



# Catalytic performance of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst in ozonation of 2-(2,4-dichlorophenoxy)propionic acid, nitrobenzene and oxalic acid in water

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## Abstract

$\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalyst was prepared by incipient wetness impregnation using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the precursors, and its catalytic performance was investigated in ozonation of 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP), nitrobenzene and oxalic acid. The experimental results indicated that  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalyst enabled an interesting improvement of ozonation efficiency during the degradation of each organic pollutant, and the  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation system followed a radical-type mechanism. The kinetics of ozonation alone and  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation of three organic pollutants in aqueous solution were discussed under the mere consideration of direct ozone reaction and OH radical reaction to well investigate its performance. In the catalytic ozonation of 2,4-DP, the apparent reaction rate constants ( $k$ ) were determined to be  $1.456 \times 10^{-2} \text{ min}^{-1}$  for ozonation alone and  $4.740 \times 10^{-2} \text{ min}^{-1}$  for  $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ . And  $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  had a larger  $R_{\text{ct}}$  ( $6.614 \times 10^{-9}$ ) calculated by the relative method than  $\text{O}_3$  did ( $1.800 \times 10^{-9}$ ), showing  $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  generated more hydroxyl radical. Similar results were also obtained in the catalytic ozonation of nitrobenzene and oxalic acid. The above results demonstrated that the catalytic performance of  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  in ozonation of studied organic substance was universal to a certain degree.

**Key words:** catalytic ozonation;  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ ; 2,4-DP; nitrobenzene; oxalic acid; kinetics

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## Introduction

Ozone, due to its high oxidation and disinfection potential, has recently received much attention in water treatment technology (Kasprzyk-Hordern et al., 2003). It has been applied to improve taste and color of water as well as to remove organic or inorganic compounds in water. Despite several advantages of using ozone, there are a few disadvantages which limit its application in water treatment. The main disadvantages of ozonation are cost of generation and its highly selective oxidation power. With the development of ozone generation technology and the stringent regulation for outlet standard, ozonation has been gradually accepted as a conventional deep treatment method. In order to overcome the selectivity of its oxidation power, some ozone-based advanced oxidation processes have been developed recently, among which catalytic ozonation is considered as the most promising method to completely mineralize pollutants.

Ozone combined with certain catalyst (called catalytic ozonation) can improve the degradation efficiencies of organic contaminants, especially for small carboxylic acids that can not be easily removed by conventional chemical oxidation processes (Legube and Karpel Vel Leitner, 1999;

Beltran et al., 2003). Catalytic ozonation (more specifically, heterogeneous catalytic ozonation) is a popular research subject in last several decades, which has high efficiency in removing pollutant from water. However, because of significant differences in both target organic pollutants and catalysts, the mechanism of  $\text{O}_3/\text{catalyst}$  is still in a state of conjecture. Few studies have established a catalytic ozonation system with higher oxidative efficiency than that of ozonation alone during degradation of different organic pollutants.

Chlorophenoxy herbicides such as chlorophenoxyacetic and chlorophenoxypropionic acids are used on a large scale as the plant growth regulators for agricultural and non-agricultural purposes. Chlorophenoxy herbicides have potential toxicity towards human beings and animals (Hoover et al., 1986), and are considered as the moderately toxic compounds (class II or class III) by the World Health Organization. Because of their intensive use and poor biodegradability, chlorophenoxy herbicides have been detected as the major pollutants in ground or surface water (Aaron and Oturan, 2001; Hamilton et al., 2003). Among these compounds, 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) is a selective pre- and post-emergence herbicide widely utilized for the control of broad-leaved aquatic weeds, annual and perennial weeds in cereals, pastures,

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and forestry.

Nitrobenzene (NB) is a major environmental pollutant due to its carcinogenesis and mutagenesis (Mantha et al., 2001; Mu et al., 2004). The commercial uses of NB include solvent, synthetic products of benzene (Zhao et al., 2001), metal polishes, shoe-black, perfume, dye intermediates (Contreras et al., 2001; Sarasa et al., 1998), plastics, explosives, pharmaceuticals (Bell et al., 2003), pesticides (Rodriguez et al., 2002) and a combustible propellant (Mantha et al., 2001). The remediation of NB-contaminated water is of environmental concern because of its toxicity and widely application.

Some carboxylic acids (oxalic acid (OA), acetic acid, pyruvic acid, etc.) resulting from chemical oxidation process, always exist as the remaining chemical oxygen demand (COD) in wastewater. Compared with other organic acids, OA is very difficult to oxidize even in the presence of hydroxyl radicals (Beltran, 2003; Beltran et al., 2002, 2004).

In this study, a novel catalyst of  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  was prepared, and its catalytic performance in ozonation of 2,4-DP, NB and OA was investigated.

## 1 Experimental

### 1.1 Materials and reagents

The agents  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Nanhui Peng Barracks Chemical Plant, Shanghai, China) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Hanson Chemical Reagent Co. Ltd., Shanghai, China) of analytical grade were used to prepare the catalyst. The average size of aluminum oxide particle (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) used as the catalyst carrier was 0.9 mm. All the other reagents such as 2,4-DP (Zhixin Chemical Co. Ltd., Shanghai, China), NB (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), OA (Xingta Jinshan Chemical Plant, Shanghai, China), sodium hydroxide (Hangzhou Xiaoshan Chemical Reagent Factory, Zhejiang, China), sulfuric acid (Quzhou Juhua Reagent Co. Ltd., Zhejiang, China) were of analytical grade without any further purification. All solutions were prepared with double-distilled water. The used flasks were soaked in chromic acid and then rinsed with distilled water.

### 1.2 Preparation of the catalyst

The catalyst was prepared by wet impregnation process according to the following procedures: firstly,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in a concentration of 1 mol/L in two 1 L vessels, respectively; secondly, 25 g aluminum oxide particle, 15 mL of 1 mol/L  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 30 mL of 1 mol/L  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 50 mL of 60% polytetrafluoroethylene latex and 2 mL alcohol were mixed in a beaker. After being static for 5 hr, the mixture was condensed at 90°C to obtain a solid; finally, the condensed solid was dried at 110°C for 2 hr and baked at 450°C for 12 hr. The catalyst powder was cooled down for further use.

X-ray diffraction (Thermo ARL X'TRA, Switzerland) was used to characterize the catalyst powder (hereafter

known as  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  ).

### 1.3 Ozonation procedure

The ozonation system (Fig. 1) consisted of an oxygen cylinder, oxygen pretreatment apparatus, ozone generator (CFS-1A, Ozonia, Switzerland), ozonation reactor (inside diameter of 50 mm and the volume of 1.5 L) and ozone destructor (ODF-003, Ozonia, Switzerland). The ozonized oxygen passed from the ozone generator into the ozone reactor through the sintered inlet that enabled small bubbles to be produced at the bottom of reactor. The activity of  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalyst was evaluated by semi-continuous test. Before any experimental operation, the reactor was pre-ozonized for 4 min, and then was washed for several times with distilled water to exclude possible side effects of impurities. In each ozonation experiment, the model water with a concentration of 100 mg/L 2,4-DP, NB or OA was 500 mL. A suitable sample was withdrawn at certain intervals and centrifuged to determinate the concentration of target compound.

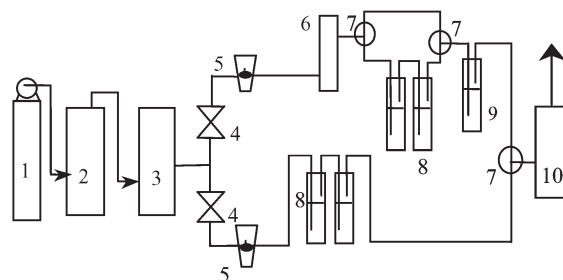
The possible removal mechanism in  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation of organic compound might involve adsorption of catalyst, direct oxidation of ozone, indirect oxidation of hydroxyl radical and other specific reactions (Karpel vel Leitner et al., 1998). In order to clarify the catalytic performance of  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ , the degradation efficiencies by ozonation alone, ozonation plus adsorption and catalytic ozonation in the presence or absence of *t*-butanol were compared in each catalytic ozonation process.

### 1.4 Analytical method

The concentration of ozone in gas was measured by the iodometric titration method (Pires and Carvalho, 1998). The dissolved ozone was detected by a spectrophotometer using the indigo method (Bader and Hoigne, 1981). The COD concentration of sample was titrated by  $\text{K}_2\text{Cr}_2\text{O}_7$  (China Environmental Protection Bureau, 1998).

The XRD pattern of the catalyst was recorded using a Thermo ARL X'TRA XRD diffractometer under the conditions of  $\text{Cu } K_\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) and the scan angle from 15° to 75° at the scanning rate of 4° per min. The accelerating voltage was 45 kV, and the emission current was 40 mA.

The concentration of 2,4-DP and NB in water were



**Fig. 1** Diagram of the experimental setup. (1) oxygen cylinder; (2) oxygen pretreatment; (3) ozone generator; (4) needle valve; (5) flow meter; (6) ozone reactor; (7) three way valve; (8) 2% KI traps; (9) balance bottle; (10) ozone destructor oven.

determined by a high performance liquid chromatography (Waters 1525-2996, USA) with a symmetry C-18 column (5  $\mu$ m). The mobile phase was 70/30 (V/V) methanol/water at a flow rate of 1 mL/min. The concentration of OA in water was determined using an ion chromatograph with an AS14 separation column (Dionex DX1500, USA). The mobile phase was Na<sub>2</sub>CO<sub>3</sub>:NaHCO<sub>3</sub> = 3.5 mmol/L:1.0 mmol/L. The pH value of solution was adjusted by adding 1 mol/L H<sub>2</sub>SO<sub>4</sub> or NaOH.

## 2 Results and discussion

### 2.1 Characterization of the catalyst

X-ray diffraction (XRD) (Fig. 2) analysis showed that the powder sample consisted of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and CoO.

This catalyst was characterized as Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> in this study.

### 2.2 Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of 2,4-DP

#### 2.2.1 Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of 2,4-DP

Figure 3 shows the removal rates of 2,4-DP by ozonation alone and the catalytic ozonation. Compared with ozonation alone, Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation had a higher degradation efficiency. The removal rates of 2,4-DP after 30 min increased from 29.56% by ozonation alone and to 95.94% by O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub>. The amount of 2,4-DP adsorbed by Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> was only 2.42%, which was negligible compared with the total removal rate. The above results demonstrate that Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> is an excellent catalyst in ozonation of 2,4-DP.

#### 2.2.2 Kinetics of ozonation and catalytic ozonation of 2,4-DP

Ozonation of wastewater is a gas/liquid two phase reaction, therefore the amount of ozone input and gas flow rate will greatly affect ozonation efficiency. It was found that the 2,4-DP removal rates were almost unchanged when the amount of ozone input was higher than 98.5 mg/min at a gas flow rate of 0.97 L/min, indicating that Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of 2,4-DP was controlled by a kinetic step here.

The chemical of *t*-butanol was added in excess (43.17 and 129.51 mmol/L) to investigate the role of hydroxyl radical in Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of 2,4-DP (Fig. 4). It can be seen that adding *t*-butanol to solution lead

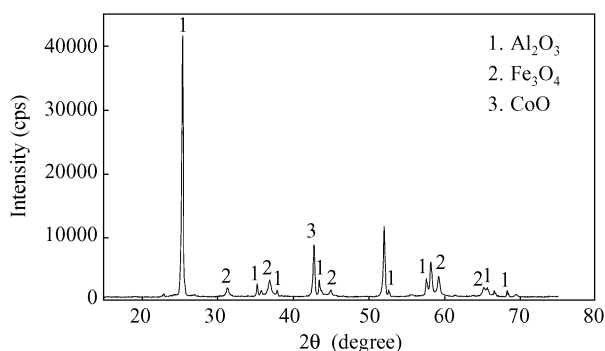


Fig. 2 XRD pattern of the catalyst.

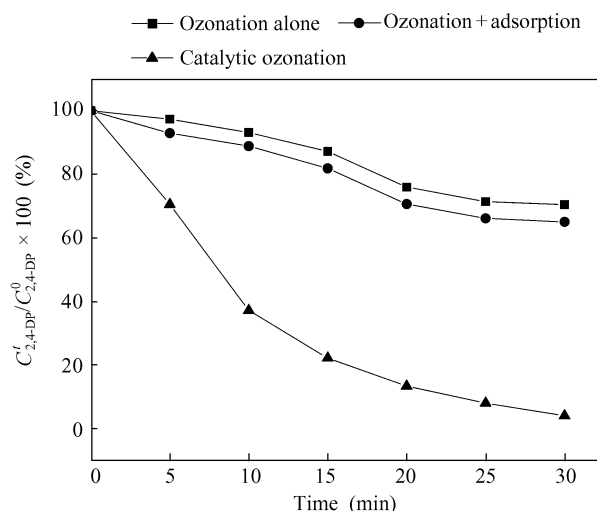


Fig. 3 Removal rates of 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) by ozonation alone and catalytic ozonation. Reaction conditions: temperature 20°C; solution pH 3.3; initial concentration of 2,4-DP: 100 mg/L; concentrations of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalysts: 20 g/L.

to a great decrease in 2,4-DP removal rate. The removal rates of 2,4-DP after 30 min decreased from 95.94% to 54.55% with 43.17 mmol/L *t*-butanol and 53.97% with 129.51 mmol/L *t*-butanol. These experimental results demonstrate that the catalytic ozonation system might comply with the mechanism of hydroxyl radical reaction.

A catalytic ozonation process might include direct oxidative reaction by ozone, indirect oxidative reaction by hydroxyl radical and some other possible reactions (named the third pathway here), and the total removal of organic compound is the sum of those by these three pathways. However, the third pathway is specific for a catalytic ozonation and probably does not exist in some cases. Therefore, the efficiency of a catalytic ozonation is always dependent on the speeds of the preceding two pathways during degradation of an organic compound. The removal of organic compound by the third pathway can

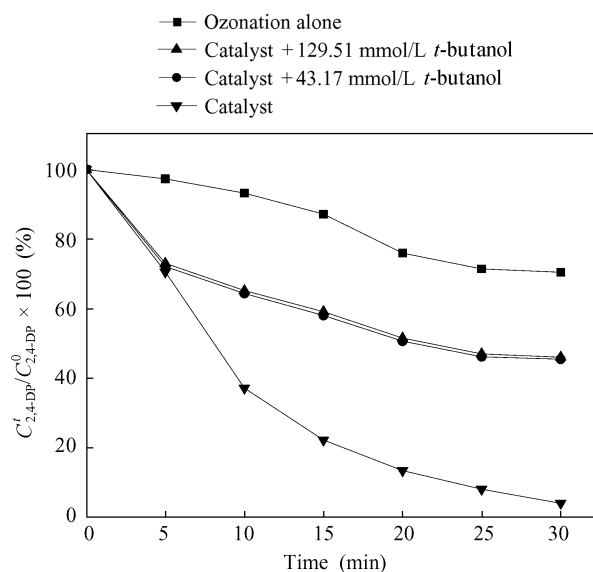


Fig. 4 Effect of *t*-butanol on the removal rate of 2,4-DP. Reaction conditions: temperature 20°C; solution pH 3.3; initial concentration of 2,4-DP: 100 mg/L; concentration of Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalyst: 20 g/L.

be obtained from subtracting that by ozonation alone from that by catalytic ozonation in the presence of *t*-butanol. In order to well investigate the characteristics of this catalytic ozonation system, we merely considered ozone reaction and hydroxyl radical reaction when discussing its kinetics. The plots of  $\ln(C_{2,4\text{-DP}}^t/C_{2,4\text{-DP}}^0)$  versus reaction time for representing the kinetics of 2,4-DP removal rate by ozone reaction plus hydroxyl radical reaction are shown in Fig. 5, and the corresponding pseudo first-order kinetic constants of  $O_3$  and  $O_3/Fe_3O_4\text{-CoO}/Al_2O_3$  are calculated. The calculated results indicate that  $O_3/Fe_3O_4\text{-CoO}/Al_2O_3$  has a larger apparent reaction rate constant than  $O_3$  alone does.

The knowledge of  $\cdot OH$  concentration evolution versus reaction time presents more problems, since there is no suitable method for direct measuring the concentration of this very active species. Elovitz and von Gunten (1999) have proposed a very interesting experimental approach to measure the concentrations of the transient  $\cdot OH$  radical and  $O_3$ . For this purpose, they have introduced a parameter  $R_{ct}$ , which is defined as the ratio of hydroxyl radical concentration and ozone concentration during the reaction (Eq. (1)):

$$R_{ct} = \int C_{OH}^t dt / \int C_{O_3}^t dt \quad (1)$$

where,  $C_{OH}^t$  and  $C_{O_3}^t$  represent hydroxyl radical concentration and ozone concentration in water at any time, respectively, and  $t$  represents reaction time. Under the conditions of a steady-state,  $C_{OH}^t$  and  $C_{O_3}^t$  always remain constant, and then can be marked as  $C_{OH}$  and  $C_{O_3}$ , respectively.

An excellent catalytic ozonation system must be universal in degradation efficiency, which means it must have a large  $R_{ct}$  because of the non-selectivity of hydroxyl radical's oxidation power. In order to calculate  $R_{ct}$  correctly by the relative method, the amount of organic removal by the third pathway must be excluded from the total removal one. Therefore, the rate of a given compound disappearance that represents the removal rate by ozone reaction

plus hydroxyl radical reaction is merely considered here. The kinetics of two reactions are assumed to be second-order (first-order in the concentrations of ozone or  $\cdot OH$ , and the given compound that reacts with the former) (Joon and Hoffmann, 1998). The degradation rate of 2,4-DP by ozonation alone or catalytic ozonation can be expressed as Eq. (2):

$$\ln(C_M^t/C_M^0) = -k_{O_3-M}C_{O_3}t - k_{OH-M}C_{OH}t \quad (2)$$

where,  $C_M^t$  and  $C_M^0$  represent organic compound concentrations at the initial and any reaction time, respectively, and  $k_{O_3-M}$  is the rate constant for organic compound and ozone.  $k_{OH-M}$  is the reaction rate constant of organic compound with hydroxyl radical.

As shown in Fig. 5, the apparent kinetics of  $Fe_3O_4\text{-CoO}/Al_2O_3$  catalytic ozonation of 2,4-DP after subtracting the contribution of the third pathway follows a pseudo first-order reaction, therefore the degradation rate of 2,4-DP can be expressed as Eq. (3):

$$\ln(C_M^t/C_M^0) = -k_{app}t \quad (3)$$

where,  $k_{app}$  is the apparent reaction rate constant. Comparing Eq. (3) with Eq. (2),  $k_{app}$  can be obtained by Eq. (4):

$$k_{app} = k_{O_3-M}C_{O_3} + k_{OH-M}C_{OH} \quad (4)$$

Substituting Eq. (1) into Eq. (4) results in Eq. (5):

$$k_{app} = (k_{O_3-M} + k_{OH-M}R_{ct}) \times C_{O_3} \quad (5)$$

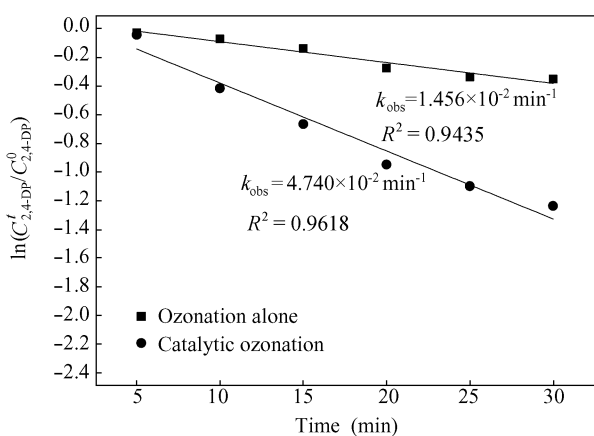
According to Eq. (5), the  $R_{ct}$  value can be experimentally calculated from the knowledge of decreases in the concentrations of both organic compound and dissolved ozone. Once the  $R_{ct}$  value and the ozone exposure are experimentally obtained, the evaluation of the  $\cdot OH$  radicals' exposure at any reaction time can be calculated. This method is very helpful to deduce the knowledge of evolution of  $\cdot OH$  radical concentration in an ozonation process.

The concentrations of dissolved ozone under the controlled conditions were determined to be 0.0486 mmol/L and 0.0482 mmol/L in  $O_3$  and  $O_3/Fe_3O_4\text{-CoO}/Al_2O_3$  systems, respectively. Therefore, according to the data in Fig. 1 and Eq. (5), the  $R_{ct}$  values in ozonation alone and  $Fe_3O_4\text{-CoO}/Al_2O_3$  catalytic ozonation of 2,4-DP are calculated to be  $1.800 \times 10^{-9}$  and  $6.614 \times 10^{-9}$ , respectively. These experimental results indicate that  $O_3/Fe_3O_4\text{-CoO}/Al_2O_3$  produce more hydroxyl radical ( $\cdot OH$ ) than  $O_3$  alone, which is in accordance with the degradation efficiencies of 2,4-DP by ozonation alone and  $Fe_3O_4\text{-CoO}/Al_2O_3$  catalytic ozonation.

In order to test its applicability,  $Fe_3O_4\text{-CoO}/Al_2O_3$  catalytic ozonation was used to degrade NB and OA in water, and the kinetics of their degradation were also discussed by similar method.

### 2.3 Kinetics of ozonation and catalytic ozonation of nitrobenzene and oxalic acid

As shown in Fig. 6, the removal rates of NB after 30 min increased from 20.54% by ozonation alone and to



**Fig. 5** Pseudo first-order plots of 2,4-DP degradation by direct ozone reaction plus OH radical reaction. Reaction conditions: temperature 20°C; solution pH 3.3; initial concentration of 2,4-DP: 100 mg/L; concentration of  $Fe_3O_4\text{-CoO}/Al_2O_3$  catalyst: 20 g/L.

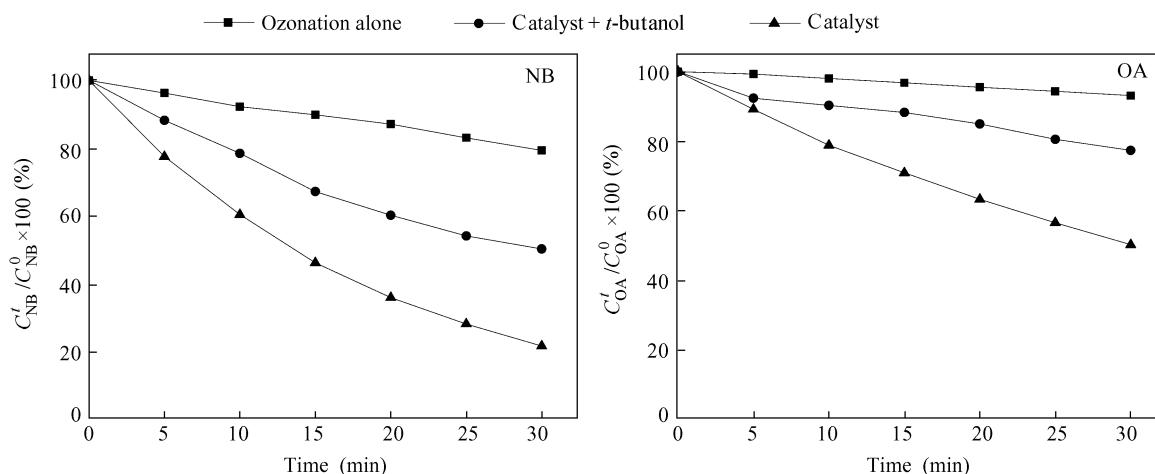
78.14% by O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub>. The adsorptive amount of NB on the catalyst was negligible compared with the total removal one. The test of OA degradation had similar results (Fig. 6), the removal rates of OA after 30 min increased from 6.9% by ozonation alone and to 49.76% by O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub>. The results of adding *t*-butanol to NB and OA solution indicated that Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of NB and OA might comply with the mechanism of hydroxyl radical's oxidation reaction, showing that Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> also had good catalytic performance in ozonation of NB and OA.

Using similar method discussed in Section 2.2,  $R_{ct}$  values in ozonation and catalytic ozonation of NB and OA were calculated. The plots of versus reaction time for representing the kinetics of NB and OA removal rates by ozone reaction plus hydroxyl radical reaction are shown in Fig. 7. The corresponding pseudo first-order kinetic constants of ozonation and Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of NB and OA are calculated (Fig. 7). The concentrations of dissolved ozone under the experimental conditions were determined to be 0.0925 mmol/L in

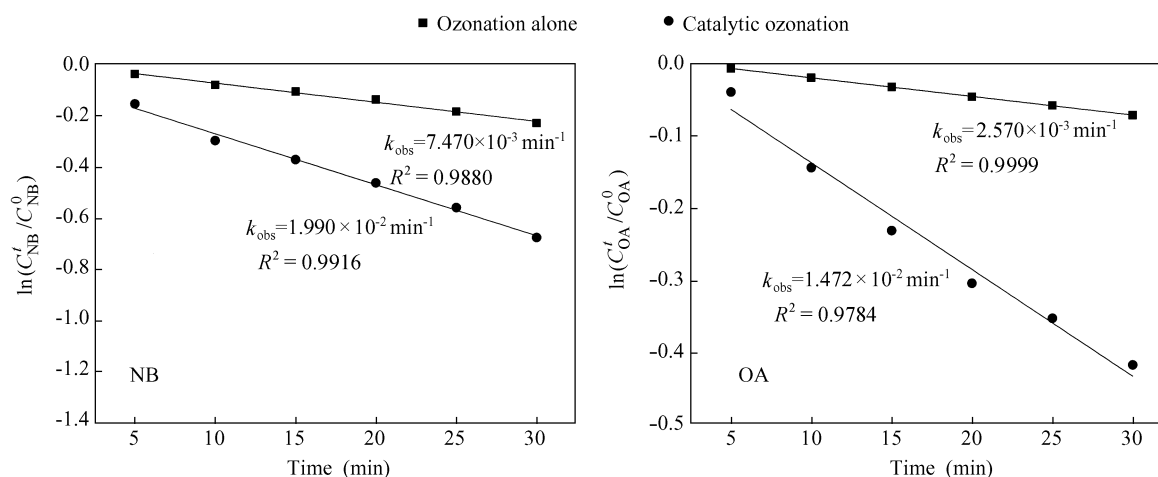
ozonation alone and 0.0918 mmol/L in Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of NB. Therefore, according to the data in Eq. (5), the  $R_{ct}$  values in ozonation alone and Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of NB can be calculated to be  $3.220 \times 10^{-10}$  and  $9.034 \times 10^{-10}$ , respectively. The concentrations of dissolved ozone were determined to be 0.0849 mmol/L in ozonation alone and 0.0843 mmol/L in Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of OA. Similarly, the  $R_{ct}$  values in ozonation alone and Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalytic ozonation of OA are calculated to be  $3.315 \times 10^{-7}$  and  $2.050 \times 10^{-6}$ , respectively. The  $R_{ct}$  values calculated all indicate that more hydroxyl radical is produced in O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub>.

### 3 Conclusions

In order to investigate the catalytic performance of Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub>, three kinds of organic substance, 2,4-DP, NB and OA were selected in the catalytic ozonation system. The experimental results indicate that the use of Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalyst during ozonation of 2,4-DP,



**Fig. 6** Ozonation and catalytic ozonation of nitrobenzene (NB) and oxalic acid (OA). Reaction conditions: temperature 20°C; solution pH 3.3 for NB and pH 2.5 for OA; initial concentration of NB or OA: 100 mg/L; *t*-butanol concentration: 110.88 mmol/L for NB and 0.0544 mmol/L for OA; concentration of Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalyst: 20 g/L.



**Fig. 7** Pseudo first-order plots of NB and OA degradation by direct ozone reaction plus OH radical reaction. Reaction conditions: temperature 20°C; solution pH 3.3 for NB and pH 2.5 for OA; initial concentration of NB or OA: 100 mg/L; concentration of Fe<sub>3</sub>O<sub>4</sub>-CoO/Al<sub>2</sub>O<sub>3</sub> catalyst: 20 g/L.

NB or OA can obtain an improvement of degradation efficiency, and  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation of three kinds of organic substance all follow a radical-type mechanism. The kinetics of ozonation and  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation of three organic pollutants in aqueous solution were discussed under the mere consideration of two reactions (direct ozone reaction and OH reaction) to well investigate its catalytic performance. In the catalytic ozonation of 2,4-DP, the apparent reaction rate constants were determined to be  $1.456 \times 10^{-2} \text{ min}^{-1}$  for ozonation alone and  $4.740 \times 10^{-2} \text{ min}^{-1}$  for  $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ . And  $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  had a larger  $R_{\text{ct}}$  ( $6.614 \times 10^{-9}$ ) calculated by the relative method than ozonation alone did ( $1.800 \times 10^{-9}$ ). Similar results could be obtained in the catalytic ozonation of NB and OA. The  $R_{\text{ct}}$  values in ozonation alone and  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  catalytic ozonation of NB were  $3.220 \times 10^{-10}$  and  $9.034 \times 10^{-10}$ , respectively. And those for OA were  $3.315 \times 10^{-7}$  and  $2.050 \times 10^{-6}$ , respectively. The above results indicate the catalytic performance of  $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$  in ozonation of three kinds of organic substance is universal to a certain degree.

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