

# Manganese Oxide Synthesis of Birnessite Type Using Sol-Gel Method for Methylene Blue Degradation

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**Abstract**—The need for catalysts for effective and environmentally friendly waste degradation is increasing. Manganese oxide has a layered structure which is theoretically capable of producing catalysis properties. The synthesis was done through variation of mole ratio of precursors and time of washing. The variations ratio of moles of precursors and washing determined the type of manganese oxide. Synthesis of birnessite type manganese oxide has been successfully performed using  $\text{KMnO}_4$  and citric acid precursors via sol-gel method. The optimum condition of birnessite synthesis through sol-gel method was obtained in a precursor mole ratio of  $\text{KMnO}_4$  and citric acid 3:1, single washing, with a time of calcination for 5 hours, and calcination temperature of  $500\text{ }^\circ\text{C}$ . The results showed that the ratio of K/Mn atoms were 3.1 to 8.0. Interpretation of infrared absorption shows a typical vibration of birnessite. Birnessite produced has a formula which was  $\text{KMn}_3\text{O}_{11}$ . Birnessite can eliminate Methylene Blue up to 97.63%.

**Keywords**—Birnessite, Manganese oxide, Sol-gel, Degradation, Methylene Blue

## I. INTRODUCTION

As the number of industries and their derivatives increases, it also unavoidably produces waste. Much effort has been made to address waste through new technologies to the use of catalysts. The need for effective catalysts to integrate organic waste continues to increase. The catalyst is expected to not only increases the speed of waste degradation but can decompose the waste into more environmentally friendly forms such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , including Manganese oxide. Manganese oxide has many applications because it has various types of structures. This material has two types of structure, namely hollow and layered [1]. Hollow structure materials have wider applications, especially in the areas of catalysts, batteries, electrodes, separations, and selective adsorption [2-7]. Manganese oxide layered structure is used as an ion-exchange material and as a cathode material for refilling in lithium batteries [8-9]. The layered structure can be used as a precursor to form a hollow structure manganese

oxide [10]. One manganese oxide layered structure that has many applications in the environmental field is birnessite.

In this research, birnessite type manganese oxide has been synthesized using the sol-gel method. The effectiveness of catalysis is known for its high degradation ability of methylene blue and short degradation time.

## II. EXPERIMENTAL SECTION

### 2.1. Materials

The materials used for this study were  $\text{KMnO}_4$  (p.a Merck), citric acid (p.a Merck), HCl (p.a Merck), Methylene blue, Whatman No. filter paper. 42, and distilled water.

### 2.2. Instrumentation

The equipment used in this research is analytical balance (METTLER type AE 200), oven (Memmert), furnace, Philips PW 3710 BASED Diffractometer, AAS AA-700F, Avatar 300 FT-IR, SEM-EDX JSM-6510LV (low vacuum).

### 2.3. Manganese oxide synthesis procedure

Synthesis of manganese oxide using  $\text{KMnO}_4$  and citric acid precursors was through the sol-gel method and variations in synthesis conditions. A total of 4.7412 g (0.03 mol) of  $\text{KMnO}_4$  was dissolved into 250 mL of distilled water while stirring. Then it was mixed with citric acid as much as 6.304 grams (0.03 mol) to form a solution with a ratio of  $\text{KMnO}_4$  and citric acid 1:1. The pH of the mixture solution is determined. After 10 minutes, a sol is formed which will then turn into a gel. After one hour, the gel formed was filtered and washed with 250 mL of distilled water as much as 4 repetitions (washing before calcination), then dried at  $110\text{ }^\circ\text{C}$  for one night. The xerogel product, calcined at a temperature of  $500\text{ }^\circ\text{C}$  for five hours. The product formed was mashed for 3 times each with 10 mL 0.1 M HCl and 10 mL distilled water (washing after calcination). The product was dried at  $110\text{ }^\circ\text{C}$  to be characterized [12].

### 2.4. Characterization of manganese oxide

The chemical characteristics include the structure of manganese oxide carried out by X-ray diffraction. Data were taken using PHILIPS PW 3710 BASED X-ray diffractometer, using Cu K $\alpha$  radiation with a scan speed of 1° every 0.2 seconds and an angle of 2 $\theta$  ranging from 0-80°, using a voltage of 40 kV with a strong current of 30 mA. The atomic ratio K and Mn were analyzed by the AAS instrument. A total of 0.1 gram of the sample was destructed using concentrated sulfuric acid so that all manganese oxide can dissolve and form a purple solution. After forming a homogeneous solution, oxalic acid is added to form a clear solution. Before being finalized using AAS, the solution is diluted to 1 mg / L. The absorption peaks of a characteristic functional group were analyzed by FT-IR spectrophotometer. Synthesized samples were mixed with KBr powder and pressed to form pellets. Samples were analyzed at 400-4000 cm<sup>-1</sup> to obtain infrared spectra from the synthesized manganese oxide in the form of a % T path to the wavenumber. The composition of the surface was bacterized with Energy Dispersive X-Ray Spectroscopy (EDS or EDX). This tool was coupled together with SEM, so sample preparation was done in conjunction with SEM. Morphological analysis was performed using a Scanning Electron Microscope (SEM). After coating, the sample was placed in an SEM sample container and analyzed. The magnification of the image was 1000 to 20,000 times using a voltage of around 8-15 kV.

## III. RESULTS AND DISCUSSION

### 3.1. Synthesis of manganese oxide

The reaction of KMnO<sub>4</sub> solution and citric acid is exothermic and produces CO<sub>2</sub> gas. After calcining, the manganese oxide gel turns blackish powder. The manganese oxide formation reaction is shown in reaction 1:



### 3.2. Characterization of manganese oxide

#### 3.2.1. Manganese oxide structure

Variations in the mole ratio of KMnO<sub>4</sub> and crystalline acid carried out showed differences in the angle of 2 $\theta$  and the degree of crystallinity (Fig. 1). The 5:1 ratio shows a diffractogram that is not crystalline with an angle of 2 $\theta$ : 12.51; 25,15; and 44.30 typical birnessite and there are impurities at an angle of 2 $\theta$ : 51.51. The 7:1 ratio has a low level of birnessite crystallinity with an angle of 2 $\theta$ : 12.64; 25.33; and 37.30, and some impurities at 28.73; 43.22, 48.27 and 51.79. Whereas the ratio of 1: 1 has an angle of 2 $\theta$  at: 23.10; 32.95; 38.22; 45.20; 49,30; 55.21; and 65.83, showing characteristics for crystalline bixbyite. Comparison of 3: 1 with an angle of 2 $\theta$ : 12.64; 18.05; 25.62; 28.66; 37.45; 41.95; 49.73; 56.23; 60.01; 65.22; 69.45; and 72.97 which shows a 2 $\theta$  angle typical for crystalline crystals, pure without impurities. Based on the diffractogram, it is known that the variation of the mole will determine the type of manganese oxide formed. If the number of moles of KMnO<sub>4</sub> gets higher, birnessite will be formed. However, if the KMnO<sub>4</sub> mole ratio is too high (7:1), a non-crystalline structure will be produced. This is due to the large number of KMnO<sub>4</sub> molecules that do

not react with citric acid to form manganese oxide, making the formation of crystallinity of manganese oxide difficult. If the mole ratio of KMnO<sub>4</sub> and citric acid is reduced, another type of manganese oxide will form, ie at a ratio of 3:1 producing cryptomelane and 1:1 forming bixbyite. This condition is in line with research by Ching et al. [5]. The number of K atoms is not only a balancing ion in the cavity or between layers of manganese oxide but also plays a very significant role in structuring the structure of manganese oxide. This fact is also supported by AAS and EDX data in this study (Table 1 and Fig. 4) which shows the ratio of the higher K / Mn atoms will form birnessite, whereas if the concentration is lowered it will produce cryptomelane.

Washing factor determines the type of manganese oxide which will be produced (Fig. 2). Manganese oxide made without washing (B4) produces birnessite with high intensity at 12.50; 25.29; 37.35; and 65.59. Washing after calcination in sample B1 has an angle of 2 $\theta$ : 12.58; 25.31; 37.29, and 65.14, which shows the higher crystallinity of birnessite. Washing before and after the C3 sample has an angle of 2 $\theta$ : 12.64; 18.05, 25.62; 28.66; 37.45; 41.95; 49.73; 56.23; 60.01; 65.22; 69.45; and 72.97 and show typical cryptomelane crystallinity levels. This fact shows that leaching affects the type of manganese oxide produced. Washing carried out before the calcined gel will produce a type of cryptomelane, whereas if not carried out washing at this stage will produce birnessite.

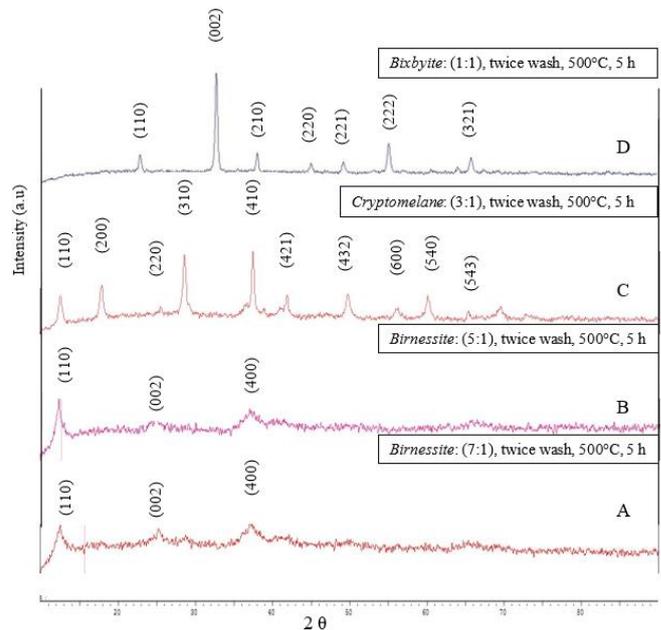


Fig 1. Manganese oxide diffractograms based on mole variations

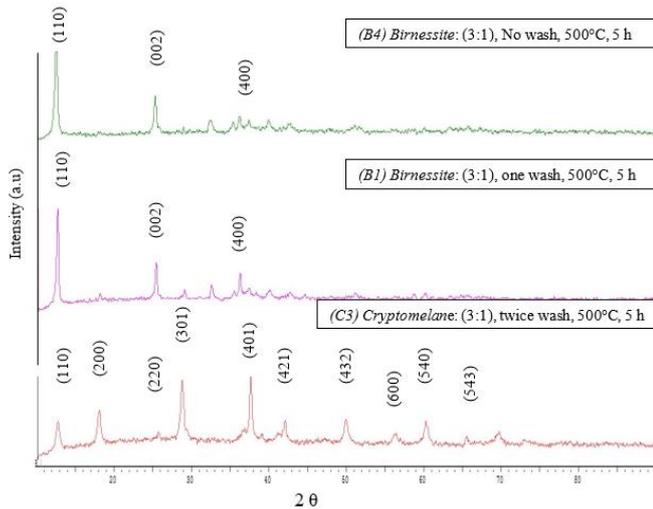


Fig 2. Manganese oxide diffractograms based on variations in washing

Washing after calcination is expected to increase the surface area as it will dissolve  $K^+$  ions which do not enter the main structure of manganese oxide or are present on the surface so that it covers the pore of manganese oxide produced. The molecular formula of cryptomelane and birnessite shows that the ratio of the number of moles of K atoms was stoichiometrically smaller than Mn atoms [20-21]. If the  $KMnO_4$  precursor is used which has the same mole ratio of K atoms as Mn atoms, then manganese oxide will produce excess K atoms. The excess of this K atom will cover the pore and surface of manganese oxide. Through washing it is expected that the K atom can be removed, so that the surface area of the manganese oxide produced increases.

### 3.2.2. The number of atoms K and Mn

AAS data (Table 1) explains the effect of leaching on the number of K and Mn atoms in the synthesized manganese oxide. Although both form birnessite, the washing process causes differences in the atomic content of K and Mn. In birnessite, without washing (B4) the K atom content is around 0.276 ppm and one washing (B1) is around 0.228 ppm. Cryptomelane produced through twice washing (C3) has a K content of around 0.200 ppm. The information clearly shows that washing causes the element K to dissolve in water so that when washed, some K atoms are missing. The more often the washing, the more K atoms are lost. In line with diffractogram data, the K atom has an important role in determining the type of manganese oxide produced.

TABLE I. Effect of leaching on atomic ratio K and Mn

NO	Sample Code	Atomic levels of K		Atomic levels of Mn		Ratio K/Mn
		(mg/L)	(g/39,10) = (mol)	(mg/L)	(g/54,94) = (mol)	
1.	C3	0.200	0.005	0.882	0.016	2.5/8
2.	B4	0.276	0.007	0.460	0.008	7.0/8
3.	B1	0.228	0.006	0.814	0.015	3.1/8

The K / Mn atom ratio based on AAS data can be used to estimate the molecular structure of the manganese oxide produced. The K / Mn ratio in birnessite without washing (B4) is around 7.0 / 8; on birnessite one washing (B1) around 3.1 / 8; and on cryptomelane twice washing (C3) around 2.5/8. Thus we can estimate the molecular formula of birnessite without washing (B4), namely  $K_7Mn_8O_x$ ,

birnessite one washing (B1)  $K_{3.1}Mn_8O_x$ , and cryptomelane one washing (C3)  $K_{2.5}Mn_8O_x$ . The molecular formula of birnessite one washing (B1) approaches the estimate of potassium birnessite by Frías et al. (2007) namely  $K_{0.46-0.5}Mn_2O_4 \cdot (H_2O)_{0.5-1.4}$  [13]. The cryptomelane twice washing (C3) molecular formula approaches the molecular formula estimated by Gao et al. (2008), namely  $A_xMn_8O_{16}$  (where A is a cation in the cavity  $(2 \times 2)$  and  $0 \leq x \leq 2$ ) [14]. Whereas the birnessite molecule formula without washing (B4) has a K / Mn ratio greater than the standard because without washing process, there are still residual K atoms and contribute to accumulate the surface and cover the pores of manganese oxide.

### 3.2.3. Characteristic of function groups

The results of the infrared spectrum interpretation in Fig. 3 of the manganese oxide sample were identified as birnessite. The infrared spectrum shows a relatively strong absorption of around  $3449.50 \text{ cm}^{-1}$ , which is caused by the adsorbent interlayer hydrate and some hydroxyl groups, not from hydrates but is bound directly to the interlayer of a metal ion. Absorption of about  $3400 \text{ cm}^{-1}$  in manganese oxide is caused by an overlap between the antisymmetric stretching vibrations and the symmetry of different water in the manganese oxide interlayer. Uptake in the region of between 400 and  $800 \text{ cm}^{-1}$  shows Mn-O lattice vibrations. The distinctive feature of manganese-coated oxide, indicated by the appearance of three strong peaks in the infrared spectrum fingerprint area around 444.16; 489.00 and  $520.98 \text{ cm}^{-1}$  [15]. The wavenumber of birnessite sample (B1) after the addition of HCl can change occurs, i.e. the wavenumber that appears shifts to a larger value and the absorption band becomes wider. These are proven by Kang et al. (2007), in birnessite the characteristic wave number for Mn-O vibrations became higher. The results of spectra interpretation show that the addition of bases does not affect the vibrational characteristics of the Mn-O contained in birnessite (B1) samples. This is evidenced by the value of the wavenumber that does not change. However, in birnessite (B1) samples there was a widening of the absorption band.

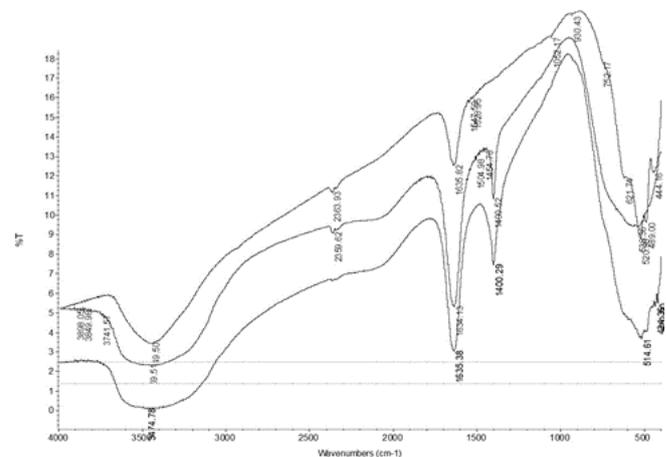


Fig 3. Initial IR spectrum of birnessite (B1) (A), after the addition of HCl (B) and NaOH (C) solution

### 3.2.4. Morphology

The SEM photo of manganese oxide produced shows the morphology of the synthesized birnessite especially at particle size around 0.4 - 1.2  $\mu\text{m}$ . The same thing was also

shown by Frias (2007) by making birnessite through the sol-gel method of  $\text{KMnO}_4$ -polyvinyl alcohol and  $\text{KMnO}_4$ -glucose also having grain morphology [13].

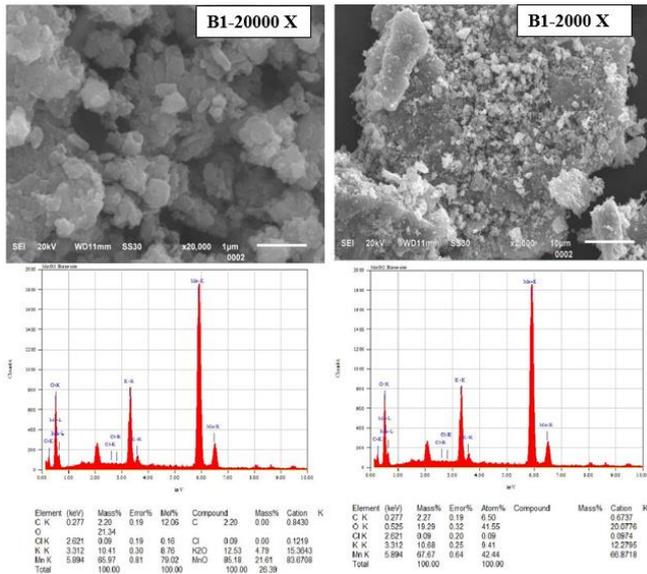


Fig 4. Photographs of SEM and EDX Birnessite with various sizes of magnification

### 3.2.5. Types of elements on the surface

The results of the analysis using EDX (Fig. 4) provide information on the types of elements present on the surface of the synthesized manganese oxide. The EDX spectrum shows that birnessite samples have three main types of elements (Mn, O, and K) and there are impurities, such as C from citric acid which is trapped in the structure of manganese and are strongly bonded to manganese, consequently these elements are not easily released during calcination.

TABLE II. Spectrum of oxide and pure birnessite

No	Spectrum of oxide			Pure Spectrum		
	Element	% Mass	% Mol	Element	% Mass	% Atom
1	Mn	65.97	79.02	Mn	67.67	42.44
2	K	10.41	8.76	K	10.68	9.41
3	O	21.34	-	O	19.29	41.55

Note: (-) was not detected

The percentage of elemental mass found on the surface of birnessite manganese oxide is K (10.41 %), Mn (65.97 %), and O (21.34 %) in the oxide spectrum, and K (10.68 %), Mn (67.67 %), and O (19.29 %) in the pure spectrum. Comparison of the percentage of the number of elements in birnessite namely: K (9.41 %), Mn (42.44 %), and O (41.55 %). If the value is divided by the relative atomic mass of each element, then it can be estimated the number of moles of each element in a semi-quantitative manner namely K (0.24), Mn (0.77), O (2.60). The molecular formula for birnessite is predicted to be  $\text{KMn}_3\text{O}_{11}$ . This molecular formula approaches the estimation of potassium birnessite by Frias (2007), namely  $\text{K}_{0.46-0.5}\text{Mn}_2\text{O}_4 \cdot (\text{H}_2\text{O})_{0.5-1.4}$  [13]. The excess number of moles of O atoms in birnessite synthesized is due to the accumulation of O contained in hydrates trapped between birnessite layers. The EDX instrument has limitations because it cannot distinguish between O hydrated or O in the main structure of manganese oxide, consequently, the ratio of O atoms is theoretically about 8 to 11.

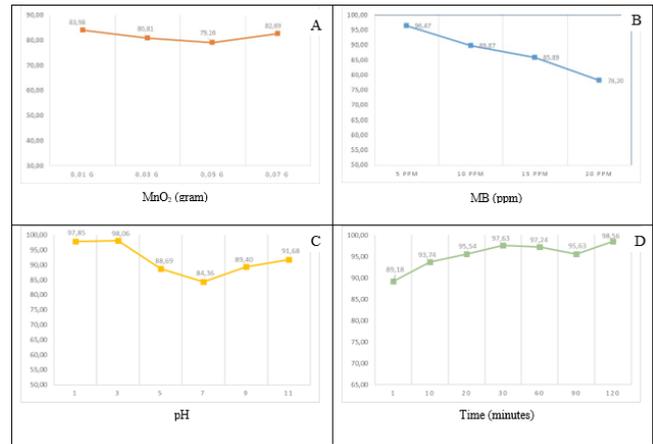


Fig 5. Percentage of degradation of methylene blue with variations in the dose of  $\text{MnO}_2$  (A), MB dose (B), pH (C), and time (D)

### 3.2.6. Methylene Blue degradation test

The degradation test results of Fig. 5 show that birnessite is effective as a catalyst for the degradation of Methylene Blue. In the variation of  $\text{MnO}_2$  dose seen in the amount of only 0.1 g was able to degrade up to 83.98%. Doses varying of MB from 5, 10, 15 to 20 ppm showing a declining trend from 96.47% to 78.20%. The effectiveness of methylene blue degradation by birnessite in the entire pH range tested showed results > 84.36%. Even for pH 1 and 3 respectively 97.85 and 98.06%. The degradation time also showed that within 1 minute, it was able to reduce Methylene Blue levels up to 89.18% and continue to increase until 30 minutes reaching 97.63 %. There was an increase in the effectiveness of catalysis for MB degradation compared to cryptomelane doped with Fe (54.82 - 77.82 %) [16], cryptomelane doped with Cu (57.82 - 94.64 %) [17], and birnessite (78.89 - 97.73 %) [18].

## IV. CONCLUSION

Synthesis of manganese oxide birnessite-type hollow structure can be carried out by the sol-gel method. The conditions of synthesis mostly determined the characterization of the chemical and physical properties of manganese oxide hollow structures. Comparison of the number of moles and washing determines the type of manganese oxide produced. The results revealed that variations in the ratio of moles of precursors and washing determined the type of manganese oxide. The optimum condition of birnessite synthesis through sol-gel method was obtained in a precursor mole ratio of  $\text{KMnO}_4$  and citric acid 3: 1, single washing, with a time of calcination for 5 hours, and calcination temperature of 500 °C. The results showed the ratio of K/Mn atoms were 3.1 to 8.0. Interpretation of infrared absorption shows a typical vibration of birnessite. Birnessite produced has a formula which was  $\text{KMn}_3\text{O}_{11}$ . Birnessite can eliminate Methylene Blue up to 97.63%.

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