



Kinetics of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalytic ozonation of the herbicide 2-(2,4-dichlorophenoxy) propionic acid

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ABSTRACT

The presence of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ can improve degradation efficiency significantly during the ozonation of the herbicide 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP). The main factors affecting degradation efficiency, such as pH, the catalyst concentration and addition of the scavenger, were investigated. The kinetics of the catalytic ozonation are also discussed. The results indicate that two factors, the oxidation after adsorption of 2,4-DP and the oxidation of hydroxyl radicals ($\cdot\text{OH}$), lead to a great enhancement in ozonation efficiency during the catalytic ozonation of 2,4-DP in the presence of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$, in which the oxidation of the $\cdot\text{OH}$ plays an important role. Under controlled conditions, the apparent reaction rate constants for the degradation of 2,4-DP were determined to be $2.567 \times 10^{-4} \text{ s}^{-1}$ for O_3 and $1.840 \times 10^{-3} \text{ s}^{-1}$ for $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$. The results from the analysis of the reaction kinetics using the relative method showed that $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ possessed a larger R_{ct} (R_{ct} is defined as the ratio of the $\cdot\text{OH}$ exposure to the O_3 exposure, $R_{\text{ct}} = \int C_{\text{OH}}^t dt / \int C_{\text{O}_3}^t dt$) than O_3 , indicating that $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ produced more hydroxyl radicals.

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1. Introduction

Chlorophenoxy herbicides, such as chlorophenoxyacetic and chlorophenoxypropionic acids, are used worldwide as plant growth regulators in both agricultural and non-agricultural applications. However, chlorophenoxy herbicides, classified as moderately toxic compounds (class II or III) by the World Health Organization, are potentially harmful to human beings and other animals [1]. Because of their extensive use and poor biodegradability, chlorophenoxy herbicides have been detected as major pollutants in ground and surface water [2,3]. Among these herbicides, the compound 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) is a selective pre- and post-emergence herbicide widely utilized to control broad-leaved aquatic weeds, and annual and perennial weeds in cereals, pastures and forests. Over the past few years, some research efforts have been undertaken to develop powerful oxidation methods to efficiently degrade 2,4-DP in aqueous medium efficiently [4–8].

Ozone, a strong chemical oxidant, is widely used to convert herbicides and other relatively biorefractory organic contaminants into CO_2 and inorganic ions in water [4–9]. However, applications of ozonation in wastewater treatment are limited. In addition

to the cost, the high selectivity of its oxidative power is another major disadvantage of ozonation (O_3 system). Consequently, various advanced oxidation processes (AOPs), such as $\text{O}_3/\text{H}_2\text{O}_2$, UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and UV/Fenton reagents, photo-catalytic oxidation with TiO_2 , wet air oxidation and wet peroxide oxidation processes, electron beam and catalytic ozonation, have been developed as potential methods for degrading organic compounds [10]. Catalytic ozonation is considered a promising method for pollutant control due to its environmental friendliness and high efficacy. Catalytic ozonation can be homogeneous or heterogeneous, the latter being more applicable to wastewater treatment [11]. However, few studies have been carried out to degrade 2,4-DP by using ozone in the presence of a composite dual-metal oxide. In this study, we used $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$, which was prepared by a wet impregnation process, as the catalyst to improve the efficiency of the ozonation of 2,4-DP.

The primary objective of this study was to determine the optimum conditions of the catalytic ozonation of 2,4-DP using $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ and to further investigate the behaviour of its apparent kinetics.

2. Experimental

2.1. Materials and reagents

Analytical grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to prepare the catalyst. Aluminium oxide particles with an aver-

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age size of 0.9 mm were used as the catalyst carrier. All the other reagents, such as 2,4-DP, sodium hydroxide and sulphuric acid, were of analytical grade and used without any further purification. All solutions were prepared with double-distilled water. All flasks in the experiments were first washed by soaking them in chromic acid and then rinsing with distilled water before use.

2.2. Preparation of the catalyst

The $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst was prepared by a wet impregnation process according to the following procedures: First, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were each dissolved into a 1 L vessel at a concentration of 1 M. Then, 25 g of aluminium oxide powder, 15 mL of 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 30 mL of 1 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 50 mL of 60% polytetrafluoroethylene latex and 2 mL of ethyl alcohol were combined in a beaker. After being kept in a static state for 5 h, the mixture was condensed at 90°C to obtain a solid of the chemicals-impregnated aluminium oxide. Finally, the condensed solid was dried at 110°C for 2 h and baked at 450°C for 12 h. The catalyst powder was cooled for further use. The $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{CoO/Al}_2\text{O}_3$ catalysts were prepared by a similar process, using 45 mL of 1 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as impregnation solutions, respectively.

X-ray diffraction (Thermo ARL X'TRA, Switzerland) was used to characterize the catalyst powder (hereafter referred to as $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$).

2.3. Ozonation procedure

The ozonation system (Fig. 1) consisted of an oxygen cylinder, an oxygen pretreatment apparatus, an ozone generator (CFS-1A, Ozonia, Switzerland), an ozone reactor (inside diameter of 50 mm and a volume of 1.5 L) and an ozone destructor (ODF-003, Ozonia, Switzerland). The ozonized oxygen passed from the ozone generator into the ozone reactor through a sintered inlet that enabled small bubbles to be produced at the bottom of reactor. The activity of the $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst was evaluated by different semi-continuous tests. Before each experiment, the reactor was pre-ozonized for 4 min and then washed for several times with distilled water to exclude potential side effects of the impurities. For every ozonation experiment, 500 mL of model water containing 100 mg L^{-1} of 2,4-DP was used. A suitable sample was withdrawn at a certain interval and centrifuged to determine the concentrations of 2,4-DP and chemical oxygen demand (COD).

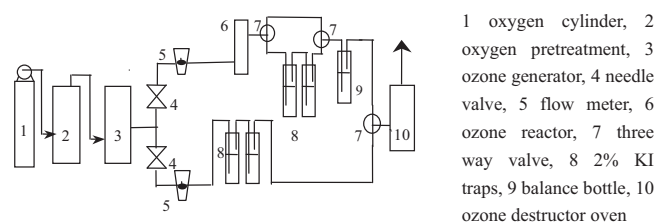


Fig. 1. Diagram of the experimental setup.

2.4. Analytical method

The concentration of ozone in gas was measured by the iodometric titration method (Ozone Standards Committee Method) [12]. The dissolved ozone in water was detected by the indigo method [13]. The COD concentration of the sample was titrated by $\text{K}_2\text{Cr}_2\text{O}_7$ [14], and the concentration of Fe leaching from the catalyst was measured by phenanthroline spectrophotometry [15].

The XRD pattern of the catalyst was recorded by a Thermo ARL X'TRA XRD diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.1542\text{ nm}$) and was scanned at angles from 15° to 75° at a rate of 4° per minute. An accelerating voltage of 45 kV and an emission current of 40 mA were used.

The concentration of 2,4-DP in water was determined by HPLC (Waters 1525-2996, USA), in which a Symmetry C-18 column ($5\ \mu\text{m}$) was used. The mobile phase was 70/30 (v/v) methanol/water at a flow rate of 1 mL min^{-1} . The pH value of solution was measured and controlled by a pH analyzer (PHS-3C, General Instrument Co., Ltd., Shanghai, China).

3. Results and discussion

3.1. Characterization of the catalyst

The results of X-ray diffraction (XRD) (Fig. 2) showed that the catalyst consisted of Al_2O_3 , Fe_3O_4 and CoO , and it can therefore be characterized as $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$. The amount of oxides of Fe and Co per gram of Al_2O_3 particles were 0.05 and 0.09, respectively.

3.2. $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalytic ozonation of 2,4-DP

Fig. 3 shows COD removal rates of 2,4-DP by O_3 , $\text{O}_3/\text{Al}_2\text{O}_3$, $\text{O}_3/\text{CoO/Al}_2\text{O}_3$, $\text{O}_3/\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$. Compared with that of ozonation alone, the ozonation efficiencies of $\text{O}_3/\text{Al}_2\text{O}_3$, $\text{O}_3/\text{CoO/Al}_2\text{O}_3$, $\text{O}_3/\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ and $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ all increased, of which $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ had the highest COD removal rate. For instance, after 30 min,

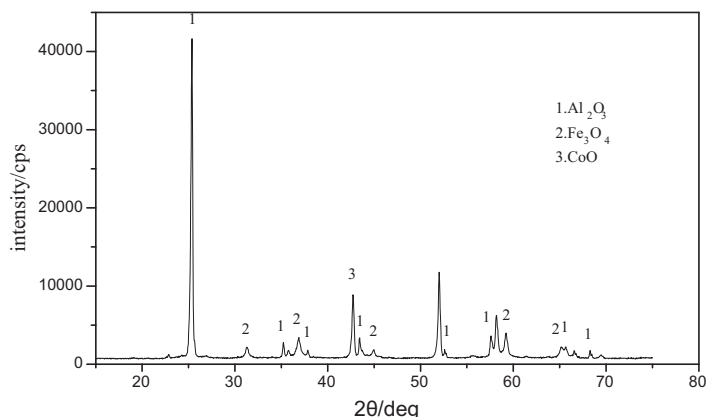


Fig. 2. XRD pattern of the catalyst.

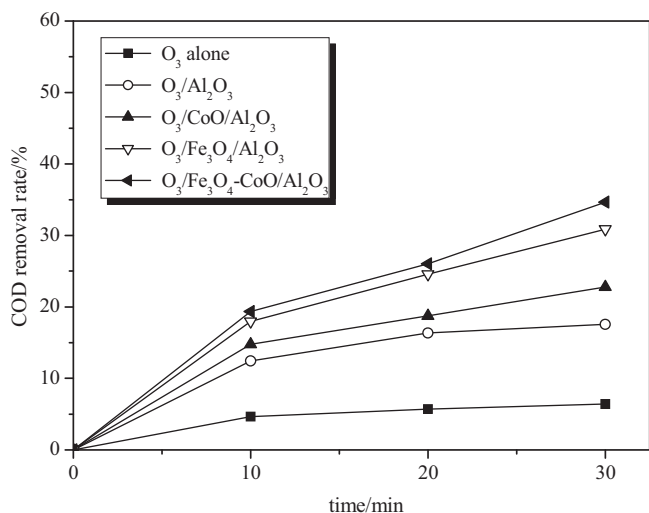


Fig. 3. The COD removal rates of 2,4-DP by ozonation and catalytic ozonation. Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L⁻¹; rate of ozone input: 98.5 mg min⁻¹; concentration of Al₂O₃, CoO/Al₂O₃, Fe₃O₄/Al₂O₃ and Fe₃O₄-CoO/Al₂O₃ catalyst: 20 g L⁻¹.

COD removal rates of 2,4-DP after 30 min increased from 6.42% by O₃ to 17.55% by O₃/Al₂O₃, 22.78% by O₃/CoO/Al₂O₃, 30.89% by O₃/Fe₃O₄/Al₂O₃ and 34.66% by O₃/Fe₃O₄-CoO/Al₂O₃. In addition, it can be seen that both CoO/Al₂O₃ and Fe₃O₄/Al₂O₃ have good catalytic activities in the ozonation of 2,4-DP, where Fe₃O₄/Al₂O₃ has higher activity. The tests on catalyst adsorption showed that the COD removal rate by Fe₃O₄-CoO/Al₂O₃ was negligible (less than 1.6%). The analysis of the concentration of 2,4-DP gave similar results: the removal rates of 2,4-DP also increased from 29.56% by O₃ to 95.94% by O₃/Fe₃O₄-CoO/Al₂O₃ after 30 min. These results indicate that Fe₃O₄-CoO/Al₂O₃ is an excellent catalyst for the ozonation of 2,4-DP.

The removal pathways in a catalytic ozonation system generally involve direct oxidation by ozone, indirect oxidation by hydroxyl radicals and oxidation after adsorption of organic [16]. Hence, the mechanism of Fe₃O₄-CoO/Al₂O₃ catalytic ozonation of 2,4-DP is discussed, and the contribution ratios (CRs) of the three pathways are calculated.

3.3. Effect of t-butanol addition

To completely rule out the role of the hydroxyl radicals in the ozonation of 2,4-DP, t-butanol was added to the solution in excess (43.17 mmol L⁻¹). The reaction rate constant for t-butanol with hydroxyl radicals is $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and the reaction rate constant for ozone is less than $0.003 \text{ M}^{-1} \text{ s}^{-1}$ [17]. The effect of the addition of t-butanol on the removal rate of 2,4-DP is shown in Fig. 4. It can be seen that the presence of t-butanol leads to a significant decrease in the 2,4-DP removal rate, indicating that O₃/Fe₃O₄-CoO/Al₂O₃ might comply with a radical-mechanism. The removal rates of 2,4-DP by catalytic ozonation after 30 min were 95.94% in the absence of t-butanol and 54.55% in the presence of t-butanol. However, the ozonation efficiency of catalytic ozonation in the presence of t-butanol was still higher than that of ozonation alone, which implies the existence of another reaction pathway, namely oxidation after adsorption of 2,4-DP. The role of t-butanol in catalytic ozonation may include two effects: the scavenging of hydroxyl radicals and a competitive adsorption which reduces the adsorptive amount of 2,4-DP. Therefore, the effect of t-butanol on the adsorption of 2,4-DP need to be analyzed. Adsorption tests indicated that adding 43.17 mmol L⁻¹ t-butanol almost had no effect on the adsorptive mass of 2,4-DP on the catalyst, showing that the

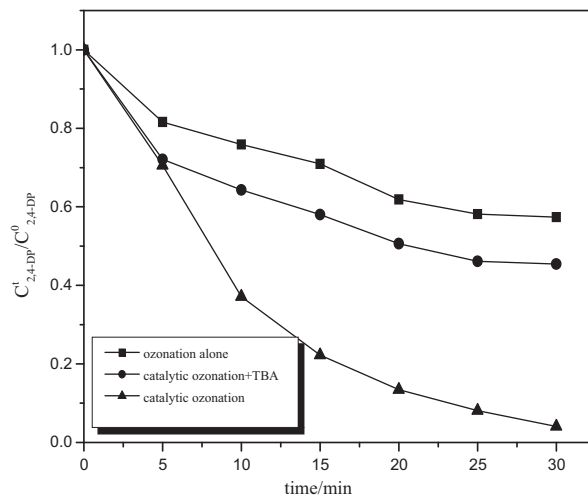


Fig. 4. Effect of t-butanol on the removal rate of 2,4-DP. Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L⁻¹; t-butanol concentration: 43.17 mmol L⁻¹; concentration of Fe₃O₄-CoO/Al₂O₃ catalyst: 20 g L⁻¹.

function of t-butanol is mainly to scavenge the hydroxyl radicals generated by the decomposition of ozone.

The CRs of O₃ and •OH on the removal rate of 2,4-DP at a pH 3.3 can be determined to clarify the mechanism. The removal rate of 2,4-DP by •OH can be obtained by subtracting the removal rate of 2,4-DP by the catalytic ozonation in the presence of t-butanol from the total removal rate. The removal rate of 2,4-DP by oxidation after adsorption can be obtained by subtracting the removal rate of 2,4-DP by ozonation alone from that by the catalytic ozonation in the presence of t-butanol. The CRs of the three pathways on the removal of 2,4-DP are: 30.81% for direct ozonation, 43.14% for oxidative reaction of •OH, and 26.05% for oxidation after adsorption.

As discussed above, an increase in ozonation efficiency for O₃/Fe₃O₄-CoO/Al₂O₃ resulted from two main factors: oxidation after adsorption of 2,4-DP and the oxidation reaction of hydroxyl radicals, the latter playing a more important role.

3.4. Effect of ozone amount

Ozonation of wastewater is a two-phase reaction involving both gases and liquids. Thus, both the rate of ozone input and the rate of gas flow greatly affect ozonation efficiency. The effect of the rate of ozone input on the remaining rate of 2,4-DP and removal rate of COD are shown in Fig. 5(A) and (B) at a gas flow rate of 0.97 L min⁻¹. Fig. 5(A) shows that an increase in the rate of ozone input can improve the removal rate of 2,4-DP. However, the enhancement in the removal rate of 2,4-DP was negligible when the rate of ozone input was higher than 98.5 mg min⁻¹, implying that the Fe₃O₄-CoO/Al₂O₃ catalytic ozonation of 2,4-DP had been controlled by a kinetic step. Similar results were obtained for the COD removal rate of 2,4-DP (Fig. 5(B)). The COD removal rates of 2,4-DP after 30 min were 16.20% for 62.7 mg min⁻¹ of ozone, 24.11% for 87.2 mg min⁻¹, 35.86% for 98.5 mg min⁻¹ and 37.4% for 116.0 mg min⁻¹ when the gas flow rate was kept constant at 0.97 L min⁻¹. At the same time, the consumed ozone per litre of water, calculated by subtracting the volume of ozone in outlet gas from the volume in the inlet gas, were 72.0, 102.0, 198.0 and 200.0 mg L⁻¹ when the rates of ozone input were 62.7, 87.2, 98.5 and 116.0 mg min⁻¹, respectively. One could draw similar conclusions based on the results of the amount of consumed ozone.

Thus, in order to conveniently study the kinetics of the catalytic ozonation of 2,4-DP, an ozone input rate of 98.5 mg min⁻¹ and a gas flow rate of 0.97 L min⁻¹ were used for the following experiments.

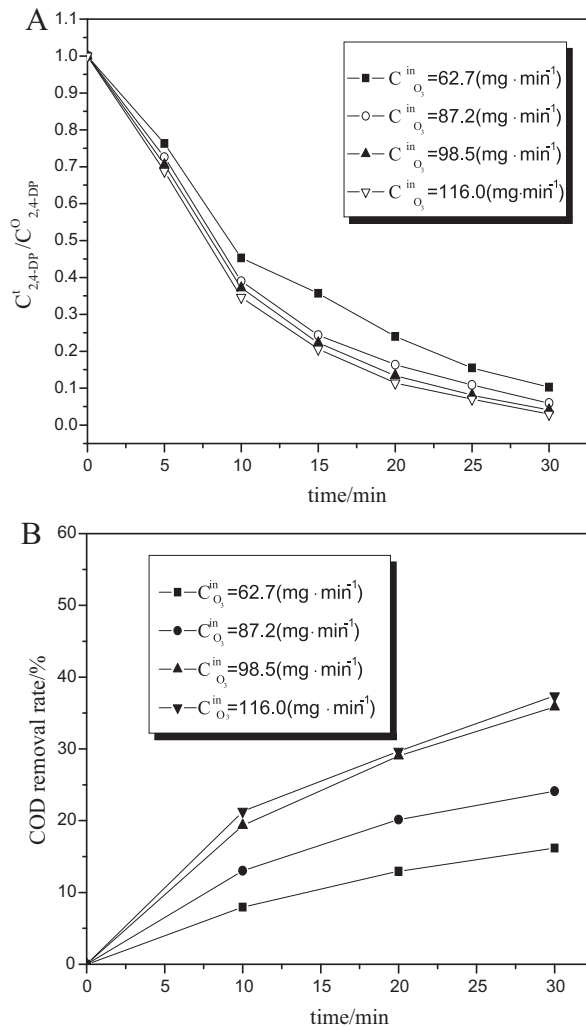


Fig. 5. Effect of the rate of ozone input on the remaining rate of 2,4-DP (A) and removal rate of COD (B). Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L^{-1} ; concentration of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst: 20 g L^{-1} .

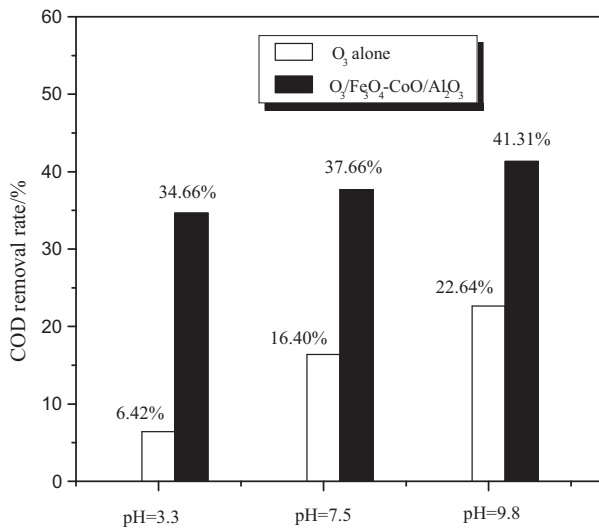


Fig. 6. Effect of pH on the COD removal rates of 2,4-DP by ozonation and catalytic ozonation. Reaction conditions: temperature 293 K; solution pH 3.3, 7.5, 9.8; initial concentration of 2,4-DP: 100 mg L^{-1} ; amount of ozone input: 98.5 mg min^{-1} ; concentration of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst: 20 g L^{-1} .

Table 1

Contribution ratios of ozone and $\cdot\text{OH}$ on the removal of COD at pH 7.5 and 9.8.

pH	CR (%)		
	O ₃	$\cdot\text{OH}$	Oxidation after adsorption
7.5	29.16	56.56	14.28
9.8	33.36	58.78	7.86

3.5. Effect of pH

The pH of the solution can affect the decomposition rate of the dissolved ozone and the existing state of a dissociable organic compound, thus leading to a change in ozonation efficiency. The results of the catalytic ozonation of 2,4-DP using $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ at different pHs are shown in Fig. 6. It was found that the higher the pH of the solution, the higher the COD removal rate was. This result is a well-known phenomenon owing to OH^- catalytic decomposition of ozone to produce the hydroxyl radicals [18]. A comparison between the COD removal rates by $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ and those by O_3 at different pHs indicates that the greatest improvement was achieved when the solution was at pH 3.3, showing that $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ is more suitable for use in acidic solutions.

The CRs of direct ozonation, oxidation of hydroxyl radicals and oxidation after adsorption for COD removal at pH 7.5 and 9.8 were determined by a similar method to that described in Section 3.3,

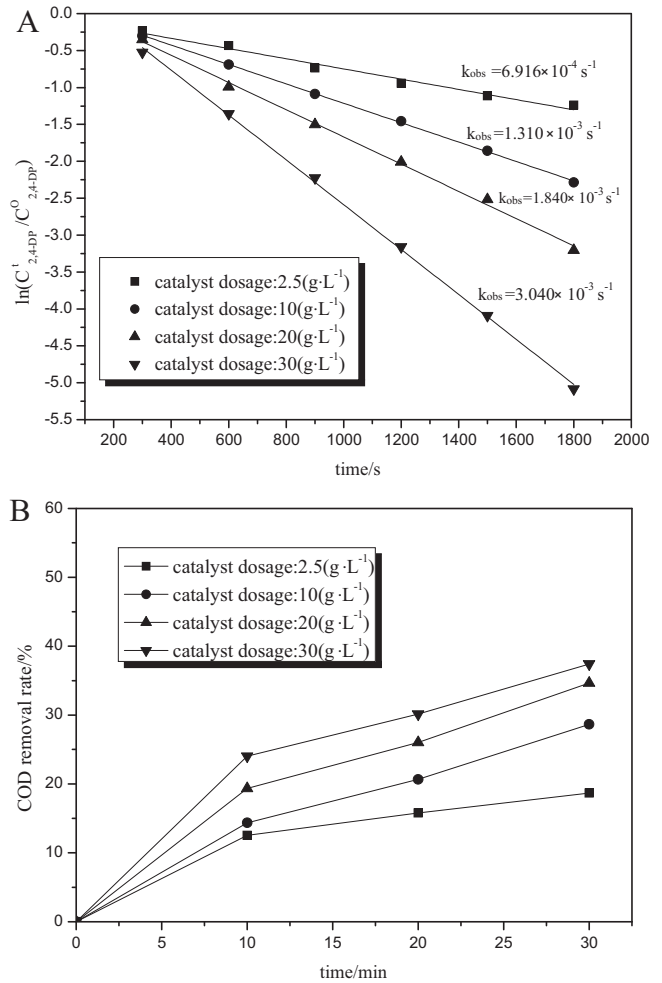


Fig. 7. Effect of catalyst concentration on the degradation rate of 2,4-DP (A) and the removal rate of COD (B). Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L^{-1} ; amount of ozone input: 98.5 mg min^{-1} .

using sodium carbonate ($119.9 \text{ mmol L}^{-1}$) as the scavenger. The results (Table 1) indicate that oxidation of hydroxyl radicals has the highest CRs for both pHs during catalytic ozonation.

3.6. Effect of catalyst concentration

As shown in Fig. 7(A), the kinetics of the catalytic ozonation of 2,4-DP using $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ follow a pseudo-first-order reaction. The effect of the catalyst concentration on the apparent reaction rate constant of the $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalytic ozonation was investigated (Fig. 7(A)). The results indicate that the concentration of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ greatly affects the apparent kinetics of 2,4-DP degradation. The higher the concentration of the catalyst, the larger the apparent reaction rate constant for the catalytic ozonation would be [19]. For example, the apparent reaction rate constants of 2,4-DP degradation by catalytic ozonation were $6.916 \times 10^{-4} \text{ s}^{-1}$ at a catalyst concentration of 2.5 g L^{-1} , $1.310 \times 10^{-3} \text{ s}^{-1}$ at 10 g L^{-1} , $1.840 \times 10^{-3} \text{ s}^{-1}$ at 20 g L^{-1} and $3.040 \times 10^{-3} \text{ s}^{-1}$ at 30 g L^{-1} . Fig. 7(B) shows effects of catalyst concentration on the COD removal rate with similar results. The above phenomenon might be attributed to the following facts: high concentrations of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ provides faster reaction rates for the oxidation after adsorption of 2,4-DP and ozone decomposition reactions to produce hydroxyl radicals. According to the experimental results and based on the previous discussion (Section 3.3), the latter plays an important role for the enhancement of ozonation efficiency. In addition, although low concentrations of the catalyst lowered the efficiency of catalytic ozonation, this still had a higher COD removal rate than ozonation alone.

3.7. Kinetics study

The experimental results reported previously demonstrate that the mechanism for the enhancement of ozonation efficiency includes an indirect oxidative reaction by hydroxyl radicals and the oxidation reaction after adsorption. The oxidation reaction of hydroxyl radicals is more significant because of its importance as a universal reaction in catalytic ozonation. The oxidation after adsorption is specific to a given compound and likely does not exist in some cases. In order to thoroughly investigate the characteristics of the $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalytic ozonation system, we solely considered the oxidative reactions of ozone and hydroxyl radicals when discussing its kinetics.

The knowledge of the $\bullet\text{OH}$ concentration evolution with respect to reaction time presented more problems, because there is no suitable method for directly measuring the concentration of this very active species. Elovitz and von Gunten [20] have proposed a very interesting experimental approach to measure the concentrations of the transient $\bullet\text{OH}$ and O_3 . For this purpose, they introduced a R_{ct} parameter, which is defined as the ratio of the $\bullet\text{OH}$ concentration and the O_3 concentration at any given time during the reaction. In order to use this parameter conveniently, R_{ct} is defined as the ratio of the $\bullet\text{OH}$ exposure to the O_3 exposure in this study:

$$R_{\text{ct}} = \frac{\int C_{\text{OH}}^t dt}{\int C_{\text{O}_3}^t dt} \quad (1)$$

where C_{OH}^t and $C_{\text{O}_3}^t$ represent the concentrations of $\bullet\text{OH}$ and O_3 in water, respectively, at any time. Under steady-state conditions, C_{OH}^t and $C_{\text{O}_3}^t$ always remain constant, and can be marked as C_{OH} and C_{O_3} , respectively. The kinetics of a given compound reacting with either O_3 or $\bullet\text{OH}$ is assumed to be second-order (first-order in the concentrations of O_3 or $\bullet\text{OH}$, and the given compound that reacts with the former) [21]. Therefore, the degradation rate of the given

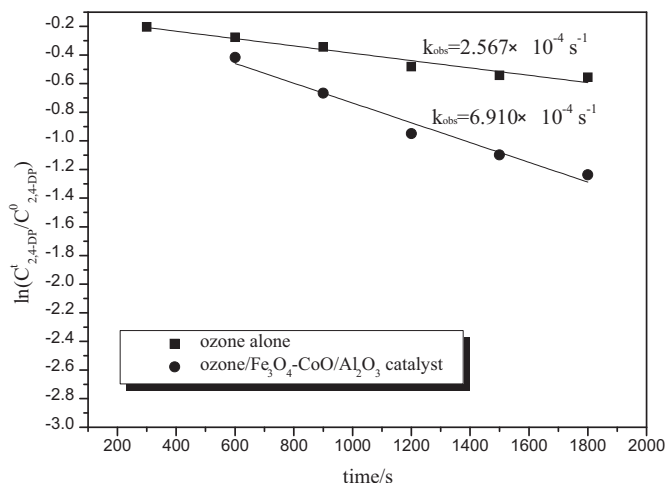


Fig. 8. Pseudo-first-order plots of 2,4-DP degradation by the oxidative reactions of O_3 and $\bullet\text{OH}$. Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L^{-1} ; concentration of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst: 20 g L^{-1} .

compound by ozonation and catalytic ozonation can be expressed as Eq. (2):

$$\ln \left(\frac{C_{\text{M}}^t}{C_{\text{M}}^0} \right) = -k_{\text{O}_3\text{-M}} C_{\text{O}_3} t - k_{\text{OH-M}} C_{\text{OH}} t = -k'_{\text{app}} t \quad (2)$$

where C_{M}^t and C_{M}^0 represent the organic compound concentrations at the initial time and at time t , respectively. $k_{\text{O}_3\text{-M}}$ is the reaction rate constant for the given compound with ozone. $k_{\text{OH-M}}$ is the reaction rate constant for the given compound with the hydroxyl radicals. k'_{app} is the pseudo-first-order kinetic constant of the catalytic ozonation. Substituting Eq. (1) into Eq. (2), one can obtain Eq. (3):

$$k'_{\text{app}} = (k_{\text{O}_3\text{-M}} + k_{\text{OH-M}} R_{\text{ct}}) \times C_{\text{O}_3} \quad (3)$$

According to Eq. (3), the R_{ct} value can be experimentally calculated based on the knowledge that the concentrations of both the organic compound and the dissolved ozone decreases. Once the R_{ct} value and the ozone exposure are experimentally determined, the evaluation of the $\bullet\text{OH}$ exposure at any given reaction time can be calculated. This method is very useful in deducing a knowledge of the $\bullet\text{OH}$ exposure in an ozonation process.

The kinetics of 2,4-DP removal by the oxidative reactions of ozone and hydroxyl radicals are represented by the plots of $\ln(C_{2,4\text{-DP}}^t / C_{2,4\text{-DP}}^0)$ versus reaction time (Fig. 8). In order to calculate the R_{ct} value, the dissolved ozone concentrations in O_3 and $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ systems were measured to be $0.0597 \text{ mmol L}^{-1}$ and $0.0486 \text{ mmol L}^{-1}$, respectively (Supporting information in Table S1). According to our previous work [22], the reaction rate constants of 2,4-DP with O_3 and $\bullet\text{OH}$ were $0.733 \pm 0.163 \text{ L mol}^{-1} \text{ s}^{-1}$ and $2.367 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. Therefore, the R_{ct} values of ozonation and $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ of 2,4-DP are calculated as 1.507×10^{-9} and 5.697×10^{-9} , respectively. These experimental results demonstrate that $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ produce more $\bullet\text{OH}$ species than O_3 alone, which is also in accordance with their corresponding degradation efficiencies.

3.8. Stability of catalyst

The stability of a catalyst is an important feature from the view of practical applications in the industry. Therefore, the effect of consecutive reaction cycles of the catalyst on ozonation efficiency was

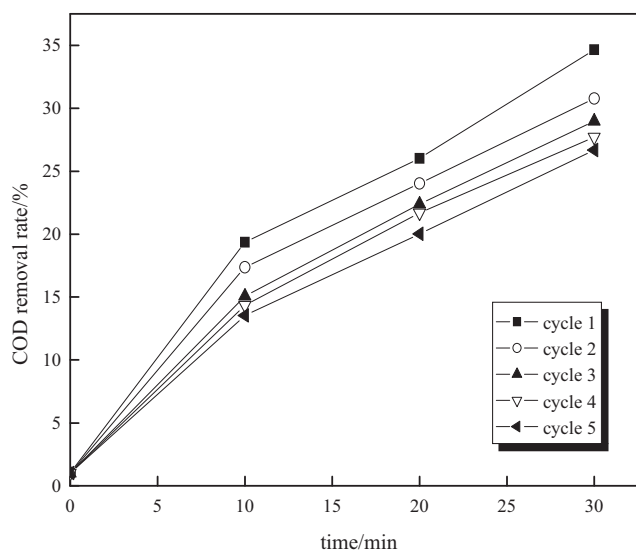


Fig. 9. Effect of the consecutive reaction cycles of the catalyst on the ozonation efficiency. Reaction conditions: temperature 293 K; solution pH 3.3; initial concentration of 2,4-DP: 100 mg L^{-1} ; amount of ozone input: 98.5 mg min^{-1} ; concentration of $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst: 20 g L^{-1} .

tested (Fig. 9). Compared with that of a fresh catalyst, the activity of the catalyst was slightly decreased after five consecutive cycles. For instance, after 30 min, the COD removal rates of the catalytic ozonation of 2,4-DP decreased from 34.66% for a fresh catalyst to 26.68% after the fifth cycle. According to the result of iron ion concentration analysis (Supporting information in Table S2) and Fig. 9, we speculate that the main reason for the decrease of ozonation efficiency is due to the leaching of Fe, thus indicating that the $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst is relatively stable.

4. Conclusions

The use of a $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalyst in the catalytic ozonation of model wastewater containing 2,4-DP was found to improve degradation efficiency. The pH of the solution greatly affected the degradation rate of 2,4-DP, and it was shown that the greatest improvement in COD removal was observed at pH 3.3. The pseudo-first-order rate constant of catalytic ozonation of 2,4-DP with $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ increased from $6.916 \times 10^{-4} \text{ s}^{-1}$ at a catalyst concentration of 2.5 g L^{-1} to $1.310 \times 10^{-3} \text{ s}^{-1}$ at 10 g L^{-1} , to $1.840 \times 10^{-3} \text{ s}^{-1}$ at 20 g L^{-1} and to $3.040 \times 10^{-3} \text{ s}^{-1}$ at 30 g L^{-1} . The mechanism for catalytic ozonation includes two factors: the oxidation after adsorption of 2,4-DP and the oxidation by $\cdot\text{OH}$, where the latter plays a more important role for the enhancement of ozonation efficiency. The apparent reaction rate constants of the degradation of 2,4-DP by ozonation and $\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ catalytic ozonation were $2.567 \times 10^{-4} \text{ s}^{-1}$ and $1.840 \times 10^{-3} \text{ s}^{-1}$, respectively. According to the relative method, $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ has a larger R_{ct} (5.697×10^{-9}) than ozonation alone (1.507×10^{-9}). These results indicate that $\text{O}_3/\text{Fe}_3\text{O}_4\text{-CoO/Al}_2\text{O}_3$ produces more hydroxyl radical ($\cdot\text{OH}$) species than ozonation alone.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.09.013.

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