

Synthesis and catalytic activity of Birnessite-Type Manganese Oxide synthesized by solvent-free method

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Abstract. Redox reaction between KMnO_4 and glucose using solvent-free method produces the octahedral layer birnessite-type manganese oxide. The effects of mole ratios, temperatures, and calcinations time on the structures and crystallinity of the oxides were studied through the X-ray powder diffraction analysis. The mole ratio of KMnO_4 /glucose (1:3) produces the pure birnessite with low crystallinity, whereas the mole ratio of KMnO_4 /glucose (3:1) yields high crystalline birnessite with minor components of hausmannite-type manganese oxide. The increasing of the temperature and calcinations times (300-700 °C and 3-7 h, respectively) will improve the crystallinity and the purity of the as-synthesized oxide. Further experiments also showed that the as-synthesized octahedral layer birnessite-type manganese oxides have catalytic activity on the degradation of methylene blue (MB) dye with H_2O_2 as oxidant. The results revealed that the effective degradation could be achieved only in the presence of both the birnessite and H_2O_2 , whereas without the addition of catalyst (H_2O_2 only) or addition of H_2O_2 (catalyst only), the 3.5% and 15.5% of MB removal were obtained, respectively.

1. Introduction

Synthetic dyes are widely used in textile, paper, printing, and plastic industries. The wastewater generated from this industry contains residual dyes with low biodegradability [1]. The dye wastes become a major source of water pollution and may cause many significant environmental problems. Thus, dye wastewater must be processed to remove or reduce dyestuff content before released into water body. Methylene blue dye is one of the most commonly used synthetic dyes in a textile industry. The use of methylene blue may cause adverse effects, such as nausea, vomiting, cyanosis, irritation to the gastrointestinal tract and skin in direct contact [2]. This compound is relatively stable, therefore is difficult to oxidize using conventional method.

Removal of organic dyes from natural and industrial wastewater has drawn attention because of the highly toxic effect of these contaminations on animals, plants, and human beings. One of effective methods currently being used for dye removal is called Fenton-like process using a metal oxide as a heterogeneous catalyst and hydrogen peroxide (H_2O_2) as an oxidant. Octahedral layer manganese oxides having similar structure with birnessite mineral is known to have catalytic activities on dye degradation. These oxides have been prepared using a wide range of methods, resulting various physicochemical properties. In the Fenton-like process, the oxide reacts with H_2O_2 to produce various types of active radicals as an intermediate for dye degradation [3]. Formation of $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and $\text{HO}_2\bullet$ to degrade methylene blue by $\beta\text{-MnO}_2/\text{H}_2\text{O}_2$ was reported, this $\beta\text{-MnO}_2$ were synthesized by



reflux and hydrothermal methods [4-5]. Birnessite (δ - MnO_2) prepared by hydrothermal [6] and sol gel [7] method can also be used for methylene blue degradation by using H_2O_2 as an oxidant.

Different synthesis methods of manganese oxide can produce different types of polymorphs. The conditions of preparation and precursor also affect the morphology, surface area, pore volume, and crystallinity of manganese oxide [8]. These structures and surface properties give a considerable effect on the catalytic activity in methylene blue degradation [9-10]. Herein, we introduce a simple one-step solvent-free method for preparing of manganese oxide. This synthetic method eliminates the use of the solvent, give short synthesis time, low cost, and high yield. To date, few reports have been made on preparation of manganese oxide via this method [11-12]. In this study, we synthesized manganese oxide using KMnO_4 and glucose as a precursor using free-solvent method. Moreover, the effect of various mole ratio between KMnO_4 and glucose, time and temperature of calcination on the crystallinity of the products were investigated. Further experiments revealed that the as-synthesized birnessite exhibited excellent catalytic efficiency for the degradation of methylene blue (MB, used as the model) by a Fenton-like reaction.

2. Experimental

2.1. Materials

All the chemical reagents were purchased from Merck (Germany), the used of analytical purity is without any further purification.

2.2. Synthesis

The manganese oxide was prepared via solvent-free method. The appropriate amount of KMnO_4 and glucose are shown in Table 1. The resulting fine-powder of KMnO_4 and glucose were then mixed and ground in one mortar. The mixture was calcined at the certain condition (Table 1). The final product was cooled up to room temperature, washed using HCl 0.1 M and distilled water. The black product was dried at 110°C .

2.3. Characterization

X-ray powder diffraction (XRD) was performed on a Shimadzu 700 Maxima X X-ray diffractometer operating at 40 kV and a current of 30 mA with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$). The data were collected with scan speed 2° per minute in 2θ , from $2\theta = 10^\circ$ to 90° . The scanning electron microscopy (SEM) images were taken on a ZEISS EVO-50 instrument. The Brunauer-Emmett-Teller (BET) surface area measurements and Barret-Joyner-Halenda (BJH) adsorption were carried out using a Quantachrome Nova nitrogen adsorption apparatus. Prior to the adsorption measurements, the samples were degassed under vacuum for 3 h at 120°C .

2.4. Catalytic activity

The catalytic reaction was carried out in the Beaker glass, contained 25 mL MB dye solution (100 mg/L), 60 mL deionized water, and 25 mg catalyst. The suspension was continuously stirred magnetically for 30 min to achieve adsorption/desorption equilibrium. Following adding 15 mL of 30 wt% H_2O_2 solution, the mixture was allowed to react at room temperature. At given time intervals, 2.5 mL of the mixture was pipetted into a volumetric flask, quickly diluted with distilled water to 25 mL, and placed in iced bath. For optical absorption measurements, the diluted solution was immediately centrifuged at 10000 rpm for 3 min to remove the catalyst particles. Then the centrifuged dye solution put into a quartz cell, and the changes of absorptions at 664 nm were taken to identify the concentrations of MB, using a Shimadzu UV mini 1240 UV-vis spectrophotometer.

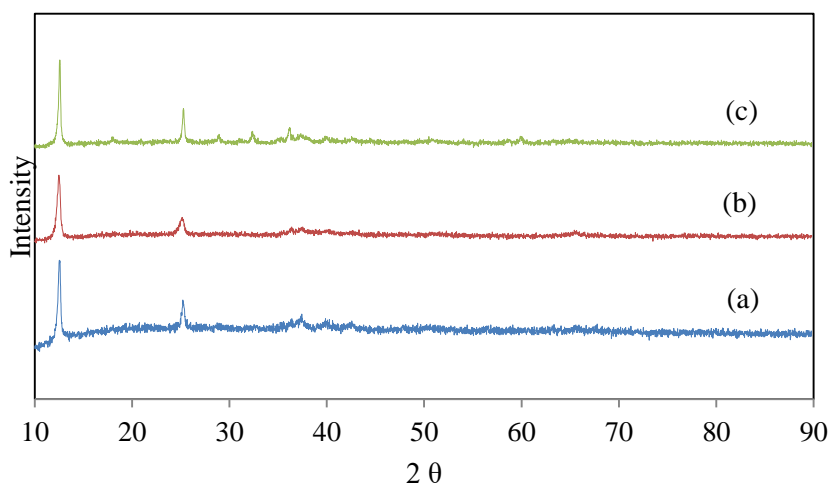
Table 1. Variation condition of synthesis birnessite-type manganese oxide

| Mole ratio KMnO ₄ :glucose | Temperature of calcination (°C) | Time of calcination (h) |
|--|------------------------------------|----------------------------|
| 1 : 3 | 500 | 5 |
| 1 : 1 | 500 | 5 |
| 3 : 1 | 500 | 5 |
| 3 : 1 | 300 | 5 |
| 3 : 1 | 700 | 5 |
| 3 : 1 | 700 | 3 |
| 3 : 1 | 700 | 7 |

3. Results and discussion

3.1. Characterization of manganese oxide

Octahedral layer Manganese oxide birnessite was synthesized using free-solvent method. This method was realized by mixing two different precursors (KMnO₄ and glucose) to form solids followed with the heating process. Prior to the mixing process, each precursor in the ground separating with mortar, then KMnO₄ and glucose were mixed in a single mortar. This process is a exothermic reaction, it generates sparks when KMnO₄ and glucose were in the ground together in one mortar. The variation of mole ratio, temperature, and time of calcination in the synthesized of manganese oxide can be seen in Table 1.

**Figure 1.** XRD patterns of the obtained products at different mole ratio (KMnO₄:glucose): (a) 1:1; (b) 1:3; (c) 3:1

X-ray diffraction was used to characterize the phase and crystallinity of the as-synthesized manganese oxide samples. Figure 1 shown that the XRD patterns of the resulting manganese oxide products synthesized under different mole ratio of KMnO₄ and glucose. The diffraction peaks of these manganese oxide match well with the standard pattern of monoclinic phase of birnessite (JCPDS card no. 80-1098). The diffraction peaks at 2θ values of 12.59°; 25.23°; 37.40°; and 42.54° can be ascribed to the reflections of (001), (002), (-111), and (-112) planes of the birnessite. As shown in Figure 1, the peaks at 2θ values of 12.59, and 25.23° increase in intensities of the mole ratio of KMnO₄/glucose. The mole of KMnO₄ is higher than mole of glucose (Figure 1c), it will generate birnessite-type manganese oxide with relatively good crystallinity, with small impurities due to hausmannite-type manganese oxide at 2θ values of 17.98°, 28.58°; and 32.35°. However, if mole ratio of KMnO₄ is

1:3 in Figure 1b, the impurities peaks will be disappeared and resulting more pure birnessite phase. This results indicate that the small ratio of KMnO_4 /glucose facilitates the formation of more pure birnessite phase with lower crystallinity, whereas the high mole ratio of KMnO_4 /glucose produce more crystalline phase of birnessite with minor impurities. The different crystal phases of manganese oxide are known to correlate with the potassium content. Ching et al., reported that the high concentration of KMnO_4 generates octahedral layered birnessite, and the lower concentration of KMnO_4 produces cryptomelane-type manganese oxide octahedral molecular sieve [13].

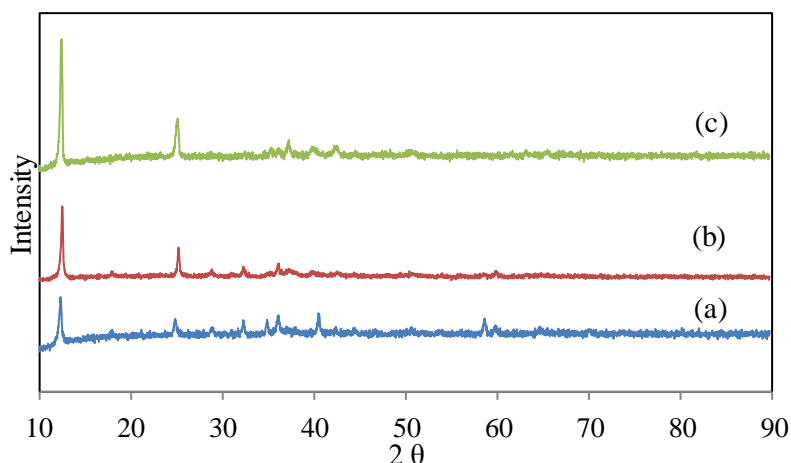


Figure 2. XRD patterns of the obtained products with mole ratio of KMnO_4 :glucose = 3:1 at different temperature of calcination: (a) 300; (b) 500; (c) 700 °C

The effect of temperatures on the structure and crystallinity of as-synthesized manganese oxides is shown in Figure 2. The calcination temperatures have a sizably impact in the structure and crystallinity of the as-synthesized manganese oxide. The increasing of the calcination temperature increases the intensity of the main reflection peaks of birnessite (2θ values of 12.38° ; 24.91°). At low temperature (300 °C), the oxide consists of mixtures of birnessite and hausmannite. The increasing of the temperature (700 °C in Figure 2), the intensities of two main peaks of birnessite also increases, reflecting more crystalline phase of birnessite and the peaks due to hausmannite phase disappear. Thus, the higher temperature produces more crystalline and pure birnessite.

Effect of the calcination time on the structure and crystallinity of the manganese oxides can be seen in the Figure 3. When the calcination time is 3 hours, the intensities at 2θ value of 12.54° ; 25.26° ; 35.30° ; 37.33° ; 39.90° and 42.66° are relatively low, indicating the low crystallinity of birnessite phase. For a 5-hour calcination, the diffraction peaks at 2θ of 12.50° ; 25.12° of birnessite phase increase substantially. Further increasing of the calcinations time (7 hours) reduces the intensity at 2θ of 12.50° , but produces sharper peaks. The calcinations times from 5 and 7 hours do not give significant effect in the crystallinity of birnessite.

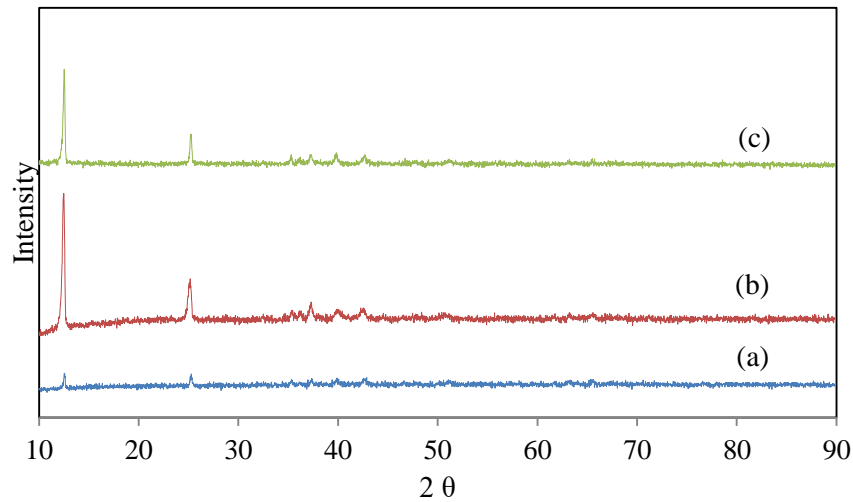


Figure 3. XRD patterns of the obtained products with mole ratio of KMnO_4 :glucose = 3:1 at different time of calcination: (a) 3; (b) 5; (c) 7 hours

The morphologies of the as-synthesized birnessite were observed by SEM images, as shown in Figure 4(a) and 4(b), respectively. From the low-magnification SEM image (Figure 4(a)), the birnessite consisted of aggregate particles with irregular sizes.

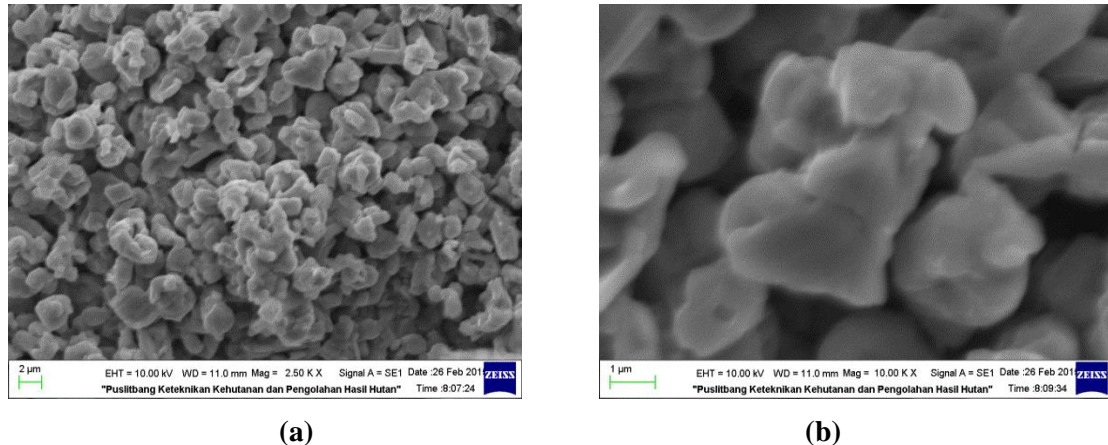


Figure 4. SEM images of the birnessite as-synthesized at 700 °C for 7 hours, Mag.x (a) 2,500 (b) 10,000 (mole ratio of KMnO_4 :glucose = 3:1)

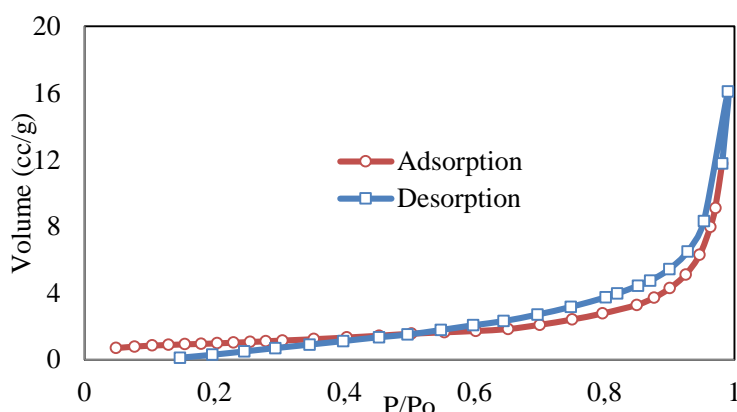


Figure 5. N₂ adsorption/desorption isothermal plot of the birnessite synthesized at 700 °C for 7 hours.

Figure 5 shown the adsorption-desorption isothermal plot of the as-synthesized birnessite prepares at 700 °C for 7 hours. The pore volume and pore size distribution were obtained using the Barrett, Joyner and Halenda (BJH) method from desorption branch of the isotherms and surface area were determined by the BET method using N₂ adsorption-desorption isotherms. The isotherm obtained is type III according to the IUPAC classification with the Brunauer-Emmett-Teller (BET) specific surface area of 23.1278 m²/g. Figure 6 shown the mesopore size distributions calculated by BJH method. The BJH plots show a pore size distribution in the range of 20-80 Å, indicating mesoporous materials.

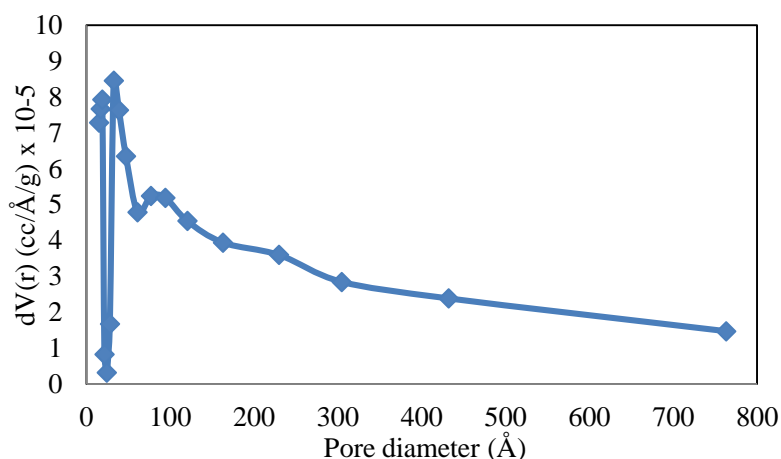


Figure 6. Mesopore size distribution plot by BJH method of the birnessite synthesized at 700 °C for 7 hours.

3.2. Catalytic degradation of methylene blue

Previous studies have reported that manganese oxides with various structures exhibited excellent catalytic properties in degradation of dyes using oxidizing agent such as H₂O₂[3-7]. Several species are responsible for the degradation, included the free radical species, such as •OH, O₂•⁻, and HO₂•. The degradation of dyes using the manganese oxides proceeds by an adsorption–oxidation–desorption mechanism [3,14,15]. Herein, the as-synthesized birnessite-type manganese oxides were tested for their catalytic performance in the degradation of methylene blue as a model under controlled conditions. In the absence of a catalyst (only MB+H₂O₂), no obvious dye degradation was observed after 120 min. With the as-synthesized birnessite as catalyst but no H₂O₂ (only MB+ birnessite), the

degree of decoloration reaches to 15% within 60 minute and then tends to be saturated, which can be ascribed to adsorption of the dye molecules on the birnessite. In the contrast, the presence of the birnessite and H_2O_2 , the degree of degradation reached to about 50% within 90 min (Figure 7).

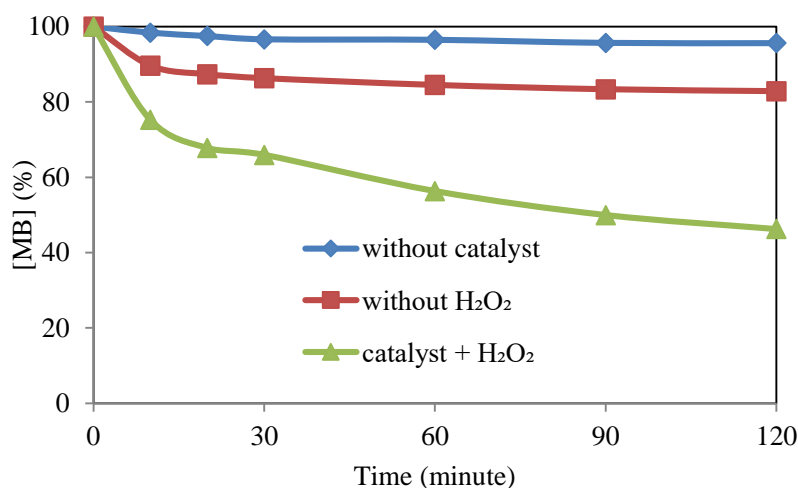


Figure 7. Time profile of MB degradation: (◆) only MB + H_2O_2 (■) only MB + birnessite (▲) MB + birnessite + H_2O_2 (reaction condition: $[\text{MB}]_0 = 25 \text{ mg/L}$; $[\text{Birnessite}] = 0.25 \text{ g/L}$; $[\text{H}_2\text{O}_2, 30 \text{ wt\%}] = 15 \text{ mL}$; at room temperature.

The UV-vis spectra of the MB solution and the dye degradation at different reaction time are showed in figure 9 and 10. In this study, the characteristic absorption peak at about 664 nm of MB was used as a monitored parameter during the catalytic degradation process. The absorption spectra at $t = 0$ minute is used for the starting solution of MB with a concentration of 25 mg/L (without the birnessite and H_2O_2). The four characteristic absorption peaks (245, 292, 614, and 664 nm) of the MB dye could be observed in the absorption spectrum. As soon as H_2O_2 was added to the mixture of MB and birnessite, the characteristic absorption peak of MB (664 nm) dropped (in 10 minute observation), and became very broad and weak with the time prolonged. In addition, the peaks at 614 and 663 nm are not observed in the spectrum even in the early of 10 minute reaction. The color of the reaction mixture slowly turned from deep blue to blackish, indicating that most of the MB dye was degraded with the degradation efficiency 95.67%.

Figure 10 shown that UV-Vis spectra of MB with the birnessite (no addition H_2O_2) with different reaction times. The four characteristic absorption peaks of methylene blue decrease considerably, but remain even after 180 minutes of reaction time. This process indicates that the MB is believed to be only adsorbed on the surface of the birnessite-type manganese oxide.

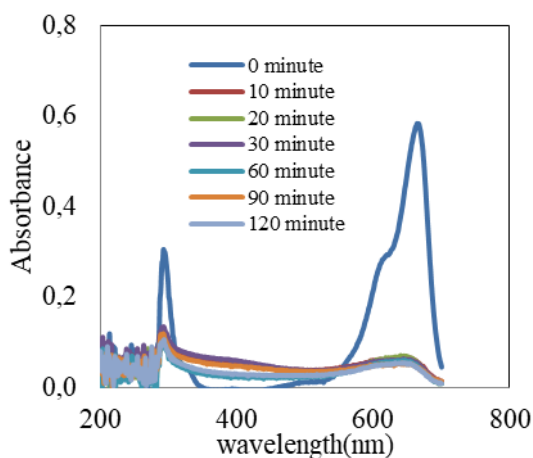


Figure 8. UV-Vis spectra of MB with addition of birnessite and H₂O₂, (reaction condition: [MB]₀ = 25 mg/L; [birnessite] = 2 g/L; [H₂O₂, 30 wt%] = 5 mL; at room temperature)

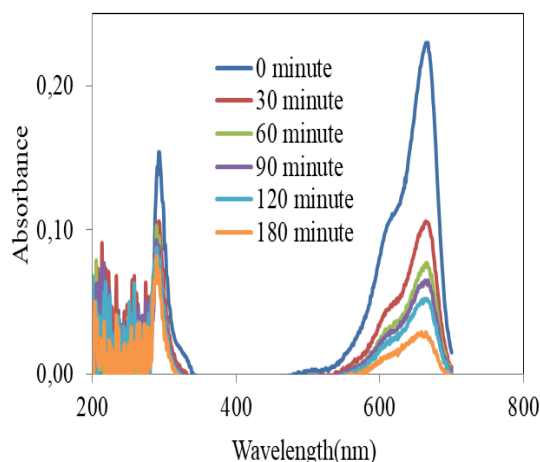


Figure 9. UV-Vis spectra of MB without addition of H₂O₂ (only birnessite); (reaction condition: [MB]₀ = 25 mg/L; [birnessite] = 2 g/L; at room temperature)

Dye molecules comprise of two key components, the chromophore, responsible for producing color, and the auxochrome, which is a functional group of atoms attached to the chromophores. This functional group is able to modify the ability of the chromophore to absorb light. Changes in the chemical structure of MB dye molecule are detected by decreasing color intensity (decolorization) that can be used as early indicators of dye degradation[16]. Further analysis with GC-MS is required to find out the final product and mechanism of the catalytic degradation of MB using the birnessite.

4. Conclusion

A solvent-free synthetic method of the octahedral layer birnessite-type manganese oxide has been developed from the redox reaction between KMnO₄ and glucose. The Mole ratio KMnO₄/glucose is critical in this process, where small mole ratio of KMnO₄/glucose (1:3) generates pure birnessite with low crystallinity. However, when mol ratio of KMnO₄/glucose is high (3:1), high crystalline birnessite is produced with minor contaminant. In addition, higher calcination temperatures lead to substantial improvements of the both crystallinity and purity of the as-synthesized oxides. The as-synthesized octahedral layer birnessite manganese oxides have catalytic activities on the degradation of MB dye using Fenton-like reaction. To obtain the optimal performance in degradation, appropriate amount of catalyst and H₂O₂ should be applied.

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