Homogeneous catalytic ozonation of C.I. Reactive Red 2 by metallic ions in a bubble column reactor

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Abstract

This study elucidates the decolorization of C.I. Reactive Red 2 (RR2) by homogeneous catalytic ozonation. The effects of pH and catalyst dosage were evaluated in O_3/Mn(II), O_3/Fe(II), O_3/Fe(III), O_3/Zn(II), O_3/Co(II) and O_3/Ni(II) systems. In O_3/Mn(II), O_3/Fe(II) and O_3/Fe(III) systems, increasing the catalyst concentration increased the rate of RR2 decolorization; however, further increasing the catalyst concentration caused no further significant increase. When 0.6 mM catalyst was added, the decolorization rates of O_3/Mn(II), O_3/Fe(II), O_3/Fe(III), O_3/Zn(II), O_3/Co(II) and O_3/Ni(II) systems at pH 2 were 3.295, 1.299, 1.278, 1.015, 0.843 and 0.822 min^{-1}, respectively. Under all of the experimental conditions, the decolorization efficiency of catalytic ozonation exceeded that of ozonation alone. The decolorization rate markedly exceeds the TOC removal rate in all tested systems. The effect of the radical scavenger on the catalytic ozonation processes suggests that the decolorization reaction in catalytic ozonation systems proceeds by mainly radical-type mechanisms, except in the O_3/Mn(II) system.
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Keywords: O_3; Mn(II); Fe(II); Fe(III); Zn(II); Co(II); Ni(II); Catalytic ozonation

1. Introduction

The textile dyeing and finishing industry generates large amounts of discharge effluent, which is regarded as a major industrial polluter. The pollution constituents that present in large quantities are unreacted dyeing compounds, dispersing agents and organics that are washed out of the dyed material. Textile preparation, dyeing and finishing plants are currently being forced to treat their effluents. Since small quantities of dyes are clearly visible and detrimentally influence the water environment; hence, removing the color from wastewater is more important than treating other colorless organics. Biological treatment is cheaper than other methods, but it decolorizes less efficiently because the wastewater is toxic. Such treatments as adsorption, flotation and coagulation merely transform the pollutants from one form to another but do not destroy them. In recent years, ozonation has emerged as a process for removing the color of dyes, since the chromophore groups with conjugated double bonds, which are responsible for color, can be broken down by ozone either by direct oxidation by ozone molecules or by indirect radical oxidation [1–7]. Ozone has a great advantage over other oxidants because of its strong oxidizing property. The efficiency of the combination of direct oxidation by ozone molecules and radical oxidation by hydroxyl and/or hydroperoxyl radicals depends on the pollutants, the solution pH and the dose of fed ozone. The oxidation potential of hydroxyl radicals significantly exceeds that of ozone molecules; therefore, radical oxidation is faster and more efficient than direct oxidation.

A disadvantage of using only ozonation for treating wastewater is the large amount of energy that is required for its generation, such that any improvement that reduces the required reaction time would be welcomed from a practical perspective. Metal-catalyzed homogeneous ozonation of organic substrates is currently attracting considerable interest, because of the intent to improve ozonation efficiency and optimize economic efficiency. Catalytic ozonation allows a quicker removal of organic pollutants, because catalysts improve the oxidizing power of ozone, markedly reducing the economic cost. Several cat-

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alytic ozonation systems, such as O_3/Mn(II) [8–13], O_3/Fe(II) [8–13], O_3/Fe(III) [14,15], O_3/Zn(II) [8,10–12], O_3/Co(II) [11,12,16,17] and O_3/Ni(II) [10–13], have been investigated. The degradation efficiency of organics in catalytic ozonation systems exceeds that in ozone alone. However, some studies have demonstrated that the degradation efficiency of organics in O_3/Mn(II) [13], O_3/Ni(II) [11,12], O_3/Zn(II) [11,12] and O_3/Fe(II) [11] systems does not exceed that in ozone alone, suggesting that the catalytic performance in ozonation is quite compound-selective. Additionally, the observed effects depend on such treatment conditions as pH and the ozone/catalyst ratio. Although the aforementioned catalysts have been extensively examined to elucidate their ability to destroy various pollutants, their effectiveness in the decolorization of azo dyes has seldom been examined. Hence, C.I. Reactive Red 2 (RR2) azo dye with the most commonly used anchor – the dichlorotriazine group – was adopted as the parent compound herein. Despite growing interest of the scientific community and intensive studies, catalytic ozonation remains insufficiently studied. Therefore, more work must be conducted with numerous pollutants and different catalysts. This investigation employed Mn(II), Fe(II), Fe(III), Zn(II), Co(II) and Ni(II) as the catalysts in the catalytic ozonation of RR2. The objectives of this study are (i) to compare the decolorization efficiency of different homogeneous catalytic ozonation systems; (ii) to evaluate the effects of pH and catalyst dosage in homogeneous catalytic ozonation systems; (iii) to propose possible reaction mechanisms for various metal-catalyzed ozonation systems based on the experimental results and the literature.

2. Materials and method

2.1. Materials

Parent compound RR2 was obtained from Aldrich and used without further purification. The formula, molecular weight and maximum light absorption wavelength of RR2 were $C_{19}H_{10}Cl_2N_6Na_2O_7S_2$, 615 g/mol and 538 nm, respectively. In homogeneous catalytic ozonation experiments, $MnSO_4 \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3$, $ZnSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ were the sources of Mn(II), Fe(II), Fe(III), Zn(II), Co(II) and Ni(II), respectively, and all were purchased from Merck. The pH of the solution was controlled using H_3PO_4 (J.T. Baker) and NaOH (Merck). In inhibition experiments, ethanol (C_2H_5OH), obtained from Merck, was employed as the radical scavenger. All experimental chemicals were of analytical grade. A dielectric barrier discharge (DBD) reactor was utilized to produce ozone. The DBD reactor, which consumed 10 W of power at a gas flow rate of 200 ml/min, was used in the catalytic ozonation process. The schematic diagram of the ozone generator herein is the same as that of Wu et al. [6] and Wu and Chang [7].

2.2. Homogeneous catalytic ozonation experiments

Homogeneous catalytic ozonation experiments were performed in a bubble-column reactor, which is a cylindrical quartz reactor (1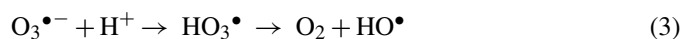00 cm high and 3.1 cm in diameter). The reaction system was aerated with ozone at a flow rate of 200 ml/min and the solution was pumped at a flow rate of 110 ml/min in continuum mode. The schematic catalytic ozonation apparatus was given in our previous study [18]. The dye concentration in each experiment was 100 mg/l and the pH was adjusted in the initial reaction. In the experiments on the effect of the catalyst dosage, each species metallic ion was added to concentrations of 0.2, 0.6 and 1 mM, to elucidate the effects of the catalyst dose in catalytic ozonation. In the experiments on the effect of pH, pH 2 and pH 5 were set in each catalytic ozonation system with the addition of 0.6 mM metallic ions. In radical scavenging experiments, ethanol (5%, (v/v)) was added to catalytic ozonation systems (metallic ion = 0.6 mM) at pH 2. A 15 ml-aliquot was withdrawn from the sampling pores in the bubble-column reactor. The suspension was separated by centrifugation at 5000 rpm for 10 min, and then filtered through a 0.22 μm filter. The decolorization of RR2 was measured using a spectrophotometer (HACH DR/4000U) at 538 nm. The decolorization efficiency was determined from the difference between dye concentrations before and after each experiment. The mineralization of RR2 was identified by the reduction in total organic carbon (TOC), determined using an O.I. 1010 TOC analyzer.

3. Results and discussion

3.1. Effects of metallic ion dosage in metal-catalyzed ozonation systems

3.1.1. O_3/Mn(II) system

Fig. 1 presents the effects of metallic ion dosage in various catalytic ozonation systems. Fig. 1(a) plots the decolorization efficiency of the O_3/Mn(II) system. The correlation coefficient (r^2) is regarded as an index of the goodness-of-fit to the pseudo-first-order kinetics; the r^2 values for RR2 decolorization in all catalytic ozonation systems are generally greater than 0.960 (Table 1). As has been reported elsewhere for dye decolorization [5,7,18,19], decolorization rates (k) followed pseudo-first-order kinetics. Incorporating Mn(II) into the O_3 system markedly accelerated the RR2 decolorization rate. Ozone oxidizes organics via two possible degradation routes; (i) at basic pH, it decomposes rapidly to yield hydroxyl and other radicals in solution, as specified by Eqs. (1)–(3), and (ii) at acidic pH, ozone is stable and reacts directly with organic substrates [20].

$$O_3 + OH^- \rightarrow O_2^{\bullet -} + HO_2^{\bullet} \tag{1}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_2 + O_3^{\bullet -} \tag{2}$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet} \rightarrow O_2 + HO^{\bullet} \tag{3}$$

Since the reaction pH is 2 herein, the main decolorization agents are ozone molecules, but not radicals in the O_3 alone system. In the O_3/Mn(II) system, the decolorization rate increased with the Mn(II) dosage in the range 0.2–1 mM. Accordingly, experiments were performed with the addition of 1.8 and 2.7 mM Mn(II). In the O_3/Mn(II) system, the k values with the addition of 0.2, 0.6, 1, 1.8 and 2.7 mM Mn(II) were 1.418, 3.295, 3.957, 3.173 and 3.087 min^{-1}, respectively. The k values increased with the
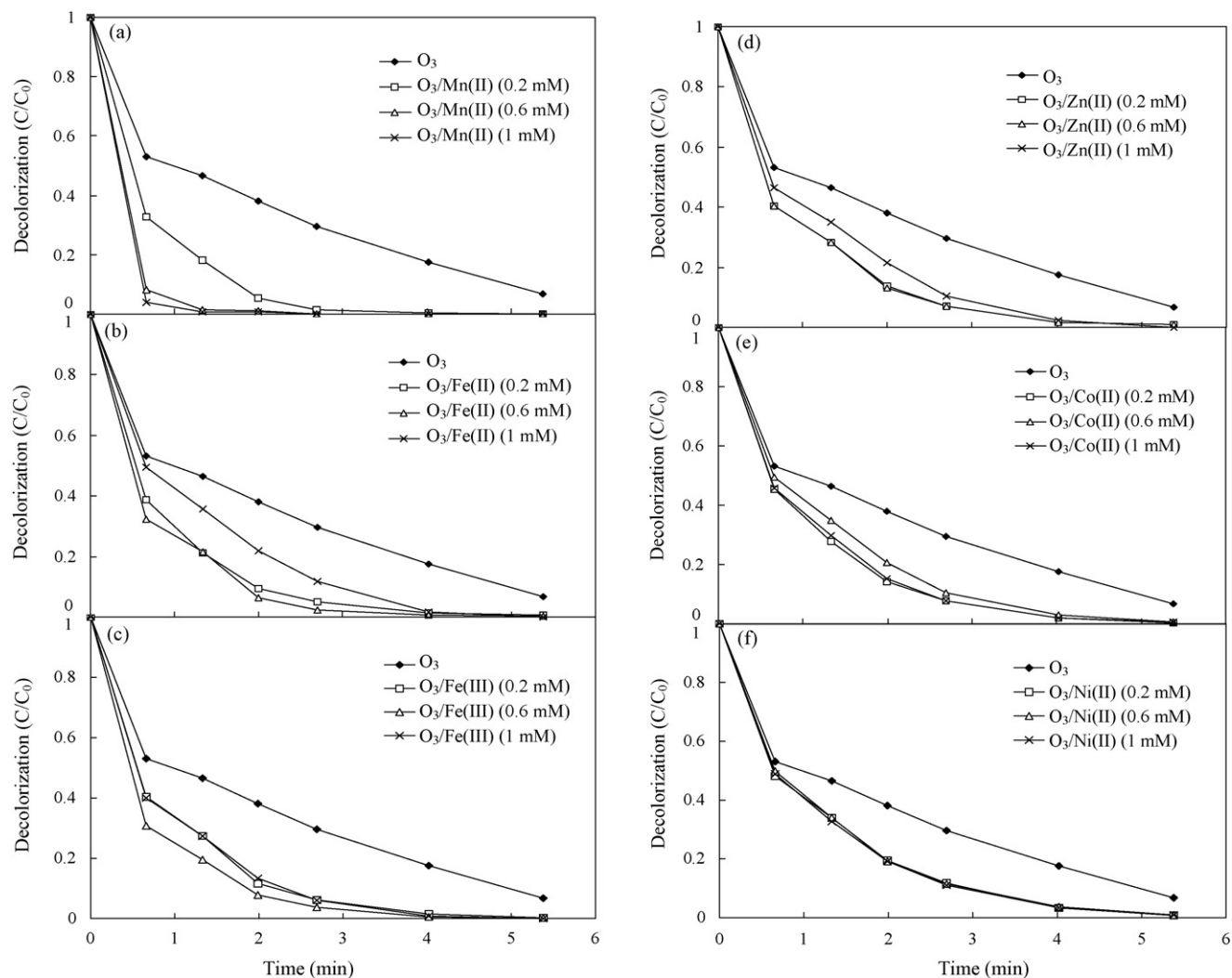
Fig. 1. Effects of metallic ion dosage in catalytic ozonation systems (a) O_3/Mn(II), (b) O_3/Fe(II), (c) O_3/Fe(III), (d) O_3/Zn(II), (e) O_3/Co(II) and (f) O_3/Ni(II) (RR2 = 100 mg/l and initial pH 2).

Mn(II) concentration in the range 0.2–1 mM and then declined as the Mn(II) concentration increased further. Ma and Graham [21] also stated that the optimal Mn(II) concentration for the degradation of atrazine was in the range 0.3–0.6 mg/l; the extent of degradation varied slightly in this range and decreased as the concentration increased above 0.6 mg/l. In the Mn(II) catalytic ozonation of citric acid, increasing Mn(II) concentration in the range 0.05–0.5 mg/l increased the rate of removal of cit-
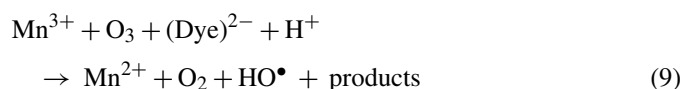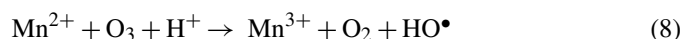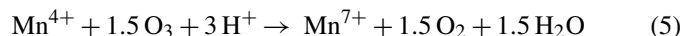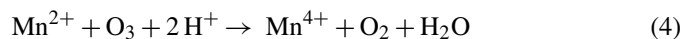
ric acid; however, further increasing the Mn(II) concentration had no significant effect [12]. Li et al. [9] indicated that adding a small amount of Mn(II) slightly increased the removal percentage of alachlor; however, oxidation was clearly inhibited when the concentration of Mn(II) reached 1.0 mg/l. The decolorization rate in the O_3/Mn(II) system exceeded that of ozone alone. Various studies have also demonstrated that Mn(II) catalytic ozonation was more effective in degrading organics than

Table 1
Pseudo-first-order decolorization rate constants (k, min^{-1}) and correlation coefficients (r^2) of different systems at pH 2

Systems	0 mM		0.2 mM		0.6 mM		1 mM	
	k	r^2	k	r^2	k	r^2	k	r^2
O_3/Mn(II)	0.481 (0.034)	0.962 (0.839)	1.418 (0.057)	0.987 (0.923)	3.295 (0.064)	0.987 (0.943)	3.957 (0.070)	0.960 (0.931)
O_3/Fe(II)	0.481	0.962	1.096	0.988	1.299 (0.039)	0.986 (0.901)	0.793	0.986
O_3/Fe(III)	0.481	0.962	1.044	0.994	1.278 (0.041)	0.991 (0.886)	1.036	0.986
O_3/Zn(II)	0.481	0.962	1.011	0.993	1.015	0.993	0.881	0.983
O_3/Co(II)	0.481	0.962	0.959	0.997	0.843	0.995	0.959	0.998
O_3/Ni(II)	0.481	0.962	0.834	0.993	0.822	0.996	0.841	0.996

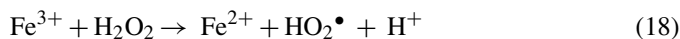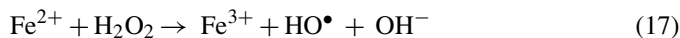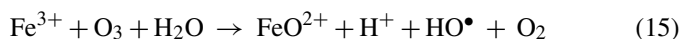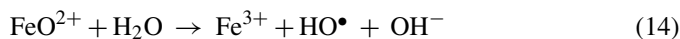Values in the parentheses denoted the results of TOC degradation.

ozone alone [9,11,12,21–26]. Furthermore, the optimum Mn(II) dosage has been suggested to vary with the parent compound. This investigation summarizes the suggestions of previous studies [11,23–26] and proposed possible reaction pathways for O$_3$/Mn(II) (Eqs. (4)–(10)).

$$Mn^{2+} + O_3 + 2H^+ \rightarrow Mn^{4+} + O_2 + H_2O \tag{4}$$

$$Mn^{4+} + 1.5O_3 + 3H^+ \rightarrow Mn^{7+} + 1.5O_2 + 1.5H_2O \tag{5}$$

$$Dye + Mn^{7+} + 1.5H_2O \rightarrow Mn^{4+} + 3H^+ + products \tag{6}$$

$$Mn^{2+} + Mn^{4+} \rightarrow 2Mn^{3+} \tag{7}$$

$$Mn^{2+} + O_3 + H^+ \rightarrow Mn^{3+} + O_2 + HO^\bullet \tag{8}$$

$$Mn^{3+} + O_3 + (Dye)^{2-} + H^+$$
$$\rightarrow Mn^{2+} + O_2 + HO^\bullet + products \tag{9}$$

$$Dye + HO^\bullet \rightarrow products \tag{10}$$

Mn(II) can react with O$_3$ to generate hydrous manganese oxide, which attacks pollutant molecules and accelerates degradation [22]. Legube and Leitner [24] suggested that Mn(II)-catalyzed oxidation proceeds by complexing between the pollutant and Mn(III), forming an intermediate product, which may be easily oxidized by ozone, which reoxidizes the Mn(II) to Mn(III, IV). This fact may reveal that the improvement in the catalytic ozonation performance is caused by additional ozone decomposition in the presence of the catalyst, resulting in the supplementary formation of reactive species and improved ozone utilization [13].

3.1.2. O$_3$/Fe(II) and O$_3$/Fe(III) systems

Fig. 1(b) and (c) plots the effects of iron dosage in O$_3$/Fe(II) and O$_3$/Fe(III) systems, respectively. The k values in O$_3$/Fe(II) with 0.2, 0.6 and 1 mM Fe(II) addition were 1.096, 1.299 and 0.793 min^{-1}, respectively, and those in O$_3$/Fe(III) for 0.2, 0.6 and 1 mM Fe(III) addition were 1.044, 1.278 and 1.036 min^{-1}, respectively (Table 1). The optimum Fe(II) and Fe(III) doses were both 0.6 mM; moreover, the decolorization efficiency of O$_3$/Fe(II) exceeded that of O$_3$/Fe(III). A synergetic effect was observed in both O$_3$/Fe(II) and O$_3$/Fe(III) systems, implying that Fe(II) and Fe(III) catalyze the decomposition of ozone to species that are more active than ozone molecules. This study proposes possible reaction pathways for O$_3$/Fe(II) (Eqs. (11)–(14)) [9,10,20,26–28] and O$_3$/Fe(III) (Eqs. (15) and (14)) [14], based on suggestions made in earlier works. Moiseeva et al. [29] noted that HO$_2^\bullet$ formed in Eq. (1) can recombine spontaneously to yield H$_2$O$_2$, as described in Eq. (16). Even though the amount of H$_2$O$_2$ formed in Eq. (16) may be limited, the Fenton and/or Fenton-like reactions caused by Fe(II) or Fe(III) accelerate decolorization (Eqs. (17) and (18)). All of the reactions in O$_3$/Fe(II) and O$_3$/Fe(III) systems clearly reveal that the mechanism of catalytic ozonation with Fe(II) and Fe(III) involves an ozone decomposition reaction that is followed by the generation of radicals.

$$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^{\bullet-} \tag{11}$$

$$O_3^{\bullet-} + H^+ \rightarrow O_2 + HO^\bullet \tag{12}$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \tag{13}$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{14}$$

$$Fe^{3+} + O_3 + H_2O \rightarrow FeO^{2+} + H^+ + HO^\bullet + O_2 \tag{15}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{16}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{17}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{18}$$

If the Fe(II) dose exceeds the optimal amount, then Eqs. (19) and (20) apply and inhibit the decolorization in O$_3$/Fe(II) [9,20,27]. Since Fe(II) undergoes additional scavenging reactions, the decolorization rate of O$_3$/Fe(II) declined more significantly than O$_3$/Fe(III) when more than the optimum amount of catalyst was added (>0.6 mM) (Table 1). Various investigations have also shown that the addition of iron catalyst accelerated the ozonation and a particular dose was optimal [9,15,20,26].

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \tag{19}$$

$$Fe^{2+} + FeO^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{20}$$
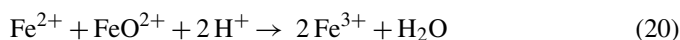
3.1.3. O$_3$/Zn(II), O$_3$/Co(II) and O$_3$/Ni(II) systems

Fig. 1(d), (e) and (f) plots the decolorization efficiency as a function of catalyst dose in O$_3$/Zn(II), O$_3$/Co(II) and O$_3$/Ni(II) systems, respectively. The effects of Ni(II) dosage are negligible in the O$_3$/Ni(II) system (Fig. 1(f)). When either 0.2 or 0.6 mM catalyst was added, the decolorization rates followed the order O$_3$/Zn(II) > O$_3$/Co(II) > O$_3$/Ni(II). Mn(II), Fe(II), Fe(III), Co(II) and Ni(II) metallic ions can all be oxidized to higher valences by ozone. Accordingly, the mechanisms of metal-catalyzed ozonation (except Zn(II)-catalyzed) herein can be briefly expressed as Eq. (21). If the catalyst dosage exceeds the optimum, then hydroxyl radicals will be scavenged and the decolorization rate declined (Eq. (22)).

$$M^{(n-1)+} + O_3 + H^+ \rightarrow M^{n+} + HO^\bullet + O_2 \tag{21}$$

$$M^{(n-1)+} + HO^\bullet \rightarrow M^{n+} + HO^- \tag{22}$$
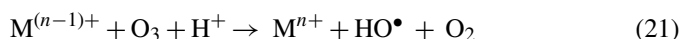
Based on the suggestions of Rakitskaya et al. [16], this study proposes possible reaction mechanisms of O$_3$/Co(II) and O$_3$/Ni(II) systems in Eqs. (23)–(25). However, to our knowledge, no satisfactory hypothesis concerning the mechanism in the O$_3$/Zn(II) system has been presented. Hence, the details of the mechanisms for O$_3$/Zn(II) system remain unknown.

$$Co^{2+}/Ni^{2+} + O_3 + H_2O$$
$$\rightarrow Co(OH)^{2+}/Ni(OH)^{2+} + O_2 + HO^\bullet \tag{23}$$

$$HO^\bullet + O_3 \rightarrow HO_2^\bullet + O_2 \tag{24}$$

$$HO_2^\bullet + Co(OH)^{2+}/Ni(OH)^{2+} \rightarrow Co^{2+}/Ni^{2+} + H_2O + O_2 \tag{25}$$
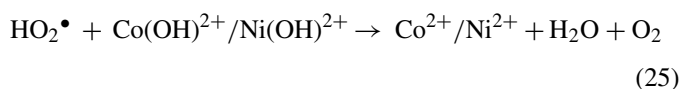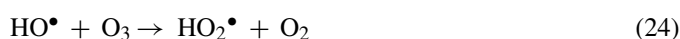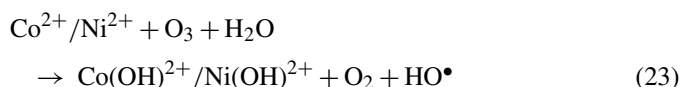
Table 2
Effects of pH on pseudo-first-order decolorization rate constant (k, min^{-1}) in ozone-based systems (metallic ion = 0.6 mM)

Systems	pH 2		pH 5	
	k	r^2	k	r^2
O_3	0.481	0.962	0.532	0.960
O_3/Mn(II)	3.295	0.987	0.666	0.940
O_3/Fe(II)	1.299	0.986	1.046	0.991
O_3/Fe(III)	1.278	0.991	1.657	0.898
O_3/Zn(II)	1.015	0.993	0.683	0.982
O_3/Co(II)	0.843	0.995	0.682	0.951
O_3/Ni(II)	0.822	0.996	0.701	0.974

3.2. Comparisons of various metal-catalyzed ozonation systems

The pH effects of various metal-catalyzed ozonation systems were evaluated with the addition of 0.6 mM catalyst. Table 2 demonstrates the effects of pH on k for various ozone-based systems. The k values at pH 2 and pH 5 in ozone alone were 0.481 and 0.532 min^{-1}, respectively. When ozonation was conducted at pH 2, the decomposition of ozone was too weak and the formation of hydroxyl radicals was therefore limited. At a higher pH, $HO_2{}^{\bullet}$ was generated from the reaction between O_3 and OH^-, accelerating the production of $HO^{\bullet}$, and $HO^{\bullet}$ which was more active than molecular ozone (Eqs (1)–(3)). Therefore, the k value at pH 5 exceeded that at pH 2 in the O_3 system (Table 2). Catalytic decomposition depends substantially on the
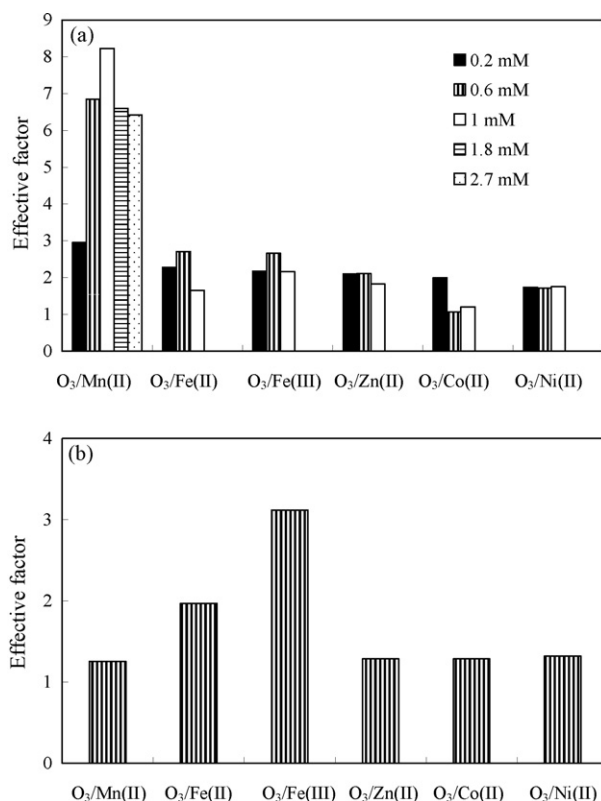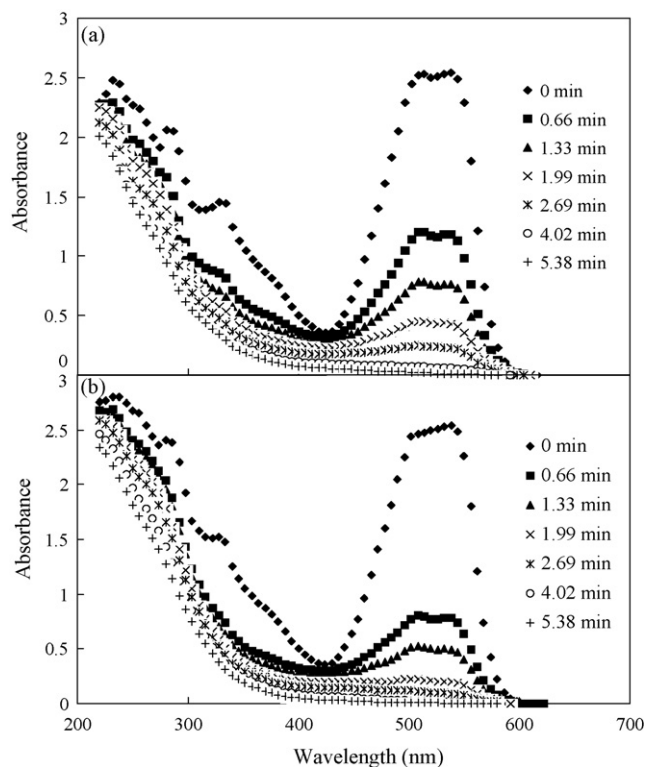

Fig. 3. UV–vis spectral changes of RR2 (a) O_3 and (b) O_3/Fe(III) (RR2 = 100 mg/l, Fe(III) = 0.6 mM and initial pH 2).

pH value. Typically, at pH < 4, direct ozonation dominates; in the range pH 4–9, both are important, and above pH > 9 the indirect pathway dominates [30]. In ozonation alone, as the solution becomes more acidic, the decolorization rate declines markedly. However, in metal-catalyzed ozonation, the situation reversed, such that decolorization was better at pH 2 than at pH 5 except in the O_3/Fe(III) system (Table 2). At pH 5, insoluble iron hydroxides (Fe(OH)$_3$) precipitated when the concentration of Fe(III) exceeded 2.79×10^{-12} M. When 0.6 mM Fe(III) was added, Fe(OH)$_3$ precipitated and acted as a coagulant. Hence,
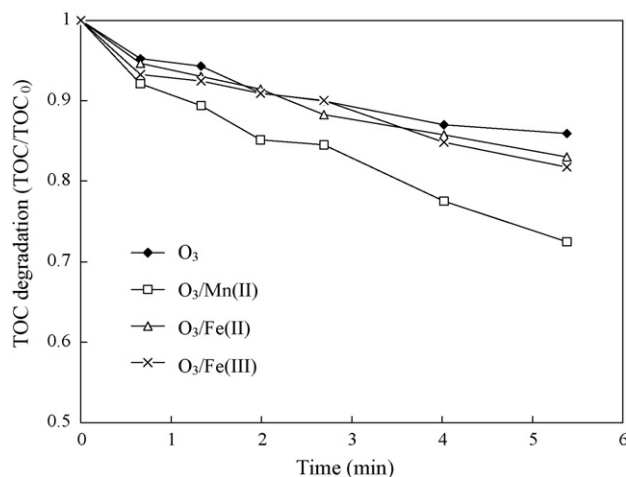

Fig. 2. Comparisons of effective factors in catalytic ozonation systems (a) pH 2 and (b) pH 5 (RR2 = 100 mg/l).

Fig. 4. Comparisons of TOC removals in O_3, O_3/Mn(II), O_3/Fe(II) and O_3/Fe(III) systems (RR2 = 100 mg/l, metallic ion = 0.6 mM and initial pH 2).

the decolorization efficiency at pH 5 exceeded that at pH 2 in the O$_3$/Fe(III) system.

The effective factor was defined herein as (k value in catalytic ozonation)/(k value in ozonation alone). Fig. 2 compares the effective factor in catalytic ozonation systems at different pH. At pH 2, the effective factor was in the range 1.1–8.2 (Fig. 2(a)); and at pH 5, the effective factor was in the range 1.3–3.1 (Fig. 2(b)). The enhancement of catalytic ozonation was more significant at pH 2 than at pH 5. Ni et al. [8] revealed that the rate of improvement of catalytic ozonation at the initial pH 3 clearly exceeds that at pH 7 or pH 9. Moreover, O$_3$/Mn(II) and O$_3$/Fe(III) were associated with the highest effective factor at pH 2 and pH 5, respectively. When 0.6 mM catalyst was added, the effective factors at pH 2 followed the order Mn(II) > Fe(II) ≥ Fe(III) > Zn(II) > Ni(II) > Co(II) and those at pH 5 followed the order Fe(III) > Fe(II) > Ni(II) ≥ Zn(II) ≥ Co(II) ≥ Mn(II). El-Raady et al. [12] stated that the order of catalytic efficiencies of metallic ions in ozonation followed the order Mn(II) > Co(II) > Fe(II). Other studies have proposed other orders, such as Mn(II) > Fe(II) > Zn(II) [8],

Fe(II) > Mn(II) > Zn(II) > Ni(II) [10], Co(II) > Mn(II) [11] and Co(II) > Ni(II) ≥ Fe(II) > Mn(II) [13]. A particular catalyst is active only under specific conditions and in the oxidation of a particular group of organic compounds [31]. Based on the experimental results for pH and metallic ion dosage, this study suggests that ozone decomposition rates depend strongly on the concentration of the catalyst and the pH. Trapido et al. [13] also indicated that a particular catalyst is active only under certain conditions of pH, ozone-to-catalyst ratio, amount of by-products in solution and surface area of the catalyst.

Fig. 3(a) and (b) displays the UV–vis spectral changes of RR2 at pH 2 in O$_3$ and O$_3$/Fe(III), respectively. Before treatment, the UV–vis spectra of RR2 have three main absorption bands—two in the UV region (285 and 330 nm) and one in the visible region (538 nm). The UV band is characteristic of two adjacent rings, whereas the visible band is associated with a long conjugated π system that is linked by two azo groups [32]. After 4 min of reaction, the intensity of absorption at 538 nm declines extremely rapidly from 2.54 to 0.06 in O$_3$ alone and from 2.54 to 0.01 in O$_3$/Fe(III). The UV bands at 285 nm and
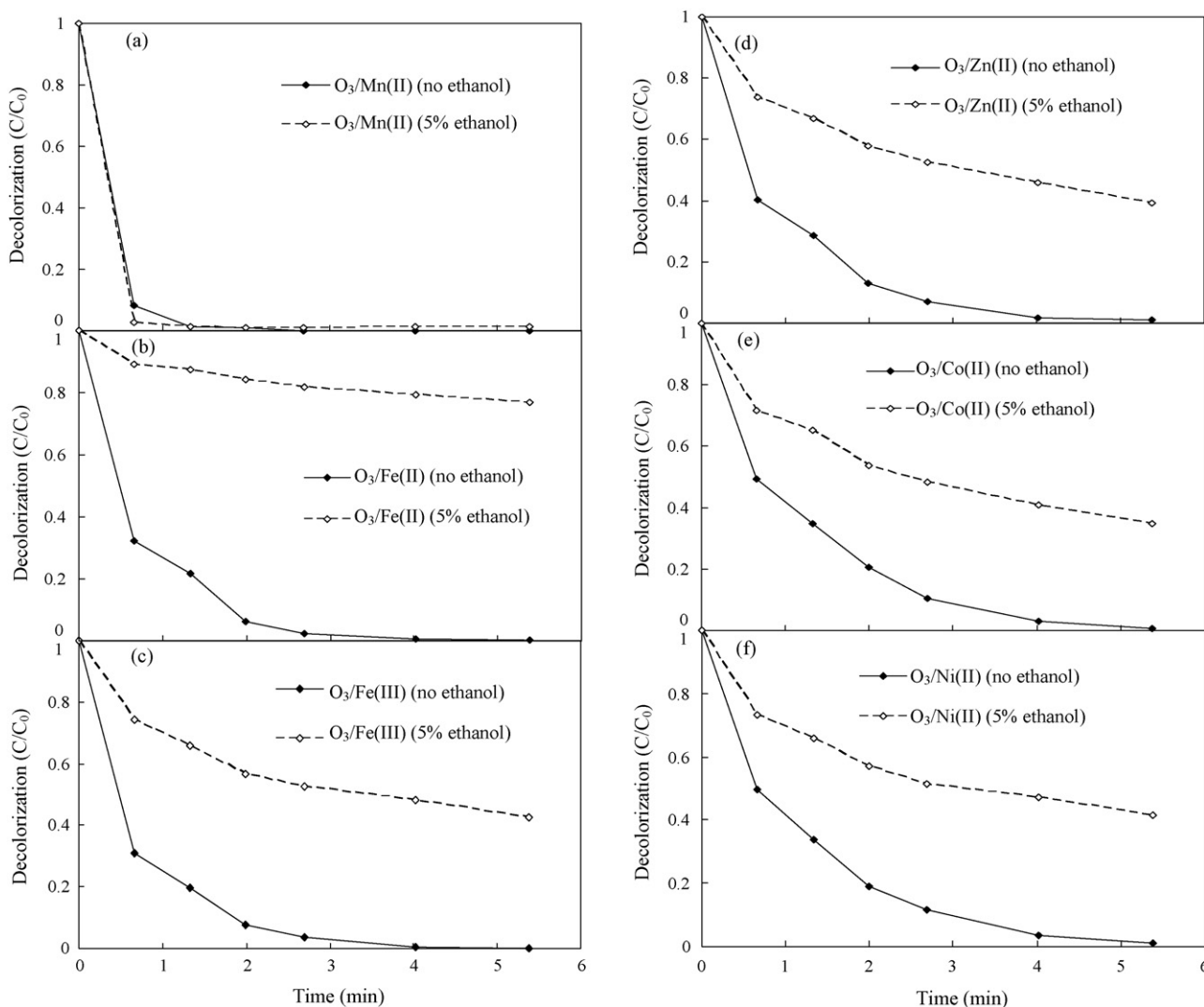

Fig. 5. Effects of ethanol addition in catalytic ozonation systems (a) O$_3$/Mn(II), (b) O$_3$/Fe(II), (c) O$_3$/Fe(III), (d) O$_3$/Zn(II), (e) O$_3$/Co(II) and (f) O$_3$/Ni(II) (RR2 = 100 mg/l, ethanol = 5% (v/v), metallic ion = 0.6 mM and initial pH 2).

330 nm disappeared after 4 min of reaction at a slower rate than did the visible band in the O_3 and O_3/Fe(III) systems. The experimental results imply that the N=N bonds more easily destroyed than aromatic structures. Lucas and Peres [33] obtained a similar result for Reactive Black 5 in a photo-Fenton system.

Since adding Mn(II), Fe(II) and Fe(III) markedly promoted RR2 decolorization at pH 2, only these metal-catalyzed ozonation systems determined the TOC removal efficiency. After 4 min of reaction, the TOC removal efficiencies of O_3, O_3/Mn(II), O_3/Fe(II) and O_3/Fe(III) were 13%, 23%, 14% and 16%, respectively (Fig. 4). Additionally, the TOC removal rates of O_3, O_3/Mn(II), O_3/Fe(II) and O_3/Fe(III) were 0.034, 0.064, 0.039 and 0.041 min^{-1}, respectively (Table 1). The O_3/Mn(II) system exhibited the highest decolorization and TOC removal rates. The decolorization rate markedly exceeded the TOC removal rate in all tested systems, and the extents of TOC removal did not vary significantly among the O_3, O_3/Fe(II) and O_3/Fe(III) systems. In the mineralization of RR2, the triazine ring of RR2 was converted to cyanuric acid, which was very stable [19]. Arslan [34] also showed that no significant TOC reduction occurred in the ozonation or the catalytic ozonation system for dispersed dye-bath effluent. This study suggests that metal-catalyzed ozonation systems can complete decolorization for RR2; however, a reduction in the color does not necessarily imply a reduction in TOC.

Fig. 5 depicts the effects of adding ethanol in catalytic ozonation systems. Ethanol is known to react with hydroxyl radicals faster ($k_{\text{ethanol, hydroxyl}} = 1.7\text{--}2.2 \times 10^9 \, M^{-1} \, s^{-1}$) than at other organic compounds [35]. Accordingly, ethanol was selected as the scavenger for hydroxyl radicals. If the catalytic ozonation was to proceed by the hydroxyl radical reaction mechanism, then the presence of ethanol would rapidly consume hydroxyl radicals and reduce the decolorization rate. Previous works have shown that ethanol quenches hydroxyl radicals, reducing the photodegradation rate [18,36–38]. The decolorization rates of 5% ethanol addition in O_3/Fe(II), O_3/Fe(III), O_3/Zn(II), O_3/Co(II) and O_3/Ni(II) were 0.060, 0.191, 0.201, 0.227 and 0.195 min^{-1}, respectively. Adding ethanol substantially reduced the decolorization rate except in the O_3/Mn(II) system. Based on the experimental results, hydroxyl radicals may be assumed not to be the dominating active species in catalytic O_3/Mn(II) ozonation, because the effect of adding ethanol was negligible. This study suggests that Eqs. (6) and (9) were the primary reaction pathways and Mn^{7+} and Mn^{3+} were the major oxidants in the O_3/Mn(II) system. The experimental findings imply that the hydroxyl radicals participate importantly in decolorization in O_3/Fe(II), O_3/Fe(III), O_3/Zn(II), O_3/Co(II) and O_3/Ni(II) systems. However, decolorization is not completely prevented by adding 5% ethanol. This experimental result suggests that another reactive species, which does not react with ethanol, participates in the decolorization. This species is most likely molecular ozone that was involved in direct ozonation in catalytic ozonation systems. Sanchez-Polo and Rivera-Utrilla [10] presented the degradation of 1,3,6-naphthalenetrisulfonic acid in a metal-catalyzed ozonation system by a radical mechanism, while catalytic ozonation by Mn(II) proceeded mainly

by the mechanism of "active sites" [9]. No clear conclusion has yet been drawn regarding the catalytic oxidation mechanism. The effect of the radical scavenger on the catalytic ozonation processes herein suggests that the decolorization reaction in metal-catalyzed ozonation systems, except the O_3/Mn(II) system, involved mainly radical-type mechanisms.

4. Conclusion

This study employed Mn(II), Fe(II), Fe(III), Zn(II), Co(II) and Ni(II) ions to catalyze ozonation. The experimental results revealed that these metallic ions can increase the efficiency of ozone in RR2 decolorization. In ozonation alone, as the solution becomes more acidic, the decolorization rate declines markedly. However, in metal-catalyzed ozonation, the situation was reversed: decolorization was better at pH 2 than at pH 5, except in the O_3/Fe(III) system. When 0.6 mM catalyst was added, the effective factors at pH 2 followed the order Mn(II) > Fe(II) ≥ Fe(III) > Zn(II) > Ni(II) > Co(II) and those at pH 5 followed the order Fe(III) > Fe(II) > Ni(II) ≥ Zn(II) ≥ Co(II) ≥ Mn(II). Based on the experimental results for pH and metallic ion dosage, this investigation suggests that ozone decomposition rates depend strongly on the catalyst concentration and the pH. This work indicated that the metal-catalyzed ozonation systems can complete decolorization for RR2; however, the diminution of the color does not necessarily imply a reduction in TOC. The experimental findings concerning the radical scavenger indicate that the hydroxyl radicals participate importantly in decolorization in O_3/Fe(II), O_3/Fe(III), O_3/Zn(II), O_3/Co(II) and O_3/Ni(II) systems.

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