Removal of methylene blue from water by $\gamma$-MnO$_2$

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**ABSTRACT**

Methylene blue (MB) is a cationic dyestuff, which is particularly resistant to biodegradation. The molecular sieved $\gamma$-MnO$_2$ was used as an adsorbent/oxidant to remove the MB at room temperature and in visible light. The removal efficiency was mainly evaluated by X-ray diffractometer (XRD), UV–Vis spectrometer (UV–Vis), total organic carbon (TOC). The results revealed that the mechanisms of MB removal by $\gamma$-MnO$_2$ are significantly influenced by the pH. In acidic conditions, hypsochromic effects (i.e. blue shifts of UV–Vis spectra) resulting from N-demethylation of the dimethylamino group in MB may occur concomitantly with oxidative degradation by $\gamma$-MnO$_2$. However, the TOC in solution after $\gamma$-MnO$_2$ treatment in acidic conditions did not show a dramatic decrease. At near neutral pH conditions, there was almost no UV–Vis absorption for the MB solution, however, only 50% TOC removal was observed. It indicated that MB was not only adsorbed onto $\gamma$-MnO$_2$ but also partially oxidatively degraded to other organic compounds which were colourless for UV–Vis.

**Key words** | adsorption, manganese oxide, methylene blue, oxidative-degradation

**INTRODUCTION**

Methylene blue (MB) plays a significant role in testing materials in analytical chemistry, as a sensitizer in solar energy conversion, as a surface modifier of semiconductor colloids, and in medical photodynamical therapy (Wainwright et al. 1997; Zhang et al. 2002; Matsuda et al. 2005). MB is a cationic dyestuff, which is particularly resistant to biodegradation. Although there have been numerous reports of photocatalytic MB degradation over the TiO$_2$-based photocatalysts, most of the studies were performed under UV light irradiation (Lakshmi et al. 1995). Recently, some investigations demonstrated that some dyes could be degraded under visible light irradiation on TiO$_2$ by a self-photosensitized process, but MB could not be degraded by this process. Up to now, only a few studies have been reported on MB dye degradation under visible light irradiation (Zhang et al. 2002). Furthermore, the catalytic efficiency is limited by the light absorption characteristics of the TiO$_2$-based photocatalysts. Because of the significant difficulty concerning dye-containing wastewater treatment, the criterion for effluent colority in Taiwan have been raised from below 400 ADMI to below 550 ADMI.

Manganese oxides have been proven to be a potential oxidant in soil and mainly govern the abiotic degradation of a number of organic pollutants due to their high reducing potential (Zhu et al. 2008; Nakayama et al. 2009). With a rather complex oxide system, forming several oxidation state phases and molecular structures, manganese oxides are of considerable importance in many technological applications (Suib 2008). One of the most important properties of the manganese oxides is the mixed valence. Mixed valence which leads to conductivity often results from first row transition metal ions which can have multiple oxidations states especially those that are 1 electron jumps such as V$^{4+}$/V$^{5+}$, Mn$^{4+}$/Mn$^{3+}$, and others. All of the manganese oxides are octahedral based molecular. Generally, manganese oxides can be divided into layered or molecular sieve (or tunnelled) structures depending on whether the octahedral MnO$_6$ ions are connected via edges or vertices, respectively. Recently, the tunnelled manganese oxides have attracted considerable attention because they have potential applications and reaction selectivities in wide-ranging sectors including catalysis, sensing, electronics and photoelectronics (Yang et al. 2006). The layered manganese oxides, such as birnessite have usually been utilized as the adsorbent/catalyst/oxidant for the removal of organic pollutants because it’s the most commonly identified in soils and...
sediiments (Khraisheh et al. 2004). However, to the best of our knowledge, the application of molecular sieve manganese oxides in organic pollutant control is still lacking. Therefore, a kind of tunnelled manganese oxide, commercial γ-MnO₂ was employed as an adsorbent/oxidant to remove the MB at room temperature and visible light in this study. The efficiency of removal was mainly evaluated by X-ray diffractometer (XRD), UV–Vis spectrometer (UV–Vis), zeta potential measurements and total organic carbon (TOC) analyzer.

**MATERIALS AND METHODS**

Methylene blue, NaOH, HNO₃, and all other chemicals were of AnalaR grade. The MnO₂ particles were obtained from the TOSOH Co. and proved to be γ-MnO₂ (pyrolusite) by X-ray diffractometer (XRD) with a specific surface area of 41 m²/g.

Batch experiments of MB removal by MnO₂ were carried out in 125-mL Erlenmeyer flasks. Before the batch experiments, the MnO₂ suspensions were aged at room temperature under a N₂ atmosphere for 2 h. The initial concentration of MB was 10 mg/L and the MnO₂ concentration was maintained at 0.2 g/L. All experiments were conducted under natural room light irradiation, maintained at 25 °C by the water circulating temperature controller, and adjusted to the desired pH by NaOH and HNO₃ solutions. A preliminary test of pH effect on MB stabilization was also conducted. The procedures of the stabilization test were the same as those of MB removal experiments but without MnO₂(s) in the reactor. The samples were also taken at various times and analyzed by UV–Vis scan of full wavelength. Figure 1 displays the results carried out at pH 12, an extreme case for elucidating the alkaline-degradation of MB. The absorbance and peak positions of original MB solution (0 min) are almost overlapped with those of MB solution sampled at 30 min. However, the absorbance of MB solution was slightly decreased for the 90 min sample and significantly decreases (35%) at 665 nm for the 5 h sample. According to the results of pH effects on MB stabilization, the alkaline-degradation of MB occurred significantly the over pH 10. Therefore, the experimental pH of this study was set in the acidic to neutral range.

After the reaction period, a subsample from the suspension was taken for the zeta potential measurements; the other part of the suspension was filtered through a Millipore membrane filter with pore size of 0.2 μm and the filtrate was preserved at 4 °C for advanced analysis. To determine the change in MB concentration in solution during the process, a UV–Vis spectrometer (Varian Cary 50 Bio) served as the major instrument, and three kinds data of UV–Vis spectrometry were selected to illustrate the reaction in this study. Firstly, the absorbance at 665 nm was a prevalent method to represent the MB concentration in the literature and was also used in this study. Secondly, because the MB could be transformed or degraded to other forms of organic compound by MnO₂, the full spectra scan was necessary and was also adopted in this study. Thirdly, the colority is a criterion of wastewater effluent, especially for dye wastewater in Taiwan. The measurement of colority followed the standard method 2,120E (APHA/AWWA/WEF 1998), which was conducted by integrating the absorbance of 590, 540, 438 nm and then calculating the ADMI value.

Change in total organic carbon (TOC) was determined using a O-I total organic carbon analyzer (Carbon Model 1010). Zeta potential of the particles in selected suspensions was measured with a laser doppler electrophoretic light-scattering apparatus (Malvern Nano-ZS90).

**RESULTS AND DISCUSSIONS**

The zeta potential of MnO₂ suspensions with and without MB over a range of pH is shown in Figure 2. The pH of zero particle mobility, which is referred to as the isoelectric point (IEP), is 4.7 for a γ-MnO₂ particle. This value is close to the pH of tetragonal MnO₂ reported in the literature (Park 1965). Because the MB is a kind of cationic dye, it could compete with H⁺ ion for the surface adsorption site on MnO₂. Therefore, the point of zero charge (pH_{pzc}) of MB in MnO₂ suspension shifted to pH 6.

The absorbance of vis-665 nm was conventionally used to evaluate the MB amount in solution because a maximum
absorbance peak was yielded at this spectrum (Albarelli et al. 2009; Chang et al. 2009; Valdés et al. 2009). Figure 3 shows the kinetics of MB removal and decoloration profiles by MnO₂ at various pHs. The removal efficiency was evaluated by the measurement of solution absorbance before and after reaction at vis-665 nm. Because the preliminary test (shown in Figure 1) indicated that the alkaline-degradation of MB occurred over pH 10 this study chose pH 4.8 and 7.2 as the representations of acidic and neutral condition respectively. The colority is a practical parameter to determine the removal efficiency of dye, and this parameter is evaluated by the ADMI value. The initial true colour of 10 ppm MB solution was 4,600 ADMI. At pH 4.8 the true colour decrease to 2,400 ADMI in the initial 5 min and slightly decreased to 1,600 ADMI at 30 min. The decoloration of MB at pH 7.2 decreased remarkably from 4,600 to 160 ADMI in 1 min. The results quite coincided with that of the MB removal percentage based on the 665 nm. The removal percentage had a sharp increase in the initial 1 min and reached a pseudo-steady state in about 10 min both at pH 4.8 and 7.2. The pseudo-steady state removal percentage of MB at pH 7.2 was 100% and that at pH 4.8 was around 80%, respectively. The pseudo-steady state removal percentage of MB at pH 7.2 was 100% and that at pH 4.8 was around 80%.

According to the vis-665nm analysis for the sample of pH 4.8, 1 g γ-MnO₂ possesses a removal quantity of 50 mg MB. Even though the MB isotherms have not been performed in this study yet, this value yielded by rough calculating revealed that the potential of γ-MnO₂ for MB removal is higher than that of layered MnO₂. Zhu et al. (2008) investigated the oxidative decolorization of MB using pelagite, which was referred to as natural marine Mn nodule and composed of layered birnessite and tunneled todorokite. The results displayed that the maximum capacity of pelagite for MB removal was 25 mg MB/g pelagite. Nakayama et al. (2009) studied the removal of MB from aqueous solution using nanolayered manganese oxide and indicated the uptake capacity of manganese oxide for MB was 45.3 mg per 1.0 g of MnO₂. The increase of MB removal from pH 4.8 to 7.2 can be ascribed to the evolution of surface charge. The γ-MnO₂ surface possessed net negative charged sites when the pH conditions were over pHiep 4.7 (see Figure 2). The cationic MB was more strongly adsorbed onto γ-MnO₂ at pH 7.2 than at pH 4.8 because of electrostatic attraction. On the contrary, the MB was also removed as high as 80% at pH 4.8 at which the net surface charge of γ-MnO₂ was almost zero. Mn-oxides are Lewis acids and deprotonating at different pH values. Therefore, the surface possessed net positive charge and negative charge under and over pHpzc, respectively. The surface with net positive charge prefers to adsorb negatively charged ions, and vice versa. While sorption occurred around pHpzc, complex formation could possibly be one of the removal mechanisms. Sorption of MB at pH 4.8, which value is very close to pHpzc of γ-MnO₂, occurred as the formation of surface complex because of little electrostatic attraction between MB and MnO₂ (Dzombak & Morel 1990). However, there could be some other mechanisms predominantly controlling the reaction.

Because of the multi-oxidation states of manganese, the MB could be adsorbed, degraded catalytically or oxidized by γ-MnO₂. The predominant mechanism was strongly dependent on the forms of manganese oxide (Suib 2008). The MB removal by layered manganese oxides has been widely studied in the literature, however, the mechanisms of MB removal by molecular sieve (tunnelled) manganese oxides are still uncertain (Yang et al. 2006; Nakayama et al. 2009). Figure 4 displays the pH effect on MB removal by γ-MnO₂. The absorption of UV–Vis radiation generally arises from the excitation of bonding electrons in all
molecules in solution. The original MB showed four main absorption peaks at 247, 293, 615, and 665 nm for both the solution conditions of pH 4.8 and 7.2. UV–Vis absorption peaks at 665 and 615 nm correspond to the monomer and dimer of MB respectively (Matsuda et al. 2003; Nakayama et al. 2009). Therefore, both of the absorption spectra were mainly discussed in this study. These two spectra considerably shifted towards the blue region (short wavelength spectra) for the system of MB after treatment by γ-MnO₂ at pH 4.8 (Figure 4(c)). Additionally, a new and remarkable peak occurring at 458 nm was also observed in the pH 4.8 treated system. The absorption intensity decrease only indicates the decrease of MB in solution but did not refer to the removal mechanisms. However, the blue shift (hyposchromic effect) and a new arising peak could evidence the oxidation degradation and new organic products occurring in this system. Figure 3 shows that at pH 4.8 (line a and c in Figure 4) the spectral band at 665 nm blue-shifts by as much as 18 nm from 665 to 647; this suggests the N-demethylation of MB (Zhang et al. 2002). N-dealkylation of dyes containing auxochromic alkylamine groups plays a significant role in catalytic degradation. The colour of MB solution turned less intense during the gradual degradation of all or part of the auxochromic groups (methyl or methyamine). Comparing the absorption spectrum 615 nm of original MB in solution with that of MB treated by γ-MnO₂ at pH 4.8, it is found that this spectrum also has a blue shift of about 10 nm. Related to the present observations, blue shift of 615 nm has been reported to be the H-type aggregation of MB dimer. At pH 7.2 there was almost no UV–Vis absorption for the MB after treating with γ-MnO₂ (line d in Figure 4). This indicates that the MB was almost totally removed from solution, however, the mechanisms of removal could be adsorption or oxidative degradation by γ-MnO₂. The uncertainty of the removal mechanism at pH 7.2 needs more advanced experiments to discern.

Figure 5 shows the evolution of the remaining TOC in solution with time. The TOC of the original MB solution was 5.71 ppm. The TOC removal percentage in the considered time was 13 and 50% at pH 4.8 and 7.2 conditions respectively. Comparing with the results of UV–Vis absorption, the low TOC removal percentage was expected for pH 4.8 conditions but not for pH 7.2 conditions. At pH 4.8, MB was oxidatively degraded to small organic compounds evidenced as a new arising peak and blue shifts of 665 and 615 nm, therefore, the TOC remaining was contributed by different small organic compounds. However, 50% TOC removal for pH 7.2 conditions was unexpected because of the almost zero UV–Vis absorption. These results might imply that the MB not only was adsorbed but also partially oxidatively degraded by γ-MnO₂ at pH 7.2 conditions; and the degradation products were colorless for UV–Vis. In addition, both of the pH conditions showed a trend of sharp decrease of TOC in the initial 1 min, but a slight increase after 10 min. These results could be ascribed to MB being firstly adsorbed to the γ-MnO₂ surface then oxidatively degraded, with and finally the products of degradation being finally released from the solid surface to solution.

CONCLUSIONS

MB removal by γ-MnO₂ was significantly pH dependent. The pH_{ep} of γ-MnO₂ was around 4.8, for which value the surface possessed net negative charge. At pH 4.7 conditions,
the cationic MB was less adsorbed because the surface was almost neutrally charged; however, the oxidative degradation was evidenced by the newly arising peak at 458 nm and the blue shifts (hypoergic effects) of the absorption peaks 615 and 665 nm respectively, corresponding to the monomeric and dimeric MB. The oxidation of MB at pH 4.7 could be attributed to the N-demethylation of MB monomer and H-type aggregation of MB dimer. At pH 7.2 there was almost no UV–Vis absorption for the MB solution treated by γ-MnO₂. However, the 50% TOC removal at pH 7.2 implied that the MB was not only adsorbed onto γ-MnO₂ but also partially oxidatively degraded to other organic compounds which were colourless for UV–Vis. According to the UV–Vis spectra, the intermediates were significantly generated at acidic conditions but not at neutral-circum implying that intermediates analysis and a broader pH range study are necessary to elucidate the accurate mechanisms of MB removal by γ-MnO₂ in future work.

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REFERENCES


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