The Effect of Support on the Catalytic Efficiency of MnO$_2$/Activated Carbon for degradation of Methylene blue

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Abstract. Methylene blue (MB) is a blue cationic thiazine dye which is widely used in cotton fiber, wood and textile industries, but has an adverse effect to environment and living organism. It is urgent to find an alternative and effective solution for this recalcitrant compound. The Fenton process-based advanced oxidation process is considered as an effective method for the degradation of organic contaminants such as dyes. In this study, the composite $\alpha$-MnO$_2$/activated carbon (AC) was first synthesized by a facile, one-pot synthesis using sol-gel method and characterized by X-ray diffraction (XRD) and BET surface areas. The XRD results indicated that the tunnel cryptomelane-type manganese oxide ($\alpha$-MnO$_2$) was successfully synthesized as the minor phase in the activated carbon support. The composite $\alpha$-MnO$_2$/AC has higher specific surface area than the single $\alpha$-MnO$_2$. The catalytic studies indicated that the $\alpha$-MnO$_2$/AC has a much higher catalytic efficiency over single $\alpha$-MnO$_2$ for degradation of MB. The presence of the support and the increase in surface area of $\alpha$-MnO$_2$/AC could be responsible for its higher catalytic efficiency compared to single $\alpha$-MnO$_2$. In the optimum condition, the $\alpha$-MnO$_2$/AC was able to degrade 98.48 % and 99.2 % of MB within 10 and 120 minute of reaction time, respectively.

1. Introduction
Synthetic dyes are widely applied in various industries for colouring their products. The effluents of these industries contain various dye stuffs that are very polluting, harmful to environment and any forms of aquatic life[1]. A dye is a coloured organic compound that absorbs a light in visible region and attached to a fiber by a chemical or physical bonding. A dye contains chromophore group that is responsible for producing colour, while auxochromes group determines the intensity of colour and enhances affinity toward fibers. Most dyes comprise of a complex polymeric structure and are recalcitrant compounds, thus are difficult to degrade naturally. Some dyes are highly toxic even in low concentration (less than 1 mg/L) due to the presence of metals, chloride and etc in their structure. Therefore, it requires urgent and effective solution to handle these problems. Among several methods reported for the degradation of dye effluents, the biological process is considered the most economical way to solve this global issue. However, the method is time-consuming [2], and cannot be used in the most dye effluents due to their toxicity to the organisms used in the degradation process. Advanced oxidation process (AOP) is emerging method, which is based on the production of hydroxyl radical as...
the most powerful oxidant (second after fluorine), for the degradation of the highly stable organic contaminants. Fenton process as apart of AOP method is a simple, easy to be used, and requires short-period time to readily oxidize recalcitrant compounds such as dyes. The conventional Fenton or homogeneous Fenton reaction, however, suffers from its inherent limitations since it requires highly acidic condition, narrow working pH and produce Fe(OH)3 sludge by-product. Thus, the heterogeneous Fenton process was introduced and widely used to overcome the drawbacks of homogeneous counterpart. The method uses heterogeneous catalyst, mainly transition metal oxides, instead of homogeneous Fe3+ catalyst for the activation of oxidant such as hydrogen peroxide. Among the transition metal oxides, porous manganese oxides have been widely studied for the degradation of dyes.

Manganese oxides have been studied as Fenton catalyst for the degradation of organic pollutants [4-12]. Manganese oxides have tunnel or layer structures, depending upon the arrangements of MnO6 octahedral units, which result in the formation of 1x1, 2x1, 2x2, and 3x3 tunnels[3 and 4]. The oxides are also readily synthesized by most synthetic method available, such as sol-gel [5-8], solid-state [4], precipitation [9-12], reflux [13] and hydrothermal [14]. The presence of mixed valences Mn (Mn3+/Mn4+) in the tunnel or layer structures of manganese oxides could promote a redox reaction (electron transfer) that are needed in a Fenton reaction. The Mn3+ ion in the framework of manganese oxide also could result in defects due the charge imbalance (negative charge in the framework of MnO2) created by replacement of Mn4+ by Mn3+ and must be overcome by the adsorption of cations or creation of oxygen vacancies. The defects due to the Mn3+ or oxygen vacancies in MnO2 could provide more active sites, thus enhance the catalytic activity of MnO2. Defect also could be created by addition of a dopant into parent manganese oxides. The doping α-MnO2 with transition metals has been reported, which enhances the degradation rates of dyes. [5-8 and 15].

Another way to enhance the catalytic efficiency of a catalyst could be done by the formation of a composite. A composite could avoid the agglomeration of the catalyst and facilitates the electron transfer in a catalytic reaction. In the current study, the composite α-MnO2/AC was first synthesized using a facile, one-pot using sol gel method and was then applied as a heterogeneous Fenton catalyst for the degradation of MB. Although similar studies for the degradation of MB using MnO2 catalyst have been reported by previous studies, the one-pot synthesis of α-MnO2/AC using KMnO4, glucose and activated carbon via sol-gel method has never been reported. Different synthetic approach and different precursors often resulted in the unique properties of MnO2, thus affecting its catalytic activity.

2. Experiment Section

2.1. Synthesis. The composite α-MnO2/AC was prepared by sol-gel method by mixing all reactants together to form final product. The solutions of KMnO4 and glucose in the 3:1 mole ratio was first mixed together, and the product was added with commercial activated carbon to form a sol after several minutes. The sol was then polymerized to generate a gel, which was washed with distilled deionized water several times. The calcination process was conducted to the gel to obtain final product, which is the composite α-MnO2/AC. The as-synthesized composite were finally characterized by X-ray powder diffraction (XRD) and Brunauer-Emmett-Teller (BET). The synthesis of α-MnO2 was reported elsewhere.

2.2. Catalytic Activity. The degradation of MB by the composite was studied under different concentration of hydrogen peroxide within the interval time: 10, 20, 30 40, 40, 50, 60, 90, and 120 minutes using 50 mg of the catalyst, and 100 ml 50 ppm MB. The catalytic activities of α-MnO2 and α-MnO2/AC was also studied at the similar interval time using the optimum concentration of hydrogen peroxide obtained from the previous study, 50 mg of catalyst and 100 ml 50 ppm MB. The remaining concentration of MB in the solution was taken at the interval time of 10, 20, 30 40, 40, 50, 60, 90, and 120 minutes and measured using a UV-Vis spectrophotometer.
3. Result and Discussion
The XRD patterns of pure cryptomelane (α-MnO₂), commercial AC and α-MnO₂/AC are shown in Figure 1. The characteristic XRD pattern for AC appears at 2θ = 21.61° and 29.91°, whereas the cryptomelane-type tunnel manganese oxide appears at 2θ = 12.8°; 18.19; 28.84; 37.67; 42.13; and 49.89° which correspond to the diffraction planes of (110), (200), (310), (211), (301) and (411), respectively. The XRD pattern of single α-MnO₂ indicated sharpness of peaks, reflecting high crystallinity of α-MnO₂. Upon loading α-MnO₂ into AC, the AC peaks remained unchanged, whereas most cryptomelane peaks disappeared completely. The α-MnO₂ peaks in α-MnO₂/AC appeared with much lower intensity at 2θ = 12.78° and 18.27°, correspond to diffraction planes of (110) and (200), respectively. The reduction in peak intensity for cryptomelane in the composite α-MnO₂/AC is due to the lower proportion of cryptomelane over AC (1:20), which was also reported by previous studies [16].

Table 1. summarizes the specific surface areas and pore volumes of the α-MnO₂, α-MnO₂/AC and AC respectively. The surface area of the composite is higher than that of α-MnO₂, which is about 1.2-fold

Figure 1. XRD of the α-MnO₂, α-MnO₂/AC and AC
increase in surface area compared to single $\alpha$-MnO$_2$. It is advantageous for the composite to have high surface area to facilitate the adsorption, which is a key step prior to a catalytic reaction.

Table 1. BET values of $\alpha$-MnO$_2$, $\alpha$-MnO$_2$/AC and AC

| No | Sample       | Specific surface area (m$^2$/g) | Pore Volume (cm$^3$/g) |
|----|--------------|---------------------------------|------------------------|
| 1  | AC           | 82.916                          | 0.4911                 |
| 2  | $\alpha$-MnO$_2$/AC | 644.247                      | 0.143                  |
| 3  | $\alpha$-MnO$_2$ | 590.759                        | 0.135                  |

The effect of hydrogen peroxide concentration on the degradation of MB is shown in Figure 2. The maximum degradation of MB was 99.962% achieved with the initial MB concentration of 50 ppm, the addition of 0.67 H$_2$O$_2$ within 120 minute. Further increase in the H$_2$O$_2$ concentration to 1.34M resulted in the decrease of MB degradation. The decrease in the MB degradation after optimum H$_2$O$_2$ concentration could be explained by the following reaction:

\[
\begin{align*}
\text{H}_2\text{O}_2 & + \text{HO}^* \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \\
\text{HO}_2^* & + \text{HO}^* \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{HO}^* & + \text{HO}_2^* \rightarrow \text{H}_2\text{O}_2 
\end{align*}
\]

The excess H$_2$O$_2$ concentrations have an adverse effect and could act as HO$^*$ radical scavenger as shown in the equation (1), thus decreasing MB degradation. The HO$^*$ radical also could react between themselves (equation 3) or with HO$_2^*$ hydroperoxyl radical (equation 2), which further decrease the concentration of the HO$^*$ radicals. The similar observation was also reported by previous studies [13 and 17], where there is a optimum concentration of H$_2$O$_2$ for degradation of MB.

![Figure 2](image_url)

**Figure 2.** The effect of H$_2$O$_2$ concentration of the degradation of MB

The Figure 3 displays the MB degradation using the single $\alpha$-MnO$_2$ and the composite $\alpha$-MnO$_2$/AC. The Figure also shows the adsorption of MB by the AC without the addition on H$_2$O$_2$. The removal of MB by AC occurs through the adsorption process since the AC contains no active species for the degradation to occur. It is noticeable that the presence of support AC in the composite $\alpha$-MnO$_2$/AC could substantially improve the degradation of MB. The considerable increase in the MB degradation by $\alpha$-MnO$_2$/AC over single $\alpha$-MnO$_2$ could be explained by several aspects. The increase in the surface area of $\alpha$-MnO$_2$/AC as seen in the table 1, could be responsible for its higher catalytic activity. The high surface area of $\alpha$-MnO$_2$/AC over single MnO$_2$ could facilitate more adsorption of the dye.
molecules and H$_2$O$_2$, leading to increase in its catalytic reaction [16]. Another aspect could be the presence of more defects in the α-MnO$_2$/AC over single α-MnO$_2$. The defects may be due to more proportion of Mn$^{3+}$/Mn$^{4+}$ or oxygen vacancies in α-MnO$_2$/AC over α-MnO$_2$[18]. The oxygen vacancies often promotes adsorption of oxygen in surface of a catalyst, as reported previously [19]. It is believed that the higher surface oxygen vacancies of α-MnO$_2$/AC over single α-MnO$_2$ was also responsible for its high degradation efficiency. The presence of a support in the composite has been reported to have positive effect for its catalytic activity. A support such as carbon-based material in the composite α-MnO$_2$/AC may facilitate charge transfer processes, thus enhancing the degradation of dyes[16]

![Figure 3](image_url)

**Figure 3.** The effect of different catalysts: MnO$_2$, MnO$_2$/AC and AC (adsorption process) for the degradation of MB

4. Conclusion

The synthesis of composite α-MnO$_2$/AC was successfully conducted via a facile, one-pot of sol-gel synthetic method. The XRD pattern of the composite confirmed the presence of tunnel cryptomelane-type (α-MnO$_2$) manganese oxide in the composite α-MnO$_2$/AC. The presence of activated carbon as a support in the composite α-MnO$_2$/AC increased the specific surface area compared to single α-MnO$_2$ and was responsible for the marked increase in degradation of MB. The activated carbon (AC) in composite MnO$_2$/AC plays a key role for facilitating the adsorption-degradation process, thus enhancing the degradation of MB.

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References

[1] Nidheesh P V, Gandhimathi R and Ramesh S T 2013 Env Sci PollutRes 20 2099–2132
[2] Permana I, Awaluddin A and Saryono 2019 Biodiversitas 20 2693–97
[3] Awaluddin A, Agustina M, Aulia RR, Muhdarina2017AIP Conf. Proc.1823020108
[4] Siregar S S and Áwaluddin A 2018 IOP Conf. Ser.: Mater. Sci. Eng 345 012005
[5] Awaluddin A, Astuti L, Linggawati, Siregar S S, Prasetya , SaputraLeo 2018 AIP Conf. Proc 2026020075
[6] Awaluddin A, Anggraini R, Siregar S S, Muhdarina and Prasetya 2019 MATEC Web Conf 276
[7] Awaluddin A, Amiruddin E, Anggraini R, Indriyani N and Siregar S S 2020 IOP Conf. Ser.: Mater. Sci. Eng 845 012014
[8] Awaluddin A, Janah SR, Anggraini R, Siregar SS 2019. J. Phys. Conf. Ser 1351 012041
[9] Absus S, Zulfa R, Awaluddin A, Anita S, Siregar S S and Prasetya 2018 AIP Conf. Proc 2049 020009
[10] Awaluddin A, Zulfa R, Absus S, Nurhayati, Linggawati A and Siregar S S 2019 IOP Conf. Ser.: Mater. Sci. Eng 509 012011
[11] Kurniati S, Linggawati A, Siregar SS, Awaluddin A 2019. J. Phys. Conf. Ser 1351 012035
[12] Asleni, Kurniati S, Linggawati A, Siregar SS and Awaluddin A 2019. J. Phys. Conf. Ser 1351 012038
[13] Cui H J, Huang H Z, Fu M L, Yuan B L and Pearl W 2011 Catal. Commun 12 1339-1343
[14] Cheng G, Lin T, Yang R, Sun M, Lan B, Yang L and Deng F 2014 J. Solid State Chem 217 57-63
[15] Sandra I, Anggraini R, Siregar SS, Awaluddin A 2019 J. Phys. Conf. Ser. 1351 0120337
[16] Ahuja P, Ujjain SK, Kanojia R and Attri P 2021 Compos. Sci. 5 82
[17] Eduardo Manuel Cuerda-Correa, María F. Alexandre-Franco and Carmen Fernández-González. 2019. Water 12 102
[18] Xiaoman L, Longsheng Y, Qinglin Z, Lihua Z, Yuanhong X, Miao L, Tao L and Qian W 2019 Env. Tech 1 28
[19] Wang F, Dai H and Deng J 2012 Environ Sci Tech 46 4034–4041