The Tremendous Catalytic Activities of the Cryptomelane-Type Manganese Oxide Octahedral Molecular Sieve Prepared Without Calcination Process for Degradation of Methylene Blue

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Abstract. The cryptomelane-type manganese oxides octahedral molecular sieve with different crystalline phases have been successfully synthesized and characterized. The oxides were synthesized using precipitation method through the redox reaction between KMnO₄ and C₆H₈O₇ with a mole ratio of 5:1 by the variation of flow rates (1, 2, and 3 mL/min). The prepared catalysts were characterized by XRD to determine their phase structures, purity, and crystallinity. The XRD results indicated that the samples without heat treatment (calcination) displayed the poor tunnel structures of cryptomelane-type manganese oxides with low intensities and broad peaks. Upon the thermal treatment at 600°C for 4 hours, the much more crystalline phases of similar cryptomelane structures were obtained. The high flow rate results in the more crystalline cryptomelane for calcined samples, whereas the flow rate has no substantial influence on the crystallinity of uncalcined samples. The catalytic activities of both oxides were evaluated for the degradation of methylene blue (MB) with H₂O₂ as an oxidant. The catalytic degradation of MB greatly enhanced using the uncalcined cryptomelane compared to calcined cryptomelane. The high flow rate has a positive impact on the degradation of MB for calcined samples, but the effect of flow rate results in the higher degradation of MB until a certain flow rate. The 98.4% degradation of MB was achieved by uncalcined samples under the optimum condition.

1. Introduction
The manganese oxides have been extensively studied due to their unique structures and physicochemical properties [1]. These materials have been used over a wide range of applications like supercapacitor [2], ion exchange, biosensor [3], and environmental remediation [4]. The manganese oxides mainly consist of two-type structures, layer and tunnel structures which are created from the basic structural units of MnO₆ octahedral. Tunnel structures were formed from edge-sharing of MnO₆ octahedral, resulting in the formation of single, double and triple chains which are connected together to form tunnel like 1x1 tunnel (pyrolysite), 2x2 tunnel (cryptomelane), and 3x3 tunnel (todorokite). Layer structures of manganese oxides are generated from the stacked sheets of edge-sharing of MnO₆ octahedral, such as birnessite and busserite.

The various structures, morphologies, and physicochemical properties are successfully synthesized by several methods such as sol-gel [5-7], ceramic [8], hydrothermal, reflux, and precipitation [9-11].
Different precursors have also been used to prepare these oxides, resulting in various structures and unique properties. Lately, different mixing modes have been applied to synthesize the layer and tunnel structures of manganese oxides with different morphologies and crystallinity. Some of these oxides have been used as heterogeneous catalysts for remediation of wastewater using Fenton reaction.

The contaminations of water with dye effluents pose severe environmental issues. These effluents are difficult to treat using a conventional method like biodegradation since they contain dyestuffs with complex aromatic structure. Dyes are also unusually resistant to light, heat, oxidizing agent, and most of them are toxic to human and aquatic life. The presence of color, even in small quantity, is highly visible and undesirable in water for any use. It is reported that more than 2-20% of the dyes are discharged into the environment as wastewater. Therefore, it is important to have simple, acceptable, efficient, and environmentally friendly methods for dye removal.

Fenton process-based advanced oxidation processes have emerged as one of the most efficient ways for remediation of dye effluents. This method is characterized by the generation of hydroxyl radicals from the reaction between H₂O₂ and a catalyst. Different catalysts have been applied successfully for the treatment of wastewater containing dyes. There have been growing interests to use a heterogeneous catalyst instead of the homogeneous catalyst due to the limitation of homogeneous catalyst possessed such as high sludge production and difficult separation. Among the solid catalyst, manganese oxides have received much attention due to high catalytic activities, easy to prepare with a simple method and unique structures.

In the current work, the tunnel structures of cryptomelane-type manganese oxides have been successfully synthesized by simple precipitation methods. The use of citric acid as a reducing agent for the preparation of cryptomelane have rarely been reported by previous reports. The effect of flow rates and thermal treatment on crystalline natures of the as-synthesized manganese oxides were correlated with their catalytic activities for the degradation of methylene blue.

2. Experimental Method

2.1. Synthesis of KMnO₄ and citric acid
Manganese oxides were synthesized by the reaction between solutions of KMnO₄ and C₆H₈O₇ (citric acid) the precipitation method [2] with a variation of a flow rate of 1, 2, and 3 mL/min of citric acid solution. The solution was added dropwise into 250 mL KMnO₄ in a laboratory beaker glass. After complete addition of 250 mL of citric acid solution with constant stirring (300 rpm) for 30 minutes at 60°C. The turbid solution was obtained filtered with 250 mL DDW four-time and heated at 120°C for 12 hours and referred to as uncalcined samples. Some of the solid product was then calcined at 600°C for 4 hours, then washed with an aqueous solution of HCl and distilled deionized water and heated 120°C for 1 hour and denoted as calcined samples. Both uncalcined and calcined products were placed in a desiccator before further uses like characterization and degradation studies.

2.2. The powder X-ray diffraction (XRD) and crystallite size
The structure, crystallinity, and phase purity of the prepared manganese oxides were characterized by X-ray diffraction. The patterns of all manganese oxide samples were recorded using Shimadzu XRD 7000 maxima. The crystallite size of the synthesis catalyst was estimated using Scherrer’s equation:

\[
D = \frac{0.54 \lambda}{\beta \cos \theta}
\]

2.3. Catalytic Activity Studies
About 25 ml of 50 ppm solution of methylene blue was added with 70 mL of distilled water. The resulting solution was added with 50 mg of the as-synthesized catalyst and stirred with a magnetic stirrer at 400 rpm for 30 minutes. The slurry was then added with 5 mL of 30% H₂O₂ and taken for the interval of 2, 4, 6, 8, 10, 30, 60, 90, and 120 minutes and placed in a laboratory glass tube for centrifugation separate the catalyst from the degraded methylene blue solution. Analysis of the
remaining concentrations of methylene blue was performed with an Optima SP-300 Spectrophotometer at a wavelength of 660 nm. The amount of MB degradation was determined using the equation:

\[ \% \text{ decrease MB} = \frac{C_0 - C_t}{C_0} \times 100 \]  

(2)

Where \( C_0 \) and \( C_t \) are initial and final concentration of MB, respectively.

3. Result and Discussion

The redox reaction between \( \text{KMnO}_4 \) solution and citric acid is an exothermic reaction, resulting in a temperature increase of the reaction system and \( \text{CO}_2 \) production as evidenced by the formation of air bubbles. The resulting reaction was solid black products, which were then characterized by X-ray diffraction. X-ray diffraction patterns of as-synthesized manganese oxides for uncalcined samples are displayed in figure 1, and the corresponding calcined samples are shown in figure 2. It is obvious from figure 1 that the uncalcined samples showed poor crystalline structures with low intensities and wider peaks, whereas the calcined samples displayed the crystalline structures with high intensities and sharp peaks. The XRD patterns of uncalcined samples are in good agreement with the cryptomelane-type layered manganese oxides (JCPDS 29-1020). Upon the heat treatment, the cryptomelane phase remained unchanged, but their crystalline natures altered remarkably. The calcination samples show much higher crystalline cryptomelane compared to uncalcined samples.

![Figure 1. XRD patterns of manganese oxides synthesized by precipitation method with the variation of flow rate (1, 2, and 3 mL/min) for uncalcined samples.](image)

Subramanian reported the conflicting results, that is, the phase transformation from layer occurs from birnessite into tunnel cryptomelane after calcination process, but using different precursor (oxalic acid) [2]. Other previous studies reported that the birnessite phase was obtained using the same method and precursor (citric acid) even after the calcination process [9]. The difference with the current study is that no washing treatments were conducted before calcination process for the previous studies [9]. The transformation from birnessite to cryptomelane seems to correlated with \( K^+ \) content since the layer birnessite structure accommodates more \( K^+ \) than that for cryptomelane [12]. The effect
of flow rates on crystallinity is also shown in figures 1-2. Figures 1-2 also displayed the effect of flow rates on the crystallinity of the as-synthesized manganese oxides. The XRD patterns of uncalcined samples remain unchanged after different addition rates of citric acid into KMnO₄. However, the higher flow rates resulted in higher crystalline manganese oxides for calcined samples [2].

![Figure 2](image.png)

**Figure 2.** XRD patterns of manganese oxides synthesized by precipitation method with the variation of flow rates (1, 2, and 3 mL/min) for calcined samples.

Table 1 showed the crystal sized of the as-synthesized manganese oxides with different flow rates of citric acid for uncalcined and calcined samples. The uncalcined cryptomelane displayed smaller particle sizes compared to calcined cryptomelane, indicating that more surface areas for uncalcined samples. The results are consistent with the XRD results, which indicated that poor crystalline natures are associated with higher surface areas.

| No | Sample (KMnO₄+Citric acid) | Flow rates (mL/min) | Treatment | Crystallite Sizes (nm) |
|----|----------------------------|---------------------|-----------|-----------------------|
| 1  | Cryptomelane               | 1                   | uncalcined | 6.529                 |
| 2  | Cryptomelane               | 2                   | uncalcined | 8.713                 |
| 3  | Cryptomelane               | 3                   | uncalcined | 8.655                 |
| 4  | Cryptomelane               | 1                   | calcined   | 15.330                |
| 5  | Cryptomelane               | 2                   | calcined   | 15.969                |
| 6  | Cryptomelane               | 3                   | calcined   | 17.893                |

The results of methylene blue degradation using uncalcined samples were displayed in figure 3. The degradation of methylene blue increased using the sample synthesized with higher flow rates until certain rates (from 1 mL/min to 2 mL/min) but dropped at the flow rate of 3 mL/min. For the calcined samples, however, the degradation improved using samples prepared with high flow rates (3 mL/minute). It is also noticeable that the uncalcined catalysts show higher degradation of methylene blue than calcined catalysts. These results suggested that the low crystalline nature of uncalcined
samples is responsible for high catalytic activities for the degradation of methylene blue. The similar results are also reported by previous studies in which the uncalcined samples have higher catalytic activities that calcined samples [9,10]. At the current study, no comprehensive explanation is given for the trends of the degradation due to the influences of flow rates since more studies are required such as morphologies, BET surface areas, pore-volume, and other related surface properties. It is believed that the higher degradation of methylene blue is related to the higher surface area, pore-volume, and morphologies of the catalysts. In general, a catalyst with high surface area and pore-volume have higher catalytic activity than that with low surface area and pore volume. This correlates with more active sites for the interaction between the catalyst and H₂O₂, resulting in high degradation rates.

Figure 3. The amount of MB degraded using cryptomelane uncalcined (1, 2, and 3 mL/min) with [MB] = 50 ppm, catalyst weight = 50 mg, volume of H₂O₂ = 5 mL at room temperature.

Figure 4. The amount of MB degraded using cryptomelane calcined (1, 2, and 3 mL/min) with [MB] = 50 ppm, catalyst weight = 50 mg, volume H₂O₂ = 5 mL at room temperature.
4. Conclusion
In this study, cryptomelane type manganese oxides were successfully synthesized by the redox reaction between KMnO$_4$ and citric acid via precipitation method. The calcination processes have a tremendous influence on crystalline nature and catalytic performance of the as-synthesized cryptomelane-type manganese oxides. The samples with a calcination process display higher crystalline phase, but lower catalytic activities compared with the samples without calcination process. The highest degradation of MB is achieved over 98% under the optimum condition.

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