Influencing Parameters for degradation of Methylene Blue using the catalyst bentonite supported manganosite MnO synthesized via facile, one-pot Sol-Gel Route

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Abstract. Textile industries consume considerable amounts of water in dyeing process, thus generating the enormous quantities of wastewater. The wastewater is a highly harmful to environment if discharged untreated or partially treated, since it contains wide range of hazardous compounds and is also very difficult to treat. The structure of dye residues in wastewater is mostly complex polymeric structures, which is highly resistant to biodegradation. The Fenton-based advanced oxidation process (AOP) was widely studied to treat recalcitrant organic contaminant and based on the production of .OH following H₂O₂ activation by a catalyst. Manganese oxides are reported to be an active catalyst for degradation of a dye via Fenton process. Herein, bentonite supported MnO (MnO/bentonite) was synthesized via one-pot sol-gel synthesis and its catalytic activity was evaluated for the degradation of methylene blue (MB) using Fenton process. The X-ray diffraction results revealed the formation of the rock-salt MnO manganosite as crystalline phase of manganese oxide. The MnO/bentonite composite displayed higher performance for the degradation of MB than pure MnO. The maximum degradation of MB by MnO/bentonite composite was achieved by evaluating the process variables and compared to MnO (manganosite) as a control. In the optimum condition, the MnO/bentonite composite was able to degrade 92.97% MB using 15 ml H₂O₂, 50 mg of catalyst and 25 ml MB (75 ppm) in 100 mL solution of initial MB concentration. Both catalyst concentration and H₂O₂ concentration seem to play a significant role for the degradation of MB using the composite MnO/bentonite.

1. Introduction
Over the last few decades the industrial development such as textile, paper, plastic and cosmetics increases significantly and these industries are connected with the release of the massive amounts of organic contaminants, which are harmful to environment (air, plants, water, soils) and human health if discharged untreated or partially treated. The effluents of textile industries contain a wide range of dye stuffs which are highly polluted and harmful as reflected with toxicity, unpleasant odour and highly visible in nature and high concentrations of chemical oxygen demand and biochemical oxygen...
demand. Therefore, the removal of colour has become an environmental concern for the ecological sustainability.

Several strategies have been developed and applied to treat dye contaminations, which mostly include biological, physical and chemical processes with their inherent advantages and disadvantages. Although the biological process is considered the most economical way to treat organic contaminations and widely used in the industrial scale, it has some drawbacks such as time-consuming [1], and could not be applied to a treatment process which is toxic to the organisms used. In the other hand, the physical processes such as adsorption and coagulation could create a side effect (second contaminant) due to the attachment of dyes residues to adsorbent or coagulant via chemical or physical interactions. Thus, an additional cost is needed to separate a dye with adsorbent or coagulant.

In the past few years, the advanced oxidation process (AOP) has been developed and widely studied for the degradation of organic contaminants. The AOP is a collection of various methods, which basically generates \( \cdot \text{OH} \) radicals through the activation of an oxidant such as \( \text{H}_2\text{O}_2 \). The Fenton-based AOP is regarded as a simple, cost-effective, efficient, and environmentally friendly method to treat organic contaminations via the activation of an oxidant by a catalyst. The convention Fenton process applies a homogeneous \( \text{Fe}^{2+} \) catalyst, but has inherent limitations such as narrow working pH, requires highly acidic condition and generates \( \text{Fe(OH)}_3 \) sludge as a by-product. The Fenton-like reaction, on the other hand, uses a heterogeneous catalysts, which is usually transition metal oxides.

Manganese oxides are earth-abundant and environmental friendly oxides and contains various structures as well as could be synthesized with ease. Various synthetic approaches such as solid-state [2], sol-gel [3-6], precipitation [7-11], reflux [12] and hydrothermal [13] have been successfully used to synthesize the oxides. Mn in oxides has various valence such as +2 in MnO (manganosite), +3 in MnO\(_2\) (hausmanite) and +4 in polymorph MnO\(_2\) with different tunnel structure. Among the manganese oxides reported in the previous studies, the rock-salt structure of MnO manganosite was less widely reported and intensively studied. Herein, the MnO-type manganosite and the bentonite supported MnO (MnO/bentonite) were synthesized via a facile, one-pot synthetic approach using sol-gel method and their catalytic performances were investigated and compared for the degradation of MB. The experimental parameters such as \( \text{H}_2\text{O}_2 \) concentration and the catalyst dosage were also investigated to optimize the degradation of MB.

2. Material and Method

2.1. Synthesis. The synthesis of Manganese/bentonite was carried out via one-pot approach of sol-gel route. Briefly, KMnO\(_4\) and glucose were mixed together in the 3:2 mole ratio, and added with bentonite. The mixture was turned into a sol, which then polymerize to generate gel over time and the gel was washed until no K\(^+\) ions were detected. Following calcination process at 700°C for 4 hours of the resulting gel, the product was characterized by X-ray powder diffraction (XRD). The pure MnO was synthesized according to the method reported previously.

2.2. Catalytic Activity. The catalytic performance of pure MnO and composite MnO/bentonite was evaluated for the degradation of MB in batch experiment in the different reaction time intervals: 10, 20,30, 60, 90, and 120 minutes using 50 mg of composite catalyst, 15 mL \( \text{H}_2\text{O}_2 \) and 25 mL MB (50 ppm) in 100 mL of solution. Furthermore, the effect of MB initial concentration, volume of \( \text{H}_2\text{O}_2 \) and the dose of Mn/bentonite catalyst was studied on the degradation of MB.

3. Results and Discussion

XRD is used to identify crystalline phase, purity and crystal size of a solid material. The XRD patterns of as-synthesized manganosite MnO, bentonite and MnO/bentonite were displayed in figure 1. The pure manganese oxide shows peaks at 2\( \theta \) of 34.90, 40.53, 58.71, 70.19 and 73.79 correspond to the diffraction planes of (111), (200), (220), (311) and (222), which are a typical rock-salt manganosite-type MnO (JCPDS card number 733-739). The as-synthesized MnO was high and sharp in intensities, suggesting its highly crystalline nature. The commercial bentonite used in this study
consists of montmorillonite (M), quartz (Q) as main crystalline phase and Kaolinite (K). Following the formation of the composite (bentonite supported MnO), the amorphous nature of bentonite (broad peaks) turns to more crystalline phases (sharper peaks), suggesting the presence of strong interaction between manganosite and bentonite support. In contrast, some peaks due to manganosite disappear, but peak at reflection plane (220) still exist, indicating the presence of manganosite phase in the composite.

**Figure 1.** XRD of the XRD of the MnO, MnO/bentonite and bentonite

The catalytic performance of as-synthesized MnO/bentonite composite was evaluated as the function of reaction time for the degradation of MB and compared to that of pure MnO as a control displayed in Figure 2. It is apparent that the composite has higher catalytic performance over single manganosite and is able to degrade 63.90% and 91.06% of MB compared to 55.61% and 79.69% MB (single manganosite) at 10 minute and 120 minute of reaction time, respectively. The better catalytic performance of the composite over pure MnO could be associated with higher surface area of the composite than the single catalyst. Bentonite, which is 2:1 layered aluminosilicate and known to have a high surface area, is a widely used as an adsorbent for treatment of organic contaminants. The
presence of bentonite in the MnO as a support could enhance the adsorption and activation of H$_2$O$_2$ and MB molecule by providing lower adsorption energy and facilitating the reaction between MB and OH radicals. Support may facilitate an electron transfer for an efficient redox reaction, thus enhancing degradation (oxidation) of a dye. Also, a support could avoid agglomeration between catalyst particles that may hamper degradation rate. Therefore, the presence of a support is believed to provide more active sites for the adsorption, which is the first step in a catalytic reaction.

**Figure 2.** The degradation of MB by single MnO and MnO/bentonite catalyst as function of time using the following condition: 25 mL MB (50 ppm), 50 mg catalyst and 15 mL H$_2$O$_2$ in 100 mL of solution.

In a Fenton reaction, oxidant such as H$_2$O$_2$ is highly important since its activated species mainly OH radical is responsible for the degradation of a dye. As a result, the optimal condition for H$_2$O$_2$ concentration is required for the maximum degradation of a dye. Figure 3 displayed the effect of H$_2$O$_2$ concentration of the catalytic performance of the composite over interval time used in this study. It is apparent from figure 3 that high H$_2$O$_2$ concentration engendered the increase in the degradation of MB, except for the addition of 20 mL of H$_2$O$_2$ where the degradation of MB remained relatively the same as the addition of 15 mL of H$_2$O$_2$. The previous reports indicated that there is an optimum condition for the addition of H$_2$O$_2$ concentration for a Fenton process as explained by the following reactions:

$$\begin{align*}
H_2O_2 + HO^* & \rightarrow HO_2^* + H_2O \\
HO_2^* + HO^* & \rightarrow H_2O + O_2 \\
HO^* + HO^* & \rightarrow H_2O_2
\end{align*}$$

The addition of an excessive amount of H$_2$O$_2$ could have a negative impact as it may act as a scavenger for the \textquoteleft OH radical (equation 1), the main and the most powerful oxidant. This process may reduce the degradation rate of MB, thus decrease the degradation of MB. Following the generation of HO$_2^*$ radicals from the reaction 1, they also could react with the HO$^*$ radical (equation 2), which further reduce the amount of HO$^*$ radicals. In addition, the each HO$^*$ radical may react between themselves, as shown in the equation 3. All above-mentioned reactions have a negative effect for the degradation of a dye in the Fenton process. From the results indicated in the figure 3, it is noticeable that the addition of 15 mL of H$_2$O$_2$ is the optimum condition for the degradation of MB.
A catalyst concentration in a catalytic reaction plays a key role since it provides more active sites for the adsorption and degradation of a contaminant. The degradation performance of the composite as a function of the catalyst concentration was shown in Figure 4. Without the addition of the catalyst, no appreciable degradation occurred (Figure 4, blue line). The constant removal of MB (about 20%) in this condition is believed to be the degradation of MB by H₂O₂ as an oxidant. Following the addition of catalyst till 50 mg, the degradation rate significantly increased as more active sites available for the adsorption-degradation to occur. Further increase in the catalyst concentration resulted in the initial increase of MB degradation until 30 minute of degradation time, but longer reaction time led to the decrease in the degradation of MB. The high concentration of the catalyst may result in the agglomeration of catalyst particles, thus declining the surface active sites available for the adsorption-degradation to occur.

Figure 3. The effect of the H₂O₂ concentration in the degradation of MB as a function of time using the following condition: 25 mL MB (75 ppm) and 50 mg catalyst in 100 ml of solution

Figure 4. The effect of the catalyst dosage in the degradation of MB as a function of time using the following condition: 25 mL MB (75 ppm) and 15 mL H₂O₂ in 100 ml of solution
4. Conclusion
The bentonite supported manganosite MnO was successfully synthesized via a one-pot approach of sol gel route. The composite was applied for the degradation of MB via activation of H$_2$O$_2$. The MnO/bentonite had better catalytic performance than pure MnO and was able to degrade 91.06% of MB within 120 minutes of reaction time. The concentration of H$_2$O$_2$ an the catalyst dose seem to play a decisive role for the effective degradation of MB. In the optimum condition, the MnO/bentonite composite was able to degrade 92.97% MB using 15 ml H$_2$O$_2$, 50 mg of catalyst and 25 ml MB (75 ppm) in 100 mL solution of initial MB concentration.

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