Effect of Precursors on Morphology and Catalytic Activities of Birnessite for Methylene Blue Degradation

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Abstract. Manganese oxides having birnessite structure have been successfully synthesized by precipitation method. These materials were fabricated based on the reaction between KMnO₄ and citric acid or oxalic acid as reductant. The precipitated solid products were heated up to 120 °C and calcined up to 600 °C. The materials were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), and its average oxidation state (AOS) together with the zero point charge (pH_zpc) were also determined. The XRD results showed the calcined citric-prepared birnessite displayed more crystalline structure than oxalic-prepared birnessite. The SEM results indicated that the citric precursor produced aggregation particles with needle-like appearance on its crystal faces, while oxalic acid generated irregular aggregation particles. The catalytic activities of as-prepared birnessite prior to and following to calcinations were evaluated for the degradation of methylene blue (MB) with H₂O₂ as an oxidant. The un-calcined samples displayed much higher catalytic degradation for MB compared to calcined samples. The maximum of MB degradation obtained using un-calcined catalyst from citric acid precursor was 98%, whereas the oxalic acid was 90%. The high catalytic activity of un-calcined samples especially for citric-prepared birnessite was correlated with high defect concentration due to its low AOS Mn and small crystal size.

1. Introduction
Manganese oxides (MnO₂) had become an important materials extensively studied in various domains due to their outstanding structural flexibility combined with novel chemical and physical properties [1]. Manganese oxide can be synthesized with various synthetic methods, such as sol-gel [2], hydrothermal [3], reflux [4], solvent-free method [5], and precipitation methods [6]. Compared with the other methods, the precipitation method was relatively short time synthesis, simple and rapid preparative method, easy control of particle size and composition. There were also various possibilities to modify the particle surface state and overall homogeneity using the method [7]. In general, the different synthesis methods, precursors, reaction conditions lead to different structure, morphologies, and surface properties of manganese oxide [8].

The MnO₂ comprises a large family of naturally occurring and synthetic materials with many kinds of crystallographic polymorphs including α-MnO₂ (cryptomelane), β-MnO₂ (pyrolusite), γ-MnO₂ (nswtite), and δ-MnO₂ (birnessite) types. Among them, birnessite-type manganese oxide (δ-MnO₂₃) possesses a two dimensional (2D) layered structure, which consists of edge-sharing MnO₆ octahedral and interstitial cations [9,10]. These cations balance the negative charge arising from the layers that was caused by Mn site vacancies and substitution of Mn (III) for Mn (IV) [10]. Additionally, the exchangeable interstitial cations and the facile interconversion of Mn oxidation state (+2, +3 and +4)
assure this material can readily engage in cation exchange and oxidation reduction reactions [10]. Due to these unique physicochemical properties, 6-MnO₂ has been widely utilized in many applications, such as catalysts [11], ion exchange, molecular adsorption, biosensor [7], supercapacitors [6] and so forth.

Among the applications stated above, the dye degradation using birnessite as a catalyst was one of the hottest topics, because organic dye pollutant in water had become a major source of environmental pollution due to their structure stability and resistance to degradation [1]. Dyes created adverse problems to the environmental and human health. Therefore, it was very urgent to solve this problem. So far, numerous studies had reported on how to deal with dye wastewaters including physical and chemical processes [1]. Advanced Oxidation Processes (AOP) was one of currently available method to oxidize dye wastewater into benign products such as CO₂ and H₂O.

In this study, birnessite catalysts were synthesized through a redox-precipitation method using potassium permanganate and two different reducing agents (citric acid or oxalic acid) with un-calcined and calcined process. The birnessite catalysts were tested for catalytic oxidation of methylene blue dye with H₂O₂ as an oxidant. The presence of more defects as shown in the lower average oxidation state (AOS) in the as-synthesized birnessite samples seems to improve the catalytic activities for MB degradation either for the samples with or without calcination process. For example, the as-synthesized birnessite samples prepared from citric acid precursor either without calcinations (CA-UC samples) or with calcinations (CA-C samples) with lower AOS (3.50-3.66) displayed enhanced catalytic activities compared with those of prepared from oxalic acid precursor with higher AOS (3.62-4.00).

2. Experimental

2.1. Synthesis of birnessite from citric acid and oxalic acid

Birnessite-type octahedral layer manganese oxide (OL-1) samples were synthesized by redox-precipitation method with the chemical reduction of KMnO₄ using citric acid or oxalic acid as a reducing agent under alkaline conditions [6]. The new redox-precipitation route was as follows: The 250 mL of 0.2 M KMnO₄ solution was added dropwise to 250 mL of 0.04 M citric acid solution with the rate of 1 ml min⁻¹ under constant stirring (300 rpm) at room temperature. After the complete addition, the obtained black-brown turbid suspension was digested at 60 °C for 30 min and dried at 120 °C for 6 h. The dried powder product was brittle and denoted as un-calcined catalyst. The un-calcined catalyst was calcined at 600 °C for 4 h and denoted as calcined catalyst. For the synthesis birnessite from oxalic acid as a reducing agent using the same method, but different mole ratio, a typical synthesis is as follows: the 250 mL of 0.2 M KMnO₄ solution was added dropwise to 250 mL of 0.3 M oxalic acid and the precipitated product was either heated to 120 °C or calcined at 600 °C. The as-synthesized catalysts were denoted as CA-UC birnessite for citric acid-prepared un-calcined birnessite, CA-C birnessite for citric acid-prepared calcined birnessite, OA-UC birnessite for oxalic acid-prepared un-calcined birnessite, and OA-C birnessite for oxalic acid-prepared calcined birnessite.

2.2. Synthesis of birnessite from citric acid and oxalic acid

The un-calcined and calcined birnessite catalyst samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic absorption spectroscopy (AAS), determine the average oxidation state (AOS) and zero point charge (pH_zpc).

2.2.1. The Powder X-ray diffraction (XRD). The structure, crystallinity and phase purity of the manganese oxides were analyzed by XRD. Patterns of all manganese oxide samples were recorded using Shimadzu XRD 7000 maxima using Cu Kα radiation (λ = 1.5406 Å) as the X-ray source.
2.2.2. **Scanning Electron Microscope (SEM).** The morphologies of the samples were characterized using SEM JEOL JSM-6330F with acceleration potential was 15-20 kV. Samples were deposited on thin amorphous carbon films supported by copper grids from ultra-sonicated ethanol on the product.

2.2.3. **Atomic Absorption Spectroscopy (AAS).** The total amount of potassium (K) and manganese (Mn) of the samples were determined by atomic absorption spectroscopy (Shimadzu AA-7000 series). About 10 mg of manganese oxide catalyst was placed into glass beaker and added 10 mL of H₂SO₄ and diluted with DDW up to 100 mL. The mixture was then analyzed using an Atomic Absorption Spectrophotometer (AAS) to determine potassium (K) and Manganese (Mn) content.

2.2.4. **Average Oxidation State (AOS).** A potential voltametric titration method was developed to determine the average oxidation states of manganese in the samples [12]. The titration method includes two steps. The first step, a 10 mg (W₁) sample with 2 mL of concentrated hydrochloride acid was added to a 50 mL Erlenmeyer flask covered with a watch glass. The samples were dissolved completely and the resulting solution was transferred into a 100 mL volumetric flask and diluted to the 100 mL mark with DDW. The diluted solution (25 mL) and 50 mL of the saturated sodium pyrophosphate solution were then added into a 200 mL beaker. When the pH value of the system reached about 7 when adjusted with a 1 M NaOH solution, the system was titrated with a 0.001 M potassium permanganate solution. The KMnO₄ used at the highest pH was recorded as V₁. The potential change (in mV) of the system during the course of titration was monitored with a D-71G pH meter with a pair of electrodes (Calomel and Pt). The second step, about 10 mg (W₂) samples were weighed and transferred into a 100 mL Erlenmeyer flask and 10 mL of 0.001 M (NH₄)₂Fe(SO₄)₂ was added. When all solids were dissolved, the solution was titrated with the potassium permanganate solution, the volume of consumed KMnO₄ solution for the titration of the sample was recorded as V₃. As for the blank titration, 10 mL of ferrous ammonium sulphate was titrated using KMnO₄ 0.001 M. The volume used for the blank titration was recorded as V₂. The average oxidation state of manganese oxide can be calculated using equation:

\[
\text{AOS} = 1.25 \times \frac{(V_2 - V_3)}{V_1} \times \frac{W_1}{W_2} \tag{1}
\]

2.2.5. **Zero Point Charge (pH_{zpc}).** Prolonged salt titration (PST) method was used to determine point of zero charge (pH_{zpc}) of manganese oxides [13]. With this method, 10 mg sample was added with 10 mL DDW and mixed with 0.01 M HCl or 0.01 M KOH to obtain the appropriate pH range (pH 2-6). The mixtures were equilibrated for 3 to 4 days at 25°C, shaken for 1 h/d. After settling, the pH values of the supernatant in each tube were measured and denoted as pHᵢ. The next step, 0.5 mL of 2 M KCl was added to the mixture and 4 h shaking followed. After settling, the pH was recorded again and denoted as pHₖ. The pH_{zpc} was obtained from the plot of ΔpH (= pHₖ - pHᵢ) against pHᵢ as point where ΔpH was zero.

2.2.6. **Catalytic activities.** The catalytic reaction was carried out in a 250 mL batch reactor, which contained 25 mL of 50 ppm methylene blue, 70 mL of DDW, and 50 mg of birnessite catalyst. The mixture was stirred using a magnetic stirrer at 400 rpm for 30 minutes and added 5 mL hydrogen peroxide 30%. The optical absorbance measurements were taken by pipetting 5 mL aliquots of the reaction mixture at various time intervals during the reaction. The solution was immediately centrifuged for 15 min at 3000 rpm to remove any solid particulates. The absorbance of the solution was analyzed using Optima SP-300 Spectrophotometer at a wavelength of 660 nm. The results were determined using the equation [14]:

\[
\% \text{ decrease MB} = \frac{C_o - C_t}{C_o} \times 100 \tag{2}
\]

Where C₀ was initial concentration and Cᵣ was final concentration in the reaction mixture at a given time respectively.
3. Result and Discussion

3.1. Synthesis of birnessite-type manganese oxide

When KMnO₄ solution was added dropwise to the solution of citric acid or oxalic acid, the colour of solution mixture slowly turned from colourless to yellow. The solution was flocculated and formed a brown to black supernatant. This observation indicated that KMnO₄ solution was completely reduced to manganese oxide solid. The reduced Mn species induced the formation of precipitated products, which were mainly oxides of manganese. Following heating and calcination of the solid product at the certain temperatures, the crystalline phases of manganese oxides were produced and referred to as uncalcined and calcined catalyst, respectively. The as-synthesized manganese oxide catalysts were stored in desiccators and tested for the catalytic oxidation of MB dye.

3.2. The crystallinity and morphology of as-synthesized birnessite

The Powder X-ray diffraction (XRD) used to identify phases and crystallinity of the as synthesized manganese oxide samples [11]. The wide-angle XRD patterns of the as-synthesized manganese oxides were showed in Fig.1. Typical diffraction peaks of citric acid-prepared manganese oxide were observed at 2θ of 12.62°, 25.37° and 37.41° and for oxalic acid-prepared manganese oxide at 2θ of 12.65°, 25.31° and 37.47°. The three peaks in XRD pattern synthesized in this study was in good agreement with characteristic Bragg diffraction at 12°, 25° and 37° that can be easily identified for the (001), (002) and (111) planes of birnessite [15] (JCPDS No. 80-1098), characteristic of the birnessite intercalated with K⁺ ion and H₂O molecules [6].

In Fig 1, the XRD patterns of CA-C and OA-C birnessite reflect the crystalline nature, indicating the CA-C birnessite was much more crystalline than that of OC-C birnessite. Thus, the different reducing agents (citric or oxalic acid, in this case) lead to different crystalline structures of birnessite produced. The XRD pattern for calcined catalyst showed similar pattern to turbostratic birnessite. On the other hand, the weak and broad peaks with low intensities in XRD patterns of the as-synthesized CA-UC and OA-UC birnessite samples reveal the poor crystalline nature of the un-calcined catalyst. It was common that calcined manganese oxides have much higher crystallinity compared to un-calcined ones, which was related to certain energies required to attain more ordered structures [6,11].

![Figure 1. Diffractogram of manganese oxide type birnessite synthesized with potassium permanganate and citric acid/oxalic acid. The oxalic acid-prepared un-calcined birnessite (black line), citric acid-prepared un-calcined birnessite (red line), oxalic acid-prepared calcined birnessite (blue line) and citric acid-prepared calcined birnessite (green line)](image-url)
The different or same synthetic methods, precursors and reaction conditions may result in the same or different crystal structures. The as-synthesized manganese oxide synthesized in this study had similar crystal phase (birnessite) with prepared-birnessite manganese oxide by sol-gel, reflux and simple-redox method using KMnO₄ and various reducing agents such as glucose and Na-Lactate [2,16], HCl [4] and oxalic acid [11], respectively. In other studies indicated that even with the same synthetic route and the precursors it resulted in the different crystal structure. For example, reaction between HCl, HNO₃, or H₂SO₄ as the reducing agents and KMnO₄ as oxidant using reflux method produced birnessite at low acid concentration. The similar reactions using the same method produced cryptomelane at high acid concentration. Similarly, the sol-gel synthesis of KMnO₄ and polyvinyl alcohol or glucose produced birnessite (OL-1) [2], whereas using KMnO₄ and oxalic acid generated cryptomelane (OMS-2) [17]. Other studies using the same synthetic strategy, but different precursors, reaction time and temperatures generated different crystalline structures as shown by hydrothermal synthesis using different precursors (MnSO₄, (CH₃COO)₂Mn-4H₂O, MnCl₂-4H₂O, Mn(NO₃)₂-4H₂O), which produced pyrolusite (β-MnO₂) with high crystallinity at long reaction time and high temperature [3].

The crystallite size of as-synthesized birnessite was estimated using Scherrer’s equation:

\[ D = \frac{0.941 \lambda}{\beta \cos \theta} \]  

Where \( D \) was the average grain size, \( \lambda \) was the X-ray wavelength (0.15406), \( \theta \) and \( \beta \) were the diffraction angles and Full-Width at Half-Maximum (FWHM, in radian) of an observed peak, respectively [18]. The results of calculated average crystallite sizes were found to be 21.56 nm for CA-C birnessite and 10.79 nm for OA-C birnessite. For the un-calcined birnessites, however, the sizes for CA-UC (1.17 nm) and OA-UC (1.21 nm) were both much smaller. This result consisted with the theory that the grain size decreased with line width increasing in XRD peaks [18]. The crystallite sizes of birnessites were found to be in the range 6.71-12.38 nm [15].

The Scanning Electron Microscopy (SEM) was used to investigate the surface morphology of the as-synthesized birnessite [10]. The SEM image of the un-calcined prepared birnessite sample showed marked different morphology from that of calcined prepared birnessite. The CA-UC birnessite produced individual particles (Fig. 2a), whereas CA-C birnessite revealed needle-like appearance on the top aggregations (or like nanofibres appearance) (Fig. 2b). Similarly, the morphology of OA-UC birnessite showed the aggregated particles without any specific morphology as shown in Fig. 2c, and globular shape with irregular aggregation for OA-C birnessite (Fig. 2d). Figures 2a-2d also revealed that the different reducing agents (citric or oxalic acid) generated remarkable differences in the morphologies for the as-synthesized birnessite. SEM images of calcined oxalic acid-synthesized birnessite displayed the morphology similar to that of birnessite and cryptomelane prepared from the previous studies synthesized using the precipitation method [6]. Also, the morphology of the CA-C birnessite was similar to that of cryptomelane prepared by sol-gel method and pyrolusite obtained using hydrothermal method. In contrast to the observation that the difference in synthetic method lead to the similar morphology of birnessite, other studies indicated that the opposite was true. Furthermore, the different synthetic route produced the same crystal structure with different morphology. For examples, the synthesized of the three dimensional hierarchical microsphere birnessite and nanowires birnessite by reflux method [4,19]. The use of citric or oxalic acid as reductant and KMnO₄ as oxidant had been used for the synthesis of birnessite using sol-gel method. The different surface morphologies were also observed, where oxalic acid precursor showed disc-like appearance with smooth faces [17] and citric acid precursor showed nanorod faces [20]. In summary, various factors were known to affect the surface morphology of manganese oxides.
Figure 2. SEM images of birnessite synthesized with potassium permanganate and citric acid or oxalic acid. (a) citric acid-prepared un-calcined birnessite, (b) citric acid-prepared calcined birnessite, (c) oxalic acid-prepared un-calcined birnessite and (d) oxalic acid-prepared calcined birnessite.

3.3. The K/Mn ratio, Average Oxidation State (AOS) and Zero Point Charge (pH_{zpc}) of as-synthesized Birnessite

Atomic Absorption Spectroscopy (AAS) was used to analyze potassium to manganese ratio in birnessite catalysts. The potassium to manganese (K/Mn) atomic weight ratio in CA-C birnessite and CA-C birnessite were 0.64 and 0.97, respectively. These results suggested that the synthesis conditions employed to generate birnessite facilitate the compositional differences between them. The sheets of birnessite were comprised of edge sharing MnO$_6$ octahedral and carry a negative charge. There were two reasons for charge imbalance in birnessite sheets: (1) presence of Mn$^{3+}$ ions in the sheets and (2) cations vacancies generated by the absence of Mn$^{4+}$ ions in their octahedral sites thus creating a tetravalent negative charge at each site [11]. High Mn content in manganese oxide means more Mn$^{3+}$ presence in the framework and thus lower the ratio of potassium to manganese. It was possible that at higher temperature, some Mn$^{3+}$ oxidize to Mn$^{4+}$ by oxygen due to more mobile oxygen in the framework.

The average oxidation state of manganese (Mn) was analyzed to determine the portion Mn$^{4+}$ relative to Mn$^{3+}$, which also indicated the presence of defect in a manganese sample and correlate the ratio with the catalytic activities of as-synthesized birnessite for the MB degradation. The average oxidation state of as-synthesized birnessite calculated was 3.50 – 4.00, which indicated that more Mn$^{4+}$ ions presence in the framework than Mn$^{3+}$ ions. The citric acid-prepared birnessite had the AOS of Mn of 3.50 and 3.66 for un-calcined and calcined samples, respectively and 3.62 and 4.00 for OA-UC and OA-C samples. In sort, the oxalic acid prepared birnessites had higher Mn$^{4+}$ content than Mn$^{3+}$ compared to citric acid prepared birnessite, indicating the presence of the less defects for the samples prepared using oxalic acid precursor. The more defect contents, which were due to Mn$^{3+}$ or oxygen vacancy, had been claimed to be responsible for the enhanced catalytic activity of birnessite by the previous report [21]. Also, the results suggested that both Mn (IV) and Mn (III) ions presence in the as-synthesized birnessite [6]. Although an ideal hexagonal birnessite does not contain Mn (III) in the MnO$_2$ layers, most naturally occurring hexagonal birnessite contains a significant amount of Mn (III).
in the octahedral layers. Mn (III) was considered to be an intermediate product formed during Mn (IV) reduction or Mn (II) oxidation [21]. Manganese oxides can adopt different structure such as MnO₂, Mn₂O₃, and MnO in which the oxidation states of Mn were +4, +3, and +2, respectively [2]. Among them, birnessite-type octahedral layer (OL-1) was a part of MnO₂ structure. In generally, the AOS of some birnessite using another methods were 3.5 (sol-gel) [16], 3.63 (simple-redox) [11] and 3.71 (reflux) [4].

Zero point charge (pHₚzp) was a pH where the surface charge of a solid is zero. The pHₚzp of as-synthesized birnessite in this study was found to be 2.4 – 4.09. These results were similar with the pHₚzp of birnessite from previous study that varying from 1.4 to 4.5. Manganese oxides mostly had a high negative charge at normal pH values [13]. The highest negative charge was found at pH >3.69 due to deprotonation. Whereas at pH < pHₚzp, the surface of manganese oxides were positively charge due to protonation, and the positive charge increases with decreasing pH values [22].

3.4. Catalytic activity

The catalytic activity of the as-synthesized birnessites was evaluated for oxidation of MB with H₂O₂ in aqueous solution. The MB degradation by as-synthesized birnessites under several reaction times was displayed in Figure 3.

The MB degradation using citric acid-prepared birnessites with calcination and un-calcination were 98% and 84%, respectively. On the other hand, the MB degradation using oxalic acid-prepared birnessites were much lower that was 90% and 83% for un-calcined and calcined sample, respectively. The data also indicated that un-calcined birnessite showed the higher catalytic activities compared to calcined birnessite. The high degradation using un-calcined catalyst was observed after 10 min reaction, the MB dye had been successfully degradation up to 90%. This suggested that crystalline nature of as-synthesized birnessite play an important role for the MB degradation. Soejima et al reported the similar observation where the amorphous structure of cryptomelane showed very high degradation ability toward RhB compared with crystalline cryptomelane [23].

The higher degradation efficiency on MB was found by birnessite with lower AOS of Mn. This is due to more Mn³⁺ presence in the birnessite framework to convert H₂O₂ into hydroxyl radicals, the second highest powerful oxidant after fluorine. These radicals are very reactive and attack most MB molecules in the solution. The citric acid-prepared birnessite had a lower AOS than oxalic acid-prepared birnessite, thus had better catalytic activities. Also, the presence of Mn (III) content and vacant site in the Mn oxide layers can substantially affect of birnessite reactivity, such as oxidising ability [21].
The MB degradation depends also on the charge on the surface and the formation of hydroxyl radicals as well as the probability of hydroxyl radicals to react with methylene blue. Manganese oxide materials in nearly neutral solutions (pH > pH_{zc}) were abundant in hydroxyl groups on their surfaces. The better adsorption ability was thought to be the strong electrostatic attraction between the surface hydroxyl groups and the cationic groups (R–S') of MB [24]. The hydroxyl group on the surface of the manganese oxide will be deprotonated and the surface become negative charge [22], which will facilitate the degradation of MB. The pH can affect the degradation of MB due to electrostatic repulsion [22]. The degradation should be enhanced with increased pH, which was consistent with the experimental results.

4. Conclusion
In this paper, the octahedral layer birnessite-type manganese oxides were successfully synthesized by a redox-precipitation method via the reaction of KMnO₄ and citric or oxalic acids as reducing agents. The as-synthesized birnessites had different crystallinity, crystal morphology, Mn⁴⁺/Mn³⁺ ratios and surface charges. This resulted in different catalytic activities for MB degradation. The un-calcined prepared birnessite showed higher activity than calcined material and citric prepared birnessite displayed higher activities than oxalic acid prepared birnessite. The high catalytic activity of CA-UC birnessite was related to amorphous nature of as-synthesized birnessite, well-developed morphology, low AOS and small crystal size.

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**Acknowledgment**

The ministry of Research, Technology and Higher Education has helped fund this research through postgraduate research grant in accordance with the number of research contract 337/UN.19.5.1.3/TT/2018.