

Decolorization of C.I. Reactive Red 2 by catalytic ozonation processes

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Abstract

This study adopted O₃, UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems to assess the decolorization efficiency of C.I. Reactive Red 2 (RR2). The decolorization rate increased with concentrations of Mn(II) and MnO₂ in the ranges 0.05–0.1 and 0.05–0.8 g/l, respectively. However, when 0.5–3 g/l TiO₂ was added, the effect of TiO₂ dosage for RR2 decolorization was insignificant in the UV/TiO₂/O₃ system. At pH 2, the decolorization rate constants of O₃, O₃/Mn(II) (0.05 g/l), O₃/Mn(II) (0.1 g/l), O₃/Mn(II) (0.15 g/l), O₃/MnO₂ (0.05 g/l) and O₃/MnO₂ (0.8 g/l) were 0.816, 2.001, 3.173, 3.087, 1.040 and 1.648 min⁻¹, respectively. After 5 min of reaction, the decolorization rates followed the order O₃/Mn(II) > O₃/MnO₂ > O₃ > UV/TiO₂/O₃; however, the TOC removal did not vary among these systems. Adding ethanol reduced the decolorization rate of the UV/TiO₂/O₃ and O₃/MnO₂ systems and did not affect the decolorization rate of O₃/Mn(II). Decolorization in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems is suggested to proceed by mainly radical-, surface- and radical-type mechanisms, respectively. Additionally, direct ozonation cannot be ignored in O₃/Mn(II) and O₃/MnO₂ systems.

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1. Introduction

Azo dyes are the most widely used dyes and are normally major pollutants in dye effluents. The textile and dyestuff industries are the main sources of dyes that are released to the environment. Because 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. Conventional treatment cannot efficiently remove dyes from textile wastewater, because they are stable against light and biological degradation. Such treatments as adsorption, flotation and coagulation only alter the phases of pollutants but do not destroy them. Advanced oxidation processes (AOPs) are alternative methods for decolorizing and reducing recalcitrant wastewater loads that are generated by textile companies. Considerable progress has been made in the development of AOPs for textile effluent in recent years, especially in ozone-related processes [1–8]. Ozonation has excellent

potential in decolorization for the following reasons. (i) Decolorization and degradation occur in one step; (ii) danger to humans is minimal; (iii) no sludge remains; (iv) all residual ozone can be decomposed easily into oxygen and water; (v) little space is required and (vi) ozonation is easily performed [9].

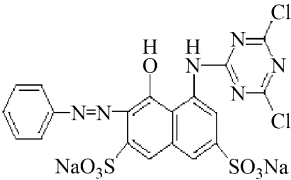
Ozone oxidizes organics through two possible degradation routes; (i) at basic pH, it decomposes rapidly to yield hydroxyl and other radical species in solution, according to Eqs. (1)–(3), and (ii) at acidic pH, ozone is stable and can react directly with organic substrates [10]. UV radiation can decompose ozone in water, generating highly reactive hydroxyl radicals [4]. The hydroxyl radicals are known to be powerful oxidizing agents and oxidize organics more rapidly than ozone itself. The effects of dye concentration [2,8], ozone dose [1,2], pH [2,6,8], the presence or absence of UV [4,8] and UV intensity [4] in ozone-based systems have been evaluated.



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Table 1
Structure and characteristics of RR2 (Wu and Chang [8])

Structure	Formula	Molecular weight (g/mol)	λ_{\max} (nm)
	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$	615	538

Combining various AOPs commonly produces interesting synergistic effects that can significantly reduce the reaction time. Various studies have explored the synergistic effects of the decolorization of dyes in ozone-based systems, such as O_3/H_2O_2 [3], O_3/Fe^{2+} [7], $UV/O_3/H_2O_2$ [5] and $UV/TiO_2/O_3$ [5,6]. Metal-catalyzed ozonation is effective in organic degradation. In some catalytic ozonation systems, such as O_3/Mn^{2+} [11–21], O_3/Co^{2+} [18–21], O_3/MnO_x /granular activated carbon (GAC) [22,23], O_3/MnO_2 [8,14,20,24–26,28] and $UV/TiO_2/O_3$ [5,6,29–34], the degradation efficiency of organics exceeds ozone alone. Radical-type mechanisms [12,13,15,17,22,34] or surface-type mechanisms [14,16,23,24,28,33] are responsible for this increased efficiency. The performance of catalytic ozonation depends strongly on the compound. A particular catalyst is active only under certain conditions of pH, ozone to catalyst ratio, temperature and species of by-products in solution [20]. Accordingly, more work must be undertaken with a variety of pollutants and different catalysts. Although the aforementioned catalysts were extensively investigated to elucidate their capacity to destroy various pollutants, their effectiveness in decolorization has been seldom examined for azo dyes. Furthermore, the efficiencies of O_3 , $UV/TiO_2/O_3$, $O_3/Mn(II)$ and O_3/MnO_2 in decolorizing dyes from wastewater have still not been clearly compared. Hence, in this work, homogeneous ($O_3/Mn(II)$) and heterogeneous (O_3/MnO_2 and $UV/TiO_2/O_3$) catalytic ozonation systems were employed to decolorize the C.I. Reactive Red 2 (RR2). The objectives of this investigation were (i) to determine the dosage effects of TiO_2 , $Mn(II)$ and MnO_2 in $UV/TiO_2/O_3$, $O_3/Mn(II)$ and O_3/MnO_2 systems, respectively; (ii) to compare the effectiveness of decolorization for RR2 in $UV/TiO_2/O_3$; $O_3/Mn(II)$ and O_3/MnO_2 systems and (iii) to propose possible reaction pathways for $UV/TiO_2/O_3$, $O_3/Mn(II)$ and O_3/MnO_2 systems.

2. Materials and method

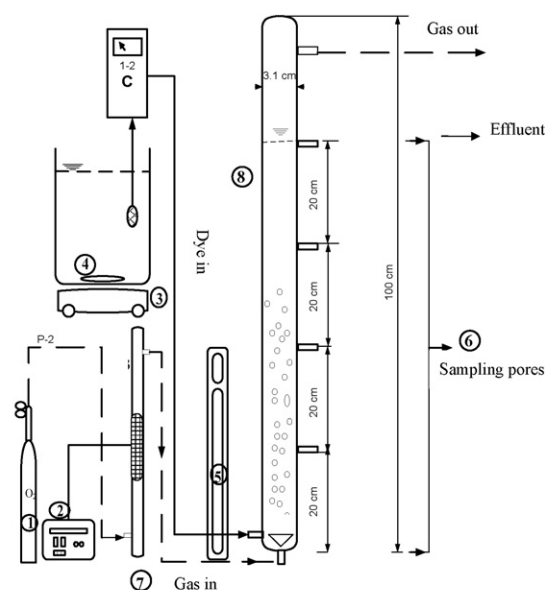
2.1. Materials

Parent compound RR2 was obtained from Aldrich and used without further purification. The structure and characteristics of RR2 was presented in Table 1. In heterogeneous catalytic ozonation experiments, MnO_2 and TiO_2 P25 were purchased from Merck and Degussa, respectively. The mean particle size and specific surface area of TiO_2 was 24 nm and $54.2\text{ m}^2/\text{g}$ [35] and that of MnO_2 was $48\ \mu\text{m}$ and $29.3\text{ m}^2/\text{g}$ [36], respectively. In homogeneous catalytic ozonation experiments, $MnSO_4 \cdot H_2O$,

obtained from Aldrich, was the source of $Mn(II)$. The pH of the solution was adjusted using H_3PO_4 (J.T. Baker) and $NaOH$ (Merck). In inhibition experiments, ethanol (C_2H_5OH), obtained from Merck, was adopted as the radical scavenger. All experimental chemicals were of analytical grade. The source of irradiation in the $UV/TiO_2/O_3$ system was a 10 W, 365 nm UVA-lamp (Philips). A dielectric barrier discharge (DBD) reactor was utilized to generate ozone. The DBD reactor, which consumed 10 W of power at a gas flow rate of 200 ml/min, was used to perform 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 [8].

2.2. Catalytic ozonation experiments

Catalytic ozonation experiments were conducted in a bubble-column reactor, which is a cylindrical quartz reactor (100 cm in height and 3.1 cm in diameter). Fig. 1 schematically depicts



1. oxygen cylinder
2. power supply
3. mixer
4. magnetic bar-stirrer
5. UV light
6. sampling point
7. dielectric barrier discharge (DBD) reactor
8. ozonation reactor

Fig. 1. Schematic diagram of catalytic ozonation apparatus.

the catalytic ozonation apparatus. 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 dye concentration in each experiment was 100 mg/l and the pH was adjusted in the initial reaction. The dosage of TiO_2 was controlled at 0.5, 1, 2 and 3 g/l; that of Mn(II) was kept at 0.05, 0.1 and 0.15 g/l, and that of MnO_2 was maintained at 0.05 and 0.8 g/l, to elucidate the effects of the TiO_2 , Mn(II) and MnO_2 doses in catalytic ozonation. Since Andreozzi et al. [26] revealed that using heterogeneous catalytic MnO_2 particles or dissolved Mn ions helped promote the reaction at pH 2.0 to 4.0, pH was maintained at 2.0 herein to perform $\text{O}_3/\text{Mn(II)}$ and O_3/MnO_2 catalytic ozonation experiments. Experiments on $\text{UV}/\text{TiO}_2/\text{O}_3$ system were performed at the solution initial pH (pH = 6.9). In radical scavenging experiments, ethanol (5%, v/v) was added to $\text{UV}/\text{TiO}_2/\text{O}_3$, $\text{O}_3/\text{Mn(II)}$ and O_3/MnO_2 systems. 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 (cellulose nitrate, Millipore). 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), using an O.I. 1010 TOC analyzer.

3. Results and discussion

3.1. O_3 , UV/TiO_2 and $\text{UV}/\text{TiO}_2/\text{O}_3$ systems

Fig. 2 plots the decolorization efficiency of O_3 , UV/TiO_2 and $\text{UV}/\text{TiO}_2/\text{O}_3$ systems. The reaction time is very short; consequently, decolorization efficiency of UV/TiO_2 is insignificant (Fig. 2a). Experimental data (Fig. 2a) indicates that the difference in RR2 decolorization efficiency between O_3 and $\text{UV}/\text{TiO}_2/\text{O}_3$ was insignificant. Fig. 2b plots the regression of first-order kinetics. The correlation coefficients are regarded as an index of the goodness-of-fit to the first-order kinetics; the r^2 values for RR2 in O_3 , UV/TiO_2 and $\text{UV}/\text{TiO}_2/\text{O}_3$ systems are typically ≥ 0.980 (Table 2). As has been reported elsewhere for dye decolorization [5,8,37], reaction rates (k) followed first-order kinetics. The decolorization rate constants follow the order $\text{O}_3 \geq \text{UV}/\text{TiO}_2$ (1 g/l)/ $\text{O}_3 > \text{UV}/\text{TiO}_2$ (2 g/l)/ $\text{O}_3 \geq \text{UV}/\text{TiO}_2$ (3 g/l)/ $\text{O}_3 > \text{UV}/\text{TiO}_2$ (0.5 g/l)/ $\text{O}_3 > \text{UV}/\text{TiO}_2$ (0.5 g/l). In the $\text{UV}/\text{TiO}_2/\text{O}_3$ system, the decolorization rate increased with TiO_2 dose to a maximum value, before decreasing as the dosage was increased further. Numerous studies [29,30,32] have proposed possible reaction pathways for $\text{UV}/\text{TiO}_2/\text{O}_3$ system (Eqs. (4)–(9)). Hernandez-Alonso et al. [30] found that ozone strongly interacts with TiO_2 , leading mainly to the formation of ozonide radicals ($\text{O}_3^{\bullet-}$). Ozone can generate hydroxyl radicals on the TiO_2 surface via the formation of an ozonide radical [29]. The production of hydroxyl radicals on the irradiated surface of TiO_2 is more effective in the presence of ozone than in oxygen [31] since ozone can trap photogenerated electrons and suppress the recombination of

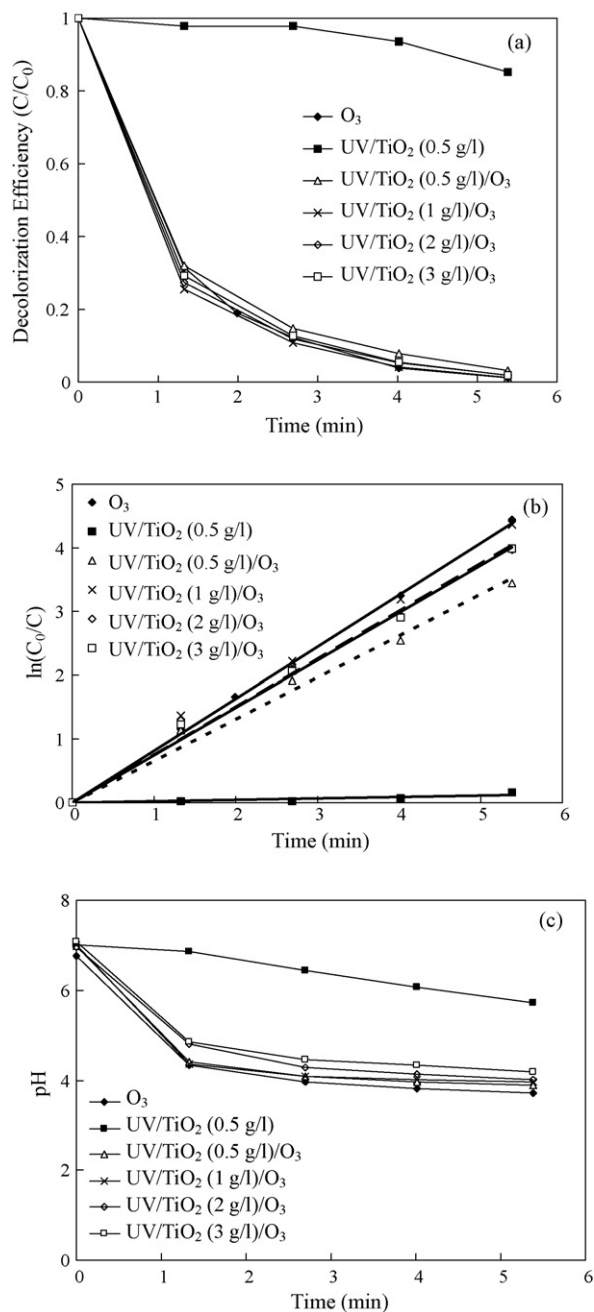


Fig. 2. Effects of TiO_2 dosage in $\text{UV}/\text{TiO}_2/\text{O}_3$ system on (a) decolorization efficiency, (b) first-order kinetics regression and (c) pH variation (RR2 = 100 mg/l and initial pH = 6.9).

photogenerated electrons and holes. Therefore, the yield of hydroxyl radicals is increased, improving the decolorization efficiency. However, adding a large amount of TiO_2 reduces UV penetration and has a UV-screening effect. Therefore, the yield of photogenerated holes and hydroxyl radicals declines, reducing the decolorization rate. Trapido et al. [20] indicated that a particular catalyst is active only under certain conditions of pH, ozone to catalyst ratio, amount of by-products in solution and the surface area of the catalyst. Yang et al. [34] stated that the increase of the TiO_2 dose did not significantly increase the oxidation rate in a catalytic ozonation system. The experimental

Table 2

First-order reaction rate constants (k) and correlation coefficients (r^2) for various ozone-based systems

Systems	k (min ⁻¹)	r^2
O ₃ = 10 W and pH = 6.9		
O ₃	0.817	0.998
UV/TiO ₂ (0.5 g/l)/O ₃	0.655	0.984
UV/TiO ₂ (1 g/l)/O ₃	0.815	0.992
UV/TiO ₂ (2 g/l)/O ₃	0.751	0.988
UV/TiO ₂ (3 g/l)/O ₃	0.745	0.993
O ₃ = 10 W and pH = 2		
O ₃	0.816	0.985
O ₃ /Mn(II) (0.05 g/l)	2.001	0.956
O ₃ /Mn(II) (0.1 g/l)	3.173	0.947
O ₃ /Mn(II) (0.15 g/l)	3.087	0.882
O ₃ /MnO ₂ (0.05 g/l)	1.040	0.997
O ₃ /MnO ₂ (0.8 g/l)	1.648	0.989

results indicated that the synergistic effect was not observed in 0.5–3 g/l TiO₂ adding in UV/TiO₂/O₃ system.

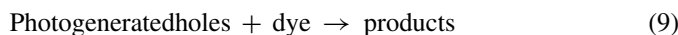
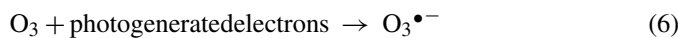
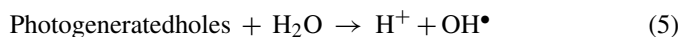
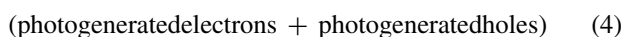
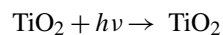


Fig. 2c plots the pH variations during decolorization process. In O₃, UV/TiO₂ and UV/TiO₂/O₃ systems, the pH of the solutions decreased during the decolorization of RR2. The most important contribution to the decline in pH during decolorization is the generation of acidic intermediates or final products. The major intermediates of azo dyes in a UV/TiO₂ system were organic aromatic and aliphatic carboxylic acids [37,38], which reduce pH. Koch et al. [1] degraded azo dye in an ozone system and identified the main oxidation products as sulfate, nitrate, formate and oxalate. These products were responsible for the drop in pH.

3.2. O₃/Mn(II) and O₃/MnO₂ systems

Figs. 3 and 4 demonstrate the effects of Mn(II) and MnO₂ concentrations in O₃/Mn(II) and O₃/MnO₂ systems, respectively. At pH 2, the k values of O₃, O₃/Mn(II) (0.05 g/l), O₃/Mn(II) (0.1 g/l), O₃/Mn(II) (0.15 g/l), O₃/MnO₂ (0.05 g/l) and O₃/MnO₂ (0.8 g/l) were 0.816, 2.001, 3.173, 3.087, 1.040 and 1.648 min⁻¹, respectively (Table 2). In O₃/Mn(II) systems, the k values increased with the Mn(II) concentration in the range 0.05–0.1 g/l and then decreased as the Mn(II) concentration increased further (Fig. 3). Ma and Graham [13] also reported that the optimal value of Mn(II) concentration for the degradation of atrazine was in the range 0.3–0.6 mg/l; the extent of

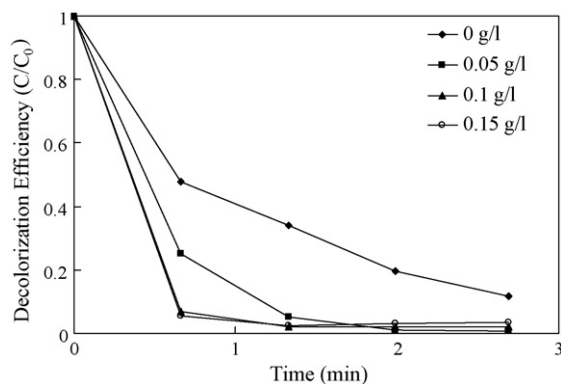


Fig. 3. Effect of Mn(II) dosage in O₃/Mn(II) system (RR2 = 100 mg/l and initial pH = 2).

degradation varied slightly in this range and declined above a concentration of 0.6 mg/l. In a previous study, 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 citric acid; however, further increasing the Mn(II) concentration had no significant effect [19]. In O₃/MnO₂ systems, the k values increased with the MnO₂ concentration in the range 0.05–0.8 g/l (Fig. 4). Andreozzi et al. [24] presented a similar result in the range 0–0.2 g/l for oxalic acid in the O₃/MnO₂ system. In both O₃/Mn(II) and O₃/MnO₂ systems, the decolorization rate exceeded that of ozone alone. Additionally, the decolorization rate of O₃/Mn(II) exceeded that of O₃/MnO₂. Several studies also established that the O₃/Mn(II) was more effective in degrading organics than O₃/MnO₂ [11,12,14,28]. Various works have also demonstrated that Mn(II) [11–21] and MnO₂ [8,14,20,24–28] catalytic ozonation was more effective in degrading organics than ozone alone. This study summarizes the suggestions made in previous works and proposed possible reaction pathways for O₃/Mn(II) (Eqs. (10)–(15)) [15,18,26,39] and O₃/MnO₂ systems (Eqs. (16)–(20)) [15–17,40].

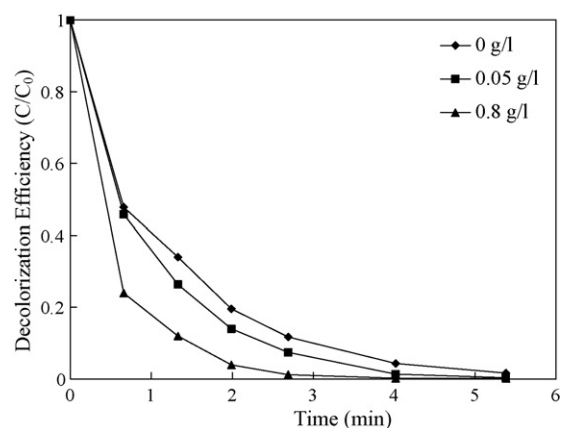
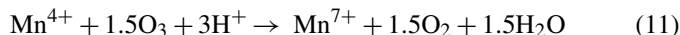
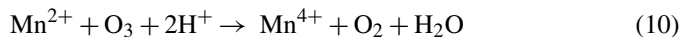
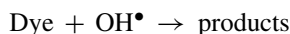
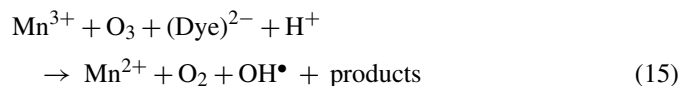
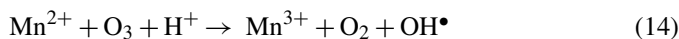
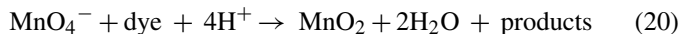
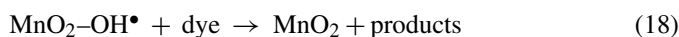
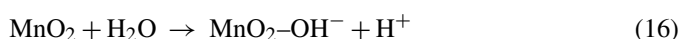


Fig. 4. Effect of MnO₂ dosage in O₃/MnO₂ system (RR2 = 100 mg/l and initial pH = 2).



Mn(II) can react with O₃ to produce hydrous manganese oxide (Mn(OH)₂) in situ, which subsequently attacks the pollutant molecules and accelerates degradation [11]. Legube and Leitner [39] suggested that Mn(II)-catalyzed oxidation proceeds via complexing between the pollutant and Mn(III), forming an intermediate product which may be easily oxidized by ozone. Ozone reoxidizes the Mn(II) to Mn(III, IV). Ma and Graham [12] claimed that ozone reacts with the MnO₂ surface-bound OH⁻ ions, inducing the production of hydroxyl radicals on the surface of MnO₂. Like the hydroxyl radicals, MnO₄⁻ is also a decolorization agent in the O₃/MnO₂ system.



3.3. Comparisons of UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems

Fig. 5 displays the UV–vis spectral changes of RR2 in O₃, UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems (RR2=100 mg/l, TiO₂=0.5 g/l, Mn(II)=0.1 g/l, MnO₂=0.8 g/l, reaction time=1.33 min and the initial pH of UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems was 6.9, 2 and 2, respectively).

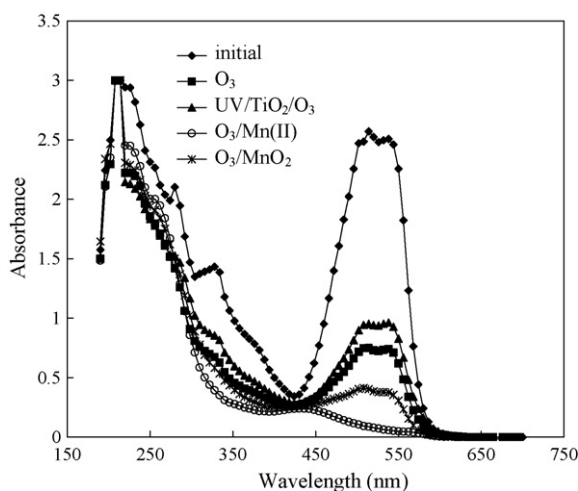


Fig. 5. UV–vis spectral changes of RR2 in O₃, UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems (RR2=100 mg/l, TiO₂=0.5 g/l, Mn(II)=0.1 g/l, MnO₂=0.8 g/l, reaction time=1.33 min and the initial pH of UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems was 6.9, 2 and 2, respectively).

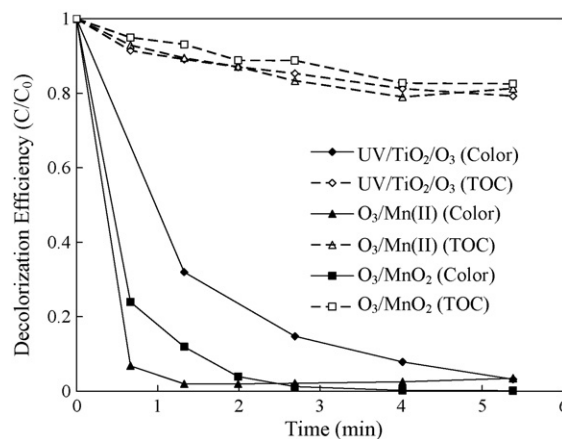


Fig. 6. Comparisons of decolorization and TOC removal in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems (RR2=100 mg/l, TiO₂=0.5 g/l, Mn(II)=0.1 g/l, MnO₂=0.8 g/l and the initial pH of UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems was 6.9, 2 and 2, respectively).

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 [41]. For all of the systems tested herein, the intensity of absorption at 538 nm declines extremely rapidly; however, the UV bands at 285 nm and 330 nm disappeared more slowly than did the visible band. The disappearance efficiency of the visible band is approximately double that of the UV band. The hydroxyl radicals and oxidizing agents initially attack azo groups and open the N=N bonds (Fig. 5); the N=N bonds are more easily destroyed than are aromatic structures. Lucas and Peres [42] obtained a similar result for Reactive Black 5 in a photo-Fenton system.

Fig. 6 compares the decolorization and TOC removal in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems. The decolorization rate substantially exceeds the TOC removal rate. Despite RR2 was over 95% decolorized, the TOC removal efficiency was 17–21% in all experiments. After 5 min of reaction, the order of decolorization rates was O₃/Mn(II) > O₃/MnO₂ > UV/TiO₂/O₃, but the extents of TOC removal did not vary significantly among these systems. In the mineralization of RR2, the triazine ring of RR2 was converted to cyanuric acid, which was very stable as reported by Hu et al. [37]. The experimental results reveal that the mineralization of RR2 was incomplete in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems. This study suggests that the rapid decolorization of the dye was followed by a much slower mineralization of the subsequently formed intermediates. Although this investigation did not identify these intermediates, Hu et al. [37] and So et al. [43] indicated that the intermediates after the decolorization of the solution of RR2 that generated in photocatalytic degradation were not toxic.

Fig. 7 depicts the effects of C₂H₅OH addition in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems. Ethanol reacts with hydroxyl radicals, producing intermediates, terminating the radical chain reaction. If the catalytic ozonation were to proceed by the hydroxyl radical reaction mechanism, then the presence of ethanol would rapidly consume hydroxyl radicals

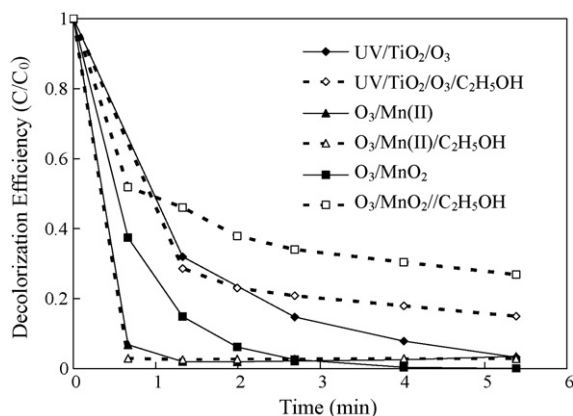


Fig. 7. Effects of C_2H_5OH addition in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems (RR2 = 100 mg/l, TiO₂ = 0.5 g/l, Mn(II) = 0.1 g/l, MnO₂ = 0.8 g/l, C₂H₅OH = 5% (v/v) and the initial pH of UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems was 6.9, 2 and 2, respectively).

and reduce the decolorization. Previous studies have shown that ethanol quenches hydroxyl radicals, reducing the photodegradation rate [44,45]. Based on the experimental results, hydroxyl radicals may be assumed not to be the dominating active species in the catalytic O₃/Mn(II) ozonation process because the effect of adding ethanol was negligible. This work suggests that Eqs. (12) and (15) were the primary reaction pathways and Mn⁷⁺ and Mn³⁺ were the major oxidants in O₃/Mn(II) system. Notably, adding ethanol reduced the decolorization rate in the UV/TiO₂/O₃ and O₃/MnO₂ systems (Fig. 7). The k values of UV/TiO₂/O₃ when no ethanol was added and when 5% ethanol was added were 0.655 and 0.514 min⁻¹, respectively, and those of O₃/MnO₂ was 1.648 and 0.666 min⁻¹, respectively. The experimental findings imply that the hydroxyl radicals are importantly involved in decolorization in UV/TiO₂/O₃ and O₃/MnO₂ 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 the photogenerated holes that are produced on irradiated TiO₂ in the UV/TiO₂/O₃ system and MnO₄⁻ in the O₃/MnO₂ systems. Moreover, direct ozonation cannot be ignored in O₃/Mn(II) and O₃/MnO₂ systems. The inhibiting effect of adding ethanol reveals that the primary decolorization pathway involves hydroxyl radicals, and that the direct oxidation by photogenerated holes is probably not negligible in the UV/TiO₂/O₃ system. Numerous studies have presented similar results for TiO₂-based systems [43,44]. This work concludes that the primary oxidants in UV/TiO₂/O₃ and O₃/MnO₂ systems was hydroxyl radicals (Eq. (8)) and MnO₂-OH• (Eq. (18)), respectively; the minor oxidants were photogenerated holes (Eq. (9)) and MnO₄⁻ (Eq. (20)), respectively. Ma and Graham [12] proposed that the Mn-catalyzed ozonation of atrazine follows a radical-type mechanism. In contrast, Ma et al. [23] assumed that the hydroxyl radicals might not be the dominating active species in the MnO_x/GAC catalytic ozonation of nitrobenzene. No clear conclusions have yet been drawn concerning the catalytic oxidation mechanism. The effect of the radical scavenger on the

catalytic ozonation processes suggests that the decolorization reaction in UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems proceeds by mainly radical-, surface- and radical-type mechanisms, respectively.

4. Conclusion

In this investigation, homogeneous (O₃/Mn(II)) and heterogeneous (O₃/MnO₂ and UV/TiO₂/O₃) catalytic ozonation systems were employed to decolorize RR2. This study determined the dosage effects of TiO₂, Mn(II) and MnO₂ on RR2 decolorization. In the UV/TiO₂/O₃ system, the decolorization rate increased with a TiO₂ dosage of 0.5–1 g/l and declined as the dosage increased. In O₃/Mn(II) system, the RR2 decolorization rate increased with a Mn(II) concentration of 0.05–0.1 g/l; moreover, this effect was observed in 0.05–0.8 g/l MnO₂ addition to the O₃/MnO₂ system. Experimental data suggest that decolorization of RR2 in the UV/TiO₂/O₃, O₃/Mn(II) and O₃/MnO₂ systems proceeded mainly by radical-, surface- and radical-type mechanisms, respectively. Both Mn³⁺ and Mn⁷⁺ were the major oxidants in the O₃/Mn(II) system. This study concluded that hydroxyl radicals and MnO₂-OH• were the primary oxidants in the UV/TiO₂/O₃ and O₃/MnO₂ systems, respectively; minor oxidants were photogenerated holes and MnO₄⁻, respectively.

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