Treatment of dye wastewater with permanganate oxidation and *in situ* formed manganese dioxides adsorption: Cation blue as model pollutant

Ruiping Liu^a, Huijuan Liu^a, Xu Zhao^a, Jiuhui Qu^{a,*}, Ran Zhang^{a,b}

^a State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b College of Environmental Science and Engineering, Hebei University of Science and Technology, Hebei Province, 050018, China

ARTICLE INFO

Article history:

Received 29 June 2009

Received in revised form

24 November 2009

Accepted 24 November 2009

Available online 1 December 2009

Keywords:

Potassium permanganate

δMnO_2

X-GRL

Adsorption

Oxidation

Dissolved Mn

ABSTRACT

This study investigated the process of potassium permanganate (KMnO_4) oxidation and *in situ* formed hydrous manganese dioxides (δMnO_2) (i.e., KMnO_4 oxidation and δMnO_2 adsorption) for the treatment of dye wastewater. The effectiveness of decolorization, removing dissolved organic carbon (DOC), and increasing biodegradable oxygen demand (BOD) were compared among these processes of KMnO_4 oxidation, δMnO_2 adsorption, and KMnO_4 oxidation and δMnO_2 adsorption. δMnO_2 adsorption contributed to the maximum DOC removal of 65.0%, but exhibited limited capabilities of decolorizing and increasing biodegradability. KMnO_4 oxidation alone at pH 0.5 showed satisfactory decrease of UV–vis absorption peaks, and the maximum BOD_5/DOC value of 1.67 was achieved. Unfortunately, the DOC removal was as low as 27.4%. Additionally, the great amount of acid for pH adjustment and the much too low pH levels limited its application in practice. KMnO_4 oxidation and δMnO_2 adsorption at pH 2.0 was the best strategy prior to biological process, in balancing the objectives of decolorization, DOC removal, and BOD increase. The optimum ratio of KMnO_4 dosage to X-GRL concentration ($R_{\text{KMnO}_4/\text{X-GRL}}$) was determined to be 2.5, at which KMnO_4 oxidation and δMnO_2 adsorption contributed to the maximal DOC removal of 53.4%. Additionally, the optimum pH for X-GRL treatment was observed to be near 3.0.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Potassium permanganate (KMnO_4) is often used for Fe^{2+} and Mn^{2+} oxidation [1], arsenite oxidation [2], taste and odor control [3], disinfection by-products formation control [4], algae removal [5], and organic chemicals degradation (e.g., TCE and MTBE) [6] during water treatment and underground water rehabilitation. In strong acid conditions, KMnO_4 exhibits high oxidative reactivity with oxidation potential (E°) of +1.51 V, and its reductive product is Mn^{2+} (Eq. (1)). However, KMnO_4 respectively shows E° values of +1.70 V and +0.59 V in acidic-neutral pH and alkaline conditions, and results in the formation of hydrous manganese dioxide (δMnO_2) (Eqs. (2) and (3)).

In strong acid condition:

In alkaline condition:

In acidic-neutral pH:

The δMnO_2 exhibited promising adsorptive activity due to its high surface area, and the active surface hydroxyl groups (i.e., $\equiv\text{Mn}-\text{OH}$). The adsorption of heavy metals, humic acid, and anions (e.g., arsenate, phosphate) has been investigated [7–10].

KMnO_4 contributes to the degradation and transformation of organics species. Simultaneously, KMnO_4 itself is reduced to δMnO_2 , which shows adsorptive reactivity towards the intermediates. However, rare studies focus on the effect of KMnO_4 oxidation on the subsequent adsorption of oxidative intermediates onto *in situ* formed δMnO_2 .

Dye wastewater, which receives great concern due to its difficulty to treat, contains high intensity of color, high chemical oxygen demand (COD); and perhaps more serious, they are toxic and carcinogenic to aquatic living organisms [11,12]. Biological process is unlikely to achieve good performance if the biodegradability is not satisfactorily increased by chemical oxidation. Adsorption could not minimize the risk to environments, due to its inability in degrading dye molecules. The advanced oxidation processes (AOPs), such as O_3 , H_2O_2 , Fenton's reagent, photo-Fenton reagent,

* Corresponding author at: State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China. Tel.: +86 10 62849151; fax: +86 10 62923558.

E-mail address: jhqu@rcees.ac.cn (J. Qu).

Table 1
Molecular structure of the studied dye.

Dye	Name	Molar mass (g/mol)	$\lambda_{\max}$ (nm)	Structure
X-GRL	Cationic blue	482	610

photo-catalysis reaction, and UV-H₂O₂, contribute to satisfactory decolorization, degradation, and mineralization of dyes [13–16]. However, AOPs are rarely used in practice, owing to the complicate reactors and high costs. The development of effective, cheap, and easy-to-handle process is of crucial importance for the treatment of dye wastewater. KMnO₄ has been proposed for the treatment of dye wastewater [17,18]. Xu et al. reported that KMnO₄ at pH 0.5 contributed to satisfactory decolorization of different dyes and the increase of BOD₅/COD [17]. However, KMnO₄ oxidation resulted in limited degradation of total organic carbon (TOC), and the pH level as low as 0.5 is often prohibited in engineering.

The study employed the azo dye of cationic blue (X-GRL) as model pollutant, and aimed: (1) to compare the variation of UV-vis spectrometry and DOC removal, and transformation of Mn species among processes of KMnO₄ oxidation, δ MnO₂ adsorption, and KMnO₄ oxidation with *in situ* formed δ MnO₂ adsorption (i.e., KMnO₄ oxidation and δ MnO₂ adsorption); (2) to investigate the effect of oxidizing X-GRL by KMnO₄ on the adsorption of intermediates onto *in situ* formed δ MnO₂; (3) to optimize the process of KMnO₄ oxidation and δ MnO₂ adsorption for the treatment of dye wastewater.

2. Materials and methods

2.1. Reagents

The blue azo dye of cationic blue X-GRL (Shanghai Huacai Fine Chemicals Co. Ltd.) was directly used without pretreatment. Table 1 presents the main characteristics and structure of X-GRL. To prepare its stock solution, X-GRL ash was first dissolved in deionized water, filtered through 0.45- μ m cellulose acetate filters, and then air-tightly kept in darkness at room temperature.

δ MnO₂ was prepared through reaction between MnSO₄ and KMnO₄ following the procedures reported by Murray [19]. X-ray diffraction (XD-3A) (Shimadzu Co., Japan) analysis showed low degree of crystallinity, indicating its similarity to what others referred to as δ MnO₂.

2.2. Experimental procedures

The initial X-GRL solution was prepared by the dilution of its stock solution in deionized water, and the concentration was controlled to be 200 mg/L. No salts were additionally added to adjust the background ionic strength, and the pH of initial X-GRL solution was determined to be 4.5. The adjustment of pH was not preceded except under the conditions that the background pH was additionally noted.

Batch experiments were conducted in capped flasks with continuous rotary shaking (125 rpm) at 25 ± 1 °C. KMnO₄ was dosed into the X-GRL solutions in the processes of KMnO₄ oxidation and KMnO₄ oxidation and δ MnO₂ adsorption. In δ MnO₂ adsorption process, δ MnO₂ was freshly prepared before dosing.

2.3. Analysis

Samples were filtered through 0.45- μ m membrane filters to remove δ MnO₂ particles and the organic species that have adsorbed onto δ MnO₂ before analysis. The initial filtrate of each sample (about 5 mL) was abandoned to avoid the side effect of filtration procedure on the experimental results. UV-vis spectra were recorded from 190 to 800 nm using a U-3010 UV-Vis spectrophotometer (Hitachi Co., Japan). Total organic carbon (TOC) was analyzed by UV-persulfate oxidation with a TOC Analyzer (Phoenix 8000) (Tekmar-Dohrmann Co.). The concentrations of Mn were determined using an atomic absorption spectrophotometer (Z-6100) (Hitachi Co., Japan).

3. Results and discussions

3.1. Comparison of X-GRL removal between KMnO₄ oxidation, δ MnO₂ adsorption, and KMnO₄ oxidation and δ MnO₂ adsorption

3.1.1. UV-vis spectrometry variation

As being indicated from UV-vis analysis in Fig. 1a, X-GRL showed three absorption peaks at wavelengths of 202, 300, and 610 nm, which were mainly attributed to benzene ring, azo linkage, and the multi-peaks of the functions within X-GRL. The ratio of absorbance at different wavelengths of 202, 300, and 610 nm ($A_{202\text{ nm}}/A_{300\text{ nm}}/A_{610\text{ nm}}$) was 1/0.24/2.04 for X-GRL molecular.

The variation of UV-vis spectrometry between different processes such as KMnO₄ oxidation, KMnO₄ oxidation and δ MnO₂ adsorption, and δ MnO₂ adsorption was also compared in Fig. 1. Generally, the oxidation effect by KMnO₄ contributed to more significant decolorization of X-GRL than the adsorption effect by δ MnO₂ did. The absorbance at 610 nm ($A_{610\text{ nm}}$), which was attributed to the azo linkage, significantly decreased to 0.01 within 4 min due to the oxidizing effect of KMnO₄ at pH 0.5 (Fig. 1b). The combined effects of KMnO₄ oxidation and δ MnO₂ adsorption (Fig. 1c) at pH 2.0 also decreased $A_{610\text{ nm}}$ to low level of 0.03 after 3.67 min. The azo linkage had been reported to be easily degraded in our former study [20]. Hu et al. [21] investigated the solid/liquid interface photodegradation mechanism of X-GRL adsorbed on the TiO₂/SiO₂ by FT-IR technique, indicating the disappearance of the characteristic C=N stretching adsorption of penta-heterocyclic alky, bands of absorption from the benzene ring, and the C-N of aromatic amide when the decolorization of X-GRL had achieved.

In comparison, KMnO₄ at pH 0.5 showed higher oxidative ability towards X-GRL than at pH 2.0. Quantitatively, after dosing KMnO₄ for 97 min, the ratios of $A_{202\text{ nm}}/A_{300\text{ nm}}/A_{610\text{ nm}}$, respectively changed to 1419/31/1 at pH 0.5 and to 928/21/1 at pH 2.0. The more significant variation of the ratios indicated the more complete degradation of X-GRL molecular. Actually, the oxidation of X-GRL by KMnO₄ at pH 0.5 led to the appearance of new absorption peaks in the wavelength ranges from 330 to 400 nm. These peaks decreased to some extent after 97 min of reaction, but the absorbance at 354 nm ($A_{354\text{ nm}}$) was still as high as 0.263, indicat-

Fig. 1. Variations of UV-vis spectrometry for KMnO_4 oxidation (500 mg/L as KMnO_4), δMnO_2 adsorption (275 mg/L as MnO_2), and KMnO_4 oxidation and δMnO_2 adsorption (500 mg/L as KMnO_4).

Fig. 2. DOC removal comparison among KMnO_4 oxidation (500 mg/L as KMnO_4), δMnO_2 adsorption (275 mg/L as MnO_2), and KMnO_4 oxidation and δMnO_2 adsorption (500 mg/L as KMnO_4).

ing the formation of new functional groups due to KMnO_4 oxidation at pH 0.5.

The adsorption effect of δMnO_2 also contributed to remarkable removal of the X-GRL, as being indicated from the steady decrease of the absorbance at different wavelengths with longer reaction time (Fig. 1d). With reaction time increasing from 4 to 30 min, $A_{610\text{nm}}$ decreased from 0.063 to 0.022. That adsorption of X-GRL onto δMnO_2 dominated the removal of X-GRL and the decrease of UV-vis absorbance. However, it was noted that δMnO_2 surfaces (i.e., $\equiv\text{MnOH}$) also exhibited oxidative activity to X-GRL, as being indicated from the shift of absorption peaks. Quantitatively, the ratio of $A_{202\text{nm}}/A_{300\text{nm}}/A_{610\text{nm}}$, respectively changed to 1/0.13/0.039 and to 1/0.13/0.022 at 30 and 110.5 min, demonstrating the interfacial reactions between δMnO_2 and X-GRL [20]. The electron transfer between Mn(IV) oxides and organics that adsorbed onto Mn(IV) oxides, mainly through interfacial oxidation/reduction reactions, had been reported before. Stone and Morgan studied the adsorption of 27 aromatic and nonaromatic compounds onto Mn(III, IV) oxide suspensions, and indicated the oxidative effect toward these organic species [22]. Comparatively, the oxidizing potential of δMnO_2 was much weaker than that of KMnO_4 . The absorbance at 500 nm ($A_{500\text{nm}}$) in the visible range was still as high as 0.23 at 110.5 min, indicating the incomplete decolorization by δMnO_2 .

3.1.2. DOC removal comparison

Fig. 2 compares the DOC removal between KMnO_4 oxidation, δMnO_2 adsorption, and KMnO_4 oxidation and δMnO_2 adsorption. KMnO_4 oxidation (pH 0.5) contributed to the steady increase of DOC removal with prolonged reaction time, which reached to maximum value of 27.4% after 97 min. Xu et al. also reported the incomplete degradation of different dyes by KMnO_4 , although the decolorization efficiency was as high as more than 85% [17]. The limited mineralization may be ascribed to the recalcitrant structures (i.e., benzene ring, $-\text{C}_2\text{H}_5$, organic acids) within X-GRL, and KMnO_4 at low pH level of 0.5 could hardly degrade these groups.

Basically, δMnO_2 contributed to more rapid and more significant removal of DOC, ascribing to its good adsorptive activity to X-GRL. DOC removal significantly increased to 56.7% at 3.75 min, and then attained to the maximum value of 65.0% at 13.5 min (pH 2.0). The longer reaction time decreased DOC removal to a certain extent, which decreased to 51.7% at 110 min. Our former study demonstrated the promisingly adsorptive activities towards X-GRL for $\equiv\text{MnOH}$, and proposed the different interfacial interactions involved in the adsorption of X-GRL onto δMnO_2 [20]. The oxidation of X-GRL and the formation of intermediates resulted in the detachment of X-GRL from $\equiv\text{MnOH}$ surfaces, as being indicated from the decrease of DOC removal with higher reaction time.

Fig. 3. Variations of filterable Mn concentrations for δMnO_2 adsorption (275 mg/L as MnO_2), and KMnO_4 oxidation and δMnO_2 adsorption (500 mg/L as KMnO_4).

As for KMnO_4 oxidation and δMnO_2 adsorption, the maximum DOC removal of 39.4% was achieved at 1.2 min at pH 2.0. After that, DOC removal decreased to 28.6% at 12.2 min and then showed no obvious variation with longer reaction time. At pH 7.2, similar trends were observed except that the maximum DOC removal was slightly lower to be 32.9%. The reactions between KMnO_4 and X-GRL were rapid, which led to the degradation of X-GRL and the formation of δMnO_2 . The DOC removal was ascribed to the combined effects of KMnO_4 oxidation and δMnO_2 adsorption. However, the intermediates from X-GRL oxidation were more difficult to adsorb onto δMnO_2 surfaces than X-GRL molecular. In the photodegradation of X-GRL on $\text{TiO}_2/\text{SiO}_2$ surfaces, Hu et al. also reported the formation of intermediates, and desorption of final products from catalyst [21]. The DOC removal of the KMnO_4 oxidation and δMnO_2 adsorption process was observed to be lower than that of δMnO_2 adsorption. These results were in accordance with the decrease of DOC removal after the formation of intermediates in δMnO_2 adsorption process.

3.1.3. Variation of aqueous Mn^{2+} concentrations

The Mn^{2+} in solution was an indicator to provide valuable information on the interactions between X-GRL and KMnO_4 and/or δMnO_2 . Fig. 3 compares the variation of dissolved Mn concentrations between the processes of δMnO_2 adsorption and KMnO_4 oxidation and δMnO_2 adsorption. It should be noted that after the interactions between KMnO_4 and X-GRL at pH 0.5, the solution was observed to be transparent and absent of any particles. It was indicated that the dissolved Mn concentrations were constant for the process of KMnO_4 oxidation at pH 0.5, owing to the complete transformation of Mn(VII) to soluble Mn(II) .

As for the δMnO_2 adsorption process, the concentrations of dissolved Mn, i.e., Mn^{2+} , increased steadily with longer reaction time and the maximal value of 66.2 mg/L was achieved after 110 min. The adsorption of X-GRL onto δMnO_2 surfaces led to the reductive dissolution of Mn(IV) oxides to soluble Mn^{2+} . The trends of Mn^{2+} concentrations variation may be fitted by logarithmic equation as follows:

$$C_{[\text{Mn}^{2+}]} = 7.66 \times \ln(t) + 21.05 \quad (R^2 = 0.8753) \quad (4)$$

However, the increasing rate of Mn^{2+} concentrations was observed to decrease with prolonged time, and was quantitatively demonstrated by the derivative formula of Eq. (4) as follows:

$$\frac{d(C_{[\text{Mn}^{2+}]})}{dt} = \left(\frac{7.66}{t} \right) dt \quad (5)$$

The increase of Mn^{2+} concentrations demonstrated the oxidative activities of δMnO_2 towards X-GRL, which led to the shift of absorption peaks in wavelength from 450 to 650 nm in Fig. 1c. Several studies have investigated the electron transfer between organics and δMnO_2 , reporting the reductive dissolution of Mn(IV) oxides and subsequent increase of Mn^{2+} concentrations [22,23].

As for the process of KMnO_4 oxidation and δMnO_2 adsorption at pH 2.0, the dissolved Mn, i.e., Mn(VII) , decreased steadily with longer reaction time, and reached to the minimum value of 5.9 mg/L after 96 min. Additionally, it was also observed that the decreasing rate of Mn(VII) concentrations reduced with longer time, and the trends of Mn(VII) variation were fitted by exponential equation as follows:

$$C_{[\text{Mn(VII)}]} = 82.59 \times e^{-0.029t} \quad (R^2 = 0.9060) \quad (6)$$

The derivative formula of Eq. (6) as follows indicated the tendency observed in Fig. 3:

$$\frac{d(C_{[\text{Mn(VII)}]})}{dt} = -2.40 \times e^{-0.029t} dt \quad (7)$$

The function groups with different reductive activities within X-GRL dominated the variation of dissolved Mn in solution. The strong reductive function groups within X-GRL (i.e., azo group) exhibited high reactivity towards oxidative species of both KMnO_4 and δMnO_2 , which contributed to the significant variation of dissolved Mn initially. After that, the recalcitrant groups within X-GRL and its intermediates were difficult to degrade and inhibited the variation of dissolved Mn.

It was interestingly observed that the dissolved Mn concentrations of the KMnO_4 oxidation and MnO_2 adsorption process were much lower than that of δMnO_2 adsorption process, indicating that most Mn(VII) had transformed to solid phase of δMnO_2 . However, the newly formed δMnO_2 from Mn(VII) reduction would not further transfer to Mn^{2+} , even in the presence of organic intermediates which were resulted from the oxidation of X-GRL molecular. This was ascribed to the less activities of δMnO_2 to the intermediates than to the X-GRL.

3.1.4. Comparison of biodegradability variation among these processes

As for the dye wastewater that is recalcitrant to biological treatment, the increase of biodegradability, through physico-chemical processes, is valuable to enable it to be treated through subsequent biological processes. The different mechanisms involved in the treatment of X-GRL by KMnO_4 oxidation, δMnO_2 adsorption, and KMnO_4 oxidation and δMnO_2 adsorption exhibited different effects on the biodegradability (Table 2).

KMnO_4 oxidation at pH 0.5 contributed to the highest BOD_5 concentration of 42.47 mg/L, which was followed by KMnO_4 oxidation and δMnO_2 adsorption at pH 0.8 and pH 2.0. The δMnO_2 adsorption at pH 2.0 led to the lowest BOD_5 concentration of 5.20 mg/L, indicating the minimum increase of biodegradability. The variation of

Table 2

Comparison of biodegradability variation among KMnO_4 oxidation, δMnO_2 adsorption, and KMnO_4 oxidation and δMnO_2 adsorption ($[\text{X-GRL}]_0 = 200 \text{ mg/L}$).

Process	Dosage	pH	BOD_5 (mg/L)	DOC (mg/L)	BOD_5/DOC
KMnO_4 oxidation	500 mg/L as KMnO_4	0.5	42.47	25.42	1.67
δMnO_2 adsorption	275 mg/L as MnO_2	2.0	5.20	16.90	0.31
KMnO_4 oxidation and MnO_2 adsorption	500 mg/L as KMnO_4	2.0	14.64	23.28	0.63
KMnO_4 oxidation and δMnO_2 adsorption	500 mg/L as KMnO_4	0.8	24.40	24.92	0.98

Fig. 4. Variation of DOC removal and filterable Mn concentrations at different ratios of permanganate to X-GRL.

ratio of BOD₅ to DOC (BOD₅/DOC) also followed same sequence to BOD₅ as follows: KMnO₄ oxidation > KMnO₄ oxidation and δ MnO₂ adsorption > δ MnO₂ adsorption, with the highest value of 1.67. Xu et al. reported that the treatment of a real textile wastewater by KMnO₄ at pH 0.5 could promisingly improved the biodegradability, which increased the ratio of BOD₅/COD from 0.0081 to 0.32 [17], and that KMnO₄ oxidation may be feasible as pretreatment before biological process.

In comparison, δ MnO₂ adsorption led to the lowest increase of biodegradability, although the residual DOC was the lowest among these processes. KMnO₄ oxidation at pH 0.5 contributed to the most significant increase of biodegradability; however, the large amount of acid for pH adjustment increased the cost for treatment, and the low pH levels inhibited the growth of bacteria for further biological processes. Consequently, the treatment by KMnO₄ oxidation and δ MnO₂ adsorption at pH 2.0, prior to the biological processes, was the optimum strategy in practice for the treatment of dyes (e.g., X-GRL) wastewaters.

3.2. Treatment of X-GRL by KMnO₄ oxidation and δ MnO₂ adsorption

3.2.1. Effects of KMnO₄ dosages on the treatment of X-GRL

The dosages of KMnO₄ impacted the treatment of X-GRL. The higher dosages of KMnO₄ improved X-GRL oxidation and provided more δ MnO₂ for adsorption. Fig. 4 presents the variation of DOC removal and dissolved Mn concentrations at different KMnO₄ dosages. With the ratios of KMnO₄ to X-GRL ($R_{KMnO_4/X-GRL}$) increasing from 0.625 to 3.125 (w/w), the DOC removal at 30 min accordingly increased from 29.9% to 53.4% (Fig. 4a). The higher $R_{KMnO_4/X-GRL}$ value of 3.75 slightly decreased DOC removal to 47.5%. The prolonged reaction time of 16 h improved DOC removal to

60.3% at $R_{KMnO_4/X-GRL}$ of 3.75, but exhibited side effects on DOC removal at $R_{KMnO_4/X-GRL}$ values of being lower than 3.125.

The variation of dissolved Mn concentrations provides valuable information on the mechanisms involved in these reactions. Fig. 4b indicates the variation of dissolved Mn concentrations at different $R_{KMnO_4/X-GRL}$ values and reaction time. At $R_{KMnO_4/X-GRL}$ values of lower than 2.5, the dissolved Mn concentrations increased to higher levels with longer reaction time, owing to the reductive dissolution effect of Mn(IV) oxides. Comparatively, the dissolved Mn concentrations at $R_{KMnO_4/X-GRL} > 2.5$ accordingly decreased to lower values, ascribing to the reduction effect of soluble Mn(VII) to Mn(IV) oxides.

At low KMnO₄ dosages, the oxidative capabilities were insufficient to oxidize the reductive functional groups within X-GRL molecular, and further resulted in the reduction of Mn(IV) oxides to aqueous Mn(II) through interfacial reductive reactions. The adsorbed organics (i.e., X-GRL, intermediates) detached from Mn(IV) oxides, together with the dissolved Mn(II), and resulted in the decrease of DOC removal. At $R_{KMnO_4/X-GRL} > 2.5$, the excess of KMnO₄ further reacted with the intermediates with longer time, and resulted in the formation of more Mn(IV) oxides for the adsorption of intermediates onto δ MnO₂ surfaces. The optimum $R_{KMnO_4/X-GRL}$ value for DOC removal was observed to be 2.5 under these conditions.

3.2.2. Effects of pH on the treatment of X-GRL

pH was an important factor affecting the treatment of X-GRL wastewater by KMnO₄ oxidation. The low pH was beneficial to the oxidation of X-GRL. However, the excessive degradation of X-GRL inhibited the adsorption of intermediate products onto δ MnO₂, as being indicated above. Additionally, the adjustment of pH to much too low levels increased the costs.

Fig. 5 presents the variation of dissolved Mn concentrations and DOC removal with pH increasing from 1.0 to 9.6 ($R_{KMnO_4/X-GRL} = 2.5$). The concentrations of dissolved Mn at pH < 2 were much lower than those in pH ranges from 2.8 to 9.6 at 30 min. The low dissolved Mn concentrations indicated the complete reaction between KMnO₄ and X-GRL, which was favored at low pH as being indicated from Eqs. (1)–(3). KMnO₄ was more reactive and showed higher oxidizing capabilities under strong acid conditions than that at elevated pH conditions.

Additionally, the species transformation of elemental Mn with longer time was indicative to the extent of reactions between KMnO₄ and X-GRL. It is observed in Fig. 5 that the concentrations of dissolved Mn at pH > 2.8 decreased with reaction time increasing from 30 min to 18 h, and this was ascribed to the reduction of excess soluble Mn(VII) to Mn(IV) oxides particles. At pH < 2, how-

Fig. 5. Variation of DOC removal and filterable Mn concentrations at different pH conditions.

ever, the concentrations of dissolved Mn accordingly increased due to the reductive dissolution of Mn(IV) oxides to soluble Mn(II).

With pH increasing from 1.0 to 9.6, DOC removal at reaction time of 30 min firstly increased from 26.9% at pH 1.0 to the maximum value of 54.6% at pH 2.8, and then steadily decreased with elevated pH values. The minimum removal of DOC of 18.9% was observed at pH 9.6. The removal of DOC by KMnO_4 adsorption and δMnO_2 adsorption was dominated by the extent of the degradation of X-GRL, and the adsorptive behaviors of the intermediates onto δMnO_2 . The dissolved Mn concentration at pH 1.0 was lower than that at pH 2.8, and indicating that KMnO_4 at pH 1.0 provided more Mn(IV) oxides than that at pH 2.8. However, the DOC removal at pH 1.0 was lower than that at pH 2.8, demonstrating that the excess degradation of X-GRL molecular was inhibitive to the removal of DOC. This result was in accordance with that in Fig. 2.

Additionally, Fig. 5 indicates that the DOC removal decreased with elevated pH in pH ranges from 2.8 to 9.6, although the concentrations of dissolved Mn were similar from pH 4.5 to pH 9.6. The higher pH decreased the surface charge of δMnO_2 , and benefited the adsorption of positively charged X-GRL molecular onto δMnO_2 surfaces [20]. In this study, X-GRL was firstly oxidized by KMnO_4 to negative species such as organic acids. The adsorption of these intermediates onto δMnO_2 at elevated pH was inhibited by the increased repulsive forces between intermediates and negative surfaces of δMnO_2 .

The optimum pH for the treatment of X-GRL wastewater was observed to be near 3.0 under these conditions.

4. Conclusions

As for the treatment of dye wastewater with high color, high COD, and low biodegradability, the addition of KMnO_4 at pH value near to 3, is shown to be feasible as a pretreatment prior to the biological process, owing to the combined effects of KMnO_4 oxidation and δMnO_2 adsorption. Basically, KMnO_4 oxidation mainly contributes to the decolorization and the increase of biodegradability, although it also leads to the DOC removal. δMnO_2 acts as adsorbent for the removal of X-GRL and its oxidative intermediates. In comparison, KMnO_4 oxidation alone at pH 0.5 requires a great deal of acid for pH adjustment, and the low pH level is inhibitive to subsequent biological units. δMnO_2 alone exhibits promising adsorptive activity to X-GRL, but showed limited capability of increasing its biodegradability. The moderate oxidation of X-GRL molecular by KMnO_4 and the formation of sufficient δMnO_2 for the adsorption of its intermediates can be achieved by adjusting the parameters (i.e., KMnO_4 dosage, pH).

Acknowledgments

This work was supported by the Funds for the Creative Research Groups of China (50621804) and the National Natural Sciences

Foundation of China (50778172). Appreciation is extended to the foundation for financial assistance.

References

- [1] T. Hedberg, T.A. Wahlberg, Upgrading of waterworks with a new biooxidation process for removal of manganese and iron, *Water Sci. Technol.* 37 (1998) 121–126.
- [2] N. Li, M.H. Fan, V.L. Johannes, S. Basudeb, H.Q. Yang, C.P. Huang, Oxidation of As(III) by potassium permanganate, *J. Environ. Sci.* 19 (2007) 783–786.
- [3] A. Bruchet, J.P. Duguet, I.H. Suffe, Role of oxidants and disinfectants on the removal, masking and generation of tastes and odours, *Rev. Environ. Sci. Biotechnol.* 3 (2004) 33–41.
- [4] B. Moyers, J.S. Wu, Removal of organic precursors by permanganate oxidation and alum coagulation, *Water Res.* 19 (1985) 309–314.
- [5] J.J. Chen, H.H. Yeh, The mechanisms of potassium permanganate on algae removal, *Water Res.* 39 (2005) 4420–4428.
- [6] K.C. Huang, G.E. Hoag, P. Chheda, B.A. Wody, G.M. Dobbs, Kinetics and mechanism of oxidation of tetrachloroethylene with permanganate, *Chemosphere* 46 (2002) 815–825.
- [7] H.S. Posselt, F.J. Anderson, J.W.J. Walter, Cation sorption on colloidal hydrous manganese dioxide, *Environ. Sci. Technol.* 2 (1968) 1087–1093.
- [8] R.P. Liu, Y.L. Yang, G.B. Li, W.J. He, H.D. Han, Adsorptive behaviors of humic acid onto freshly prepared hydrous manganese dioxides, *Front. Environ. Sci. Eng. China* 1 (2007) 1–6.
- [9] W. Yao, F.J. Millero, Adsorption of phosphate on manganese dioxide in seawater, *Environ. Sci. Technol.* 30 (1996) 536–541.
- [10] R.P. Liu, B.L. Yuan, X. Li, S.J. Xia, Y.L. Yang, G.B. Li, The oxidative and adsorptive effectiveness of hydrous manganese dioxide for arsenite removal from aqueous solution, *High Technol. Lett.* 12 (2006) 30–34.
- [11] C. O'Neill, F.R. Hawkes, D.L. Hawkes, N.D. Lourenco, H.M. Pinheiro, W. Dele'e, Colour in textile effluents—sources, measurement, discharge consents and simulation: a review, *J. Chem. Technol. Biotechnol.* 74 (1999) 1009–1018.
- [12] P.C. Vandeviere, R. Bianchi, W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, *J. Chem. Technol. Biotechnol.* 72 (1998) 289–302.
- [13] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments* 71 (2006) 236–244.
- [14] H.Y. Shu, M.C. Chang, Development of a rate expression for predicting decolorization of C.I. Acid Black 1 in a UV- H_2O_2 process, *Dyes Pigments* 70 (2006) 31–37.
- [15] Y.Z. Wang, A. Yedeler, A. Kettrup, Comparison of degradation reactions of Acid Yellow 61 in both oxidation processes of $\text{H}_2\text{O}_2/\text{UV}$ and O_3 , *J. Environ. Sci.* 13 (2001) 304–307.
- [16] F.B. Li, G.B. Gu, G.F. Huang, Y.L. Gu, TiO_2 -assisted photo-catalysis degradation process of dye chemicals, *J. Environ. Sci.* 13 (2001) 62–68.
- [17] X.P. Xu, H.B. Li, W.H. Wang, J.D. Gu, Decolorization of dyes and textile wastewater by potassium permanganate, *Chemosphere* 59 (2005) 893–898.
- [18] A. Aleboyeh, M.E. Olya, H. Aleboyeh, Oxidative treatment of azo dyes in aqueous solution by potassium permanganate, *J. Hazard. Mater.* 162 (2009) 1530–1535.
- [19] J.W. Murray, The surface chemistry of hydrous manganese dioxide, *J. Colloid Interface Sci.* 46 (1974) 357–371.
- [20] R.P. Liu, H.J. Wang, X. Zhao, S.H. Xiao, J.H. Qu, Microwave electrodeless lamp assisted catalytic degradation of X-GRL with manganese dioxides: adsorption and manganese(IV) reductive dissolution effects, *Catal. Today* 139 (2008) 119–124.
- [21] C. Hu, Y. Tang, J.C. Yu, P.K. Wong, Photocatalytic degradation of cationic blue X-GRL adsorbed on $\text{TiO}_2/\text{SiO}_2$ photocatalyst, *Appl. Catal. B: Environ.* 40 (2003) 131–140.
- [22] A. Stone, J. Morgan, Reduction and dissolution of manganese(III) and manganese(IV) oxides by organics: 2. Survey of the reactivity of organics, *Environ. Sci. Technol.* 18 (1984) 617–624.
- [23] R. Petrie, P. Grossl, R. Sims, Oxidation of pentachlorophenol in manganese oxide suspensions under controlled E_h and pH environments, *Environ. Sci. Technol.* 36 (2002) 3744–3748.