



# Catalytic ozonation for advanced treatment of incineration leachate using $(\text{MnO}_2\text{-Co}_3\text{O}_4)/\text{AC}$ as a catalyst



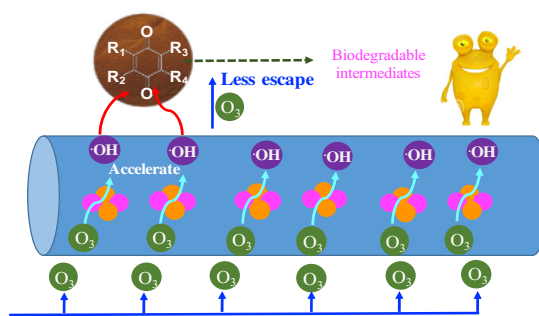
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## HIGHLIGHTS

- A novel catalyst was synthesized for effectively advanced treatment of incineration leachate.
- Biodegradability of the wastewater was obviously increased by catalytic ozonation.
- $\cdot\text{OH}$  generation were accelerated in this catalytic ozonation process.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The leachate from municipal solid waste incineration plants can be effectively treated by a combined anaerobic-anoxic-aerobic process. However, refractory humic-like and fulvic-like substances that remain in the effluent have been a challenge for advanced treatment due to the low biodegradability. In this study, catalytic ozonation was employed for the advanced oxidation treatment of this effluent by using  $(\text{MnO}_2\text{-Co}_3\text{O}_4)$  loaded activated carbon composites ( $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{AC}$ ) as a catalyst with a weight proportion of  $\text{MnO}_2:\text{Co}_3\text{O}_4:\text{AC}$  at 1:2.49:31.23. The refractory substances were partially degraded to intermediates with lower molecular weight by the catalytic ozonation. The biodegradability ( $\text{BOD}_5/\text{COD}$ ) of the effluent increased from 0.15 to 0.80 by the catalytic ozonation with 0.4 g/L of  $(\text{MnO}_2\text{-Co}_3\text{O}_4)/\text{AC}$  and 6.11 mg/(min·L) of transferred ozone within 30 min. The additional  $(\text{MnO}_2\text{-Co}_3\text{O}_4)/\text{AC}$  catalyst improved the transferred ozone dosage into the wastewater and accelerated the hydroxyl radicals ( $\cdot\text{OH}$ ) generation, which were the main mechanisms involved in its great performance on degrading the refractory pollutants.

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## 1. Introduction

Huge amount of municipal solid waste (MSW) were generated worldwide. For example, more than 178 and 260 million tons of the MSW were generated in China and USA every year [1]. Incineration has been considered as an effective method for the MSW disposal recently, as the reduction of the MSW volume and harvest of the energy can be simultaneously achieved by this technology.

However, the fresh leachate was generated during the storage step before incineration [2], which has a complex composition with a high concentration of organic pollutants [3] as well as the refractory organics, such as fulvic and humic substances [4]. As documented, the leachate has been effectively treated by the anaerobic and aerated processes, and biodegradable organic pollutants were degraded and transformed into methane and  $\text{CO}_2$  [5]. However, some pollutants, e.g. fulvic and humic substances, were refractory against the biotreatment, leading to a poor biodegradability of the effluent [6,7]. Serious environmental problems could result from the discharge of this effluent without effective

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treatment. The fulvic and humic substances can form complexes with metals, enhancing solubility of toxic compound and forming harmful products. Therefore, advanced processes is often used to further degrade these refractory organics or improve their biodegradability.

Recently, catalytic ozonation has been demonstrated to be effective for the degradation of refractory pollutants in wastewater. During the catalytic ozonation process, various catalysts play an important role in generating hydroxyl radicals and degrading pollutants. A variety of catalysts have been developed for the catalytic ozonation of refractory pollutants in wastewater such as activated carbon (AC) [8], metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}_2$ ) [9], and metals composites [10,11]. Among these catalysts,  $\text{MnO}_2$  has been shown to be effective for the catalytic degradation of several refractory organic compounds including oxalic acid [12], pyruvic acid [13], and sulfosalicylic acid [14]. In addition,  $\text{MnO}_2$  has also been useful for the degradation of humic substances [15]. 89% of COD and 79% of TOC can be removed by catalytic ozonation within 30 min by using  $\text{MnO}_2$  as the catalyst [15]. Meanwhile,  $\text{Co}_3\text{O}_4$  has also been effective for the catalytic degradation of refractory organic compounds such as toluene [16], phenol [17], 2,4-dichlorophenoxyacetic acid [18], and bezafibrate [19]. In addition, composites of  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  have been synthesized and show excellent catalytic activity for degradation of aromatics. For example, 92.0% of benzophenone-3 was degraded with an ozone concentration of 2.0 mg/L and catalyst dosage of 0.1 mg/L [20].

Although  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$ -based catalysts have been successful for the catalytic ozonation of many compounds, the majority of studies have only been conducted with low concentrations of pure pollutants. There are few reports on the application of these catalysts for the degradation of refractory pollutants in actual wastewater, such as incineration leachate, which has a complex composition. Another challenge for treating wastewater with these catalysts is that the nanosized catalyst particles are difficult to recycle after being used. Coating the nanosized catalyst on the surface of carriers with a big particle size has been a useful resolution to this issue. Granular active carbon (AC) has a large specific surface area and big particle size, thus it is considered a useful carrier for loading the nanosized catalysts [21,22].

The incineration leachate has been effectively treated by a combined UASB-anoxic MBBR-aerobic MBBR process in our previous work. However,  $\sim 390$  mg/L of COD was still remained in the effluent with a poor biodegradability ( $\text{BOD}_5/\text{COD} = \sim 0.15$ ), which mainly include the fulvic and humic substances. In this study, catalytic ozonation was used to further degrade the refractory fulvic and humic substances in this wastewater and to improve its biodegradability. The  $\text{MnO}_2$  and  $\text{Co}_3\text{O}_4$  loaded AC composites ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC was used as the catalyst in this catalytic ozonation. The objective of this study was to evaluate the performance of catalytic ozonation on the degradation of the refractory organics and improvement of the biodegradability of this effluent. The mechanisms involved in the degradation of refractory organics by catalytic ozonation were also disclosed.

## 2. Materials and methods

### 2.1. Materials

The wastewater used in this study was the effluent from the combined UASB-anoxic MBBR-aerobic MBBR process in our lab, which treated incineration leachate for more than 1 year [5]. It contained a COD concentration of  $\sim 390$  mg/L,  $\text{BOD}_5$  of 50–60 mg/L, and was approximately pH 9.

The potassium permanganate ( $\text{KMnO}_4$ ) and cobaltous nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) used for synthesis of the catalysts were purchased from Beijing chemical industry group Co., Ltd., China. The

granular AC with a BET surface area of  $440 \text{ m}^2/\text{g}$  was supplied by Beijing Kechengguanghua New Tech Co., Ltd., China. The Polyethylene glycol (PEG) with molecular weights of 2, 4, 10 and 20 kDa, used as the standard chemicals for the molecular weight test, were purchased from Merck, USA. Spin trap 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO), used for capturing the free radicals, was purchased from Sigma, USA. All the chemicals were used without any further purification.

### 2.2. Preparation and characterization of the catalysts

The ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC composites were prepared by an impregnation-precipitation method [20] with a little modification under the optimized conditions. The synthesized conditions, including the precursors ration of  $\text{Co}(\text{NO}_3)_2/\text{KMnO}_4$  and  $\text{MnO}_2\text{-Co}_3\text{O}_4$  loading, were optimized in our previous work based on the performance of the synthesized ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC catalysts on the improvement of  $\text{BOD}_5/\text{COD}$  (as shown in Figs. S1 and S2). Briefly, 2.0 g of AC, as a support for the catalysts, was washed with diluted nitric acid to remove the impurities. The AC was then dispersed into 50 mL of  $\text{KMnO}_4$  solution (0.075 M), and was stirred for 10 min. Then 50 mL of  $\text{Co}(\text{NO}_3)_2$  (0.225 M) solution was added into the above solution drop by drop. At the same time, a 5 M NaOH solution was used to adjust the pH of the solution and keep the pH between 7 and 8. The  $\text{Mn}(\text{OH})_3$  and  $\text{Co}(\text{OH})_2$  were precipitated on the surface of the AC. After being mixed for 6 h, the Mn/Co-impregnated AC was collected by centrifugation at 3000 rpm, and was washed with deionized water, then was dried in an oven at  $100^\circ\text{C}$ . Finally, the Mn/Co-impregnated AC was calcined at  $500^\circ\text{C}$  for 1 h at a heating rate of  $10^\circ\text{C}/\text{min}$ , and then was cooled to room temperature naturally, obtaining the ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC composites.

The morphology of the ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC composite and the EDS mapping was characterized by a scanning electron microscopy (SEM, Hitachi SU-8010). Before measurement, the samples were sputter coated onto a thin layer of gold (about 5 nm) to ensure good conductivity. The forms of the Mn/Co loaded on the catalyst composite were characterized by XRD and X-ray photoelectron spectroscopy (XPS). The powder XRD of the ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC composite was carried out with an XRD-7000 power diffraction instrument (Shimadzu, Japan) operating with a Cu-K $\alpha$  radiation source filtered with a graphite monochromator ( $\lambda = 1.5406 \text{ \AA}$ ). The  $2\theta$  ranged from  $10^\circ$  to  $80^\circ$  with a scanning speed of  $2^\circ/\text{min}$ . The XPS measurements were conducted in the ESCALAB 250Xi (Thermo Fisher, USA) using a monochromatic Al K radiation to investigate the elemental compositions. The Co2p and Mn2p peaks were deconvoluted into the components consisting of a Gaussian/Lorentzian line shape function (Gaussian = 80%, Lorentzian = 20%) on a linear background. For measuring the Co and Mn loadings in the catalyst, the ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC was dissolved by an acidic microwave digestion method [23], then the concentrations of the Co and Mn were measured by an inductively coupled plasma spectrometer (Agilent, 7900 ICP-MS).

### 2.3. Advanced oxidation treatment

The advanced oxidation treatment of the wastewater by using ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC as the catalyst was carried out in a stainless steel reactor with an effective volume of 400 mL (internal diameter = 50 mm and height = 250 mm). 200 mL wastewater (pH 9.0) was added into the reactor, then a desired amount of ( $\text{MnO}_2\text{-Co}_3\text{O}_4$ )/AC catalyst was added. The ozone produced from pure oxygen by a 3S-A laboratory ozone generator (Tonglin Technology, China) was bubbled into the reactor bottom at a flow rate of 300 mL/min. The ozone concentration was controlled by adjusting the electric voltage. The residual ozone in the off-gas

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