Degradation of methylene blue by natural manganese oxides: kinetics and transformation products

Shuangxi Zhou, Zhiling Du, Xiwen Li, Yunhai Zhang, Yide He and Yongjun Zhang

School of Environmental Science and Engineering, Nanjing Tech University, Pu Zhu Nan Lu 30, Nanjing 211800, People’s Republic of China

In this study, natural manganese oxides (MnO$_x$), an environmental material with high redox potential, were used as a promising low-cost oxidant to degrade the widely used dyestuff methylene blue (MB) in aqueous solution. Although the surface area of MnO$_x$ was only 7.17 m$^2$ g$^{-1}$, it performed well in the degradation of MB with a removal percentage of 85.6% at pH 4. It was found that MB was chemically degraded in a low-pH reaction system and the degradation efficiency correlated negatively with the pH value (4–8) and initial concentration of MB (10–50 mg l$^{-1}$), but positively with the dosage of MnO$_x$ (1–5 g l$^{-1}$). The degradation of MB fitted well with the second-order kinetics. Mathematical models were also built for the correlation of the kinetic constants with the pH value, the initial concentration of MB and the dosage of MnO$_x$. Furthermore, several transformation products of MB were identified with HPLC-MS, which was linked with the bond energy theory to reveal that the degradation was initiated with demethylation.

1. Introduction

Nowadays, a great deal of wastewater from industrial production is discharged into the natural environment, leading to a certain degree of contamination [1]. Dyestuff is an essential industrial ingredient, and the manufacturing processes of which release a large volume of wastewater containing dyestuff [2]. It has been estimated that 10–15% of dyestuff in the dyeing process is drained into natural water via sewage plants [3]. Among these dyestuffs, methylene blue (MB) is a traditional dyestuff and is widely applied in papermaking, textile, plastics, cosmetics, etc. [4]. However, some researchers have reported that people
exposed to MB in the environment experience nausea, chest pain, dizziness and headaches, especially infants and pregnant women [5–8]. In addition, the dyestuff wastewater containing MB can weaken intense sunlight and further affect the photosynthetic activity of aquatic life and decrease the aesthetics and diversity of the biological community [9,10].

To control the contamination of dyestuff wastewater, various technologies have been investigated, including physical methods such as micelle-enhanced ultrafiltration [11], nano-filtration [12], adsorption [13–15] and chemical methods; for instance, electrochemical degradation [8], ozone oxidation degradation [16–18], photo-catalytic degradation [4,19,20] and electrocoagulation [21]. However, the high cost and complex operation of these physical [22] and chemical methods [23] significantly hinder their wide application. In addition, dyestuff wastewater is difficult to biodegrade because it has a low B/C ratio (BOD5/CODcr of less than 0.1) [24,25]. Herein, there is an urgent need to find a method with high efficiency, economical feasibility and ease of operation to degrade dyestuff wastewater.

It has been reported that manganese dioxide possesses high oxidation–reduction potential (1.29 V, 25°C) and that synthetic MnO2 has been applied to degrade phenol and aromatic amines [26,27]. Studies have also found that it performs well in treating bisphenol A, bisphenol AF, bisphenol S and cephalosporins [28,29]. In addition, Fei et al. [30] found that synthesized MnO2 has a high removal efficiency for Congo red. Cheng et al. [31,32] reported that nano-MnO2 could completely destroy HCHO at low temperature. Furthermore, Sekine [33] has improved the performance of nano-MnO2 so that it can be practically used to remove HCHO at room temperature. However, the high cost and complex synthetic steps of synthesized MnO2 have limited its application in wastewater treatment. By contrast, manganese ores consisting of multivalent manganese oxides could be a substitute because of abundant reserves in nature. Recently, studies have demonstrated the good degradation efficiency of organic contaminants by natural manganese oxides (MnOx), such as diclofenac [34], melanin [35] and paracetamolin [36] and emerging organic contaminants [37]. MnOx was also extensively used in drinking water treatment for the removal of iron and manganese [38]. However, there are too many different and complex compositions of natural manganese ores. Therefore, it is necessary to find a kind of MnOx with high manganese content and stable effect on removing environmental containments.

In the current study, MnOx was used as an environmental material to degrade MB. The influence of pH, the dosage of MnOx and the concentration of MB was studied and the degradation kinetics was established. In addition, a degradation pathway is proposed with the transformation products identified with high-performance liquid chromatography–mass spectrometry (HPLC-MS).

2. Experiment

2.1. Materials and chemical agents

MB (98.5%), acetic acid (99.8%), sodium acetate (98%), sodium hydrogen phosphate (99%), hydrochloric acid (36–38%) and sodium hydroxide (96%) were used as purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai). Deionized water was used for preparing all solutions. Natural manganese ore (MnOx, with a relative content of MnO2 75.38%) was purchased from Qingchong Manganese Co., Ltd, Hunan Province, with a size ranging from 0.075 to 0.12 mm. MnO2 was rinsed with deionized water before tests.

2.2. Characterization of MnOx

X-ray diffraction (XRD; Rigaku Smartlab, Japan) equipped with monochromatic high-intensity Cu-Kα radiation (λ = 0.154 nm) was used to analyse MnOx. The operating conditions were as follows: voltage 40 kV, current 40 mA, small-angle range from 0.6° to 5° and wide-angle range from 10° to 80° in a scanning step of 0.02° s⁻¹. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7800F (Japan). Fourier transform infrared (FTIR) spectra were obtained with a IRAffinity-1 (Shimadzu) spectrometer. The Brunauer–Emmett–Teller (BET) surface areas were measured with a Micromeritics TriStar II 3020 nitrogen adsorption apparatus. The surface charges zeta point was measured by a zeta-meter (Malvern Nano-ZS90).

2.3. Degradation test

Aliquots containing 200 ml of MB solution were added to Erlenmeyer flasks containing 0.1 mol l⁻¹ acetic or phosphate as a buffer system. The pH of the solution was adjusted with HCl (0.1 M) or...
NaOH (0.1 M) at room temperature. With stirring on a magnetic stirrer, a certain dosage of MnO$_x$ was added to each flask. A 3.5 ml aqueous sample was collected from the flask at certain time intervals and immediately filtered with a 0.45 μm polyether sulfone (PES) membrane. The filtrate was used to determine the absorbance of the MB solution at a wavelength of 664 nm with a UV–vis spectrophotometer. All experiments were conducted twice and the average value was adopted. The MB degradation percentage was estimated by equation (2.1),

\[
\text{degradation percentage of MB (\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100,
\]

where $C_0$ and $C_t$ are the concentrations of MB at the start and at time $t$ (mg l$^{-1}$), respectively.

The concentration of Mn$^{2+}$ in the degradation was measured by atomic absorption spectroscopy (AAS; Persee TAS-990).

2.4. Identification of transformation products

The HPLC-MS system (Agilent 1200-6410B, USA) was equipped with an Agilent Poroshell EC-C18 column (100 mm × 4.6 mm packed with 2.7 μm particle size). The mobile phase consisted of 10 mM ammonium acetate (adjusted to pH 5.3 by acetic acid) and acetonitrile at a ratio of 78 : 22 (v/v), and the flow rate was 0.8 ml min$^{-1}$ with an injection volume of 20 μl. The HPLC separation was coupled with an ion trap mass spectrometer, equipped with an electrospray ionization (ESI) source and operated in positive mode. The ESI conditions were as follows: capillary voltage at 3.5 kV, endplate offset fixed at 500 V, skimmer at 40 V, trap drive at 53 V, a nebulizer pressure of 70 psi, a drying gas flow of 12 l min$^{-1}$ and a drying temperature of 350°C. The mass range was 50–700 m/z.

3. Results and discussion

3.1. Characterization of MnO$_x$

The crystalline structure of MnO$_x$ was characterized by XRD. According to the XRD patterns shown in figure 1a, the diffraction peaks (2θ) of 12.74°, 37.63°, 49.90°, 56.18°, 60.24°, 65.52°, and 73.07° correspond, respectively, to the (1 1 0), (3 1 0), (3 0 1), (4 1 1), (6 0 0), (5 2 1) and (4 5 1) crystal planes of α-MnO$_2$ (JCPDS card no. 72-1982) [39]. The diffraction peaks of 12.8°, 18.1°, 37.4°, 42°, 49.8° and 60.2° could be indexed to α-MnO$_2$ (JCPDS card no. 81-1947) [40]. The diffraction peaks of 37.12°, 42.66°, 56.02°, 66.76°, 75.02° and 78.92° match with the (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (2 0 0) crystal planes of ε-MnO$_2$ (JCPDS card no. 30-0820) [41]. The diffraction peaks of 13.45°, 18.20°, 18.59°, 21.06°, 21.32°, 37.43° and 38.28° could be indexed to todorokite (JCPDS card no. 84-1713) [42].

The sample of MnO$_x$ was also characterized using FTIR spectroscopy, which is a powerful tool to study the vibrational behaviour of lattices and provide crystalline phases of MnO$_x$ in the amorphous state. The FTIR spectra of MnO$_x$ are shown in figure 1b. MnO$_x$ has two strong bands located at 538.16 and 580.59 cm$^{-1}$, which are the characteristic adsorption peaks of MnO$_2$ (Mn–O), and two broad bands attributed to the Mn$^{3+}$–O bending–stretching vibration of todorokite could also be detected.
which were located at 468.72 and 1033.89 cm\(^{-1}\) [43–46]. In addition, the vibration peak at 3291.66 cm\(^{-1}\) was attributed to the symmetrical stretching vibration of hydroxyl (–OH) formed by physical adsorption of water molecules or ion exchange.

The N\(_2\) sorption and desorption isotherms are shown in figure 2. According to the IUPAC classification, the N\(_2\) adsorption isotherm closely resembles a type IIb isotherm [47] with a weak adsorption capacity. Within a low relative pressure (\(P/P_0 < 0.3\)), the adsorbed volume of N\(_2\) increased slowly with relative pressure. Under the effect of monolayer adsorption, the adsorption and desorption lines almost coincided with each other, which was also confirmed by Tang et al. [48]. In addition, the adsorbed volume of N\(_2\) rapidly increased under high relative pressure (\(P/P_0 > 0.3\)), which has been regarded as a character of capillary condensation (relative pressure ranging from 0.45 to 0.9) [49]. The specific surface area of MnO\(_x\) was 7.17 m\(^2\) g\(^{-1}\).

In the electronic supplementary material, figure S1 depicts the surface morphology characteristics of MnO\(_x\) by SEM. Particles with different shapes and size were spread in the field. Many grain structures were stuck to the surface of larger particles and some rod-like structures existed between the gaps of the particles. Such observations indicated that the surface morphology material is irregular.

### 3.2. Degradation of MB

#### 3.2.1. pH effects

An experiment was conducted to investigate the relationship between the value of pH and the removal efficiency of MB by MnO\(_x\), and the results are shown in figure 3a. The degradation was promoted by lower pH values and a significant gap existed between pH 5 and 6. The degradation of MB reached
66.1% in 7.5 h at pH 5 and increased to 85.6% at pH 4. However, it was less than 50% with pH values of 6, 7 and 8, in good accordance with previous reports that MnO$_x$ is more active at low pH [40,49,50].

Firstly, the value of pH would affect the surface charge of MnO$_x$ and finally influences the removal behaviour of MB on MnO$_x$ [51]. The zero point charge (pHzpc) of MnO$_x$ was measured and is shown in electronic supplementary material, figure S2. When the pH was lower than 6.13, the surface charge of the MnO$_x$ was positive owing to the protonation. Then the adsorption could be held back by the electrostatic repulsion between the cationic MB (MB$^+$) and the surface active sites of MnO$_x$. When the pH was higher than 6.13, the surface of MnO$_x$ was negatively charged owing to the de-protonation reaction, which led to the formation of precursors between MB$^+$ and MnO$_x$ by mutual attraction. However, the result showed that the removal of MB by MnO$_x$ under acidic conditions was much higher than that under alkaline conditions.

In addition, a small amount of MB adsorbed onto the surface of MnO$_x$ would subsequently be rapidly transferred by oxidation in the low-pH environment. As shown in figure 3b, the photo-spectra of the sample at pH 4 presented a blue shift after the reaction with a decrease in the absorbance peak at 664 nm and an emerging peak at 605 nm, which might belong to the intermediates from the degradation process [40,52]. On the contrary, the absorbance peak patterns did not change under alkaline conditions as the oxidability of MnO$_x$ would be restrained. A further proof came from the increased concentration of Mn$^{2+}$ with the removal of MB in the reaction solution (figure 4a) as a reduced product of MnO$_x$.

A desorption test was conducted with the reacted MnO$_x$ by adding an equal volume of methanol to the reaction solution. It was found that the adsorbed MB only accounted for 0.36% of the total removed MB. The desorption solution also showed a single absorbance peak at 605 nm (figure 4b). Therefore, it is highly possible that oxidation might play a major role in removing MB.

Figure 4. Concentration profile of Mn$^{2+}$ in the degradation of MB (a) and photo-spectra of the reaction and desorption solution (b) (pH = 4, [MnO$_x$] = 3 g l$^{-1}$, [MB] = 30 mg l$^{-1}$, reaction time = 10 h, desorption time = 24 h).

3.2.2. Dosage of MnO$_x$ and initial concentration of MB

To check the effect of MnO$_x$ dosage on the degradation efficiency, a varying dosage of MnO$_x$ from 1 to 5 g l$^{-1}$ was studied at pH 4 and MB concentration of 10 mg l$^{-1}$. As shown in figure 5a, with the increase in the amount of MnO$_x$, the degradation of MB significantly increased. It is worth noting that the degradation of MB reached 69% and 97% in 5 min and 60 min, respectively, under the dosage of 5 g l$^{-1}$ of MnO$_x$. That might be due to the availability of the reactive sites in the system [49].

The initial concentration of MB was also investigated with a range from 10 to 50 mg l$^{-1}$ at pH 4 with an MnO$_x$ dosage of 3 g l$^{-1}$ as presented in figure 5b. It can be clearly seen that the degradation percentage increases with time, and also decreases with increasing initial concentration. Over 99% of MB was degraded in 5.5 h with an initial concentration of 10 mg l$^{-1}$, much higher than that with 50 mg l$^{-1}$ MB (52%), which might be due to the limited amount of active sites of MnO$_x$. Moreover, the intermediates formed during the degradation of MB might compete with the MB molecules for the available active sites.
3.3. Kinetics analysis

The surface binding model of MnO$_2$ with organic compounds, proposed by Arimi *et al.* [35] and Stone & Morgan [53], can be used to describe the reaction process,

\[
\text{MnOH} + \text{MB} \rightarrow \text{MnMB} + \text{H}_2\text{O},
\]

(3.1)

\[
\text{MnMB} \rightarrow \text{Mn}^{2+} + \text{products}
\]

(3.2)

and

\[
\text{[total sites]} = [\text{MnOH}] + [\text{MnMB}],
\]

(3.3)

where \(\text{MnOH}\) is the number of free active sites on the surface of NMO; MB is the concentration in the aqueous solution; and \(\text{MnMB}\), a manganese–methylene blue complex, is formed on the surface of MnO$_2$ and releases Mn$^{2+}$ into the solution.

The dissolving procedure of the products in the solution can be described by equation (3.2). Therefore, the total active sites in the reaction system can be demonstrated in equation (3.3).

The second-order kinetic reaction equation is used to simulate the obtained data as follows:

\[
\frac{d[\text{MB}]}{dt} = -k \cdot [\text{MB}]^2.
\]

(3.4)

In the above equation, [MB] is the concentration of MB at time \(t\). The second-order kinetic reaction constant \(k\) can be obtained by a straight line by fitting \(1/[\text{MB}]\) versus \(t\), and the plots of the experimental results are shown in figure 6. With the above model, figure 6a shows the fitting plots. The calculated kinetic data are summarized in table 1 and the kinetic constant \(k\) of pH = 4 was far higher than that of the other four pH values, as discussed above.
Previous studies have already demonstrated that H\(^+\) in solution may promote the redox capacity of MnO\(_2\)/Mn\(^{2+}\) and a mathematical correlation exists between the kinetic constant and the pH [34,35]:

\[
\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad E^{0}_\text{H} = 1.29 \text{ V at } 25^\circ\text{C}
\]

and

\[
K' = K_{\text{pH}} \cdot [\text{H}^+]^m, \text{or } \log K' = \log K_{\text{pH}} + m \cdot [\text{H}^+].
\]

Here, \(K'\) is a constant independent of the solution pH, \(K_{\text{pH}}\) represents the constant obtained from the fitted kinetics and \(m\) is a constant standing for the reaction series. As shown in figure 6b, the results fit well with equation (3.6), and the values of \(K'\) and \(m\) are 0.2078 and 0.2809, respectively. The value of \(m\) is higher than the data in previous studies on the treatment of organic material by manganese dioxide [35].

Figure 7a,c shows the fitting plots of the second-order kinetics at various dosages of MnO\(_x\) and at different initial concentrations of MB. The kinetic constants can be seen in table 1. In addition, a double logarithmic correlation was also found between the obtained kinetic constants and the dosages of MnO\(_x\) or the initial concentrations of MB, as shown in figure 7b,d, respectively.

### 3.4. Proposed intermediates and reaction pathway

The photo-spectrum of the reaction solution indicated a highly possible chemical transformation of MB with MnO\(_x\), as shown in figure 3b. To gain further understanding of the reaction, the sample was analysed with HPLC-MS to identify the intermediates formed after a 7.5 h reaction. The mass spectra are shown in figure 8, where several \(m/z\) peaks can be clearly noted, representing the formed intermediates. Some peaks (\(m/z\) 256.1, 270.1) have also been found in other studies after the oxidation of MB [4,49].
Table 1. Parameters of second-order kinetic equations with different influencing factors.

| pH | K     | $R^2$ | s.d. | dosage of MnO$_x$ | $K$   | $R^2$ | s.d. | initial concentration | $K$   | $R^2$ | s.d. |
|----|-------|-------|------|--------------------|-------|-------|------|-----------------------|-------|-------|------|
| 4  | 0.0547| 0.9953| 0.0026| 1                  | 0.0547| 0.9953| 0.0026| 10                    | 0.3371| 0.9970| 0.0264|
| 5  | 0.0252| 0.9979| 0.0006| 2                  | 0.1590| 0.9770| 0.0217| 20                    | 0.0469| 0.9861| 0.0108|
| 6  | 0.0097| 0.9786| 0.0010| 3                  | 0.3371| 0.9970| 0.0303| 30                    | 0.0140| 0.9379| 0.0046|
| 7  | 0.0055| 0.9811| 0.0004| 4                  | 0.7723| 0.9952| 0.0424| 40                    | 0.0114| 0.9723| 0.0044|
| 8  | 0.0046| 0.9624| 0.0005| 5                  | 4.3070| 0.9736| 0.3644| 50                    | 0.0068| 0.9802| 0.0023|
As shown in figure 8a, some fragments were observed in eluent at 2.12 min by mass spectra. Those peaks are the possible reduced products in the oxidation of MB by MnO$_x$, which are eluted at the same time as one of the major products, azure A (AA). Similarly, other fragments are eluted with another major product, azure B (AB), at 3.14 min (figure 8b). But the content of these small fragments is very low relative to the other four main intermediates (azure A, azure B, azure C, thionin). Accordingly, these possible intermediates are listed in table 2.

In addition, the detected intermediates are in good accordance with the theory of molecular bond energy. In a molecule of MB, the bonds of N–CH$_3$ connected to C$_7$ or C$_{12}$ have the lowest bond energy (electronic supplementary material, table S1) and thus would be broken first in the oxidation, resulting in demethylation, such as mono-demethylation, di-demethylation, tri-demethylation and
complete demethylation of nitrogen. Ring opening might subsequently occur. Similar results were also observed previously [4,54,55]. A possible demethylation pathway of MB is shown in figure 9.

4. Conclusion

Compared with other synthetic oxidants, Fenton or ozone technology, the current study demonstrates that this kind of natural manganese oxide could be a potentially efficient low-cost oxidant for the degradation of MB in aqueous solution. The results show that the reaction preferred an acidic pH and was strongly influenced by the dosage of MnO$x$ and the initial concentration of MB. The second-order kinetic model can describe the reaction very well and a double logarithmic correlation fits well between the kinetic constants and the dosages of MnO$x$ or the initial concentrations of MB. Several intermediates have been detected, which, linking to the theory of molecular bond energy, demonstrates that the degradation of MB is initiated by the demethylation.

Data accessibility. Additional data are available in the electronic supplementary material. Authors' contributions. S.Z. carried out the degradation experiment, analysed the data and drafted the manuscript; Z.D. and X.L. carried out the analysis of the dynamic experiment data; Yu.Z. and Y.H. conducted the instrumental testing and analysis and revised the manuscript; Yo.Z. conceived of the study, designed the research, coordinated the study and helped revise the manuscript.
References

1. Zerbin Ezzeddine A. 2016 Removal of methylene blue by mesoporous CMK-3: kinetics, isotherms and thermodynamics. J. Mol. Liq. 223, 763–770. (doi:10.1016/j.molliq.2016.09.003)

2. Crini G. 2006 Non-conventional low-cost adsorbents for dye removal: a review. Bioresour. Technol. 97, 1061–1085. (doi:10.1016/j.biortech.2005.05.001)

3. Nell CO, Hawkes FR, Hawkes DL, Lourenço ND, Pinheiro HM, Delée W. 1999 Colour in textile effluents—sources, measurement, discharge consents and simulation: a review. J. Chem. Technol. Biotechnol. 74, 1009–1018. (doi:10.1002/(SICI)1097-4600(19991114)74:3<1009::AID-JCTB153>3.0.CO;2-N)

4. Rauf MA, Meertani MA, Khaledel A, Ahmed A. 2010 Photocatalytic degradation of methylene blue using a mixed catalyst and product analysis by LC/MS. Chem. Eng. J. 157, 373–378. (doi:10.1016/j.cej.2009.11.017)

5. Harvey JG. 1979 Diagnosis of gastro-esophageal reflux in infants and children by methylene-blue gel beads and their efficient adsorption for methylene blue. J. Collid Interface Sci. 506, 669–677. (doi:10.1016/j.jcis.2017.07.093)

6. Zeinab Ezzeddine A. 2016 Removal of methylene blue. J. Pediatr. Surg. 51, 33–42. (doi:10.1016/j.jpedsurg.2015.11.018)

7. Mahadevan MM, Weitzman GA, Hogan S, Breckinridge S, Miller MM. 1993 Methylene blue refractory neonatal hypotension. J. Pediatr. 123, 3476(93)70036-7

8. Park J, Dec J, Kim J, Bollag J. 1999 Effect of methylene blue on refractory neonatal hypotension. J. Pediatr. 129, 904–908. (doi:10.1016/S0022-3476(06)0032-7)

9. Samarghandi MR, Al-Muzaini TW, Mohseni-Bandpi A, Zarabi M. 2015 Adsorption of cephalazin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles. J. Mol. Liq. 211, 431–441. (doi:10.1016/j.molliq.2015.06.067)

10. Mahadevan MM, Weitzman GA, Hogan S, Breckinridge S, Miller MM. 1993 Methylene blue refractory neonatal hypotension. J. Pediatr. Surg. 28, 421–427. (doi:10.1016/j.jtice.2016.10.029)

11. Mahadevan MM, Weitzman GA, Hogan S, Breckinridge S, Miller MM. 1993 Methylene blue refractory neonatal hypotension. J. Pediatr. 123, 3476(93)70036-7

12. Yang M, Liu X, Qi Y, Sun W, Men Y. 2017 Preparation of k-carrageenan/graphene oxide nanocoated electrode. Ultrason. Sonochem. 2018 Substructure reactivity affecting the manganese dioxide oxidation of cephaloparins. Environ. Sci. Technol. 52, 9188–9195. (doi:10.1021/acs.est.8b02448)

13. Khadraoui M, Travelli H, Kibi M, Bouquera S, Ellouche B. 2009 Discoloration and detoxification of a Congo red dye solution by means of ozone treatment for a possible water reuse. J. Hazard. Mater. 161, 974–981. (doi:10.1016/j.jhazmat.2008.04.060)

14. Cheng FY, Chen J, Gou XL, Shen PW. 2005 High-performance lithium-ion batteries using γ-MnO2 nanowires/nanotubes and electrolytic zinc powder. Adv. Mater. 17, 2753–2756. (doi:10.1002/adma.200500633)

15. Cheng F, Su Y, Liang J, Tao Z, Chen J. 2010 MnO2-based nanocatalysts as catalysts for electrochemical oxygen reduction in alkaline media. Chem. Mater. 22, 898–905. (doi:10.1021/cm901698a)

16. Seikine Y. 2002 Oxiative decomposition of formaldehyde by metal oxides at room temperature. Atmos. Environ. 36, 5543–5547. (doi:10.1016/S1352-2310(02)00670-2)

17. Huguet M, Deborde M, Papat S, Gallard H. 2013 Oxidative decarbonylation of dicoflonac by manganese oxide bed filter. Water Res. 47, 5400–5408. (doi:10.1016/j.watres.2013.06.016)

18. Bandopadhyay A, Kim H, Chang P. 2000 Decolorization of wastewater. Crit. Rev. Environ. Sci. Technol. 30, 449–505. (doi:10.1080/10643380901184237)

19. Brillas E, Martinez-Huitle CA. 2015 Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: an updated review. Appl. Catal. B 157, 683–691. (doi:10.1016/j.apcatb.2014.11.016)

20. Manna S, Roy D, Saha P, Gopakumar D, Thomas S. 2017 Rapid methylene blue adsorption using modified lignocellulosic materials. Process Saf. Environ. Protect. 107, 346–356. (doi:10.1016/j.ṛrspp.2017.03.008)

21. Georgiou D, Aivazidis A, Hatiras J, Gizouhoupoulos K. 2003 Treatment of cotton textile wastewater using lime and ferrous sulfate. Water Res. 37, 2248–2250. (doi:10.1016/S0043-1354(02)00481-5)

22. Laha S, Luthy RG. 1990 Oxidation of aniline and other primary aromatic amines by manganese dioxide. Environ. Sci. Technol. 24, 363–373. (doi:10.1021/es00073a012)

23. Yang M, Liu X, Qi Y, Sun W, Men Y. 2017 Preparation of k-carrageenan/graphene oxide nanocoated electrode. Ultrason. Sonochem. 2018 Substructure reactivity affecting the manganese dioxide oxidation of cephaloparins. Environ. Sci. Technol. 52, 9188–9195. (doi:10.1021/acs.est.8b02448)

24. Laha S, Luthy RG. 1990 Oxidation of aniline and other primary aromatic amines by manganese dioxide. Environ. Sci. Technol. 24, 363–373. (doi:10.1021/es00073a012)

25. Le J, Pang SY, Zhou Y, Sun S, Wang L, Wang Z, Gao Y, Yang Y, Jiang L. 2018 Transformation of bisphenol AF and bisphenol S by manganese dioxide and effects of iodide. Water Res. 143, 47–55. (doi:10.1016/j.watres.2018.06.029)

26. Hou M, Kuo C, Chen Y, Huang C, Hsu C, Lin AV. 2018 Substructure reactivity affecting the manganese dioxide oxidation of cephaloparins. Environ. Sci. Technol. 52, 9188–9195. (doi:10.1021/acs.est.8b02448)

27. Cheng F, Su Y, Liang J, Tao Z, Chen J. 2010 MnO2-based nanocatalysts as catalysts for electrochemical oxygen reduction in alkaline media. Chem. Mater. 22, 898–905. (doi:10.1021/cm901698a)

28. Brillas E, Martinez-Huitle CA. 2015 Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: an updated review. Appl. Catal. B 157, 683–691. (doi:10.1016/j.apcatb.2014.11.016)

29. Manna S, Roy D, Saha P, Gopakumar D, Thomas S. 2017 Rapid methylene blue adsorption using modified lignocellulosic materials. Process Saf. Environ. Protect. 107, 346–356. (doi:10.1016/j.ṛrspp.2017.03.008)
