,4]. In the past, some studies focused on the biodegradation of several phthalate esters from soil, synthetic or real wastewater by activated sludge treatment [2]. However, PAEs are rather stable compounds in the natural environment, their hydrolysis half-life is estimated to be about 20 years [1].

Advanced oxidation processes (AOPs) were frequently selected as a treatment option to oxidize refractory and toxic organic compounds present in water. Because of their high cost in treatment, traditional AOPs, such as photocatalysis and catalytic wet oxidation process, can hardly meet the requirements of the practical applications [5,6]. Heterogeneous catalytic ozonation, a novel alternative to traditional AOPs, has received wide interest as a promising technology for removing refractory organic pollutants in water. It combines ozone with the adsorptive and oxidative properties of solid phase metal oxide catalysts to mineralize refractory organic compounds to carbon dioxide, water and mineral acids at ambient temperature, without UV radiation and high reaction temperature and pressure [7].

In order to improve mass transfer between catalyst and organic pollutants, different metal or its oxides (such as Ru, TiO_2 , Co_3O_4 , or other transition metals) deposited on porous materials (alumina, activated carbon, carbon fibre) were investigated [8–11]. Recently, activated carbon (AC) adsorption combined with ozone oxidative regeneration of AC offers an attractive option for organic pollutant removal. Indeed, AC presents a large surface area where organic pollutants can be adsorbed [12], while ozone readily destroys adsorbed aromatic molecules, helping to regenerate AC adsorption capacity [13]. However, the reports about Ce supported on activated carbon

* Corresponding author. Tel.: +86 20 39310213; fax: +86 20 39310187.
E-mail address: llsh@scnu.edu.cn (L. Li).

(Ce/AC) catalyst are scarce. In this work, CeO₂ was chosen as active component of catalyst because of its stability in chemical oxidation and low cost [14], its application with ozone could be considered a potential catalyst. The objective of this study was to investigate the degradation and mineralization of dimethyl phthalate (DMP) in Ce/AC catalytic ozonation.

2. Experimental

2.1. Materials

Ce(NO₃)₃ (analytical grade) and dimethyl phthalate (analytical grade) were supplied by Tianjin Damao Chemical Agent Factory (Tianjin, China). The coconut hull substratal activated carbons (industry grade) was supplied by Guangzhou Chemical Co. Ltd. (Guangzhou, China), and their particle size ranges are about 0.45 mm.

2.2. Preparation of Ce/AC catalyst

Before use, activated carbons prepared from coconut hull and coal were thoroughly washed with deionized water and dried in an oven at 105 °C for 24 h. Ce/AC catalyst was prepared by the dipping method with an aqueous solution of Ce(NO₃)₃ in a shaking incubator at 160 rpm and 30 °C for 2 h. The wet sample was dried at room temperature. And then it was heated to 450 °C at a rate of 3 °C/min in N₂ flow (400 mL/min) and calcined at 450 °C for 2 h to obtain the required catalyst.

2.3. Catalyst characterization

The crystalline phase of Ce/AC catalyst was determined using an X-ray diffractometer (Rigaku, D/max-RB, Japan) employing Cu K α radiation. The accelerating voltage and applied current were 40 kV and 120 mA, respectively. The surface morphology of the samples was visualized using a Thermal FE Environment Scanning Electron Microscope (Quanta 400) with an accelerating voltage of 20 kV. The BET surface area was determined by nitrogen adsorption using Quantasorb Surface Area Analyzer (USA). The textural properties such as surface area, pore volume, pore size were determined by nitrogen adsorption. Nitrogen adsorption and desorption isotherms were recorded on nitrogen adsorption system.

2.4. Catalytic ozonation procedure

The experimental system consisted of a 1.4 L tubular borosilicate glass oxidation reactor ($h=500$ mm, $\phi_{in}=60$ mm) equipped with gas inlet and outlet, reactive alimentation, and sampling accessories for catalytic ozonation experiments. 1.35 L DMP around 30 mg/L (initial pH 5.0) solution was added into the reactor. Simultaneously, 2 g catalyst was added (fluidized status). Ozone was produced from pure oxygen by using a DHX-SS-001 ozone generator (made in China). Ozonized oxygen (50.0 mg/h ozone input rate) was continuously bubbled into the solution through a porous glass plate and flowed upward in the annular section. The excess ozone in the outlet gas was eliminated by 5% Na₂S₂O₃ solution. Samples were taken at regular intervals to analyze DMP and total organic carbon (TOC) concentrations. Na₂S₂O₃ solution was used to stop the continuous ozonation reaction in the sample.

2.5. Analytical methods

DMP concentration was analyzed by means of a high-performance liquid chromatography (Shimadzu, LC10A HPLC) with a UV detector (SPD-10AV) at 254 nm. A Discovery C18 column (150 mm \times 4.6 mm) was used, the mobile phase was a

Table 1

The content of different metal elements in activated carbon.

Component	Fe	Cu	Zn	Pb	Co
Content (mg/g)	0.28	1.0×10^{-2}	6.1×10^{-3}	5.5×10^{-3}	1.9×10^{-4}

mixture of methanol and water at 70:30 (v:v) (eluting solvent rate = 1.0 ml/min, column temperature = 40 °C). Total organic carbon (TOC) was determined by a Shimadzu TOC 5000 analyzer after filtration through 0.45 μ m prefilter. Metal elemental analysis of activated carbon was determined by inductively coupled plasma-atomic emission spectrometry (ICP) (Thermo Scientific, IRIS Intrepid IIXSP, USA). The content of different metal elements in activated carbon prepared from coconut hull are listed in Table 1.

3. Results and discussion

3.1. Characterization of Ce/AC catalyst

Fig. 1 displays X-ray powder diffraction patterns of Ce/AC catalyst. In Ce/AC sample, the main diffraction peaks correspond to CeO₂ ($2\theta=28.6, 33.1, 47.6$ and 56.4), which is the decomposing product of Ce(NO₃)₃ at 450 °C. CeO₂ can suppose a high catalytic activity for Ce/AC catalyst in the ozonation process of DMP [14]. The other main diffraction peaks correspond to AC ($2\theta=26.5, 38.0, 44.3, 50.0, 82.1$ and so on).

The SEM micrographs obtained from AC, Ce/AC and the used Ce/AC catalyst are analysed by SEM at same magnifications and the corresponding images are presented in Fig. 2. SEM analyses of sample Ce/AC catalyst (Fig. 2b) reveals that CeO₂ particles are shown on the surface of Ce/AC catalyst, compared with the surface of activated carbon (Fig. 2a). From the comparison between SEM images of fresh activated carbon (Fig. 2a) and spent Ce/AC catalyst (Fig. 2c), it is concluded that both have identical morphology. Even though activated carbon surface is partially oxidized by ozone [8], no major differences are observed in the morphology of Ce/AC catalyst after 780 min sequential reaction in the catalytic ozonation of DMP, which suppose that Ce/AC catalyst has a high catalytic activity and stability in the ozonation process of DMP.

Table 2 shows the results of the textural characterization of activated carbon and Ce/AC catalyst. Their textural characterization is based on the corresponding N₂ equilibrium adsorption isotherms determined at 77 K. Their surface area (S_{N2}) is obtained by applying

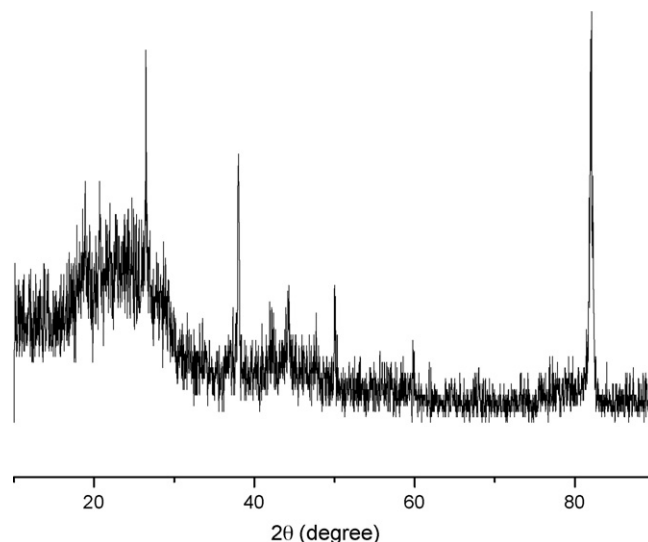


Fig. 1. The X-ray powder diffraction patterns of Ce/AC catalyst.

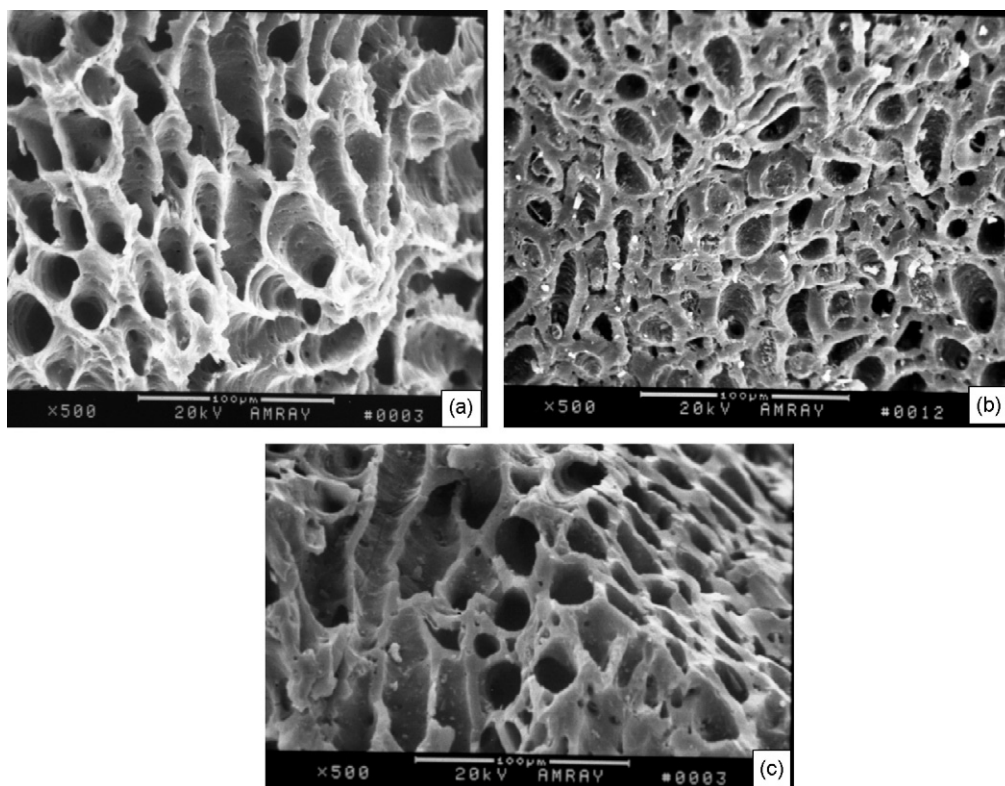


Fig. 2. The SEM micrographs obtained from AC and Ce/AC catalyst (a) AC, (b) Ce/AC, (c) the used Ce/AC.

the BET equation to N_2 adsorption isotherms. The selected activated carbon has a surface area of $632 \text{ m}^2/\text{g}$, new and spent sample Ce/AC catalyst have a surface area of 522 and $487 \text{ m}^2/\text{g}$, respectively. These results show that a higher dipping $\text{Ce}(\text{NO}_3)_3$ concentration and calcination process increase its microporous volume (V_{micro}) and surface area (S_{micro}), and decrease total pore volume (V_{tot}), mean pore diameter (D_{ave}) and special surface area, evidently its exterior surface area (S_{ext}). They indicate that the loaded Ce blocks holes in activated carbon. It is seen that special surface area, total pore volume and microporous volume (V_{micro}) of Ce/AC catalyst slightly decreased after 780 min sequential reaction, which suggests that they result in slightly decreasing of its catalytic activity in the ozonation of DMP.

3.2. Effect of cerium loading content on catalytic ozonation of DMP

Fig. 3 shows that effect of cerium loading content on catalytic ozonation of DMP with 50 mg/h ozone flow rate. It is seen from Fig. 3 that a maximum of 99% DMP and 68% TOC removal is obtained at 60 min oxidation time when cerium loading content reaches 0.2%. TOC removal rate decreases with the increase of cerium loading content when it is over 0.2%, the decrease of TOC removal rate is due to the increase of the loaded cerium content on AC, which is verified by Fig. 2. In addition, the dipping and calcination process decrease total pore volume, mean pore diameter and special surface area of Ce/AC catalyst. They illustrate that the loaded Ce enhances steric

hindrance and decreases the surface area of catalyst. So the cerium loading content plays an important role in determining catalytic activity in the ozonation of DMP, and 0.2% cerium loading content is employed.

3.3. Comparison of DMP and TOC removal among O_3 alone, AC/ O_3 and Ce/AC/ O_3 processes

Fig. 4 compares DMP and TOC removal efficiency by O_3 alone, AC/ O_3 and Ce/AC/ O_3 processes. It is clearly seen from Fig. 4 that the presence of Ce/AC catalyst and AC improves DMP and TOC removal efficiency, compared with ozonation alone. Ce/AC/ O_3 process is most efficient for DMP and TOC removal. During the ozonation (50 mg/h ozone flow rate) of a 30 mg/L DMP (pH 5.0), it can be more mineralized in the presence of Ce/AC catalyst, TOC (DMP) removal rate reaches 68% (99%) at 60 min, 48% (95%) using AC as catalyst, only 22% (86%) with ozonation alone. These results suggest that Ce is a better active component for the catalytic ozonation of DMP. The increased removal rate of this pollutant in the presence of Ce/AC catalyst is due to an increase in the ozone decomposition rate into highly oxidant species ($\bullet\text{OH}$) in the system. The active component Ce enhances ozone transformation into $\bullet\text{OH}$, which conformed with former reports [14]. The increased TOC removal rate with the presence of AC in the ozonation of DMP also suggests that AC promotes ozone transformation in aqueous phase and starts chain reactions that continue in aqueous phase, accelerating ozone transformation into $\bullet\text{OH}$ [15–18]. Previous studies

Table 2
Surface area, pore volume and pore diameter of AC and Ce/AC.

Sample	S_{N_2} ($\text{m}^2 \text{ g}^{-1}$)	S_{micro} ($\text{m}^2 \text{ g}^{-1}$)	S_{ext} ($\text{m}^2 \text{ g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{ g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{ g}^{-1}$)	D_{ave} (nm)
AC	632.16	276.09	356.07	0.450	0.125	28.45
New Ce/AC	522.98	412.46	110.52	0.272	0.190	20.79
Spent Ce/AC	486.98	387.05	99.93	0.253	0.177	20.78

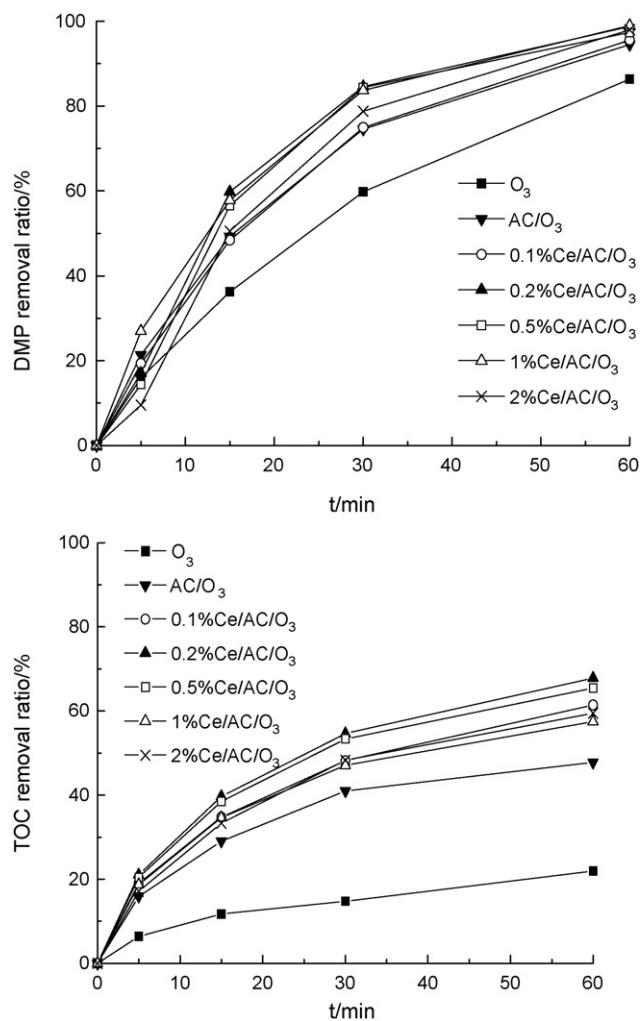


Fig. 3. Effect of cerium loading amount on catalytic ozonation of DMP.

[10,19,20] revealed that metal contents present in AC could act as catalytic sites in the ozonation process. These results indicate that the intermediate compounds (such as formic acid and oxalic acid) produced during the ozonation process of DMP are not easily mineralized. According to former research, some organic acids were produced in the ozonation process of aromatics, such as formic acid and oxalic acid, etc. Their low reaction rate constants are reported in the literature for the ozonation of formic acid and oxalic acid, and they always accumulate as final products when organic aqueous solutes are ozonized in water [21]. The compounds of low reactivity towards ozone may be oxidized by $\cdot\text{OH}$ produced during the decomposition of ozone in aqueous solution, the reaction rate constants of formic acid and oxalic acid with $\cdot\text{OH}$ are reported to be 1.3×10^8 and 1.4×10^6 ($\text{mol/L})^{-1} \text{s}^{-1}$, respectively [2].

In order to confirm that the mineral matter present in activated carbon positively contributes to its activity to enhance DMP ozonation process. Fig. 5 depicts the increase of DMP removal with oxidation time during ozonation in the presence of activated carbon prepared from coconut hull (AC) and the demineralized activated carbon prepared from coconut hull (demineralized AC, which was repeatedly washed by 6 mol/L HCl aqueous solution). It can be seen from Fig. 5 that the presence of AC is advantageous for DMP reduction, compared with the presence of the demineralized AC. For example, at 60 min oxidation time, DMP removal rate in the presence of the demineralized AC is about 82%, that in the presence of AC is about 95%. Therefore, the greater reduction in DMP concentra-

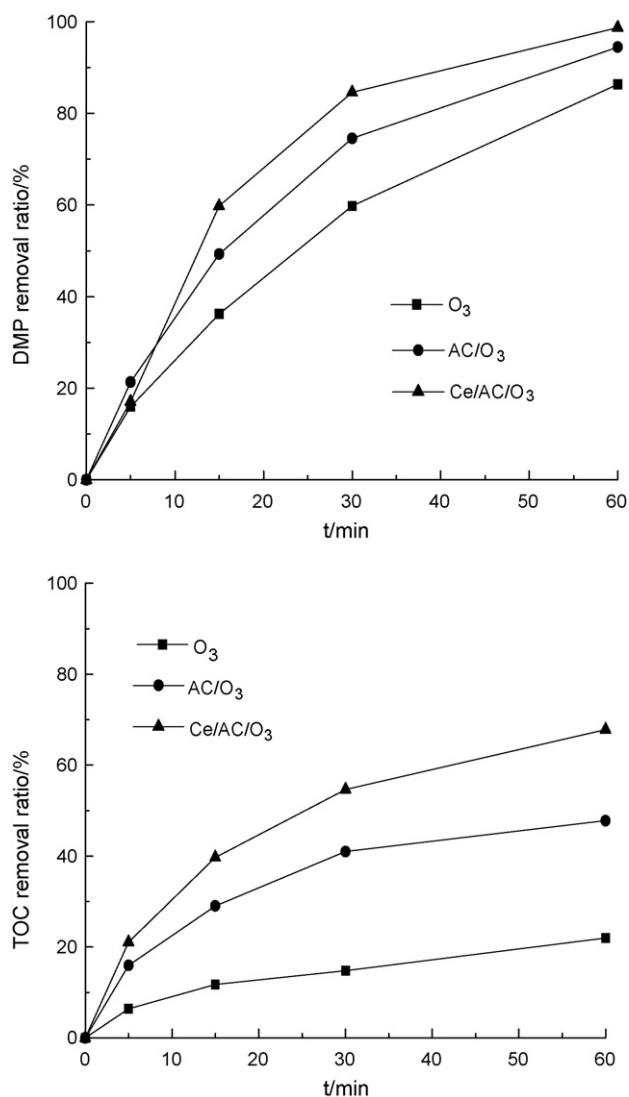


Fig. 4. Comparison of DMP and TOC removal among O₃, AC/O₃ and Ce/AC/O₃ processes.

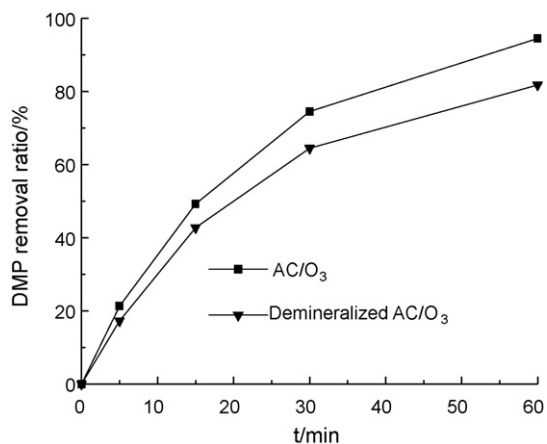


Fig. 5. The effect of the mineral matter in activated carbon and added tert-butanol on the ozonation of DMP.

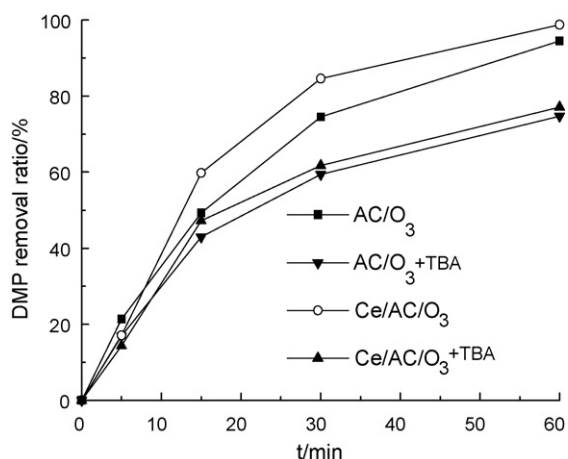


Fig. 6. The effect of added tert-butanol on catalytic ozonation of DMP.

tion (Fig. 5) observed during DMP ozonation in the presence of AC is largely due to the generation of highly oxidant species ($\cdot\text{OH}$) in the system. Furthermore, it can be deduced from the results presented in Fig. 5 that the demineralization of AC removes its capacity to promote the generation of highly oxidant species ($\cdot\text{OH}$). It could be deduced that the mineral matter (such as Cu, Fe, Zn, Pb and Co, see Table 1) of the AC presents a higher activity in ozone transformation into highly oxidant species ($\cdot\text{OH}$) [17–19], which is advantageous for degradation of DMP. These results confirm that the mineral matter present in the AC positively contributes to its activity to enhance DMP ozonation process, making AC a very interesting material for ozonation of aromatic compounds.

In order to verify whether the ozonation of DMP in the presence of Ce/AC catalyst involves $\cdot\text{OH}$ radicals, some experiments were also carried out in the presence of 10 mg/L TBA, a well known $\cdot\text{OH}$ radical scavenger. The results obtained for both Ce/AC and AC catalyst are presented also in Fig. 6. The results show that the ozonation of DMP catalyzed by Ce/AC is strongly inhibited in the presence of TBA. For example, at 60 min oxidation time, DMP removal rate in the presence of TBA is about 77%, that without TBA is about 99%. This experimental observation indicates that, in these conditions, the oxidation mechanism of DMP occurs via $\cdot\text{OH}$ radicals in the liquid bulk. It should be noted that these results are similar to those obtained with AC promoted ozonation at the same conditions.

3.4. Effect of initial DMP concentration on its catalytic ozonation with Ce/AC catalyst

Fig. 7 shows the effect of initial DMP concentration on DMP and TOC removal in the Ce/AC catalytic ozonation process. It is observed that the removal of DMP and TOC follows similar trends for the concentrations of 5 mg/L, 20 mg/L, 50 mg/L and 100 mg/L. At 60 min oxidation reaction time, DMP and TOC removal rate reduces with the increase of DMP concentration. The results demonstrate that DMP and TOC removal rate significantly depends on the initial DMP concentration at 60 min ozonation time. The results reveal that the increase of initial DMP concentration decreases DMP and TOC removal rate. This means that catalytic ozonation achieves only a limited amount of DMP and TOC removal at the highest initial DMP concentration, because an increase of the initial DMP concentration corresponds to an increase of by-product concentration in the solution. Then, the available ozone (fixed ozone flow rate, 50 mg/h) at different initial DMP concentration will start to be consumed both for oxidation of intermediates and also for the continuing degradation of original DMP. Thus, this will cause a decrease in the degradation rate of the DMP with oxidation reaction time, yielding

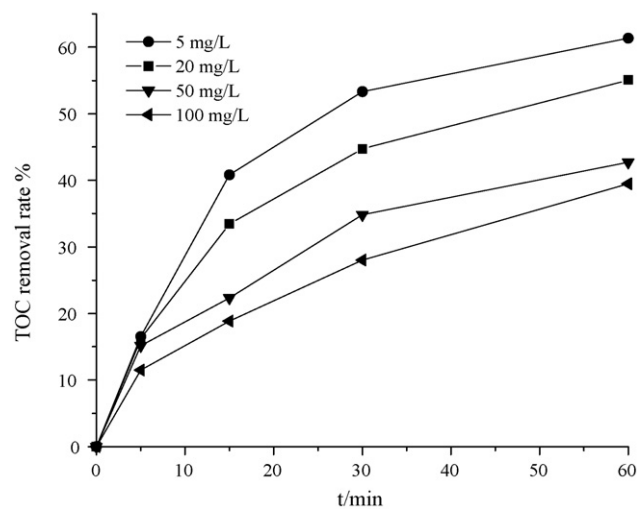
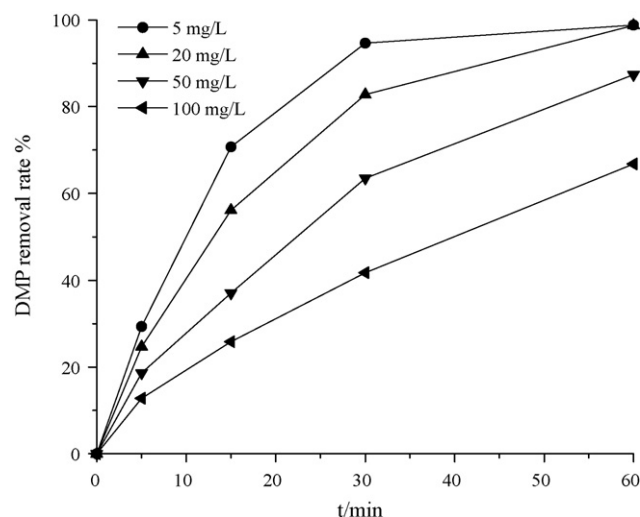


Fig. 7. Effect of initial DMP concentration on its catalytic ozonation with Ce/AC catalyst.

a lower overall TOC removal at 60 min reaction time than that of the case with a lower initial DMP concentration.

3.5. Kinetics of TOC removal in O_3 alone, AC/O_3 and $\text{Ce}/\text{AC}/\text{O}_3$ processes

The kinetic data of semi-batch experiments with various different oxidation processes are listed in Table 3. When the pseudo-second-order rate constant values were plotted against various DMP concentration, a good linearity was observed (Table 3), suggesting that the reaction is of second-order with respect to DMP concentration. The mineralization rate constant of DMP with Ce/AC/ O_3 is 2.5 times higher than that of AC/ O_3 with the same concentration of ozone, 7.5 times higher than that of O_3 alone. These results indicate that Ce/AC catalyst shows the better catalytic activity in the ozonation of p-CBA.

Table 3
TOC removal kinetics of O_3 alone, AC/ O_3 and Ce/AC/ O_3 processes.

Process	Second-order kinetics	
	K (L/mg min)	R^2
O_3	0.0002	0.9400
AC/ O_3	0.0006	0.9188
Ce/AC/ O_3	0.0015	0.9930

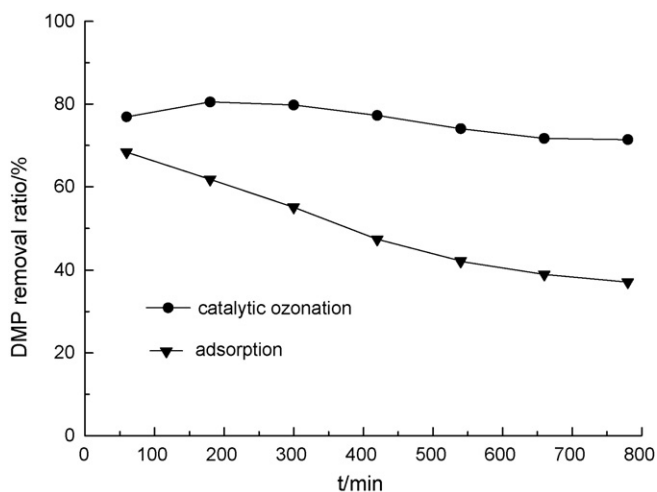


Fig. 8. Stability experiment of Ce/AC catalyst in sequential reaction for the ozonation process of DMP.

3.6. Stability experiment of Ce/AC catalyst in sequential reaction

In order to investigate stability of Ce/AC catalyst, the test was performed with a new batch of 30 mg/L DMP solution under the sequential reaction conditions (2 g catalyst, 60 min oxidation retention time, 50 mg/h ozone flow rate). The test process was performed about 780 min. And the test results are shown in Fig. 8. It is seen that DMP removal efficiency keeps to a nearly constant rate after 540 min sequential reaction when compared with Ce/AC catalyst adsorption, which suggests that the catalytic capacity of Ce/AC catalyst is not quickly decreasing with time under such treatment conditions. These results also correspond to Table 2 and Fig. 2. Table 2 illustrates the surface area of the spent sample Ce/AC catalyst after 780 min sequential reaction is 487 m²/g, which is slightly lower than that of new Ce/AC catalyst sample (522 m²/g). It is seen from Fig. 2 that new and spent Ce/AC catalysts have identical morphology after 780 min sequential reaction in the catalytic ozonation of DMP. The above results demonstrate that the Ce/AC catalyst is effective and stable in the ozonation of DMP.

4. Conclusion

The presence of either AC or Ce/AC considerably improves TOC removal during DMP ozonation. During the ozonation (50 mg/h ozone flow rate) of a 30 mg/L DMP (pH 5.0), a maximum of TOC (DMP) removal rate reaches 68% (99%) at 60 min oxidation time when cerium loading amount in Ce/AC catalyst reaches 0.2%, 48% (95%) using AC as catalyst, only 22% (86%) with ozonation alone.

DMP and TOC removal rate reduces with the increase of DMP initial concentration. The mineralization rate constant of DMP with Ce/AC/O₃ is 2.5 times higher than that of AC/O₃ with 50 mg/h ozone flow rate, 7.5 times higher than that of O₃ alone.

DMP and TOC removal efficiency keeps to a nearly constant rate after 540 min sequential reaction when compared with Ce/AC cata-

lyst adsorption, which suggests that Ce/AC catalyst shows the better catalytic activity and stability.

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