Rapid and efficient removal of methylene blue by freshly prepared manganese dioxide

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Abstract: Freshly prepared manganese dioxide was employed as an adsorbent to remove methylene blue (MB) from water. It was demonstrated that the obtained MnO₂ outperformed several adsorbents previously reported in the literatures for a rapid and effective removal of MB. The time required to reach adsorption equilibrium was as short as 2 min. The Langmuir isotherm fit well into the experimental data with a linear correlation coefficient ($R^2$) of 0.997. The maximum adsorption capacity was 627.1 mg/g. The removal efficiency of MB increased along with increasing MnO₂ dose, whereas decreased over pH 3.0–6.0. The adsorption mechanism was primarily attributed to electrostatic attraction.

1. Introduction

Water contamination caused by dye industries is of great environmental concern all over the world, since most dyes are considered as possible carcinogens or mutagens to aquatic life and humans (Yagub, Sen, Afroze, & Ang, 2014). Therefore, a variety of treatment processes such as physical separation, chemical oxidation and biological degradation have been widely employed for the removal of dyes from wastewaters (Singh & Arora, 2011). Among the treatment options applied, considerable attentions have been paid to adsorption technology due to its simplicity, easy scale-up and high efficiency over a wide concentration range. Numerous adsorbents have been investigated for dyes adsorption, including activated carbon aerogels (Yu, Li, & Wang, 2017), red mud (Coruh, Geyikci, & Nuri Ergun, 2011), activated carbon (Dahlan, Ng, & Pushpamalar, 2017), zeolite (El-Mekkawi, Ibrahim, & Selim, 2016), graphene oxide (Wu et al., 2014), agricultural residues (Balarak et al., 2015).

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PUBLIC INTEREST STATEMENT

The water contamination caused by dyes has raised concerns about the adverse effects on aquatic ecosystems and human health. The commonly used dyes removal adsorbents, such as carbonaceous materials, have several deficiencies including low adsorption capacity and/or slow dyes uptake. To overcome these obstacles, freshly prepared manganese dioxide was employed as an adsorbent to remove a typical dye methylene blue from aqueous solution. It was demonstrated that freshly prepared manganese dioxide outperformed several adsorbents previously reported in the literatures for a rapid and effective removal of methylene blue in aqueous solution. Therefore, freshly prepared manganese dioxide has a great potential for the treatment of dye polluted water.
multi-wall carbon nanotube (Gong et al., 2009). However, these established adsorbents usually have some inherent problems such as low adsorption capacity, long equilibrium time and high capital cost.

Generally, a great adsorption capacity for pollutant removal could be obtained from adsorbent with a large surface area and/or sufficient active sites, such as activated carbon (Kannan & Sundaram, 2001) and metal-organic framework (Haque, Lo, Minett, Harris, & Church, 2014). A rapid adsorption is enabled by the decrease in adsorbent particle size and/or the increase in pore diffusion. Previous studies show that smaller adsorbent particle size favor adsorption due to shorter travel distance for intraparticle radial diffusion and larger specific surface area (Matsui, Ando, Sasaki, Matsushita, & Ohno, 2009). In addition, increasing numbers of mesopores in adsorbent can reduce the length of the diffusion path to the micropores and accelerate the pore diffusion of pollutant molecules (Qin & Xu, 2016). As a result, nanoparticles such as sphere-like MnO₂ nanoparticles, iron oxide nanoparticles and mesoporous nano-TiO₂ have been successfully used as dyes adsorbents in wastewater treatment due to their large numbers of active sites, smaller particle size and high surface area (Nassar, Amin, Ahmed, & Abdallah, 2016; Saha, Das, Saikia, & Das, 2011; Tan et al., 2015; Xiong et al., 2010).

In addition, nanosized manganese dioxide has received a considerable interest because of its nontoxicity, low cost and easy obtainment (Huangfu, Jiang, Ma, Liu, & Yang, 2013; Qin, Wang, Fu, & Ma, 2011). In engineered systems, nanosized manganese dioxide can be prepared simply by oxidizing Mn²⁺ by KMnO₄ or NaOCl. This process offers many advantages for the treatment of dyes compared to other treatment processes, including: low space and energy requirements; simple plant design; easy maintenance, operation and handling; and low operational costs (Qin et al., 2011). However, it should be noted that nanosized manganese dioxide gradually aggregate in aqueous solution over time, resulting in a decrease of surface area and loss of other related properties (Huangfu et al., 2013). Accordingly, freshly prepared manganese dioxide is expected to exhibit a higher adsorptive potential than aged manganese dioxide. It has been reported that freshly prepared MnO₂ has small particle size (20–100 nm) and relatively high surface area (Huangfu et al., 2013; Qin et al., 2011; Zhang, Ma, & Yu, 2008). Therefore, freshly prepared MnO₂ might be promising adsorbent for pollutant removal in environment remediation. Up to now, to the best of our knowledge, removal of dyes by freshly prepared MnO₂ has not yet been studied.

In this current study, methylene blue (MB) was selected as a model compound for cationic dyes. Freshly prepared MnO₂ was obtained from oxidizing MnSO₄ by KMnO₄ in a basic solution of NaOH. The ability of the freshly prepared MnO₂ for MB removal in single batch system from aqueous solution under various environmental conditions was investigated. Fourier transform infrared spectroscopy (FTIR) of pure MnO₂ and MnO₂ loaded with MB were also performed to identify the possible adsorption mechanism.

2. Materials and methods

2.1. Materials

All chemicals (analytical grade) used in the study were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared using 18 MQ deionized H₂O at neutral pH (Millipore). The stock solutions containing 250 mg/L of MB were prepared by dissolving appropriate amounts of MB. The molecular structure of MB was shown in Figure 1. Stock solutions of 17.3 mmol/L MnSO₄ and 11.5 mmol/L KMnO₄ containing 23.0 mmol/L NaOH were prepared every week. Freshly prepared MnO₂ was generated by reducing KMnO₄ with a stoichiometric amount of MnSO₄ according to the reaction:

\[3\text{MnSO}_4 + 2\text{KMnO}_4 + 4\text{NaOH} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}\]  (1)
2.2. Adsorption experiments

Adsorption experiments were performed by batch technique to obtain the equilibrium time and equilibrium data. In brief, the MB adsorption experiments were all conducted in 18 MΩ deionized H₂O and room temperature at constant ionic strength of 0.01 mol/L NaNO₃ and pH 6.0, unless specified otherwise.

For adsorption kinetics, an aliquot of MnSO₄ solution was introduced into 500 mL polyethylene flask by stirring at 200 rpm. Then an aliquot of KMnO₄ solution was added and quickly mixed for 1 min (120 min was also studied to compare aged MnO₂ with freshly prepared MnO₂). Finally, an aliquot of MB solution was added into the mixture. The final solution volume was invariably kept at 250 mL. Following that, an aliquot of 5.0 mL of the solution was withdrawn at appropriate time intervals and immediately filtered through a cellulose acetate membrane of 0.22 μm pore size. The residual concentration of MB in the filtrate was subsequently determined by UV–vis spectrophotometer at the wavelength corresponding to the maximum absorbance (λ<sub>max</sub> = 660 nm). A five-point calibration curve was made with MB standard solutions ranged from 1.0–5.0 mg/L. To ensure that the adsorption of MB onto the cellulose acetate membrane was negligible, the concentrations of MB standard solutions passed through the filter membrane were measured and recalculated using the calibration curve and the differences were less than 2%.

For isotherm studies, an aliquot of MnSO₄ solution was introduced into 50 mL polyethylene flasks. Subsequently, an aliquot of KMnO₄ solution was added and quickly mixed for 1 min, into which an aliquot of MB solution with varying initial concentrations was added. The final solution volume was invariably kept at 25 mL. Following that, the flasks were shaken at 150 rpm for 30 min, using a thermostatic shaker at 25°C. The shaking time was deemed sufficient to ensure apparent equilibrium as determined by preliminary kinetic tests. After the adsorption reached equilibrium, the solutions were filtered and the remaining concentrations of MB were measured by UV–vis spectrophotometer. The samples were diluted if necessary to ensure the MB concentration in the diluted samples were within the range of the calibration curve.

For the investigation of adsorbent dosage effect, various adsorbent dosages from 10–50 mg were added to 25 mL of solution with MB initial concentration of 20 mg/L, and then the flasks were shaken under 25°C for 30 min. The effect of pH on adsorption of MB was studied in a pH range of 3.0–9.0 by agitating 25 mL of 10 mg/L MB solutions with freshly prepared MnO₂ of 10 mg/L at 25°C for 30 min. To ensure reproducibility, all MB adsorption tests were carried out in duplicate. The coefficient of variations (CV) of the data duplicates was all below 5%.

The total Mn content in the filtrate in all adsorption experiments was determined by inductively coupled plasma mass spectrometry (ICP-MS) method. It was observed that the total Mn content was less than 0.1 mg/L. In addition, Van Benschoten and colleague reported that the solid phase formed in oxidation of MnSO₄ by KMnO₄ at pH 5.5–8.0 and temperature 25°C was predominantly MnO₂(s) (Van Benschoten, Lin, & Knocke, 1992). Therefore, the dose of freshly prepared MnO₂ can be calculated directly from reaction (1). The adsorption percentage of MB was calculated by the difference of initial and final concentration using the equation expressed as follow:

\[
\text{Removal (\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]
The adsorbed amount of freshly prepared MnO₂ was calculated by the following equation:

\[ q_e = \frac{(C_0 - C_t)V}{W} \]  

(3)

where \( C_0 \) (mg/L) is the initial concentration of MB in solution, \( C_t \) (mg/L) is the concentration of MB in solution at time \( t \), \( V \) (L) is the volume of the solution and \( W \) (g) is the weight of freshly prepared MnO₂ calculated from reaction (1). For the equilibrium concentrations in these equations, \( C_e \) (equilibrium concentration) and \( q_e \) (adsorbed MB at equilibrium) must be written instead of \( C_t \) and \( q_t \). \( C_e \) and \( q_e \) have same unit with \( C_t \) and \( q_t \), respectively.

2.3. Zeta potential measurements

Zeta potential measurements were conducted using a Zeta-Sizer 3000 (Malvern Instrument). The sample containing 0.01 g/L freshly prepared MnO₂ was suspended in a 0.01 mol/L NaNO₃ solution (electrolyte). Then, the slurry was injected into the microelectrophoresis cell using disposable syringes to determine the zeta potential at different pH values. Prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with deionized water, followed by the introduction of the sample solution to be measured. The pHₜₚₗₜ (point of zero charge) of freshly prepared MnO₂ was determined to be 1.2.

2.4. FTIR analysis

Samples were obtained following the procedure used above at pH 6.0. After centrifugation, the slurry was freeze-dried and stored at a desiccator for further FTIR analysis. FTIR spectra of MnO₂ and MnO₂ loaded with MB were recorded with KBr pellets on a Perkin-Elmer Spectrum One FTIR between wave numbers of 400 and 4,000 cm⁻¹.

3. Results and discussion

3.1. Effect of contact time

Figure 2 shows the amounts of MB adsorbed as a function of contact time with an MB dosage of 10 mg/L and an initial pH value of 6.0. It is observed that the time required to reach adsorption equilibrium was as short as 2 min for freshly prepared MnO₂. The average adsorption amount of MB was 573.8 mg/g (removal by 57.4%). This short time period required to attain equilibrium suggests an excellent affinity of freshly prepared MnO₂ for MB from aqueous solution, which would be helpful in reducing the capital and operational costs for industrial applications. However, the time required to reach adsorption equilibrium for aged MnO₂ was longer than 5 min. The maximum adsorption amount of MB was 475.8 mg/g (removal by 47.6%), which is lower than that of freshly prepared MnO₂. It has been reported that freshly prepared MnO₂ could gradually aggregate in aqueous solution and the hydrodynamic diameter will increase significantly over time (Huangfu et al., 2013).
Therefore, the relatively lower adsorption amount and longer adsorption equilibrium time for aged MnO$_2$ was likely attributed to the MnO$_2$ aggregation, which might hinder MB molecules to the readily accessible binding sites as well as increase resistance to diffusion.

It should be stressed that MnO$_2$ could oxidize organic compounds in aqueous solution such as steroid estrogens (Xu, Xu, Zhao, Qiu, & Sheng, 2008), sulfamethazine (Gao, Hedman, Liu, Guo, & Pedersen, 2012), nonylphenol and octylphenol (Lu & Gan, 2013). To distinguish the removal of MB by adsorption or oxidation, UV–vis spectra of MB after treatment with freshly prepared MnO$_2$ at time intervals were investigated. As shown in Figure 3, no new peaks were observed directly, indicating that removal of MB by freshly prepared MnO$_2$ at pH 6.0 was solely resulted from adsorption.

### 3.2. Effect of freshly prepared MnO$_2$ dose

The adsorption percentage and the adsorbed amount for adsorption of MB on freshly prepared MnO$_2$ with respect to MnO$_2$ dose are illustrated in Figure 4. It is observed that there is a significant increase in percentage removal of MB with a increase in the MnO$_2$ dose due to the availability of larger surface area and more adsorption sites. The almost complete removal of MB was obtained at MnO$_2$ dose of 50 mg/L. The adsorbed amount at equilibrium decreased as MnO$_2$ dose increased from 10–50 mg/L. The results could be explained by adsorbent surface area and available adsorption sites. At low adsorbent dose, the adsorbent surface is likely saturated with MB and the residual MB concentration in the solution is large. At a higher adsorbent dose, the adsorption sites would be excessive for adsorption reaction, which led to the unsaturation of the adsorption sites, resulting in comparatively less adsorption amount at higher adsorbent dose. Moreover, the hydrodynamic diameter of freshly prepared MnO$_2$
prepared MnO₂ will increase with the increase of MnO₂ dose due to aggregation, which led to a decrease in surface area and ultimately a lower adsorption capacity (Huangfu et al., 2013).

### 3.3. Adsorption isotherm

The adsorption isotherm of MB on freshly prepared MnO₂ is shown in Figure 5. The shape of the isotherm looks rectangular because at low equilibrium MB concentration \( C_e \), the equilibrium adsorption capacity \( q_e \) of the freshly prepared MnO₂ reaches almost the same \( q_e \) as those at high equilibrium MB concentration. It indicates that a strong affinity takes place between the MB molecules and the surface sites on MnO₂. At low initial MB concentrations, sufficient adsorption sites on MnO₂ surface are available for adsorption of MB. The removal of MB with an initial concentration of 5 mg/L was 92.6%. At higher initial concentrations of MB, the uptake of MB remained unchanged due to the limited available adsorption sites.

In order to describe the adsorption isotherm, two common isotherms are selected in this study, the Langmuir and Freundlich isotherms:

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad (4)
\]

\[
q_e = K_F C_e^{1/n} \quad (5)
\]

where \( q_e \) (mg/g) is the adsorbed amount of MB at equilibrium; \( C_e \) (mg/L) is the equilibrium concentration of MB in solution; \( q_{\text{max}} \) (mg/g) is the maximum adsorption capacity; \( K_L \) (L/mg) is the Langmuir constant; \( K_F \) is an index of the adsorption capacity of the adsorbent and the slope \( n \) is a constant indicative of the degree of nonlinearity between solution concentration and adsorption.

The isotherm parameters obtained from the Langmuir and Freundlich model fits to the data are given in Table 1. It is clear that the Langmuir isotherm fit is quite well for MB adsorption under the concentration range studied (evidenced from the correlation coefficients, >0.997), suggesting that the adsorption of MB on freshly prepared MnO₂ closely follow a Langmuir isotherm. The high fit to the Langmuir model also suggests that the adsorption is limited with monolayer coverage and the

| Table 1. Parameters of adsorption isotherms of MB on freshly prepared MnO₂ |
|-----------------------------|-----------------|-----------------|-----------------|-----------------|
| **Langmuir isotherm**       | **Freundlich isotherm** |
| \( q_{\text{max}} \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \)    | \( K_F \) | \( n \) | \( R^2 \) |
| 627.1                       | 7.57            | 0.997          | 516.5         | 14.2           | 0.860           |
surface is relatively homogeneous. The maximum monolayer adsorption capacity \(q_{\text{max}}\) of freshly prepared MnO\(_2\) was 627.1 mg/g.

Adsorption capacity and adsorption rate are both crucial factors for adsorbents in practical application, which provide the basis for assessing the adsorption processes and, in particular, for adsorption system design. MB adsorption performances of other adsorbents are summarized in Table 2. Compared to that of most of other adsorbents, the adsorption capacity of freshly prepared MnO\(_2\) is considerably higher and the adsorption equilibrium time is significantly shorter, which was most likely attributed to the small adsorbent particle size. The particle size of freshly prepared MnO\(_2\) has been reported to be in the range of 20–100 nm (Huangfu et al., 2013; Zhang et al., 2008). The smaller adsorbent particle size is believed to enhance adsorption capacity and rate due to larger specific surface area and shorter travel distance for diffusion (Matsui et al., 2009). These results imply that freshly prepared MnO\(_2\) can serve as a promising and feasible adsorbent for the removal of MB from water.

### 3.4. Effect of pH

Figure 6 shows the removal efficiency of MB with respect to the equilibrium solution pH over the range of pH 3.0–9.0. Seen in Figure 6, solution pH is a crucial factor for the extent of MB removal by freshly prepared MnO\(_2\). The removal efficiency of MB decreased with increasing pH up to 6.0 and then increased slightly in the pH range 6.0–9.0. At pH 3.0, 6.0 and 9.0, MB was removed by 96.1, 56.3 and 62.2%, respectively. The removal of MB at pH 3.0 is much higher than that at pH > 6.0. This finding can be explained by the oxidation of MB by freshly prepared MnO\(_2\). Some researchers have demonstrated that MB can be oxidized by MnO\(_2\) at pH lower than 5.0 due to the high standard reducing potential (1.29 V) (Wang et al., 2014; Zhao et al., 2013). Derived from the Nernst equation, a decreased pH in the suspension results in the reducing potential of MnO\(_2\)/Mn\(^{2+}\), and followed by an increase of the oxidizing power of the system. In other words, low pH conditions apparently favor the oxidation process. In this study, the color of solution changed from blue to steel blue at pH 3.0 (seen in Figure 6). This suggests that removal of MB at low pH values (less than 5.0) might not result from pure adsorption but the oxidation by MnO\(_2\). At pH values higher than 6.0, the removal of MB was mainly due to adsorption, which was confirmed by UV–vis spectra.

The zeta potential of freshly prepared MnO\(_2\) decreased from −4.7 to −9.0 mV in the pH range 3.0–9.0, indicating that the surface of freshly prepared MnO\(_2\) was negatively charged. Under the

### Table 2. Comparison of MB adsorption performance from the literature by various adsorbents

| Adsorbent                  | pH  | Equilibrium time | \(q_{\text{max}}\) (mg/g) | References                  |
|----------------------------|-----|------------------|--------------------------|-----------------------------|
| Carbon aerogels            | 7.0 | 12 h             | 249.6                    | Yu et al. (2017)            |
| Red mud                   | 7.0 | 14 h             | 476                      | Dahlan et al. (2017)        |
| Activated carbon          | 7.0 | 24 h             | 377.6                    | Wu et al. (2014)            |
| Zeolite                    | 7.0 | 24 h             | 21.4                     | EL-Mekkawi et al. (2016)    |
| Commercial activated carbon| 7.4 | 35 min           | 57.3                     | Kannan and Sundaram, (2001) |
| Amino-MIL-101(Al)          | 7.0 | 24 h             | 16.7                     | Balarak et al. (2015)       |
| Multi-wall carbon nanotube| 7.0 | 6 h              | 15.9                     | Gong et al. (2009)          |
| Commercial activated carbon| 7.0 | 24 h             | 980.3                    | Dahlan et al. (2017)        |
| Canola residues            | 7.0 | 120 min          | 762                      | Haque et al. (2014)         |
| Commercial activated carbon| 7.0 | 24 h             | 133.3                    | Xiong et al. (2010)         |
| MCM-22                     | 7.0 | 24 h             | 57.3                     | Wang, Li, and Xu, (2006)    |
| CMK-3                      | 7.0 | 24 h             | 1,250                    | Ezzeddine, Batonneau-Gener, Pouiloux, and Hamad, (2016) |
| NaAlg-g-p(AA-co-St)/I/S    | >4.0| 30 min           | 1,797.3                  | Wang et al. (2013)          |
| Freshly prepared MnO\(_2\)| 6.0 | 2 min            | 627.1                    | This work                   |
experimental conditions, MB is positively charged. As a result, the cationic dye is favourably adsorbed by the negatively charged surface of freshly prepared MnO$_2$ with an electrostatic interaction. Moreover, as pH increased from 6.0–9.0, the removal of MB increased slightly from 56.3–62.2%. The change of removal efficiency of MB with pH (6.0–9.0) might be explained with the increased negative charge of freshly prepared MnO$_2$ at high pH values. A similar adsorption mechanism via electrostatic interaction has also been described in MB adsorption by metal oxides (Xiong et al., 2010).

### 3.5. FTIR analysis

To gain insight into the adsorption mechanism, the FTIR spectra of freshly prepared MnO$_2$ before and after MB adsorption are analyzed (Figure 7). In the case of pure MnO$_2$, the spectrum exhibited the absorption bands at 3,153, 1,034 and 514 cm$^{-1}$. The broadened band around 3,153 cm$^{-1}$ could be assigned to the bending vibration of adsorbed molecular water and stretching vibration of hydroxyl group (Qin et al., 2011; Yang, Makita, Liu, Sakane, & Ooi, 2004). The peak at 1,034 cm$^{-1}$ may be assigned to vibration of the hydroxyl group combined with Mn atoms (Qin et al., 2011; Zhang, Qu, Liu, Liu, & Li, 2007). The broadened band around 514 cm$^{-1}$ was assigned to the Mn-O stretching vibration (Qin et al., 2011; Yang et al., 2004). The adsorption bands of MB at 1,601 and 1,397 cm$^{-1}$ were ascribed to the C–C stretching vibration of aromatic cycle, and the adsorption peak at 883 cm$^{-1}$ belonged to the aromatic skeletal group (Wang, Wang, & Wang, 2013). After adsorption of MB by freshly prepared MnO$_2$, the three bands shifted to 1,607, 1,395 and 896 cm$^{-1}$, respectively. The shifts could have been caused by the interaction between MB molecules and MnO$_2$. In comparison with freshly prepared MnO$_2$, the adsorption band at 514 cm$^{-1}$ of Mn–O bond shifted slightly. Moreover, considering the rapid adsorption rate, the adsorption process might be mainly controlled by
chemical adsorption. This was also supported by the goodness to use the Langmuir isotherm, rather than the Freundlich isotherm, to fit the experimental data. Hence, it was concluded that the main adsorption mechanism of MB onto freshly prepared MnO₂ is electrostatic attraction between negatively charged MnO₂ and positively charged MB.

4. Conclusion
Manganese dioxide was freshly prepared by oxidizing MnSO₄ with KMnO₄ in alkaline medium and its application for the removal of MB from aqueous solution was investigated. The results demonstrated that freshly prepared MnO₂ exhibited a good efficiency in MB removal from aqueous solution. The isothermal data were well described by Langmuir model for the present system. The change of solution pH between 3.0 and 9.0 had a significant influence on MB removal by freshly prepared MnO₂. At pH lower than 5.0, the removal of MB was also attributed to oxidation. Compared to most of other available adsorbents, the adsorption capacity of freshly prepared MnO₂ was much higher. Moreover, the adsorption rate of MB onto freshly prepared MnO₂ was considerably more rapid than other adsorbents. Based on zeta potential measurement and FTIR analysis, the MB uptake onto freshly prepared MnO₂ might be driven solely by electrostatic attraction. Considering its high adsorption capacity and rapid adsorption rate, freshly prepared MnO₂ has a great potential for the removal of MB from water.

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