The Preliminary Studies on the Tremendous Degradation Rate of Methylene Blue with Cu-doped $\alpha$-MnO$_2$ Photocatalyst Under UV Light Irradation

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Abstract. Dye contaminations have severe impacts to environment (air, soils, plants, water) due to their adverse effects. Most dyes are toxic, carcinogenic, mutagenic and resistant to biodegradation. Photocatalysis-based advanced oxidation process (AOP) has been considered as the most effective and efficient way to treat this recalcitrant compounds. Manganese oxides are ubiquitous and environmentally friendly in natural environments and can act as semiconducting materials. Tunnel structure of manganese oxide such as $\alpha$-MnO$_2$ (cryptomelane) has been widely studied for broad applications as Fenton-based AOP. Catalytic efficiency of $\alpha$-MnO$_2$ could be further increased by doping $\alpha$-MnO$_2$ with a metal ion like the Cu ion. Although the synthesis and catalytic activity of Cu-$\alpha$-MnO$_2$ have been reported by previous studies, its photocatalytic performance using this one-pot-sol-gel approach for MB degradation has never been reported previously. Herein, Cu-doped $\alpha$-MnO$_2$ was synthesized by one-pot sol-gel method and characterized by X-ray diffraction (XRD), BET surface area and atomic absorption spectroscopy (AAS). The AAS results suggested the presence of Cu ions in $\alpha$-MnO$_2$ since the increase in doping Cu resulted in the corresponding increase in Cu content in the $\alpha$-MnO$_2$. The BET surface area indicated that the doping 10% Cu in $\alpha$-MnO$_2$ led to about two fold increase in surface area compared to undoped $\alpha$-MnO$_2$. The photo catalytic performance of Cu-$\alpha$-MnO$_2$ via UV light irradiation for the degradation of methylene blue (MB) was significantly higher that that of undoped $\alpha$-MnO$_2$ and was associated with the increased in surface area of Cu-$\alpha$-MnO$_2$ over undoped $\alpha$-MnO$_2$. The maximum degradation of MB was 97.9, 98.3, 98.7 and 99.5% achieved using $\alpha$-MnO$_2$, 1% Cu-$\alpha$-MnO$_2$, 5% Cu-$\alpha$-MnO$_2$, and 10% Cu-$\alpha$ MnO$_2$ and 10% Cu-$\alpha$-MnO$_2$.

1. Introduction
Economic growth and development in industrial processes have resulted in the prosperity, efficacy and comport of human beings in the different fields. One of the industrial processes with significant growth is dyeing process. In addition, the high demand and excessive cost for natural dye extraction led to the development of synthetic counterpart. Since then, most industries have used the synthetic dyes for the colouring their final products and the different types of the dyes have been artificially synthesized. The synthetic dyes are colour-resistant, cheap, easy to be applied to most fibers, but it is difficult to degrade in nature even in a low concentration (>1 mg/L). The severe impacts of synthetic dyes to the environment (air, soil, plants, water) and human health have been reported. They are
mostly toxic, carcinogenic, mutagenic and highly resistant to the degradation in natural environment. Therefore, it is urgent to find an effective and efficient, cost-effective, and sound environmentally friendly method to solve this ubiquitous problems.

Numerous methods have been studied and applied either in laboratory or industrial scale for the degradation of dye residues, which mostly consist of biological, physical, chemical and the combination (tandem) between them. All methods have their own inherent advantages and disadvantages as reported by previous studies. Biological processes have been regarded as the most economical way to treat most organic contaminants, but it is time-consuming [1], and could not be used in a dye which is toxic to the organisms used in the treatment process. Although physical processes such as adsorption and coagulation are easily applied and widely used to treat an environmental problem, the method could create second contaminant due to the transfer of contaminants into adsorbent or coagulant via physical or chemical bonding. In the last few years, the advanced oxidation process (AOP) has been widely studied and considered to be one of the most effective ways to treat many organic contaminants, which are based on the production of OH radicals (highly powerful oxidant) to oxidize most contaminants non-selectively into harmless water and carbon dioxide if complete oxidation is achieved.

The photocatalysis-based advanced oxidation process is one of AOP methods, which applies a catalyst with aid of irradiation to activate the catalyst referred to as photocatalyst. The wide range of semiconductors have been reported as photocatalyst, especially TiO\(_2\) by previous studies. A typical photocatalytic reaction involves the transfer of an electron from the valence band to conduction band, leaving behind the hole in valence band. Both hole and electron participate in a redox reaction to oxide an organic contaminant. Among the semiconductors used as a photocatalyst, tunnel and layer manganese oxides have been regarded as a promising photocatalytic material, since it has acceptable band gap (2.23 ev for birnessite) and readily synthesized by various methods with ease.

Earth-abundant, environmentally friendly manganese oxides are ubiquitous in natural environmental settings and reported to be an active oxidant and play a key role in biogeochemical cycles. The oxides have many applications as supercapacitor, battery materials, sensor and catalyst for various chemical reactions and environmental protection. Manganese oxides, in particular the porous ones, are mixed valence Mn, and have different structures, notably tunnel and layer structures. The tunnel structures of manganese oxides are formed by the arrangements of basic structural unit MnO\(_6\) octahedra through edge and corner sharing, generating 1x1 tunnel pyrolusite (β-MnO\(_2\)), 2x2 tunnel cryptomelane (α-MnO\(_2\)) and 3x3 tunnel todorokite, whereas layer birnessite-type of manganese oxide is formed by stacking sheets obtained from edge sharing of basic unit octahedral MnO\(_6\). The oxides have been widely prepared with ease by variety of synthetic methods such as sol-gel [2-5], solid-state [6], precipitation [7-11] and hydrothermal. The phase and properties of resulting oxides heavily depend upon the preparation method used and the experimental conditions [2-5]. For example, layer birnessite was easily prepared via solid-state method [6], while controlled synthesis of binesite or cryptomelane could be obtained by tuning the experimental condition via sol-gel or precipitation method.

The catalytic activities of manganese oxides could be enhanced by the addition of small amount of transition metals, dopants, which could create defects in the parent manganese oxide. The doping with Fe and Cu in tunnel cryptomelane-type manganese oxides has been reported to enhance the catalytic efficiency for the degradation of MB dye. The different ionic size between a dopant with parent atom and the replacement of parent atom with dopant in the framework of a solid material is believed to be responsible for the formation of defects. Defects also could be created by oxygen vacancies in the metal oxides due to doping process.

In the current study, the Cu-doped α-MnO\(_2\) was prepared via a facile, one-pot synthetic method using sol-gel route. The resulting Cu-doped α-MnO\(_2\) was applied as a photocatalyst for the degradation MB via UV irradiation and compared with pure α-MnO\(_2\) as a control. The optimum condition for MB degradation was achieved by the optimization the experimental condition.
2. Materials and Method

2.1. Synthesis. The synthesis of Cu-doped α-MnO₂ was realized by a facile, one-pot sol-gel method. The solution of KMnO₄ was prepared by dissolving 0.1 mole KMnO₄ in 1000 ml deionized water, which was added with 0.033 mole glucose. After 3 minutes, the different ratios of CuSO₄·5H₂O (the molar ratio of Cu/Mn: 0, 0.01, 0.05, or 0.10) was added to the solution mixture, which immediately formed a sol and polymerized into a blackish brown flocculants gel following 10 minute of reaction time. The gel was allowed to settle in room temperature and isolated after 1 hour by filtration and washed four times with 250 mL water. Then, the gel samples were dried at 110°C for overnight to generate brown gel (xerogel) and calcined at 450°C up to 2 hour. The resulting product was grounded into fine particles and washed three times with HCl 0.1 M and distilled water. The final powder product was dried at 110°C and then collected for characterization.

2.2. Photocatalytic experiment. The photocatalytic reaction for the degradation of MB was carried out in a glass Beaker and about 25 mL MB dye solution (60 mg/L) was added to 75 mL deionized water containing 100 mg Cu-doped α-MnO₂ catalyst. The resulting suspension was then continuously stirred with the aid of magnetic stirrer for 30 min to achieve adsorption/desorption equilibrium. The UV light irradiation with the wavelength of 254 nm was applied to the suspension. At given time intervals of 10, 20, 30, 40, 50, 60, 90, and 120 min, the 8 mL of the mixture was pipetted into a volumetric flask and transferred into a tube for centrifugation at 1000 rpm for 20 min to settle the catalyst particles. The residual concentration of the MB in the solution at different times was determined using UV spectroscopy.

3. Results and Discussion

The crystalline phases of as-synthesized α-MnO₂, 1% Cu-α-MnO₂, 5% Cu-α-MnO₂, and 10% Cu-α MnO₂ are characterized by XRD and shown in figure 1. The XRD patterns for all samples the indicated the presence of peaks at 2ϴ= 12.79º; 18.17º; 28.79º; 37.58º; 41.84º; 49.82º; 56.82º; and 60.12º, corresponding to reflection planes of 110, 200, 310, 211, 301, 411, 600, and 521, which is a typical α-MnO₂ (the International Center for Diffraction Data (ICDD) (1977) 29-1020). It is obvious from the figure 1 that the doping Cu on or into the framework of α-MnO₂ resulted in the similar reflection planes as the undoped α-MnO₂ and no additional peaks due to Cu species were detected. The previous studies also reported no additional peaks due to Cu species following the doping Cu into α-MnO₂ [12]. In this previous study, the difference between undoped and Cu-α-MnO₂ can be obtained by subtracting the differential synchrotron radiation XRD (DSXRD) of the undoped α-MnO₂ pattern from the Cu-α-MnO₂. Using this approach, the wavy and mountain-like patterns appeared in the DSXRD could be attributed with the weaker intensity and down shifting of Cu-α-MnO₂ and Cu ions were believed to be doped into the α-MnO₂.

Similar observation was reported by the previous study [13], in which doping Cu in α-MnO₂ resulted no observable change of diffraction patterns. Other study [14] revealed the similar diffraction patterns following the doping Cu in the α-MnO₂, but led to the increase in the unit cell along a-axis and the unit cell volume compared to undoped α-MnO₂.

3
The average of crystallite size of the as-synthesize \( \alpha \)-MnO\(_2\) and Cu-doped \( \alpha \)-MnO\(_2\) was estimated by Scherrer equation for the whole peaks and the formula is \( D = \frac{(0.941 \lambda)}{\beta \cos \theta} \). Table 1 summarizes the atomic percent ratios of K/Mn and Cu/Mn of the \( \alpha \)-MnO\(_2\), 1% Cu-\( \alpha \)-MnO\(_2\), 5% Cu-\( \alpha \)-MnO\(_2\), 10% Cu-\( \alpha \)-MnO\(_2\) and the corresponding crystal sizes, respectively. It is obvious from the measurement of atomic absorption spectroscopy (AAS) that doping Cu into \( \alpha \)-MnO\(_2\) resulted in the increase in Cu content as shown in the Cu/Mn ratio. Since no other relevant experiments conducted to confirm the presence of Cu in the \( \alpha \)-MnO\(_2\), it is unclear whether Cu ions replace Mn ions in the frameworks or the other sites. On the other hand, the K/Mn ratio revealed that the increase in doping Cu in the \( \alpha \)-MnO\(_2\) led to the decrease in their corresponding K/Mn ratios. It is known that Mn exists in mixed valences (Mn\(^{3+}\) and Mn\(^{4+}\)) in the \( \alpha \)-MnO\(_2\). The decrease in K/Mn ratios is believed to be associated with the decrease in Mn\(^{3+}\) content in the \( \alpha \)-MnO\(_2\) since the presence of Mn\(^{3+}\) can create charge imbalance in the \( \alpha \)-MnO\(_2\) resulting the adsorption of a cation such K\(^+\). Presence of Mn\(^{3+}\) in \( \alpha \)-MnO\(_2\) also could resulted in the formation of oxygen vacancy. Our results contradict with previous report that the increased doping Cu in \( \alpha \)-MnO\(_2\) led to the creation of more oxygen vacancies or Mn\(^{3+}\) ions.

Figure 1. XRD of the \( \alpha \)-MnO\(_2\), 1% Cu-\( \alpha \)-MnO\(_2\), 5% Cu-\( \alpha \)-MnO\(_2\), and 10% Cu-\( \alpha \)-MnO\(_2\)
Table 1. Elemental analysis and Crystal size

| No | Catalyst                  | K/Mn  | Cu/Mn | Crystal Size (nm) |
|----|---------------------------|-------|-------|-------------------|
| 1  | α-MnO₂                    | 0.8131| 0.000 | 17.67             |
| 2  | α-MnO₂/Cu 1%              | 0.7628| 0.030 | 13.48             |
| 3  | α-MnO₂/Cu 15%             | 0.5135| 0.212 | 17.70             |
| 4  | α-MnO₂/Cu 10%             | 0.3816| 0.459 | 20.80             |

Table 1 also displayed the crystal size of α-MnO₂, 1% Cu-α-MnO₂, 5% Cu-α-MnO₂, 10% Cu-α-MnO₂ and revealed that loading more Cu ions in α-MnO₂ led to the increase in the corresponding crystal size, except for 1% Cu-α-MnO₂. The specific surface area and pore volume of α-MnO₂, 1% Cu-α-MnO₂, 5% Cu-α-MnO₂, 10% Cu-α-MnO₂ were shown in Table 2. The increase in Cu doping led to the increase in surface area and pore volume, resulting about 2 fold increase in surface areas and 1.2 fold increase in pore volume for 10% Cu-α-MnO₂ compared to undoped α-MnO₂.

Table 2. BET values of α-MnO₂, 1% Cu-α-MnO₂, 5% Cu-α-MnO₂, 10% Cu-α-MnO₂

| No | Catalyst                  | Specific surface area (m²/g) | Pore Volume (cm³/g) |
|----|---------------------------|------------------------------|---------------------|
| 1  | α-MnO₂                    | 82.916                       | 0.491               |
| 2  | α-MnO₂/Cu 1%              | 81.680                       | 0.521               |
| 3  | α-MnO₂/Cu 15%             | 119.94                       | 0.677               |
| 4  | α-MnO₂/Cu 10%             | 145.78                       | 0.727               |

The photocatalytic performance of Cu-α-MnO₂ was evaluated for the degradation of MB as a function of time as shown in figure 2. The catalytic performance for Cu-α-MnO₂ was significantly higher than that of undoped α-MnO₂ and able to degrade over 98% MB within 10 minute of degradation time, whereas undoped α-MnO₂ only degraded less than 86% in the same degradation time. It is believed that the considerable increase in the surface area could be responsible for the tremendous photocatalytic performance of for Cu-α-MnO₂ over undoped α-MnO₂. The effect of defects due to oxygen vacancies or Mn³⁺ for the massive increase in catalytic performance of Cu-α-MnO₂ could be ruled out since the K/Mn ratio revealed otherwise.

Figure 2. Percentage results of methylene blue degradation
4. Conclusion
The photocatalytic performance of Cu-α-MnO₂ via UV light irradiation was conducted for the degradation of MB and revealed that the doping Cu in the α-MnO₂ resulted in the higher degradation of MB compared to undoped α-MnO₂. The considerable increase in Cu-α-MnO₂ was correlated with the corresponding increase in surface area, was not associated with the increase in oxygen vacancies or Mn³⁺ ions. The photocatalyst 10% Cu-α-MnO₂ can degrade over 98% of MB within 10 minute of degradation time.

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