

Facile decolorization of methylene blue with flower-like manganese wads

Aili Yang, Chinpao Huang, Bingqing Wei and Zhengjun Zhang

ABSTRACT

Flower-like manganese wads (MWs) were synthesized via a simple and inexpensive ultrasonic irradiation method for the first time. MWs were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray and transmission electronic microscopy. The decolorization efficiency of MWs for methylene blue (MB) azo dye was examined as a function of pH, stirring time, MW dosage and initial concentration of the MB solution. Results show that MWs have excellent decolorization performance for MB with a higher efficiency (and without using H₂O₂ or other devices such as UV light and ultrasonic irradiation) compared to other catalysts, such as the mixture of Mn₃O₄ and H₂O₂ (with a maximum decolorization rate of 99.7% in 3 h), ZnS and CdS under light irradiation (with a maximum decolorization rate of 73% in 6 h), and sulfate modified titania under solar radiation (with a maximum decolorization rate of nearly 100% in 4 h).

Key words | characterization, decolorization, manganese wads (MWs), methylene blue (MB), synthesis

Aili Yang (corresponding author)

Zhengjun Zhang

Department of Materials Science and Engineering,
Tsinghua University,
Beijing 100085,
China
E-mail: yangaili770117@126.com

Chinpao Huang

Department of Environmental Engineering,
University of Delaware,
Newark, DE 19716,
USA

Bingqing Wei

Department of Mechanical Engineering,
University of Delaware,
Newark, DE 19716,
USA

INTRODUCTION

Dyes with complex aromatic molecular structures from industrial effluents are toxic, chemically stable and not totally biodegradable which may perturb aquatic ecosystems. Methylene blue (MB), a brightly colored cationic thiazine dye, is one of the most commonly used substances for dyeing cotton, wood and silk. However, it can have harmful effects on animals and humans. Therefore, the removal of MB in wastewater has attracted considerable attention in the field of environmental remediation (Yang *et al.* 2011; Zhang *et al.* 2011).

Various treatment techniques such as electrocoagulation (Asghari *et al.* 2012), oxidation (Clarke *et al.* 2010), ozonation (Valdés *et al.* 2010), adsorption (Oyelude & Owusu 2011), and catalyst oxidation (Ge & Qu 2004) have been used to remove organic pollutants from dye effluents. Of all these available methods, catalyst oxidation technology has gained intensive attention, and is currently considered an effective and economic method for water purification. Significant attention has been placed on the use of hydrogen peroxide (H₂O₂) or the mixture of manganese oxide and H₂O₂ as active oxidants for the removal of organic pollutants in the dye wastewater (Zhang *et al.* 2010; Gemeay *et al.* 2012). However, H₂O₂ has very poor chemical stability

and decomposes completely within 20 min at room temperature, which limits its use for the degradation of hazardous organic matters in water (Gulshan *et al.* 2010; Zhang *et al.* 2011). In order to overcome this drawback, advanced oxidation processes with higher chemical stability have been developed, such as ozonation, ultrasonic irradiation and UV-Vis light irradiation photocatalytic technology (Valdés *et al.* 2010; Kobayashi *et al.* 2012; Soltani *et al.* 2012). However, these technologies need special operation equipment, which increase the cost, energy use and complexity of the treatment processes.

Manganese oxides with many excellent properties, such as being earth-abundant, inexpensive, environmentally friendly and with high stability, have attracted considerable attention because of their extensive application in many fields such as electrochemistry and environmental remediation. However, their methods of synthesis usually have some disadvantages such as high-cost, time-consuming and needing several chemicals (Xu *et al.* 2008; Qiu *et al.* 2011). In this paper, flower-like manganese wads (MWs) were synthesized via a simple and inexpensive ultrasonic irradiation method for the first time. Manganese wad is considered to be a heterogeneous manganese oxide containing MnO and

MnO₂. The multiple oxidation states of manganese oxides can greatly accelerate interfacial electron transfer and improve the reaction efficiency and catalytic activity for the removal of organic pollutants in wastewater (Yang *et al.* 2009). However, very few studies have reported the synthesis of MWs with multivalent Mn, and fewer reports have focused on their decolorization performance for the removal of azo dyes. The present study aimed to explore the feasibility of MB decolorization using as-synthesized MWs. The effects of various parameters, such as pH, reaction time, the MW dosage and initial MB concentration on the decolorization efficiency were investigated.

METHODS

Materials

KMnO₄ (Aldrich Chemicals), concentrated HCl (Fisher Scientific), KOH (Fisher Scientific), and anhydrous alcohol (Decon Labs Inc.) used were analytical grade chemicals. MB (Aldrich Chemicals) was used as the surrogate dye. Deionized water (DW) was used throughout the experiments for solution preparation.

Synthesis and characterization of MWs

MWs were prepared using KMnO₄ in the acid condition by the oxidation-reduction process under ultrasonic irradiation. KMnO₄ (0.90 g) was dissolved completely in 40 mL DW in a 250-mL conical glass reactor. Concentrated HCl (2 mL) was then added to the KMnO₄ solution at room temperature and mixed as a homogenous phase. The resulting solution was sonicated in an ultrasonic bath (Branson 2510, USA) for 30 min at 60 °C. The reaction products were centrifuged and washed several times with DW and anhydrous alcohol. Finally, the black brown precipitates were collected and dried under vacuum at 60 °C.

MWs were characterized by X-ray diffraction (XRD) (Siemens X-ray diffractometer, Germany), scanning electron microscopy (SEM) (JSM-7400F, Japan) and transmission electron microscopy (TEM) (JEM-2000F, Japan).

Decolorization experiments

A given quantity of MB was accurately weighed and dissolved in DW to prepare a stock solution at a concentration of 0.1 g L⁻¹. The desired concentrations of working solutions were obtained by successive dilutions. The catalytic reactions

of MWs were carried out in a 100-mL beaker, which contained 50 mL of the MB solution (50 mg L⁻¹) and different amounts of MWs. The mixture was stirred continuously. The solution pH was adjusted with 0.1 M HCl and 0.1 M KOH using a pH meter (pHS-25, Shanghai Hongyi Instrument Co., China). At preselected time intervals, 5 mL of the suspension were immediately centrifuged for 5 min at 4,000 rpm. In order to correctly determine the absorbance of MB when pH was above 5, the 2 mL supernatant was withdrawn carefully and diluted eight times with DW. The supernatant was analyzed using a UV-visible spectrophotometer (Diode Array 8452A, HP) at $\lambda_{\max} = 664$ nm. The decolorization rate is calculated using the following equation:

$$\text{Decolorization Rate}/\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t (mg L⁻¹) are the initial concentration and the concentration at stirring time t of MB, respectively.

RESULTS AND DISCUSSION

Characterization of MWs

Figure 1 shows the typical XRD pattern (Figure 1(a)), energy dispersive X-ray (EDX) spectrum (Figure 1(b)), SEM image (Figure 1(c)), and TEM micrograph (Figure 1(d)) of MWs. MWs display poor crystalline characteristics with two broad peaks at 2θ values of $\sim 36.7^\circ$ and $\sim 65.7^\circ$. The XRD peaks of the samples were matched with the card of MnO-MnO₂ (JCPDS-02-1070), and identified as manganese wad. As shown in Figure 1(b), MWs consist of three elements (Mn, O and K) and interlayer water. Based on the atomic ratio of Mn, O and K, the chemical formula of MWs could be expressed as K_{0.2}MnOMnO₂·1.4H₂O. As seen from Figures 1(c) and 1(d), MWs form agglomerates with porous microspheres and exhibit a flower-like structure composed of tiny interconnected nanoflakes radiating from the center. These structural properties are useful for the removal of organic compounds in wastewater.

Decolorization performance of MWs

Influence of the solution pH

To study the influence of pH on MB removal, experiments at different pH ranging from 1.5 to 10 were carried out. A given amount (0.05 g) of MWs were added to 50 mL of MB

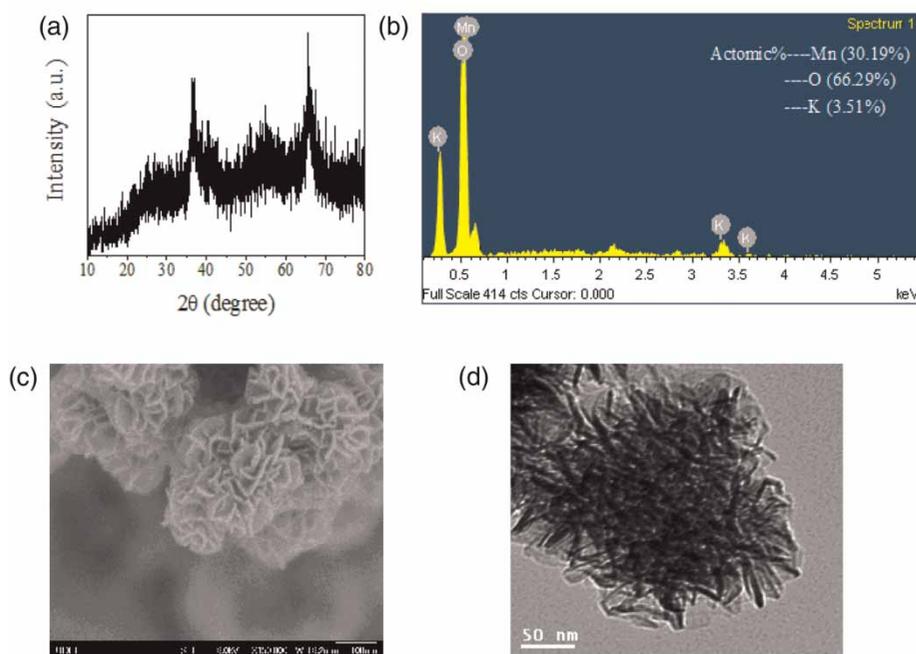


Figure 1 | XRD pattern (a), EDX spectrum (b), SEM image (c), and TEM micrograph (d) of MWs.

solution (50 mg L^{-1}) and stirred for 30 min. **Figure 2(a)** shows the effect of pH on the decolorization rate. It is evident that the decolorization rate reached above 99% when the pH was below 2. The dark blue color of the initial MB solution changes to purple, and then becomes colorless and transparent at the end of the treatment process (**Figure 2(c)** inset), which can be explained by the fact that there was a hypsochromic shift of the maximum absorption wavelength of the MB solution after treatment due to the degradation of MB. The decolorization rate of MB was highly pH dependent. The MB removal efficiency was maximal at pH 1.5 and then decreased with further increase in solution pH. **Figure 2(a)** (inset) shows that the absorption intensity of solution treated for 30 min increased gradually with the increase in pH.

From **Figure 2(a)**, it can be concluded that the optimum pH is 1.5. However, the pH of zero point of charge (pH_{zpc}) of MWs was determined to be around 3.2 (**Figure 2(b)**) by a MPT-2 multi-purpose titrator. At a lower pH, the surface sites of MWs are protonated, which would not favor electrostatic interaction with the cationic MB. As pH increases, the surface of MWs becomes deprotonated and there is also a decrease in N $(\text{CH}_3)_2$ protonation in MB (Kuan *et al.* 2011). However, the optimum pH value of 1.5 with MWs is below its pH_{zpc} value, which indicates that the reason for the enhanced activity of MWs at a lower pH could be due to

a favorable reduction potential of the Mn(IV)/Mn(II) couple for electron transfer. On the other hand, the surface charge of MWs becomes negative at $\text{pH} > 3.2$, which favors the adsorption of Mn(II) formed by the reduction of Mn(IV) during the MB decolorization process. This, in turn, inhibits the adsorption of MB on the MW surface. The combined effect of the above two mechanisms results in a decrease in oxidative decolorization of MB by MWs at a higher pH (Satapathy *et al.* 2012).

Influence of stirring time

It was found from the experiments that the optimum dose of MWs for MB removal was 2.4 g L^{-1} at pH 1.5 (**Figure 2(c)**). **Figure 2(d)** (inset) shows the UV-Vis decolorization spectra of the MB solution by MWs for a stirring period of 1, 2, 5, 15, 30, 60, 90, and 120 min and the corresponding decolorization rate. It can be seen that, after stirring for 30 min, the absorbance peak of MB drops significantly, reflecting that the MB molecules undergo a degradation reaction. It rapidly reaches high decolorization efficiency at 664 nm and the decolorization rate reaches above 99%. However, the peak intensity of MB is reduced progressively with a shift towards a lower wavelength of $\sim 600 \text{ nm}$. The color of the dye solution faded gradually with the increase of stirring time until the suspension liquid changed to colorless. A similar spectral

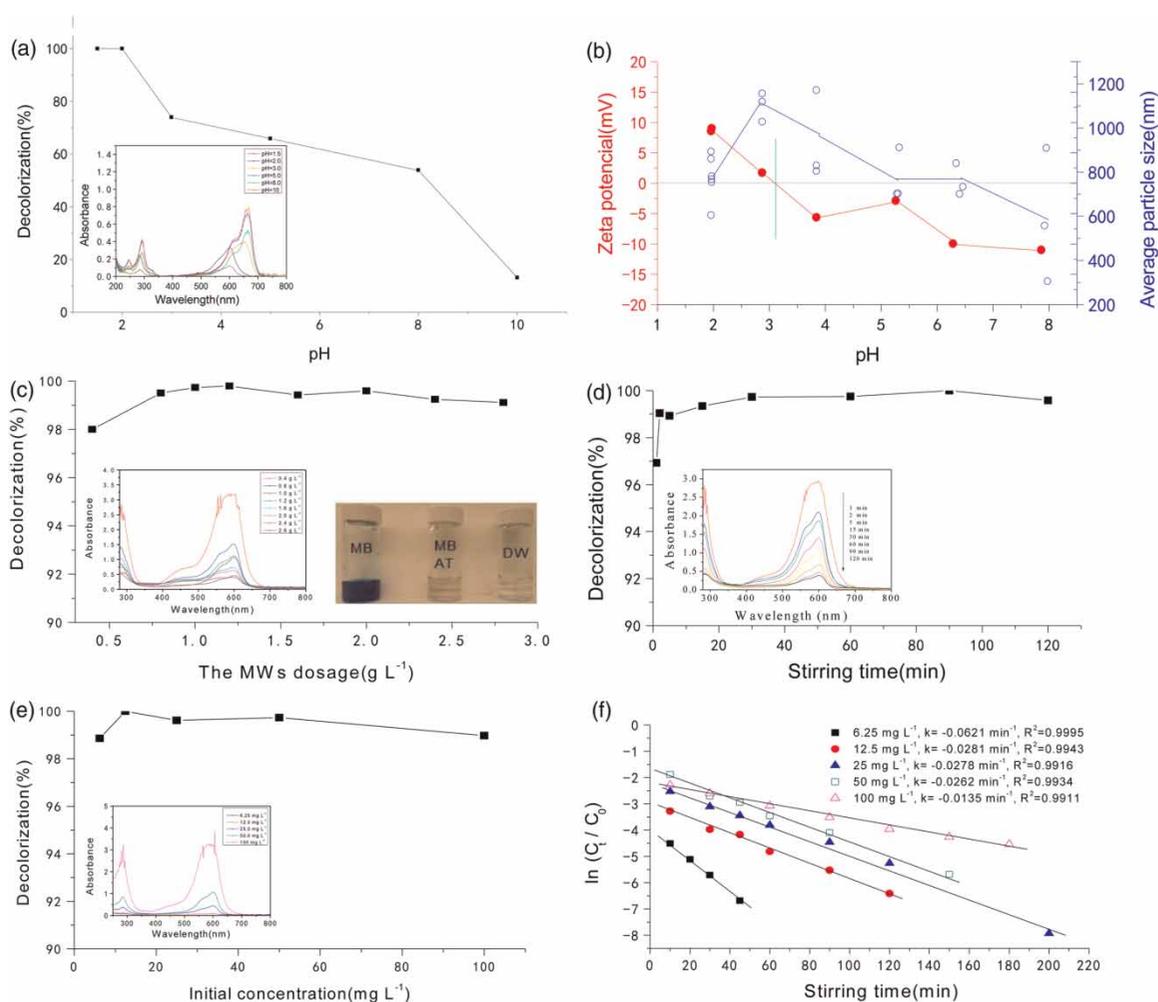


Figure 2 | Effect of pH on the decolorization rate (a); inset in (a) is UV-Vis spectral change of MB solution with pH. The pH_{zpc} value and average particle size of MWs (b). Effect of the MW dosage on the decolorization rate (c); inset in (c) is UV-Vis spectral change of MB solution treated with MWs for different MW dosage and the photographs of initial MB solution (MB), the suspension liquid being treated by MWs (MB AT) and DW. Effect of stirring time on the decolorization rate (d); inset in (d) is UV-Vis spectral change of MB solution treated with MWs for different stirring time. Effect of initial concentration on the decolorization rate (e); inset in (e) is UV-Vis spectral change of MB solution at different initial concentration. Influence of initial concentration on the decolorization kinetics of MB (f).

change has been reported for catalytic oxidation of MB by β - MnO_2 nanorods (Zhang *et al.* 2006).

Influence of initial concentration

Figure 2(e) shows the effect of initial concentration (e.g., 6.25–100 $mg\ L^{-1}$) on the decolorization efficiency of MB by 2.4 $g\ L^{-1}$ of MWs at pH 1.5. At low concentrations of 6.25 and 12.5 $mg\ L^{-1}$, MB was completely decolorized within 30 min and the absorption peaks at ~ 600 and 664 nm disappeared. On the other hand, the peak intensities of MB at ~ 290 nm were reduced progressively without any shift in their positions. As shown in Figure 2(e), the decolorization rate of MB was substantially decreased with an increase in initial concentration. When stirring

for 30 min, the decolorization efficiency of MB with a high initial concentration was significantly reduced at ~ 600 nm. This decrease might be attributed to the formation of a surface precursor complex between MWs and MB at a rate limiting step prior to electron transfer from MB to the active metal center of MWs, leading to the MB decolorization. A similar trend has also been observed for MB decolorization by Zhu (Zhu *et al.* 2008). It appears that the surface reactivity and the number of available sites are two critical factors controlling MB decolorization (Satapathy *et al.* 2012). The decrease in decolorization efficiency at a higher MB concentration might have resulted from the saturation of active surface sites on MWs, which impedes further formation of a precursor complex followed by electron transfer.

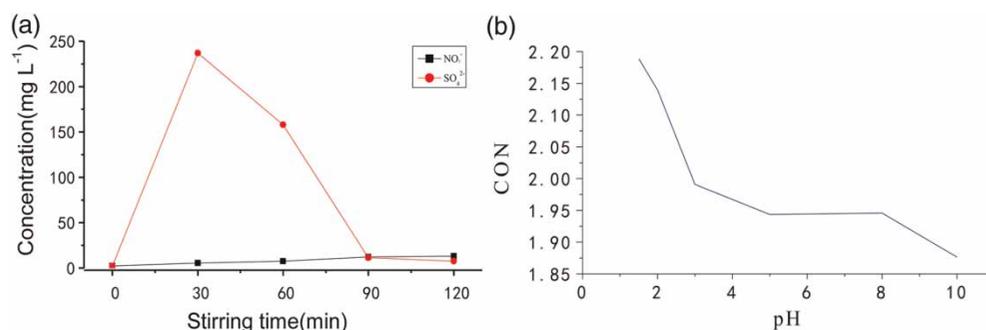


Figure 3 | Concentration change of SO_4^{2-} and NO_3^- in MB solution at different stirring times (a). Change of CON of MB oxidized by MWs at varying pH (b).

The kinetics of the MB decolorization was determined using the experimental data with initial MB concentration of 6.25, 12.5, 25, 50 and 100 mg L⁻¹. The Langmuir–Hinshelwood model was used to characterize the kinetic data (Wahi *et al.* 2005). The reaction follows the pseudo-first-order reaction: $\ln(C_t/C_0) = -kt$; where C_t and C_0 are temporal and initial MB concentration, respectively, and k is the rate constant. A plot of $\ln(C_t/C_0)$ versus t yields a slope of $-k$, as shown in Figure 2(f). A relatively higher rate constant at the lower initial concentration of 6.25 mg L⁻¹ ($6.43 \times 10^{-2} \text{ min}^{-1}$) was observed, whereas for the higher initial concentration of 100 mg L⁻¹, the rate constant was $1.35 \times 10^{-2} \text{ min}^{-1}$ under identical conditions. The correlation coefficient values (R^2) were greater than 0.99. Zhu *et al.* (2009) have also reported a decrease in k value with increase in initial dye concentration. The decrease in the decolorization rate of MB with a higher initial concentration might be partly attributed to the increase in the solution pH and the decrease in the adsorption of MB on MWs, which in turn reduce the extent of surface complexation with MB. The solution pH at the end of the reaction was found to be higher than the initial pH, owing to consumption of H^+ in the redox process.

MWs have a higher decolorization efficiency (a maximum decolorization rate of $\sim 100\%$ in 90 min) compared to other catalysts, such as Mn_3O_4 and H_2O_2 (a maximum decolorization rate of 99.7% in 3 h) (Zhang *et al.* 2010), ZnS and CdS under light irradiation (a maximum decolorization rate of 73% in 6 h) (Soltani *et al.* 2012) and sulfate modified titania under solar radiation (a maximum decolorization rate of nearly 100% in 4 h) (Mohapatra & Parida 2006).

Mechanism aspects of MB degradation

The oxidation degree of the MB solution with MWs of 2.4 g L⁻¹ at pH 1.5 was investigated (Figure 3). The

production and concentration change of SO_4^{2-} and NO_3^- in suspension liquid during the decolorization process were also determined by ion chromatography (Dionex DX500, USA). The concentrations of SO_4^{2-} and NO_3^- in the initial MB solution (50 mg L⁻¹) of 50 mL were 2.15 and 2.38 mg L⁻¹, respectively. Results shown in Figure 3(a) indicate that the formation and concentration of SO_4^{2-} and NO_3^- change with the increase of stirring time. 29.20% of the total sulfur was converted into SO_4^{2-} and the SO_4^{2-} concentration was determined to be 236.93 mg L⁻¹ when stirring for 30 min. However, when stirring time was increased to 120 min, the concentration of SO_4^{2-} was reduced to 5.46 mg L⁻¹, which might be the results of $-\text{S}-$ on the MB molecules being reduced to $=\text{SO}_2$ due to the strong deoxidization potential of Mn^{2+} (Yang & Wang 2004). Under identical conditions, the NO_3^- concentration increased with the increase of stirring time. 10.78 mg L⁻¹ of NO_3^- was generated from about 34.27% of the total nitrogen content. The results indicate that MB can be completely decolorized and partly degraded in MW suspension.

Figure 3(b) shows that the carbon oxidation number (CON) of the MB molecular oxidized by MWs at different pH. CON can be calculated based on TOC (total organic carbon) (Dohrmann Apollo 9000, TEKMAR) and COD (chemical oxygen demand) measurements (DR/2000, HACH) according to the following equation (Stumm & Morgan 1981):

$$\text{CON} = 4 \times (\text{TOC} - \text{COD}) / \text{TOC} \quad (2)$$

where TOC and COD (mM) are the TOC and COD values in MB solution after being treated by MWs at varying pH, respectively.

As seen from Figure 3(b), with the increase in pH, the CON of the MB significantly decreased, implying a decrease

in the degree of MB oxidation. At pH <2, the CON reached the highest value of 2.2 which indicated partial oxidation of the MB molecules in the solution under the optimum decolorization conditions.

CONCLUSIONS

Flower-like MWs were synthesized via a simple ultrasonic irradiation method for the first time. The XRD pattern confirmed the formation of MWs. The decolorization process was highly pH dependent, and reached the highest decolorization efficiency of nearly 100% at pH 1.5. MWs have an excellent catalytic activity and a remarkable removal efficiency of MB. The optimum treatment conditions were pH of 1.5, MW dosage of 2.4 g L⁻¹, and stirring time of 90 min for 50 mL MB (50 mg L⁻¹). MB can be completely decolorized and partly oxidized by the MW catalysts. About 29.20% of the total sulfur content was converted into SO₄²⁻ when stirring for 120 min. About 10.78 mg L⁻¹ NO₃⁻ was generated from about 34.27% of the total nitrogen content. Results demonstrated that MWs provide a more efficient, low-cost, environmentally friendly, and chemically stable process for the decolorization and degradation of azo dyes from industrial dye effluents.

REFERENCES

- Asghari, A., Kamalabadi, M. & Farzinia, H. 2012 Electrochemical removal of methylene blue from aqueous solutions using taguchi experimental design. *Chem. Biochem. Eng. Q.* **26** (2), 145–154.
- Clarke, C. E., Kielar, F., Talbot, H. M. & Johnson, K. L. 2010 Oxidative decolorization of acid azo dyes by a Mn oxide containing waste. *Environ. Sci. Technol.* **44** (3), 1116–1122.
- Ge, J. T. & Qu, J. H. 2004 Ultrasonic irradiation enhanced degradation of azo dye on MnO₂. *Appl. Catal. B: Environ.* **47** (2), 133–140.
- Gemeay, A. H., Gel-Sharkawy, R., Mansour, I. A. & Zaki, A. B. 2012 Application of polyaniline/manganese dioxide composites for degradation of acid blue 25 by hydrogen peroxide in aqueous media. *Bull. Mater. Sci.* **35** (4), 585–593.
- Gulshan, F., Yanagida, S., Kameshima, Y., Isobe, T., Nakajima, A. & Okada, K. 2010 Various factors affecting photodecomposition of methylene blue by iron-oxides in an oxalate solution. *Water Res.* **44** (9), 2876–2884.
- Kobayashi, D., Honma, C., Suzuki, A., Takahashi, T., Matsumoto, H., Kuroda, C., Otake, K. & Shono, A. 2012 Comparison of ultrasonic degradation rates constants of methylene blue at 22.8, 127 and 490 kHz. *Ultrason. Sonochem.* **19** (4), 745–749.
- Kuan, W. H., Chen, C. Y. & Hu, C. Y. 2011 Removal of methylene blue from water by gamma-MnO₂. *Water Sci. Technol.* **64** (4), 899–903.
- Mohapatra, P. & Parida, K. M. 2006 Photocatalytic activity of sulfate modified titania 3: decolorization of methylene blue in aqueous solution. *J. Mol. Catal. A: Chem.* **258** (1–2), 118–123.
- Oyelude, E. O. & Owusu, U. R. 2011 Adsorption of methylene blue from aqueous solution using acid modified calotropis procera leaf powder. *J. Appl. Sci. Environ. San.* **6** (4), 477–484.
- Qiu, G., Huang, H., Dharmarathna, S., Benbow, E., Stafford, L. & Suib, S. L. 2011 Hydrothermal synthesis of manganese oxide nanomaterials and their catalytic and electrochemical properties. *Chem. Mater.* **23** (17), 3892–3901.
- Satapathy, P. K., Randhawa, N. S. & Das, N. N. 2012 Oxidative decolorization of methylene blue by leached sea-nodule residues generated by the reduction-roasting ammoniacal leaching process. *Environ. Technol.* **33** (4–6), 515–522.
- Soltani, N., Saion, E., Hussein, M. Z., Erfani, M., Abedini, A., Bahmanrokh, G., Navasery, M. & Vaziri, P. 2012 Visible light-induced degradation of methylene blue in the presence of photocatalytic ZnS and CdS nanoparticles. *Int. J. Mol. Sci.* **13** (10), 12242–12258.
- Stumm, W. & Morgan, J. J. 1981 *Aquatic Chemistry*. 2nd edn. Wiley-Interscience, New York.
- Valdés, H., Godoy, H. P. & Zaror, C. A. 2010 Heterogeneous catalytic ozonation of cationic dyes using volcanic sand. *Water Sci. Technol.* **61** (12), 2973–2978.
- Wahi, R. K., Yu, W. W., Liu, Y., Mejia, M. L., Falkner, J. C., Nolte, W. & Colvin, V. L. 2005 Photodegradation of Congo Red catalyzed by nanosized TiO₂. *J. Mol. Catal. A: Chem.* **242** (1–2), 48–56.
- Xu, C., Li, B., Du, H., Kang, F. & Zeng, Y. 2008 Electrochemical properties of nanosized hydrous manganese dioxide synthesized by a self-reacting microemulsion method. *J. Power Sour.* **180** (1), 664–670.
- Yang, C. W. & Wang, D. 2004 The study of fenton reagent oxidation and reaction kinetics of methylene blue. *Environ. Technol.* **22** (6), 24–29.
- Yang, L., Hu, C., Nie, Y. & Qu, J. 2009 Catalytic ozonation of selected pharmaceuticals over mesoporous aluminum-supported manganese oxide. *Environ. Sci. Technol.* **43** (7), 2525–2529.
- Yang, S. T., Chen, S., Chang, Y. L., Cao, A. N., Liu, Y. F. & Wang, H. F. 2011 Removal of methylene blue from aqueous solution by graphene oxide. *J. Coll. Interf. Sci.* **359** (1), 24–29.
- Zhang, W., Yang, Z., Wang, X., Zhang, Y., Wen, X. & Yang, S. 2006 Large-scale synthesis of β-MnO₂ nanorods and their rapid and efficient catalytic oxidation of methylene blue dye. *Catal. Commun.* **7** (6), 408–412.
- Zhang, P. Q., Zhan, Y. G., Cai, B. X., Hao, C. C., Wang, J., Liu, C. X., Meng, Z. J., Yin, Z. L. & Chen, Q. Y. 2010 Shape-controlled synthesis of Mn₃O₄ nanocrystals and their catalysis of the degradation of methylene blue. *Nano Res.* **3** (4), 235–243.

Zhang, L. L., Nie, Y. L., Hu, C. & Hu, X. X. 2011 Decolorization of methylene blue in layered manganese oxide suspension with H_2O_2 . *J. Hazard. Mater.* **190** (1–3), 780–785.

Zhu, M. X., Wang, Z. & Zhou, L. Y. 2008 Oxidative decolourisation of methylene blue using pelagite. *J. Hazard. Mater.* **150** (1), 37–45.

Zhu, H. Y., Jiang, R., Xiao, L., Chang, Y. H., Guan, Y. J., Li, X. D. & Zeng, G. M. 2009 Photocatalytic decolorization and degradation of Congo red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation. *J. Hazard. Mater.* **169** (1–3), 933–940.

First received 7 October 2013; accepted in revised form 13 December 2013. Available online 21 January 2014