

Improved removal performance and mechanism investigation of papermaking wastewater treatment using manganese enhanced Fenton reaction

Yingcai Wang, Can Wang, Shuai Shi and Shuai Fang

ABSTRACT

The effects of Mn(II) on Fenton system to treat papermaking wastewater and the mechanism of Mn(II) enhanced Fenton reaction were investigated in this study. The chemical oxygen demand (COD) removal efficiency was enhanced in the presence of Mn(II), which increased by 19% compared with that of the Fenton system alone. The pseudo-first order reaction kinetic rate constant of Mn(II)/Fenton system was 2.11 times higher than that of Fenton system. 67%–81% COD were removed with the increasing Mn(II) concentration from 0 to 0.8 g/L. COD removal efficiency was also enhanced in a wider pH range (3–7), which indicated the operation parameters of Fenton technology could be broadened to a milder condition. The study of the mechanism showed that Mn(II) participated in the oxidation and coagulation stages in Fenton system. In the oxidation stage, Mn(II) promotes the production of $\text{HO}_2\bullet/\text{O}_2\bullet^-$, then $\text{HO}_2\bullet/\text{O}_2\bullet^-$ reacts with Fe(III) to accelerate the formation of Fe(II), and finally accelerates the production of $\text{HO}\bullet$. Meantime MnMnO_3 and Fe(OH)_3 forms in the coagulation stage, facilitating the removal of suspended substances and a large amount of COD, which enhances the overall COD removal of papermaking wastewater. This study provided a detailed mechanism to improve practical applications of Fenton technology.

Key words | coagulation, Fenton system, manganese, oxidation, papermaking wastewater

Yingcai Wang

Can Wang (corresponding author)

Shuai Shi

Shuai Fang

School of Environmental Science and Engineering,

Tianjin University,

135 Yaguan Road, Jinnan District,

Tianjin 300350,

China

E-mail: wangcan@tju.edu.cn

INTRODUCTION

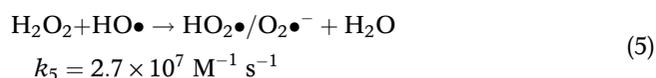
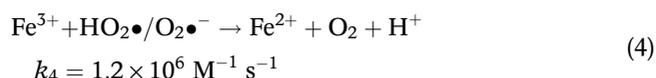
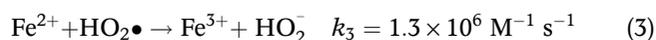
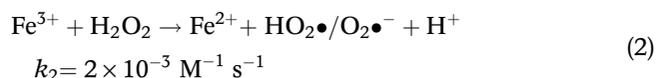
The pulp and paper industry is a high water-consumption industry in which 76 to 227 m³ water need to be utilized for each ton of product, generating huge quantities of wastewater and thereby causing concomitant problems for the environment and economy (Khansorthong & Hunsom 2009). Nowadays, in the papermaking industry, the main treatment process involves clarification as a primary process and biological treatment as a secondary process. However, these treatments could not meet the water quality requirements since high chemical oxygen demand (COD), toxicity, and color remain in the effluent (Ciputra *et al.* 2010). Besides, the COD, which consists of persistent substances, could not be further degraded by the subsequent biological process (Jamil *et al.* 2011). Considering the increasingly strict standards of environmental protection and discharge limitations, other treatment methods are needed to meet these rigorous standards. Advanced oxidation processes (AOPs) seem to be a promising alternative.

Fenton processes have produced better overall results treating pulp and paper mill effluents than other AOP-based treatment technologies (Hermosilla *et al.* 2015) due to the mild operating conditions (room temperature and atmospheric pressure), and high oxidation efficiency (Garg *et al.* 2010). The hydroxyl radical ($\text{HO}\bullet$) is generally considered as the active oxidizing intermediate in the Fenton system (Tizaoui *et al.* 2010). Fenton reactions can be initiated when hydrogen peroxide (H_2O_2) reacts with Fe(II) (Equation (1)) to produce $\text{HO}\bullet$ (Neyens & Baeyens 2003; Garrido-Ramírez *et al.* 2010).

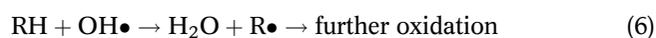


This catalytic reaction can be accelerated by more Fe(II), which reduces from Fe(III) through Equation (2), and more radicals are generated in these oxidation-reduction reactions by Equations (3)–(5) (Garrido-Ramírez

et al. 2010).



HO• can attack and oxidize organic pollutant molecules (RH) by abstracting protons. Highly reactive organic radicals (R•) are produced in this process and could be further oxidized through Equation (6).



Generally, the Fenton-coagulation reaction consists of the following stages: pH adjustment, oxidation reaction, neutralization, coagulation, and precipitation (Wu *et al.* 2010). Organic substances could be removed through the oxidation and coagulation process. Although the overall reaction rate of Fenton process is governed by the reduction rate of Fe(III) to Fe(II), the degradation efficiency is not only related to the radical oxidation process but also depends greatly on the chemical coagulation process. Thus, strategies have been considered to improve the efficiency of Fenton system. Some studies have opted for transition metals, such as copper (Nichela *et al.* 2013), manganese (Wang *et al.* 2018), and cobalt (Oturán *et al.* 2010), as iron substitutes to catalyze H₂O₂ to improve the Fenton oxidation efficiency. Among these strategies, Fenton-coagulation process is widely applied to maximize the coagulation stage (Fang *et al.* 2015).

As a common transition metal, manganese has received attention in Fenton system because of its benign environmental effect. Some researchers found that synthesized α -MnO₂, β -MnO₂, and γ -MnO₂ showed good abilities to decompose rhodamine B (RB) (Sui *et al.* 2009), methylene blue (MB) (Yu *et al.* 2014), and hexachloroethane (HCA) in the presence of H₂O₂ (Furman *et al.* 2009). Other researchers made use of Mn-incorporated Fe₃O₄/FeSO₄ to enhance the degradation of organic pollutants in Fenton system (Carvalho *et al.* 2014). The enhanced degradation

activity of an Mn(II)/Fenton system could be attributed to the production of HO₂•/ O₂•⁻ in the oxidation stage of Fenton system, showing the ability to degrade recalcitrant contaminants (Furman *et al.* 2009; Carvalho *et al.* 2014). However, the effects of Mn(II) on the efficiency of Fenton system have not been investigated in detail, the mechanism of Mn(II)/Fenton for treating papermaking wastewater is not fully reported. Besides, few studies are involved in the removal process of the oxidation and coagulation stages with the presence of Mn(II), which might inhibit its further applications. Therefore, it is imperative to determine the mechanism of manganese enhanced Fenton reaction in two stages (oxidation and coagulation stages) for its broader application in papermaking wastewater treatments.

In this study, the effects of Mn(II) on Fenton system to treat papermaking wastewater were conducted through comparing COD removal efficiencies and reaction kinetics in two different stages. In addition, the initial Mn(II) concentration and pH were selected and considered as operation parameters that might have effects on COD removal efficiencies. The objective of this study was to propose the possible mechanism of Mn(II) enhanced Fenton reaction in oxidation and coagulation stages.

MATERIALS AND METHODS

Wastewater samples and reagents

The papermaking wastewater samples were collected in a secondary sedimentation tank from a papermaking company in Shandong. The detailed information and characteristics of papermaking wastewater samples are described in Text S1, which can be found in the supplementary material (available with the online version of this paper). All chemicals and reagents used in our study were of analytical grade. Hydrogen peroxide (H₂O₂, 30%, wt %), sodium hydroxide (NaOH), hydrochloric acid (HCl) were purchased from Tianjin Kernel Chemical Reagent Co., Ltd, China. Ferrous sulfate heptahydrate (FeSO₄·7H₂O), and manganese sulfate (MnSO₄) were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Analytical method

The COD was determined according to the spectrophotometry method (Hach, Japan). The pH of the solution was measured by a pH meter (Mettler Toledo, FE28-Standard, Switzerland). The hydroxyl radicals were monitored by fluorescence method with aromatic hydroxylation

reaction and L-phenylalanine (L-Phe) was selected as a fluorescent probe for HPLC analysis. HPLC-analysis was performed on a HP1100 Hewlett–Packard system (Agilent, USA), equipped with a Zorbax Eclipse XDB-C18 (150 mm × 4.6 mm) column and an HP1100 fluorescence detector (FLD). A mixture of methanol, water and phosphoric acid (60:39:1) (v/v) was used as the mobile phase. The flow rate was 1 ml/min and the injection volume was 5 μ L. The FLD was set at 277 nm for the excitation wavelength and 306 nm for the emission wavelength. More detailed information about the analytical methods can be found in Text S2 and Text S3 (available online).

Effects of Mn(II) on papermaking wastewater degradation by oxidation system

All experiments of oxidation were performed in 100 ml glass beakers at room temperature (25 ± 1 °C) and atmospheric pressure. Fenton reactions were triggered by the introduction of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 (30%, wt%) under continuous magnetic stirring. The concentration of Fe(II), H_2O_2 and Mn(II) were 4 mmol/L, 4.8 mmol/L and 0.2 g/L, respectively. The initial pH of wastewater was adjusted to 3.0 by the addition of HCl. All these parameters were optimized in our former research (Shi *et al.* 2017). Oxidation reaction was maintained for 30 min, then excess NaOH was added into the solution to raise the pH and to quench the reaction. The wastewater sample was withdrawn for further analysis, and all experiments were performed in triplicate.

Effects of operating conditions on papermaking wastewater degradation by Mn(II) enhanced Fenton reaction

The pH and concentration of MnSO_4 were selected as the monitoring parameters for the treatment efficiency in this study. 0.2–0.8 g/L MnSO_4 was added into the solution with the pH range from 3.0 to 7.0. The initial pH of the wastewater was adjusted by the addition of HCl or NaOH. Other parameters were the same as the above method shown in the section, Effects of Mn(II) on papermaking wastewater degradation by oxidation system.

Investigation of the role of Mn(II) in Fenton system

Soluble COD and suspended COD treatment experiments were conducted to investigate the role of Mn(II) in the oxidation and coagulation stages in Fenton system, respectively. Five different systems (MnSO_4 , H_2O_2 ,

$\text{MnSO}_4 + \text{H}_2\text{O}_2$, Fenton, Fenton + MnSO_4) were used for soluble COD treatment. The solution pH was adjusted to 3.0 by HCl solutions. $\text{MnSO}_4 + \text{H}_2\text{O}_2$ system was further investigated to clarify soluble COD and suspended COD removal efficiencies with the introduction of Mn(II). Then, the Fenton oxidation processes were performed as in the above procedures. More detailed information can be found in the supplementary material (available online).

RESULTS AND DISCUSSION

Effects of Mn(II) on papermaking wastewater treatment by oxidation system

The effects of Mn(II) introduction in papermaking wastewater treatment are illustrated in Figure 1, which shows the COD removal of papermaking wastewater in H_2O_2 , Mn(II)/ H_2O_2 , Fenton and Mn(II)/Fenton system. It was clear that the treatment of papermaking wastewater by H_2O_2 oxidation system was enhanced with the presence of Mn(II), from the results. The COD removal efficiencies reached 52%, 67%, and 77% in Mn(II)/ H_2O_2 , Fenton, and Mn(II)/Fenton systems, respectively. This indicated that the standalone H_2O_2 showed little effect on COD removal whereas Mn(II)/ H_2O_2 system presented much better results to some extent. The enhancement might be concerned with the generation of $\text{HO}\cdot$ due to the introduction of Mn(II). Significantly, although the COD removal efficiency has been improved in Mn(II)/ H_2O_2 system, it is still lower than the conventional Fenton process, which means that Fe(II) in

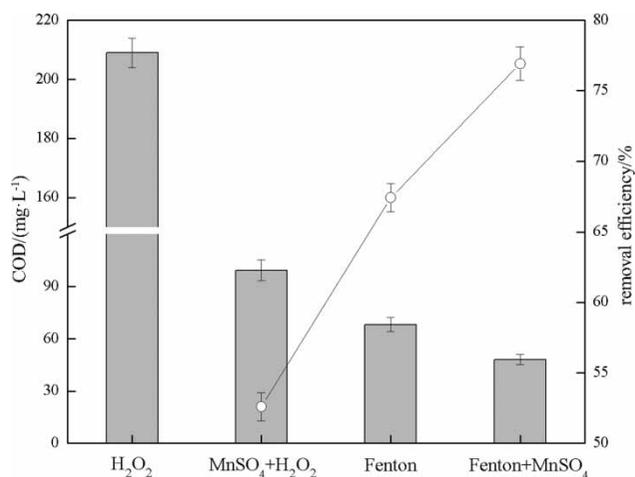


Figure 1 | COD removal of papermaking wastewater under various oxidation systems (initial concentrations: $[\text{Fe}^{2+}] = 4$ mmol/L, $[\text{H}_2\text{O}_2] = 4.8$ mmol/L, $[\text{MnSO}_4] = 0.2$ g/L, pH = 3.0, t = 30 min, COD of raw wastewater = 209 mg/L).

Fenton system cannot be substituted by Mn(II) in terms of obtaining high COD removal efficiency in Fenton system.

Generally, COD removal efficiency in Mn(II)/Fenton system was remarkably enhanced compared with that in Fenton system alone. Some studies showed that the catalytic activity of Fe(II) was enhanced by Mn(II) introduction in Fenton reactions (Liang *et al.* 2014). The manganese ion may participate in the chain reaction of radicals in Fenton system by reacting with HO• or HO₂•/O₂•, and the valence of Mn could be changed in this process, resulting in the decreased consumption of HO• by Fe(II) and other active species. Therefore, the effectivity of HO• would then be improved and COD removal could ultimately be strongly enhanced in Mn(II)/Fenton system. Similarly, some other research has reported the same results. The Mn-incorporated samples displayed enhanced efficiency in HO• production for the degradation of acid orange II and the decoloration of methylene blue (Carvalho *et al.* 2014; Liang *et al.* 2014).

The kinetics of COD removal in Fenton and Mn(II)/Fenton system are studied in Figure 2. The pseudo-first order kinetic equation (Equation (S7), available with the online version of this paper) is used for fitting the degradation data, and R² of the two fitting lines are 0.9637 and 0.9448 in Fenton and Mn(II)/Fenton system, respectively. The intercept and slope of the fitting line in Fenton system are 1.0520 ± 0.0845 and 0.0028 ± 0.0056, while the intercept and slope are 1.3197 ± 0.1185 and 0.0059 ± 0.0078 for Fenton + MnSO₄ treatment. The slope of the lines yielded the reaction rate constant of 0.0059 min⁻¹ and 0.0028 min⁻¹, which

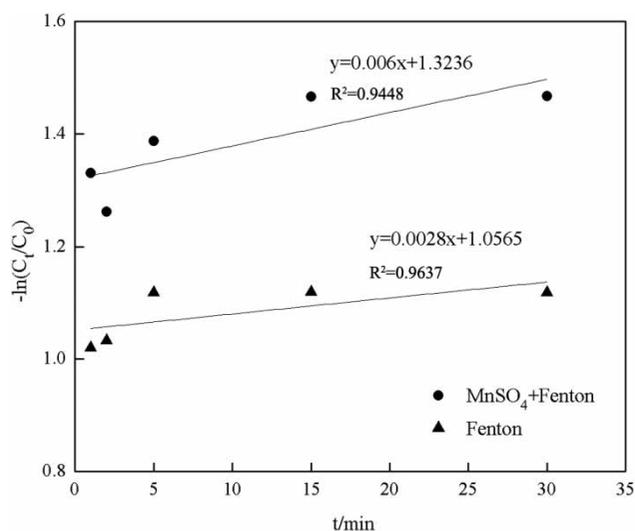


Figure 2 | The kinetics of COD removal in Fenton and Mn(II)/Fenton system (initial concentrations: [Fe²⁺] = 4 mmol/L, [H₂O₂] = 4.8 mmol/L, [MnSO₄] = 0.2 g/L, pH = 3.0, t = 30 min, COD of raw wastewater = 209 mg/L).

showed that the pseudo-first order reaction rate constant of Mn(II)/Fenton system was 2.11 times higher than that of Fenton system. The treatment efficiency of papermaking wastewater in Fenton system was improved obviously when Mn(II) was added. In Fenton system, the oxidation rate is limited by the slow formation of Fe(II) through Equation (2) ($k_2 = 2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$). In the Mn(II)/Fenton system, the increment in reaction rate may be attributed to the prompt reduction of Fe(III) to Fe(II) with the help of Mn(II), boosting the catalytic reaction of H₂O₂ by Equation (1). As a result, the treatment of papermaking wastewater was enhanced.

Effects of operating conditions on papermaking wastewater treatment by Mn(II) enhanced Fenton reaction

Effect of Mn(II) concentration

The effects of Mn(II) concentration on Fenton system are illustrated in Figure 3 and the results show that 0.2 g/L MnSO₄ exhibited obvious enhancement on COD removal for papermaking wastewater in Fenton system. COD removal efficiency increased significantly with rising Mn(II) concentration, ranging from 67% to 81% with Mn(II) concentrations from 0 g/L to 0.8 g/L. Similarly, Li *et al.* (2016) studied the removal of bisphenol A (BPA) in water using a microwave-enhanced Mn-Fenton method. They found that with an increasing concentration of Mn(II) ions, BPA removal rate was higher than that without any Mn(II) ions. BPA could be completely degraded when

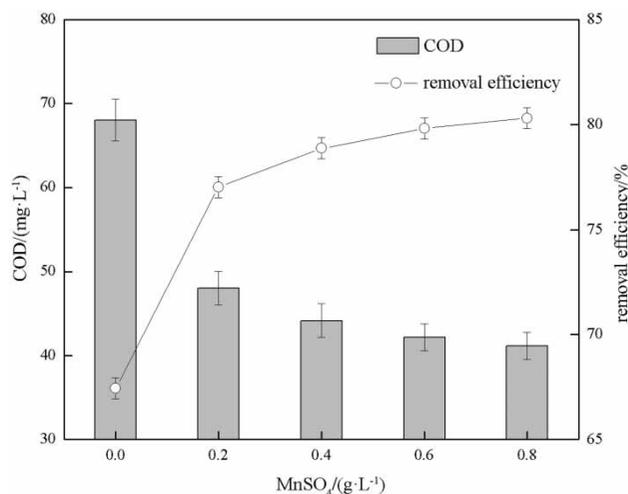


Figure 3 | Effect of Mn(II) concentration on COD removal of papermaking wastewater by Fenton system (initial concentrations: [Fe²⁺] = 4 mmol/L, [H₂O₂] = 4.8 mmol/L, pH = 3.0, COD of raw wastewater = 209 mg/L).

the concentration of Mn(II) exceeded 2.7 mg/L, which showed the highly effective utilization of $\cdot\text{OH}$. In general, a high Fe(II) concentration is unlikely to correspond to high oxidation removal in Fe(II)/ H_2O_2 system. Instead, the degradation rate decreases as Fe(II) concentration continuously increases beyond a suitable level, because a high Fe(II) concentration can cause a self-scavenging effect of $\text{HO}_2\cdot$ (Equation (3)) and induce a decrease in degradation rate of pollutants (Neyens & Baeyens 2003). Thus, it should be noted that Mn(II) could enhance the effectiveness of Fenton process in its application.

Effects of initial pH

The effect of pH on COD removal efficiency is shown in Figure 4. During the reaction, the pH value was slightly decreased and the solution became acidic after the Fenton process. The maximal removal efficiency of COD (82%) was achieved at pH of 4. In other studies, the optimum pH ranges from 2.0 to 4.0 in Fenton system (Han et al. 2012). By contrast, pH made no remarkable difference on COD removal by Fenton system in the presence of Mn(II) from Figure 4. To some extent, this mechanism broadened the application of Fenton technology to treat papermaking wastewater in a wider pH range. In general, huge quantities of acidic substances are needed as pH adjustments in Fenton system to maintain the optimal pH of 3. This result was significant for the treatment of papermaking wastewater, as it is not necessary to lower the pH of the system, thus eliminating the need for extra expenses. At the end of

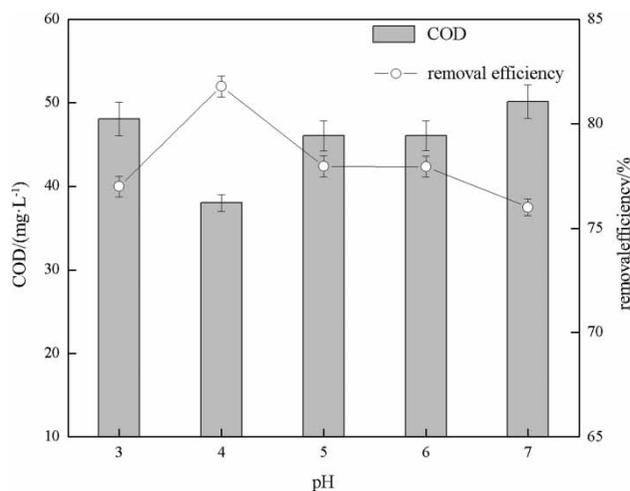


Figure 4 | Effect of pH on COD removal of papermaking wastewater by Fenton system (initial concentrations: $[\text{Fe}^{2+}] = 4 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 4.8 \text{ mmol/L}$, $[\text{MnSO}_4] = 0.2 \text{ g/L}$, COD of raw wastewater = 209 mg/L).

the reactions, pH values were 2.90, 2.91, 2.94, 3.34 and 3.70, respectively. The decreased pH might be concerned with the Equations (2) and (4) mentioned above.

Investigation of the role of Mn(II) in Fenton system

Effect of Mn(II) on enhancing $\text{HO}\cdot$ generation in Fenton system

To get a clear perspective of the role of Mn(II) in Fenton system, the papermaking wastewater was pretreated by filtration to remove the suspended COD in solution. Five different systems were used to treat soluble COD wastewater. No floc and precipitation were observed in these experiments, which could be considered as the organic compounds being mainly removed by the oxidation stage in Fenton system. As shown in Figure 5, the soluble COD removal efficiency by Fenton system was enhanced in the presence of Mn(II), and increased by 19% compared with that of a separate Fenton system. However, no evident removal of soluble COD could be observed when the system only contained Mn(II) and H_2O_2 without the participation of Fe(II). This result could be explained by the different catalytic abilities presented by Mn(II) and Fe(II). Soluble Mn(II) could catalyze H_2O_2 decomposition in a suitable condition; however, the catalytic reaction happened at a very slow rate (Richard et al. 2005). Anipsitakis & Dionysiou (2004) also found that iron is the most efficient transition metal to catalyze H_2O_2 to generate $\text{HO}\cdot$, whereas the manganese ion is very inert. The role of Mn(II) in Fenton

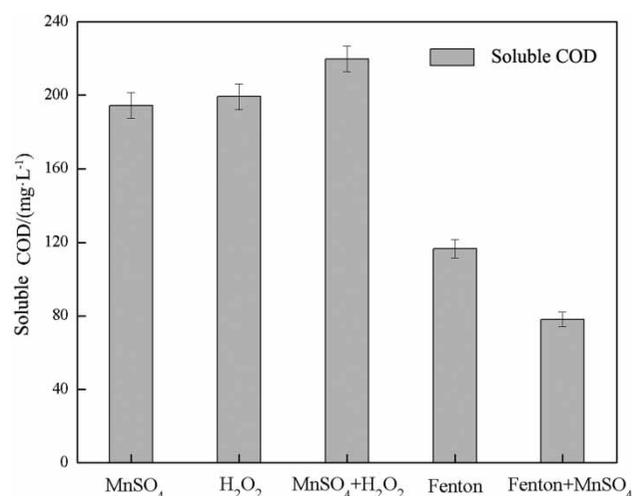


Figure 5 | Effect of Mn(II) on the oxidation of coagulation-treated effluent of papermaking wastewater by Fenton system (initial concentrations: $[\text{Fe}^{2+}] = 4 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 4.8 \text{ mmol/L}$, $[\text{MnSO}_4] = 0.2 \text{ g/L}$, pH = 3.0, t = 30 min, soluble COD of raw wastewater = 224 mg/L).

system is probably associated with the oxidation process, in which HO• production might be enhanced.

HPLC with fluorescence detection was performed to detect HO• generation in Fenton reaction in the presence of Mn(II). Fluorescence increment (ΔF) was presented as the parameter indicating HO• generation under various Mn(II) concentrations. From Figure 6, it is found that the generation of HO• was evidently promoted by Mn(II), and similar results have been reported in other studies. Fernsebner *et al.* (2014) made use of the ion chromatography coupled to inductively coupled plasma-optical emission spectrometry (IC-ICP-OES) analysis of brain samples to show that Mn(II) may trigger a shift of the Fe(II)/Fe(III) ratio to generate more Fe(II) in different oxidation reactions, such as Fenton reaction. The resulting $O_2^{\cdot-}$ further reduced Fe(III) to produce more Fe(II) through Equation (4). Then the formation of HO• was enhanced, thereby consequently accelerating the oxidation of pollutants. Besides, lower HO• generation was obtained under a higher Mn(II) concentration. The reason might be that the amount of H_2O_2 reacting with the redundant Mn(II) ion was inadequate to generate OH•. Nevertheless, the HO• production was still higher than the absence of Mn(II) in Fenton system.

Effect of Mn(II) on coagulation process in Fenton system

To further know the role of Mn(II) in Fenton system, soluble COD and suspended COD removal efficiencies by Mn(II)/ H_2O_2 system are analyzed in Figure 7. Results showed that suspended COD decreased evidently, whereas soluble COD remained unchanged after the reaction in Mn(II)/ H_2O_2

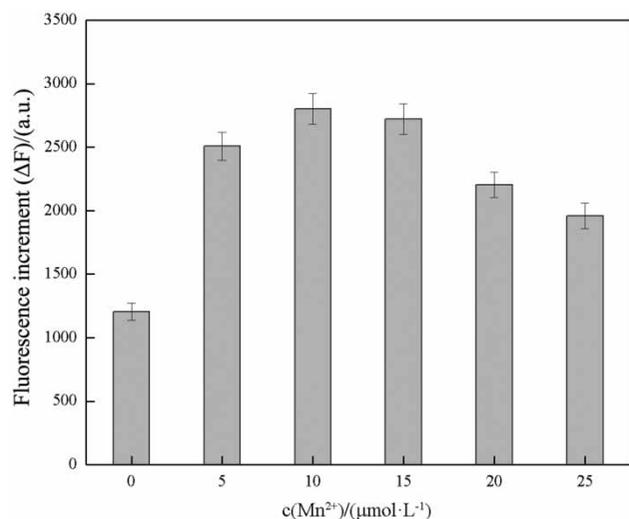


Figure 6 | Mn(II) promotes HO• in Fenton system (initial concentrations: $[Fe^{2+}] = 1.2$ mmol/L, pH = 7.4, t = 1 h, n = 3).

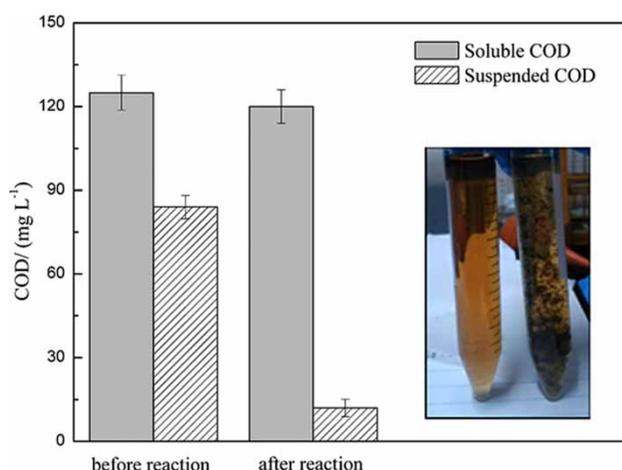
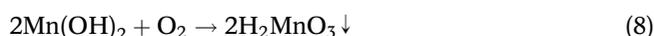


Figure 7 | Effect of Mn(II) on the treatment of soluble COD and suspended COD (initial concentrations: $[H_2O_2] = 4.8$ mmol/L, $[MnSO_4] = 0.2$ g/L, t = 30 min, COD of raw wastewater = 215 mg/L).

system. Meantime, many flocs were generated in raw papermaking wastewater. This result indicated that suspended substances precipitated in papermaking wastewater, and then a large amount of COD was removed through the coagulation process. The mechanism of the coagulation might be explained by the formation of $MnMnO_3$ through Equations (7)–(9). The surface area of the obtained precipitate from N_2 adsorption/desorption isotherms was 146.9 m²/g, which presented a good characteristic for COD removal by coagulation process.



Mechanism of Mn(II) enhanced Fenton reaction

Based on the above results, the mechanism of the enhanced treatment of organic substances in Fenton system in the presence of Mn(II) was proposed. As shown in Figure 8,

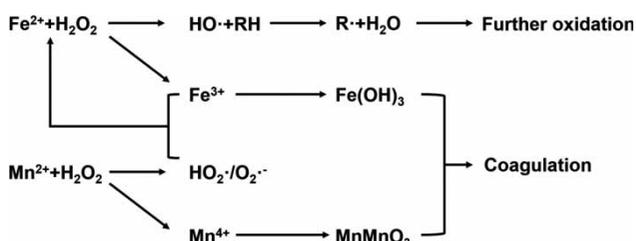
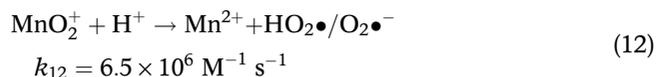
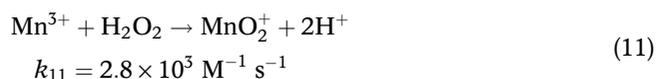
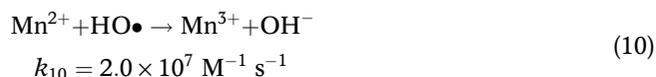
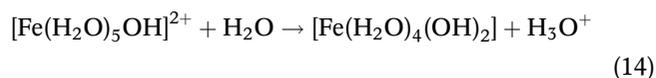


Figure 8 | Possible mechanisms during the Mn(II)/Fenton process.

Mn(II) participated in the oxidation and coagulation stages of Fenton system. Firstly, the manganese ion may participate in the chain reaction in the oxidation stage to generate $\text{HO}_2\cdot/\text{O}_2\cdot^-$, which reduced Fe(III) back to Fe(II) through Equation (4). The formation of Fe(II) and $\text{HO}\cdot$ were then accelerated, thereby increasing the oxidation of organic substances. Jacobsen et al. (1998) investigated the reactions of Mn(II) with $\text{HO}\cdot$ and $\text{HO}_2\cdot/\text{O}_2\cdot^-$ in detail as shown by Equations (10)–(12).



Secondly, after the pH was adjusted, Fe(III) and Mn(II) could form insoluble ferric hydroxy complexes (Equations (13) and (14)) and MnMnO_5 (Equations (7)–(9)) to produce a flocculent precipitate, which facilitated the separation of suspended substances in effluent in the coagulation stage (Neyens & Baeyens 2003). These complexes generated in the reactions accounted for the coagulation capability of Fenton's reagent.



CONCLUSIONS

In this study, the treatment of papermaking wastewater by Fenton system was enhanced in the presence of manganese (MnSO_4). The COD removal efficiency of papermaking wastewater was increased with the rising concentration of MnSO_4 . Soluble COD removal reached 61% at an H_2O_2 concentration of 4.8 mmol/L, $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ molar ratio of 1.2, and MnSO_4 concentration of 0.2 g/L, which were increased by 19% compared with that of the Fenton system alone. COD removal efficiency was also enhanced

in a wider pH range (3–7), which indicated the operation parameters of Fenton technology could be broadened to a milder condition.

Based on soluble COD and suspended COD treatment experiments, the possible mechanism of the enhanced removal of organic substances in Fenton system in the presence of Mn(II) was proposed. Mn(II) participated in the oxidation and coagulation stages in Fenton system. In the oxidation stage, Mn(II) promotes the production of $\text{HO}_2\cdot/\text{O}_2\cdot^-$, then $\text{HO}_2\cdot/\text{O}_2\cdot^-$ reacts with Fe(III) to accelerate the formation of Fe(II), and finally accelerates the production of $\text{HO}\cdot$. Meantime MnMnO_5 and $\text{Fe}(\text{OH})_3$ formed in the coagulation stage facilitated the removal of suspended substances and a large amount of COD, which enhanced the overall COD removal of papermaking wastewater. This study helped to elucidate the treatment of papermaking wastewater by Fenton system in the presence of Mn(II) and provided a detailed mechanism to improve practical applications of Fenton technology.

ACKNOWLEDGEMENTS

The work was supported by a grant from National Science and Technology Major Project Water Pollution Control and Treatment (No. 2012ZX07203-004-44).

REFERENCES

- Anipsitakis, G. P. & Dionysiou, D. D. 2004 Radical generation by the interaction of transition metals with common oxidants. *Environ. Sci. Technol.* **38** (13), 3705–3712.
- Carvalho, H. W. P., Hammer, P., Pulcinelli, S. H., Santilli, C. V. & Molina, E. F. 2014 Improvement of the photocatalytic activity of magnetite by Mn-incorporation. *Mat. Sci. Eng. B* **181**, 64–69.
- Ciputra, S., Antony, A., Phillips, R., Richardson, D. & Leslie, G. 2010 Comparison of treatment options for removal of recalcitrant dissolved organic matter from paper mill effluent. *Chemosphere* **81** (1), 86–91.
- Fang, S., Wang, C. & Chao, B. 2015 Operating conditions on the optimization and water quality analysis on the advanced treatment of papermaking wastewater by coagulation/Fenton process. *Desalin. Water Treat.* **57** (27), 12755–12762.
- Fersebner, K., Zorn, J., Kanawati, B., Walker, A. & Michalke, B. 2014 Manganese leads to an increase in markers of oxidative stress as well as to a shift in the ratio of Fe(II)/(III) in rat brain tissue. *Metallomics* **6** (4), 921–931.
- Furman, O., Laine, D. F., Blumenfeld, A., Teel, A. L., Shimizu, K. & Cheng, I. F. 2009 Enhanced reactivity of superoxide in water-solid matrices. *Environ. Sci. Technol.* **43** (5), 1528–1533.

- Garg, A., Mishra, I. M. & Chand, S. 2010 Effectiveness of coagulation and acid precipitation processes for the pre-treatment of diluted black liquor. *J. Hazard. Mater.* **180** (1), 158–164.
- Garrido-Ramírez, E. G., Theng, B. K. G. & Mora, M. L. 2010 Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions – a review. *Appl. Clay Sci.* **47** (3), 182–192.
- Han, J. C., Liu, X., Yang, N. Z., Ramsay, J. A., Dai, R. H., Liu, Y. & Jin, W. 2012 Biohazardous wastewater treatment by sequential combination of coagulation and Fenton oxidation. *J. Environ. Eng.* **138** (1), 74–80.
- Hermosilla, D., Merayo, N., Gascó, A. & Blanco, Á. 2015 The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: a review. *Environ. Sci. Pollut. R.* **22** (1), 168–191.
- Jacobsen, F., Holcman, J. & Sehested, K. 1998 Oxidation of manganese(II) by ozone and reduction of manganese(III) by hydrogen peroxide in acidic solution. *Int. J. Chem. Kinet.* **30** (3), 207–214.
- Jamil, T. S., Ghaly, M. Y., El-Seesy, I. E., Souaya, E. R. & Nasr, R. A. A. 2011 Comparative study among different photochemical oxidation processes to enhance the biodegradability of paper mill wastewater. *J. Hazard. Mater.* **185** (1), 353–358.
- Khansorthong, S. & Hunsom, M. 2009 Remediation of wastewater from pulp and paper mill industry by the electrochemical technique. *Chem. Eng. J.* **151** (1), 228–234.
- Li, S., Zhang, G. & Wang, P. 2016 Microwave-enhanced Mn-Fenton process for the removal of BPA in water. *Chem. Eng. J.* **294**, 371–379.
- Liang, X. L., He, Z., Wei, G. L., Liu, P., Zhong, Y. H., Tan, W., Du, P. X., Zhu, J. X., He, H. P. & Zhang, J. 2014 The distinct effects of Mn substitution on the reactivity of magnetite in heterogeneous Fenton reaction and Pb(II) adsorption. *J. Colloid Interf. Sci.* **426**, 181–189.
- Neyens, E. & Baeyens, J. 2003 A review of classic Fenton's peroxidation as an advanced oxidation technique. *J. Hazard. Mater.* **98** (1), 33–50.
- Nichela, D. A., Berkovic, A. M., Costante, M. R., Juliarena, M. P. & Einschlag, F. S. G. 2013 Nitrobenzene degradation in Fenton-like systems using Cu(II) as catalyst. Comparison between Cu(II)- and Fe(III)-based systems. *Chem. Eng. J.* **228**, 1148–1157.
- Oturan, N., Zhou, M. & Oturan, M. A. 2010 Metomyl degradation by electro-Fenton and electro-Fenton-like processes: a kinetics study of the effect of the nature and concentration of some transition metal ions as catalyst. *J. Phys. Chem. A* **114**, 10605–10611.
- Richard, J. W., Judith, S., Frank, J. L. & Teel, A. L. 2005 Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions. *J. Environ. Eng.* **131** (1), 158–164.
- Shi, S., Wang, C., Fang, S., Jia, M. & Li, X. 2017 Removal performance and water quality analysis of paper machine white water in a full-scale wastewater treatment plant. *Environ. Technol.* **38** (11), 1443–1451.
- Sui, N., Duan, Y. Z., Jiao, X. L. & Chen, D. 2009 Large-scale preparation and catalytic properties of one-dimensional α/β -MnO₂ nanostructures. *J. Phys. Chem. C* **113** (20), 8560–8565.
- Tizaoui, C., Karodia, N. & Aburowais, M. 2010 Kinetic study of the manganese-based catalytic hydrogen peroxide oxidation of a persistent azo-dye. *J. Chem. Technol. Biot.* **85** (2), 234–242.
- Wang, Y., Shi, S., Wang, C. & Fang, S. 2018 Degradation of papermaking wastewater by a heterogeneous Fenton-like catalyst Fe/Mn supported on zeolite. *Environ. Prot. Eng.* **44** (3). In press. DOI: 10.5277/epe180209.
- Wu, Y. Y., Zhou, S. Q., Qin, F. H., Peng, H. P., Lai, L. Y. & Lin, Y. M. 2010 Removal of humic substances from landfill leachate by Fenton oxidation and coagulation. *Process Saf. Environ.* **88** (4), 276–284.
- Yu, C. L., Li, G., Wei, L. F., Fan, Q. Z., Shu, Q. & Yu, J. C. 2014 Fabrication, characterization of β -MnO₂ microrod catalysts and their performance in rapid degradation of dyes of high concentration. *Catal. Today* **224**, 154–162.

First received 8 January 2018; accepted in revised form 25 April 2018. Available online 8 May 2018