



# Magnetic pyrite cinder as an efficient heterogeneous ozonation catalyst and synergetic effect of deposited Ce



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## HIGHLIGHTS

- Pyrite cinder(PyC) exerted an efficient catalytic activity in the mineralization of RB5 by O<sub>3</sub>.
- Optimized Ce deposition evidently enhanced the catalytic activity of PyC.
- PyC was found to keep quite stable catalytic activity in a wide pH range from 3 to 10.
- Surface hydroxyl and surface Ce(III) were crucial in the generation of hydroxyl radical.

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Heterogeneous catalytic ozonation was emerged to be a promising alternative in the mineralization of various persistent organic pollutants in recent decades. Magnetic pyrite cinder (PyC), which was employed as the catalyst in our investigation, was further deposited by Ce (Ce-PyC) to enhance its catalytic activity in the degradation of aqueous reactive black 5 (RB5). The results showed that additional 17.39%, 42.12% mineralization efficiency was obtained by O<sub>3</sub>/PyC, O<sub>3</sub>/Ce-PyC, respectively, in the degradation of RB5 compared to that of O<sub>3</sub> alone under identical experimental condition. The reaction mechanism involved the enhanced mineralization of aqueous RB5 at the catalyst-solution interface via hydroxyl radicals produced by the reaction between O<sub>3</sub> and catalyst surface. Besides surface hydroxyl, surface Ce(III) was crucial for Ce-PyC in the enhanced generation of hydroxyl radicals. More surprisingly, it was found that both PyC and Ce-PyC could exert quite stable catalytic activity in a wide pH range from 3 to 10, which was supposed to be combined with inherently comprised various metal oxide, such as Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> and CuO. Ozone utilization evaluation demonstrated that PyC and Ce-PyC facilitated effective ozone decomposition, as ozone utilization efficiency (mgTOC/mgO<sub>3</sub>) of O<sub>3</sub>/PyC and O<sub>3</sub>/Ce-PyC increased 64.0%, 155.0%, respectively, compared to that of O<sub>3</sub> alone. This investigation provided an effective alternative in the resource utilization of PyC, which was traditionally characterized as a waste material.

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## 1. Introduction

The distinctive advantage of heterogeneous catalytic ozonation lies in the attractive potential in the degradation and mineralization of refractory organic matters [Sui et al., 2011]. Indeed, heterogeneous catalytic ozonation was intensively explored in the degradation of various dyes, including methyl orange [Tizaoui et al., 2015], active brilliant red X-3B [Dong et al., 2007], reactive blue 5 [Yong et al., 2005]. In most cases, metal oxide (e.g. MnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>,

CeO<sub>2</sub>) [Andreozzi et al., 1996; Ikhlaiq et al., 2012; Orge et al., 2011a,b] and mixed metal oxides (e.g. TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, NiFe<sub>2</sub>O<sub>4</sub>, CuO/CeO<sub>2</sub>) [Beltran et al., 2004; Ren and Dong, 2012; Zhang and Coue, 2014] attracted worldwide attentions due to their excellent catalytic performances. For example, complete mineralization efficiency was obtained within 3 h when freshly-prepared cerium oxides were used in the ozonation of reactive dye and it was found that the high reactive species generated, predominantly HO•, at the surface of cerium oxides was crucial in the pollutants mineralization [Orge et al., 2011a,b].

Though laboratory synthesized metal oxides promoted the advance of ozonation technology as well as the perfection of ozonation mechanism, high material costs and harsh preparation

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conditions limited the large-scale employment of those metal oxides [Zhang and Croue, 2014; Yan et al., 2013]. In this case, natural minerals that contained various metal oxides provided well opportunity, as these metal oxides were known to be effective ozonation catalysts. It was previously reported that by promoting the generation of hydroxyl radicals, ceramic honeycomb (CH) could obviously quicken the nitrobenzene mineralization by ozonation [L. Zhao et al., 2008] and the reaction rate constant and the enhancement of  $\cdot\text{OH}$  formation exhibit a good correlation in the reaction temperature scope of 278–328 K [L. Zhao et al., 2009]. They also found that the conversion of initial pH determines the establishment of  $\text{pH}_{\text{pzc}}$  (at pH the catalyst surface was zero-charged), and the synergistic effect of  $\text{pH}_{\text{terminal}}$  and  $\text{pH}_{\text{pzc}}$  terminal affects the density of surface hydroxyl groups in the neutral state, which controls the concentration of  $\cdot\text{OH}$  [L. Zhao et al., 2008]. As a stable microporous material, zeolite was found to exhibit excellent repetitive-use performance even after continuous operation for 10 cycles [Dong et al., 2008]. Investigation by Valdés et al., 2010 indicated that hydrous oxide sites present on zeolite surface ( $\text{S}-\text{OH}_2^+$ ,  $\text{S}-\text{OH}$ ,  $\text{S}-\text{O}^-$ ) play a key role on the catalytic ozonation mechanism. Similarly, Ikhlaiq supposed that highest activity of zeolite was at pH close to the point of zero charge where surface hydroxyl radicals are most susceptible to conversion of ozone to hydroxyl radicals [Ikhlaiq et al., 2012]. Other natural minerals as effective ozonation catalysts include brucite [He et al., 2008, Qi et al., 2009], magnesia [Dong et al., 2007], volcanic sand [Valdés et al., 2008]. However, relatively limited catalytic activity weakened the potential of natural minerals as the cost-efficient catalysts [Valdés et al., 2008; Moussavi et al., 2012]. As a matter of fact, various attempts have been tried to promote the catalytic activity of specific natural minerals. For example, calcined magnetite attained greater catalytic potential than the raw ore, which was ascribed to the destruction of pyrite and the transformation of most of the magnetite ( $\text{Fe}_3\text{O}_4$ ) into hematite ( $\text{Fe}_2\text{O}_3$ ) under 700 °C [Moussavi et al., 2012]. In most cases, metal oxide deposited minerals were increasingly recognized because of the synergetic effect between deposited metal oxides and minerals [He et al., 2010]. For example, the modification of CH with metals, including Mn and Cu, enhanced the density of surface hydroxyl groups, which determines the initiation of  $\text{HO}\cdot$  from ozone decomposition, causing the increases in the utilization efficiency of ozone, the formation of  $\text{H}_2\text{O}_2$  and the initiation of  $\cdot\text{OH}$  [L. Zhao et al., 2009, 2010]. Nonetheless, modified or natural minerals received striking less attention, compared to synthesized catalysts. What's worse, catalytic activities of previous reported metal oxides and minerals were almost pH dependent, limiting the stability of catalytic ozonation performance in pH-variable wastewater [Andreozi et al., 1996; Orge et al., 2011a,b; Beltran et al., 2004].

Traditionally, pyrite cinder (PyC) is characterized as a waste material and poses potential environmental risk while having issues associated with disposal [Zhang et al., 2015]. Resource utilization of PyC includes using as a potential iron-based oxygen carrier [Zhang et al., 2015], extracting iron from PyC [Fan et al., 2015]. Our previous research confirmed PyC as a cost-effective heterogeneous catalyst in Fenton-like reaction [Wu et al., 2014]. Taking its feature of various metal oxides composition into consideration, PyC as an effective ozonation catalyst was forecasted and accordingly explored for the first time in our investigation. What's more, catalytic activity of PyC was further promoted by Ce deposition (Ce-PyC). Ce-PyC preparation was optimized prior to employment as the ozonation catalyst. Subsequently, both PyC and Ce-PyC were investigated intensively as effective ozonation catalysts, using reactive black 5 as the target pollutant. Their effectiveness under a wide range of pH (from acidic to alkaline) was compared and surface reaction mechanism involving surface

hydroxyl and deposited Ce were proposed. Furthermore, ozone utilization efficiencies in all three cases of  $\text{O}_3$ ,  $\text{O}_3/\text{PyC}$  and  $\text{O}_3/\text{Ce-PyC}$  were also evaluated, providing available information for the application of PyC-based catalytic ozonation technology.

## 2. Methods

### 2.1. Materials

All of the reagents, such as NaOH, KI were purchased from Sinopharm Chemical Reagent. They were all reagent grades and used without further purification.  $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  of analytical grade was obtained from Sigma-Aldrich. Simulated dyeing wastewater was prepared by spiking RB5 (Shanghai Chem. Ltd.) and the initial concentration was always 200 mg/L in our study. Ultrapure water ( $18 \text{ M}\Omega \cdot \text{cm}^{-1}$ , Millipore) was used for all experiments. The pH regulation was performed using either 1.0 mM NaOH or  $\text{H}_2\text{SO}_4$ . PyC was obtained from a chemical plant that produced  $\text{H}_2\text{SO}_4$  by pyrite ( $\text{FeS}_2$ ). It showed uniform particle size with >70% of particles ranging from 50 to 100 mesh and the XRD pattern was shown in Fig. 1 as below.

Ce-PyC was prepared by wet impregnation of PyC with an initial 0.1 mol/L  $\text{Ce}(\text{NO}_3)_3$  which was the unique concentration determined through the optimizing experiments. Firstly, PyC was washed with ultrapure water, and dried at 378.15 K overnight, and then stored in a drying vacuum oven prior to the impregnation. Then, 10.0 g dried PyC was added into 1 L  $\text{Ce}(\text{NO}_3)_3$  aqueous solution under vigorous mechanical agitation for 4 h. Afterwards, the solid-liquid was centrifuged with the supernatant being abandoned.  $\text{Ce}(\text{NO}_3)_3$  concentration of the supernatant was measured in order to calculate Ce loading content. Acquired solid was dried at 378.15 K for 12 h, and calcinated at 873.15 K for 6 h in the air. Finally, the powder particle was the catalyst prepared after air cooling overnight. As the impregnation time, calcination time, calcination temperature are key factors affecting the activity of Ce-PyC, all the three factors are optimized which will show later. In addition, the *m*-PyC mentioned below was prepared similarly, except that the aqueous solution was only ultrapure water.

### 2.2. Catalytic ozonation runs

The removal of RB5 from aqueous solutions by ozonation alone, homogeneous/heterogeneous catalytic ozonation were investigated at room temperature in semi-batch mode in a column glass reactor equipped with agitation. The catalyst (2.5 g/L) and RB5 (2.0 L, 200.0 mg/L) were added into the reactor and followed by the input of a steady ozone flow, which was generated by an ozone generator (CF-3-10 g, Qingdao Guolin). Due to relatively smaller surface area of both PyC and Ce-PyC ( $6.0 \text{ m}^2/\text{g}$ ,  $1.4 \text{ m}^2/\text{g}$ ), the adsorption effect was negligible and related data was not presented. The addition of the gaseous flow was made through an aerator placed at the bottom of the reactor. Particularly,  $\text{O}_3$  generated in the initial 4 min was abandoned to get a steady ozone flow before the experimental operation. The withdrawn samples during the reaction were centrifuged immediately at the speed of 2000 rpm for 5 min.

In view of metal ions leaching experiments, PyC (10.0 g) was added to pH adjusted ultrapure water (1.0 L, pH from 1.0 to 13.0) under vigorous mechanical agitation for 24 h. Metal ions in the supernatant were regarded as leached metal ions and the concentrations were determined.

### 2.3. Analytical method and characterization

The dissolved ozone was determined by indigo method and the

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