



# Ozonation catalyzed by cerium supported on activated carbon for the degradation of typical pharmaceutical wastewater



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## ABSTRACT

The catalyst of cerium supported on activated carbon (Ce/AC) for ozonation was prepared and the catalytic activity was evaluated by the degradation of *p*-toluenesulfonic acid (*p*-TSA). The results showed that Ce/AC catalyst could not only greatly enhance the degradation of *p*-TSA but also significantly increase the efficiency of COD removal by ozonation. The COD removal could reach 74.1% with the Ce/AC catalyst at 60 min, while the effects of activated carbon (AC) catalyst and without catalyst were only 62.4% and 50.8%, respectively. The superiority of Ce/AC catalyst was attributed to the fact that cerium increased the generation of hydroxyl radicals ( $\cdot\text{OH}$ ), which could react with *p*-TSA and intermediate to form oxidized products rapidly. Based on the intermediates detected by GC/MS, IC and HPLC, a possible degradation pathway of *p*-TSA was proposed. Our aim is to provide basic data and theoretical support for pharmaceutical wastewater treatment by catalytic ozonation.

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## 1. Introduction

With the rapid development of pharmaceutical and chemical industry, pharmaceutical wastewater has become one of the serious sources of environmental pollution [1–3]. Pharmaceutical wastewater contains highly concentrated refractory organic compounds [4,5], and would cause serious problems if discharging without suitable treatment. Pharmaceuticals, such as antibiotics and pharmaceutical intermediates, are persisting against biological degradation. They could retain their chemical structure long enough and remain in the environment for a long time. So their presence is considered dangerous in both low and high concentrations [6–8].

Ozone has attracted considerable attention due to its strong oxidizing, environmentally friendly nature and its potential applications in field of environmental science [9–11]. However, the application of single ozonation is still limited due to the oxidation selectivity and low efficiency [12]. In this regard, in order to increase the oxidizing capability by increasing the generation of more  $\cdot\text{OH}$ , various methods have been applied in combination with ozonation, such as treatment with hydrogen peroxide, UV radiation, or sonolysis [13–15]. But, these methods are not attractive because of the high energy consumption and low energy efficiency [16].

Catalytic ozonation, as an advanced oxidation process (AOP), has attracted a lot of attention because this method can enhance the removal of refractory compounds with highly efficient ozone consumption [17–19]. Catalytic ozonation includes both homogeneous and heterogeneous catalytic ozonation. Though homogeneous catalytic ozonation has been proven an effective method to remove organic pollutants, some metal ions as catalysts which are extremely harmful to human health and the environment was introduced to water environment during reaction [20–22]. However, heterogeneous catalytic ozonation, using solid heterogeneous catalysts, can overcome the drawbacks of homogeneous catalytic ozonation [23–25].

Both the catalyst and the support play important roles in heterogeneous catalysis [26,27]. Activated carbon is the most commonly used supports in catalytic ozonation because of its large surface area and good adsorption capacity [28,29]. As typical rare earth oxide, cerium and its oxide have been used as active species due to the special structure of 4f orbit and high catalytic activity in recent years [30,31]. Cerium ions can exchange between the trivalent and tetravalent states, allowing the release and uptake of oxygen [31–33]. Therefore, cerium oxide appears to be very promising as a catalyst with the help of high oxygen mobility and cerium was typically considerably more active than other rare earth oxides for heterogeneous catalytic ozonation. The catalysts loaded or composited with cerium and its oxide can enhance catalytic activity because presence of cerium oxides can decompose molecular ozone to more reactive radicals such as

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$\cdot\text{OH}$  to mineralize organic compounds [32–34]. Therefore, cerium supported on activated carbon can be a good catalyst for ozonation of pharmaceutical wastewater. However, literature extensively reports on transition metals (Co, Mn, Ti, etc.) supported on alumina or transition metal oxides to catalyze the degradation of phenol, substituted phenols and some carboxylic acids [35–38]. Few studies [39,40] on the loading of rare earth such as cerium oxide into activated carbon and catalytic ozonation of pharmaceutical wastewater by this kind of catalyst have been reported.

In this study, cerium supported on activated carbon catalyzed ozonation for *p*-TSA degradation was studied. The *p*-TSA and COD removal efficiency were compared among  $\text{O}_3$  alone, AC/ $\text{O}_3$  and Ce/AC/ $\text{O}_3$  processes. The influence of operational factors on the removal of *p*-TSA was carefully investigated. A possible degradation pathway of *p*-TSA and the reaction mechanism of ozonation catalyzed by Ce/AC were proposed. Our purpose is to improve pharmaceutical wastewater treatment by making full use of catalytic properties of rare earth and provide a reference for related research.

## 2. Materials and methods

### 2.1. Reagents

All reagents used in this study were analytical grade. *p*-TSA was obtained from Aladdin Reagent (China) Co., Ltd., (purity 99.9%). Cerous nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ; purity 99.9%) was purchased from Shanghai Yuejing Chemical Reagent (China) Co., Ltd., and AC (particle size: 40–80 mesh (0.18–0.38 mm)) was obtained from Shanghai J&K Chemical Reagent (China) Co., Ltd. The pH of solutions was adjusted by sulfuric acid and sodium hydroxide.

### 2.2. Catalyst preparation and characterization

The Ce/AC catalysts were prepared by impregnating AC with an aqueous solution of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  to give 0.5, 1, 1.5 and 2 wt% of Ce/AC. The volume of solution used was just sufficient to wet the powder completely. After impregnating, the powder was dried in a vacuum oven at 110 °C for 4 h. The dried powder was calcined in a tube furnace from ambient temperature to 450 °C at a heating

rate of 5 °C/min and kept at that temperature for 2 h. Nitrogen was used as the protective gas during calcination and the flow rate was 0.2 L min<sup>-1</sup>. After calcination, the Ce/AC catalysts were obtained. The nomenclature used for the catalysts is Ce/AC-X%-Y °C, where X refers to the weight percentage of cerium in the catalyst and Y denotes the calcination temperature.

Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were analyzed with S24700 microscope (Hitachi, Japan). The porous volume and the specific surface area (BET) of the catalysts were determined on a Micromeritics ASAP 2020 Analyzer using nitrogen adsorption at 77 K. Powder X-ray diffraction (XRD) of the catalyst was recorded on a Thermo ARL SCINTAG X'TRA diffractometer at room temperature using Cu K $\alpha$  irradiation at 45 kV and 40 mA.

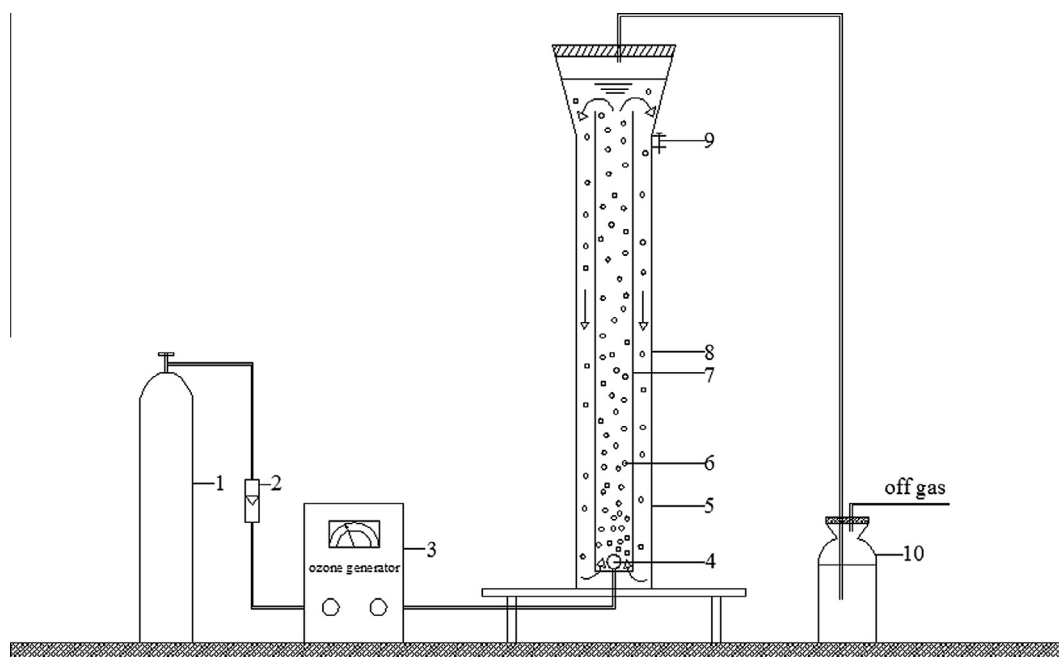
### 2.3. Apparatus and procedures

The experimental apparatus employed in this work (Fig. 1) consisted of a cylindrical Pyrex glass reactor (an internal circulation reactor; inner tube diameter 50 mm; outer tube diameter 80 mm; height 650 mm; volume 1.5 L), an  $\text{O}_3$  supply system (CFY-3, Hangzhou Rongxin Electronic Equipment Co., Ltd., China) and an exhaust treatment system. The ozone diffuser, fixed at the center of the bottom of the reactor, was a spherical unit with coarse porosity. As ozone diffusing, catalysts could be diffused well in aqueous solution. The flow rate was controlled by a rotameter and the unreacted ozone in the off gas was absorbed by sodium thiosulfate solution before it was discharged into the environment.

Experiments were carried out at 25 °C. Simulated wastewater (1.5 L) containing *p*-TSA was added into the reactor. The reaction started with simultaneous Ce/AC catalysts and ozone addition. Samples were withdrawn at predetermined time-points from the top of the reactor, and filtered through a 0.22  $\mu\text{m}$  pore size membrane filter, and then analyzed.

### 2.4. Analytical methods

The concentrations of *p*-TSA were immediately determined by HPLC (Model 1200, Agilent Technologies, USA) equipped with a



**Fig. 1.** Experimental equipment. 1. Oxygen. 2. Rotameter. 3. Ozone generator. 4. Gas dispersion equipment. 5. Reactor. 6. Catalysts. 7. Inner pipe of reactor. 8. Outer pipe of reactor. 9. Sample connection. 10. Absorption bottle.

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