The Effect of Hydrogen Peroxide on Catalytic Activity of Manganosite MnO/Oil Palm Fly Ash Catalyst for Degradation Methylene Blue

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Abstract. Dye pollutants have become a major environmental problem due their mutagenic, carcinogenic nature, toxicity and stability. The effective removal of this recalcitrant material from wastewater requires immediate solution. The Fenton-based advanced oxidation processes have been considered as highly effective and efficient method for the degradation of highly stable organic contaminants. In this work, the composite MnO/oil palm fly ash (OPFA) was first synthesized, characterized and applied as a heterogeneous Fenton catalyst for the degradation of methylene blue (MB). The composite was characterized by X-ray powder diffraction (XRD), and Brunauer–Emmett–Teller (BET). The XRD result indicated that the manganese oxide phase in the composite is the rock-salt manganese oxide of manganosite MnO. The MnO/OPFA has a surface area of 278.541 m²/g, which is much higher than those of pure manganosite or OPFA. The catalytic test indicated that the concentration of hydrogen peroxide (H₂O₂) seems to play a significant role for the effective degradation of MB. The degradation of MB was 95.31 achieved only within 10 minutes of reaction time with the addition of 5 ml of H₂O₂, 125 mg catalyst using 100 ml 12.5 ppm MB.

1. Introduction
The wastewater due to dye effluents has been reported as a major environmental concerns globally. This pollutants have increased significantly due to the increase in world population, economic development and a number and type of dyes used in the various industries especially in the textile and related industries. The wide range of methods have been studied intensively to tackle this unsolved problem with their inherent advantages and disadvantages. The biological processes have been considered as the most economical way to overcome the wastewater problems, but suffered from its limitation. The biological process is time-consuming [1], ineffective for most textile wastewater due its polymeric structures and cannot be used for the highly toxic dye effluents to the organisms used in the process.

The advanced oxidation process (AOP) has been studied widely for the degradation of organic pollutants and considered as the most effective and efficient strategies to solve this recalcitrant materials. This method is based on the production of •OH radicals as main powerful oxidant to oxidize
the organic contaminants non-selectively. Among the AOP methods, the Fenton-based AOP has been studied extensively for the degradation of most organic pollutions. This Fenton process, which is referred to as homogeneous Fenton, has major limitation as it can only be used in the highly acidic condition, narrow pH range and generated second contaminant due to the sludge formation. Therefore, the heterogeneous Fenton process or Fenton-like reaction has been studied widely to overcome the drawbacks of homogeneous Fenton process. This type of process uses the heterogeneous catalyst, mainly transition metal oxides to activate hydrogen peroxide to generate several radicals with •OH radical as the main and the most powerful radical.

The manganese oxides have been reported as the highly active heterogeneous Fenton catalyst for the degradation of dyes from water and wastewater. The oxides have various tunnel or layer structures, depending upon the arrangement of MnO₆ structural unit and could be synthesized readily by wide range of methods such solid-state [2], sol-gel [3,4], precipitation [5,6], reflux and hydrothermal [7,8]. The modification of manganese oxides through doping with transition metals [3,4] has also been studied previously to enhance their catalytic activities for the degradation of dyes. A doping could create defects in the parent crystal due the different size of the dopant atom with parent atom. Previous studies indicated that the transition metal doping into manganese oxides creates more defects due to oxygen vacancies. The highly active Fenton catalysts of manganese oxides for the degradation of dyes have been reported to correlate with their high surface areas, unique morphologies, high proportion \( \text{Mn}^{3+}/\text{Mn}^{4+} \) and oxygen vacancies. It is highly desirable to be able to control such above-mentioned properties to generate highly active catalyst for dye degradation.

This current study is aimed to investigate the effects of support in the catalytic efficiency of MnO/OPFA and the \( \text{H}_2\text{O}_2 \) concentration for the degradation of MB. Although, the similar investigations have been reported in previous studies, the use of one-pot sol-gel synthesis using \( \text{KMnO}_4 \) (oxidant) and glucose (reductant) and OPFA as support has never been reported. The different synthetic route could always results in the unique properties, thus effecting the catalytic efficiency for degradation of a dye.

2. Experiment section

2.1. Synthesis. The fly MnO/OPFA was first synthesized via a facile, one-pot technique using sol-gel method. The solutions of \( \text{KMnO}_4 \) and glucose in the 3:2 mole ratio, and OPFA in form of powder were mixed together. The suspension was allowed to form a sol, which then polymerize to generate gel. The resulting gel was then washed with deionized water several times, followed by calcination process at 700°C for 4 hours. The as-synthesized composite were finally characterized by X-ray powder diffraction (XRD) and Brunauer-Emmett-Teller (BET). The synthesis of pure manganosite MnO was reported elsewhere.

2.2. Catalytic Activity. The catalytic activities of pure manganosite Mn and composite MnO/OPFA for the degradation of MB were conducted in batch experiment in the different reaction time intervals: 10, 20, 30, 40, 50, 60, 90, and 120 minutes using 100 mg Catalyst, 5 mL \( \text{H}_2\text{O}_2 \) and 100 mL MB 12.5 ppm. The effect of \( \text{H}_2\text{O}_2 \) concentrations on the catalytic activities of pure manganosite MnO and composite MnO/OPFA was also studied at the similar interval time using 100 mg of the composite and 100 mL MB 12.5 ppm. The remaining concentration of MB in the solution at the interval time of 10, 20, 30, 40, 50, 60, 90, and 120 minutes was measured using a UV-Vis spectrophotometer.

3. Results and Discussion

Figure 1 shows the XRD patterns of as-synthesized manganosite MnO, OPFA and MnO/OPFA. The peaks at \( 2\Theta \) of 34.96 for the figure 1 (bottom) correspond to the diffraction planes of (111), which are typical manganosite-type manganese oxide MnO (JCPDS card number 733-739). The manganosite MnO is of high crystallinity as is indicated by sharpness of the peaks. The average of crystallite size of the as-synthesize MnO was estimated by Screer equation for the whole peaks and is \( D = (0.941 \lambda) / \)
(β Cos θ). The XRD patterns of OPFA is shown in figure 1 (middle), which indicate the presence of mullite (M), quartz (Q) as main crystalline phase and sodalite (S). When OPFA was impregnated with manganosite using one-pot synthesis, some manganosite peaks decreased significantly and the other peaks disappear completely as shown in figure 1 (top). The manganosite peaks at diffraction planes of (220) and (311) still appear at lower intensity, whereas the strongest manganosite peak at (111) diffraction plane disappear completely. The peaks due to mullite and sodalide peaks in the composite disappear except quartz phase at 2Θ=30.01° remain unchanged as displayed in figure 1 (top). This indicated the decrease of relative content of OPFA after loading MnO.

![Figure 1. XRD of the MnO, MnO/OPFA and OPFA](image)

Table 1 summarizes the crystal sizes of the MnO, MnO/OPFA and OPFA, respectively. The crystal size of MnO is about thirty times higher than that of composite MnO/OPFA. The higher decrease in crystal size of MnO/OPFA compared to that of pure manganosite MnO is in agreement with the increased surface area of MnO/OPFA compared to that of pure MnO as displayed in table 2.

| No | Sample    | Crystal Size (nm) |
|----|-----------|-------------------|
| 1  | MnO       | 11.9853           |
| 2  | MnO/OPFA  | 0.3951            |
| 3  | OPFA      | 1.143             |

Table 2 shows the surface areas and pore volumes of MnO, MnO/OPFA and OPFA, respectively. The composite has surface area of 278.451 m²/g, which increases by five times compared to pure MnO. The increase in surface area of composite may be attributed to its smaller crystal size than that of pure MnO. The increased surface area of MnO/OPFA than pure MnO could be explained by heterogeneous growth mechanism [9]. The support OPFA may cause rapid generation of nuclei and lead to small crystals. On the other hand, the homogeneous nucleation process of pure MnO seems to produce larger crystal particles. Thus, the stacking of smaller particles resulted in higher surface area of
MnO/OPFA than pure MnO. The higher surface area and smaller particle size for MnO/OPFA offer more accessible active sites for its catalytic activation of $\text{H}_2\text{O}_2$ [9].

**Table 2. BET values of two samples**

| No | Sample    | Specific surface area (m$^2$/g) | Pore Volume (cm$^3$/g) |
|----|-----------|---------------------------------|------------------------|
| 1  | OPFA      | 60.824                          | 0.011                  |
| 2  | MnO/OPFA  | 278.451                         | 0.077                  |
| 3  | MnO       | 11.223                          | 0.087                  |

The catalytic efficiency of composite MnO/OPFA and pure MnO is shown in figure 2. It obvious that the composite is a more efficient catalyst for the degradation of MB. The composite was able to degrade 95.31% and 99.14% of MB within 10 and 120 minutes of reaction time, whereas the pure MnO only degrade 90% and 93.35% MB in 10 and 120 minutes of reaction time. The better catalytic efficiency for the MnO/OPFA than pure MnO could be explained by three aspects: surface area, $\text{Mn}^{3+}$ concentration and oxygen vacancy. The higher surface area for the composite MnO/OPFA than pure MnO offers more accessible active sites for oxidant and dye, which enhance the removal of MB. The presence of more $\text{Mn}^{3+}$ concentration for MnO/OPFA could be another reason for higher its catalytic efficiency. The higher proportion $\text{Mn}^{3+}/\text{Mn}^{4+}$ in the composite could facilitate more electron transfer to occur, which in turn enhance the catalytic efficiency of the composite. Several studies indicated that the higher concentration of $\text{Mn}^{3+}$ in the composite could also lead to more oxygen vacancies, thus decreasing decomposition barrier for $\text{H}_2\text{O}_2$. This leads to increase the degradation efficiency for MnO/OPFA compared to pure MnO.

![Figure 2. Percentage results of methylene blue degradation](image)

The effect of $\text{H}_2\text{O}_2$ concentration on the degradation of MB is shown in figure 3. It is obvious that the concentration of $\text{H}_2\text{O}_2$ also play a significant role in the degradation of MB. Without the presence of both adsorption and oxidation may occur simultaneously. It is well-known than manganese oxide could act as strong oxidant for the degradation of many organic compounds and is also reported to play a key role in numerous biogeochemical cycles[10]. Thus, the high removal of MB without the presence of $\text{H}_2\text{O}_2$ could be attributed to the combination adsorption-oxidation process. The presence of $\text{H}_2\text{O}_2$ enhances the degradation efficiency of the composite as shown in figure 3. Several studies reported that there is the optimum concentration of $\text{H}_2\text{O}_2$ for the degradation of dyes. The excessive
concentration of H$_2$O$_2$ could have adverse effect for degradation of dyes. The high concentration of H$_2$O$_2$ could act as a scavenger for OH radicals, which is the main oxidant for the degradation of dye. In the current study, the addition of 5 ml of H$_2$O$_2$ is enough for the maximum degradation of MB. The higher concentration of H$_2$O$_2$ seems to have negligible effect for the degradation of MB in this study.

**Figure 3.** Percentage results of methylene blue degradation with variation Volume of H$_2$O$_2$.

### 4. Conclusion

The composite MnO/OPFA was successfully synthesized via the one-pot of sol gel method and used as heterogeneous Fenton catalyst for the degradation of MB. The XRD result indicated that the manganosite MnO-type of manganese oxide was formed as main phase. The MnO/OPFA seems to have better catalytic efficiency than pure MnO and is able to degrade 95.13% of MB within 10 minutes of reaction time. The concentration of H$_2$O$_2$ plays a significant role for the effective degradation of MB.

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