Synthesis of birnessite-type manganese oxide from two different reducing agents via solvent-free method and the catalytic activity in degradation of POME

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Abstract. Birnessite-type manganese oxide is multifunction material that has been used in various application and the characteristic depends heavily upon its preparation method. In this study, birnessite-type manganese oxide was synthesized using the reaction between KMnO$_4$ (oxidant) and two different reducing agents i.e., citric acid and oxalic acid via a solvent-free method. The characterization of the birnessite was carried out using X-Ray Diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX), and Surface Area Analyzer (SAA). Birnessite from this variation of reducing agents showed different levels of crystallinity, diverse morphology, crystal size, and surface area. The birnessite-type was then applied as a catalyst for the degradation of Palm Oil Mill Effluent (POME) with hydrogen peroxide (H$_2$O$_2$) as an oxidant to reduce the concentrations of Chemical Oxygen Demand (COD). The maximum reduction in COD concentration was obtained using the catalyst concentration of 400 and 800 mg/L for reducing agent of as-synthesized catalyst citric acid and oxalic acid. Birnessite-type manganese oxide shows potential as a catalyst in the degradation of POME with citric acid as reducing agents showed better degradation in reducing COD values.

1. Introduction
Palm oil is one of the world's most produced and consumed oils that can be used in a wide variety of food, cosmetic, hygiene products, and a source for bio-fuel or biodiesel. According to Indonesian Statistic Agency 2019, the production of palm oil in Indonesia has increased significantly from 26 million tonnes in 2012 to 41 million tonnes in 2018. In spite of the benefits obtained from high production and consumption of palm oil, environmental problems such as high amounts of water consumption and high toxicity of resulting effluent generated from palm oil processing mills should be concerned and treated before being released.

Palm oil mill effluent (POME) has been classified as highly pollutant-containing wastewater with thick brownish viscous liquid waste and has an unpleasant odour. The characteristics of POME typically contains large amounts of total solids (11,500–79,000 mg/L); suspended solids contents (5,000–54,000 mg/L); total volatile solid (9,000-72,000 mg/L); oil and grease (130–18,000 mg/L); total nitrogen (180–1,400 mg/L); ammoniacal nitrogen (4-80 mg/L); and high BOD and COD contents which are in the range 10,250–43,750 mg/L and 15,000–100,000 mg/L, respectively and also amounts
of N, P, K, Mg and Ca which are the vital nutrient elements for plant growth [1,2]. These characteristics depend on the quality of the raw material and production processes.

Therefore, POME requires highly efficient processing technology to ensure that waste meets the disposal requirements set by the Indonesian Ministry of Environment and Forestry. Generally, oily wastewater is discharged in open dumping ponds and it takes a very long time to reach the allowable level of COD and BOD, so these common conventional treatments (anaerobic and aerobic) cannot meet the regulations set. The main reason is due to slow microbial action, requires a large area of land even though the operating costs are low [2]. The chemical reaction is generally faster and suitable to speed up the treatment of POME. POME with a large amount of organic matter is enabled and easy to oxidized compared to wastewater containing inorganic compounds and heavy metals from heavy industrial wastewater. Hence, oxidative processes as a potential alternative technology should be developed in recovering POME.

Several chemical processes have been developed such as advanced oxidation processes (AOPs) that generate highly reactive radicals such as the hydroxyl radical (HO•) in sufficient quantities to degrade organic matter and nutrients present in the wastewater effluents [3]. Superoxide radical anions (O$_2^-$•), hydroperoxyl radicals (HO$_2$•), sulfate radicals (SO$_4^-$•), and organic peroxy radicals (ROO•) are other radicals and active oxygen species generated in AOPs. Hydroxyl radicals are an extremely reactive species, with the redox potential of 2.80 V that attack most of the organic molecules to destroy and even mineralize them to a certain extent [4,5]. Among the AOPs treatment, Fenton and Fenton-like process are extensively studied and used in industry because of their low costs, ease of operation, rapid and highly efficient.

The application of manganese oxide with porous and layered structures are being developed in recent years as a catalyst to replace Fe metal ions in Fenton reagents in the AOPs method [6]. Manganese oxide can react with H$_2$O$_2$ to produce various types of active radicals as an intermediary to degrade organic compounds, one of which is dyes [7,8]. Formation of OH•, O$_2$•, and HO$_2$• to degrade methylene blue above 90% by layered and porous manganese oxide structures reported by Siregar and Awaluddin, Cheng et al., and Cui et al. [9,10,11], which synthesized manganese oxide by solvent-free, hydrothermal, and reflux methods. Manganese oxide prepared by the sol-gel [12,13,14] and precipitation method [15,16] also shows good catalytic activity for degradation of methylene blue more than 90% in less than 30 minutes using H$_2$O$_2$ as an oxidant. In addition, manganese oxide is also used for the degradation of organic compounds, one of which is POME. Manganese oxides synthesized with different reducing agents show different properties. Therefore, in this study, manganese oxide was synthesized using two different reducing agents to see the properties effect for POME degradation. The advantages of free-solvent methods are very simple, does not require solvents, does not take a long time, and uses organic acids as a precursor that do not have toxic effects so that it is environmentally friendly.

2. Experimental

2.1. Materials
All the chemicals such as hydrogen peroxide, potassium permanganate, citric acid, oxalic acid, and reagents for COD determination were purchased from Merck and used without further purification.

2.2. Synthesis
The manganese oxide was prepared via a ceramic or solvent-free method as described by Siregar and Awaluddin but using different reducing agent [9]. The appropriate amount of KMnO$_4$ and organic acid as a reducing agent (citric or oxalic acid) with mole ratio 3:1 were mixed and ground in one mortar. The mixture was calcined at the 700°C in 5 h for citric acid and 7 h for oxalic acid (The different temperature of calcination according to our previous experiment that showed relatively good in crystallinity with small impurities). 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 Rigaku X-ray diffractometer operating at 40 kV and a current of 30 mA with Cu Kα radiation ($\lambda = 1.54060 \text{ Å}$). The data were collected with scan speed 2° per minute in 2θ, from 2θ = 10° to 80°. SEM-EDX were taken on a JSM-6510LV (low vacuum) instrument. The calcined samples were degassed at 423 K for 2 h prior to measurement. The Brunauer-Emmett-Teller (BET) surface area measurements and Barret-Joyner-Halenda (BJH) adsorption were carried out using a BELSORP-max instrument (BEL Japan) at 77 K.

2.4. Sampling of POME
The POME samples were obtained in Mei 2018 from the pond of the Palm Oil Mill in Kampar, Riau. Sampling is done by grab sampling in the palm oil mill effluent pool inlet area of 10 L. The initial stage is to analyze the pH and temperature of the waste. The handling sample method refers to Indonesian National Standard, SNI 6989.59:2008. The samples were then transported to the laboratory and kept in a refrigerator.

2.5. COD analysis
The COD analysis was performed according to the Indonesian National Standard, SNI 6989.73:2009.

2.6. Degradation of POME with $\text{H}_2\text{O}_2$ using manganese oxide as catalyst
The catalytic reaction was carried out in the reactor, contained 10 mL POME and an amount of catalyst. The suspension was continuously stirred magnetically for 30 minutes to achieve adsorption/desorption equilibrium. Following adding $\text{H}_2\text{O}_2$ (30 wt%) solution, the mixture was allowed to react at room temperature. At given time intervals, the mixture was pipetted and ready to analysis.

3. Result and discussion
3.1. Characterization of manganese oxide
The diffractogram presented in figure 1 showed the XRD patterns of as-synthesized material using potassium permanganate (oxidant) with two different reducing agents (citric and oxalic acid). The diffraction peaks of these manganese oxides match well with the standard pattern of a monoclinic phase of birnessite (JCPDS card no. 80-1098). The diffraction peaks at 2θ values of 12.52 (7.07 Å); 25.21 (3.53 Å); 37.20 (2.41 Å); 39.70 (2.26 Å); and 52.44 (2.12 Å). Diffractogram in figure 1 shows sharp peaks with high intensity. This explains that birnessite synthesized by the solvent-free method of KMnO$_4$ and citric acid (3: 1) at a temperature of 700°C has good crystallinity. While the use of the oxalic acid as reducing agent produced diffraction peak at 2θ = 12.46° (79.97 Å); 25.17° (35.37 Å); 37.11° (24.12 Å); 40.06° (22.65 Å); and 42.30° (21.24 Å) with the reflection fields (001), (002), (1-1-1), (201) and (1-1-2).
The average crystal size was determined using the Scherrer equation. The average size of the as-synthesized birnessite was 37.89 nm and 21.22 nm for citric and oxalic acid as a reducing agent, respectively. This crystal size is greater than birnessite conducted by Ye et al. with precursor KMnO$_4$ and glucose using the sol-gel method (crystal size of 20.9 nm) [17] and Cheney et al. with KMnO$_4$ and KCl as a precursor by hydrothermal method (12.38 nm) [18]. The different of crystal size may be due to differences in the precursor, mole ratio, and synthesis method.

The morphology of the as-synthesized birnessite was characterized using an SEM instrument. SEM photos of as-synthesized birnessite-type manganese oxides are shown in figure 2 with 1000x, 5000x and 10000x magnifications. The birnessite-type produced in the form of irregularly shaped granules of different sizes. These morphological results have little in common with the birnessite that synthesized by Ching et al.[19]; Siregar and Awaluddin [9].

![Figure 2. SEM images of the birnessite as-synthesized using citric acid as reducing agent, Mag.x (a) 1000 (b) 5000 dan (c) 10000 and using oxalic acid as a reducing agent, Mag.x (d) 1000 (e) 5000 dan (f) 10000](image-url)
The chemical composition of the as-synthesized material was analyzed using EDX analysis. EDX results show the presence of elements K, Mn, and O in the as-synthesized manganese oxide. Accordingly, the composition of the materials was shown in table 1. Atoms K and Mn are constituent atoms of the structure of manganese oxide, Mn is in the octahedral framework and K is in the interlayer which binds to $H_2O$.

| No. | Elements | Citric Acid | Oxalic acid |
|-----|----------|-------------|-------------|
|     |          | % Atom | % Mass | % Atom | % Mass |
| 1.  | Mn       | 16.39 | 41.37 | 10.32 | 28.52 |
| 2.  | O        | 38.10 | 27.99 | 45.63 | 36.71 |
| 3.  | C        | 36.96 | 20.39 | 38.06 | 22.99 |
| 4.  | K        | 4.12  | 7.40  | 5.99  | 11.78 |

Surface area, pore-volume, average pore diameter, and pore size distribution produced using the BET and BJH methods are shown in table 2. These surface area are smaller when compared to the surface area of other studies of birnessite which also uses the BET method, as research conducted by Ye et al. with precursor of KMnO$_4$ and glucose using a sol-gel method which produced a surface area of 42.61 m$^2$/g and a small pore size of 8.71 nm [17]. However, these surface area almost the same as the birnessite conducted by Siregar and Awaluddin with precursor KMnO$_4$ and glucose which obtained a smaller surface area of 3.56 m$^2$/g and pore size of 13.96 nm [9]. This is because the high calcination temperature in the solvent-free method causes a high level of crystallinity so that the resulting surface area getting smaller. Another factor that also causes the surface area of birnessite is relatively small, namely the presence of $K^+$ ions which cover the active site on the surface of the birnessite so that $N_2$ cannot be entered when analyzed. The surface area of birnessite generally ranges from 10-45 m$^2$/g, but there is also a surface area of more than 100 m$^2$/g [20].

| Parameter                     | Citric acid | Oxalic acid |
|-------------------------------|-------------|-------------|
| Surface area (m$^2$/g)        | 5.725       | 10.544      |
| Total pore volume (cc/g)      | 0.028       | 0.054       |
| Average pore radius (nm)      | 19.658      | 20.369      |
| Pore distribution (nm)        | 78.010      | 167.750     |

The small surface area of birnessite in this study is one of the factors that influence the performance of the catalyst in the process of degradation of palm oil mill effluent with the efficiency of decreasing the COD concentration almost 70%. It is assumed that the larger the surface area will increase catalytic activity. However, after comparing the results in other studies, the surface area is not the main reason in catalytic activity. Liu et al. reported that crystalline $\beta$-MnO$_2$ catalytic activity with a small surface area was better than amorphous $\delta$-MnO$_2$ (birnessite) [21].

3.2. Catalytic degradation of POME
The variation of catalyst concentration was carried out to determine the maximum conditions for adding birnessite-type manganese oxide as a catalyst for the degradation process of palm oil mill effluent (POME). The variation of catalyst concentration added in this study was 400; 800; 1,600 mg/L; and without the addition of a catalyst. Whereas other conditions such as the concentration of
H$_2$O$_2$ maintained in 17,000 mg/L. The initial conditions of POME for the degradation process, as listed in table 3.

### Table 3. Initial conditions of POME

| Parameter                      | Value                  |
|--------------------------------|------------------------|
| Temperature                    | 47°C                   |
| pH                             | 5.0                    |
| COD                            | 39,571-56,288 mg/L     |
| BOD$_5$                        | 14,496-14,500 mg/L     |
| Suspended solid content        | 28,102 mg/L            |
| Oil and grease                 | 15,355 mg/L            |
| Total nitrogen                 | 350 mg/L               |

Effect of variations in catalyst concentration on decreasing COD values can be seen in figure 3 and 4. Maximum degradation obtained in addition 400 mg/L catalyst, with 61% efficiency of decreasing COD concentration in 60-minute reaction using citric acid as a reducing agent, while for oxalic acid reach out 45%. In the addition of 800 mg catalyst/L, COD value achieved 56% if using a catalyst synthesized using oxalic acid of 800 mg/L compared to citric acid which only reached 59% in the 45-minute reaction. From this result, it shows that citric acid as reducing agent shows better results. Although seen from the extent of the surface, the results show little, but the catalytic activity is much better. Surface area is not the main factor affecting degradation. The small percentage in COD degradation of POME, which is <70%, maybe influenced by the characteristics of the catalyst which has a high level of crystallinity and a small surface area, because crystallinity can reduce catalytic activity.

![Figure 3](image-url)  
**Figure 3.** Effect of catalyst concentration (citric acid as a reducing agent) in COD removal of POME degradation
Figure 4. Effect of catalyst concentration (oxalic acid as a reducing agent) in COD removal of POME degradation.

The efficiency of decreasing COD concentration occurs at a catalyst concentration of 400 mg/L. This is quite efficient because in a small amount of catalyst can reduce the COD concentration by up to 70%. The results obtained are the same as the results of several studies that show the condition of the addition of large H$_2$O$_2$ and the small amount of catalyst give better results in degradation. Increasing the catalyst concentration causes in decreasing the percentage of degradation because it passes the critical concentration of the catalyst. So that, hydroxyl radicals are not able to oxidize further because the presence of Mn (II) ions in the solution is already excessive. This condition causes competition between excess Mn (II) ions and organic components to react with hydroxyl radicals. This condition is called recombination of hydroxyl radical. A significant decrease in COD concentration occurred in 15 minutes of reaction. A typical general reduction in COD waste can be divided into two stages. First, a rapid phase of decline, after that the second stage occurs a turning point where the reaction speed decreases due to the formation of organic carbon as an intermediate result. Therefore, in 30, 45, and 60 minutes of reaction, there was no significant decrease in COD concentration.

The mechanism of waste degradation, according to Yu et al. through the adsorption-oxidation-desorption stage[22]. The initial stage of the degradation process is the adsorption of H$_2$O$_2$ on the surface of manganese oxide (1.1) followed by the decomposition of H$_2$O$_2$ into free radicals such as HO•, O$_2$•‾ or HOO• (1.2) - (1.4). The high oxidative ability of free radicals (HO•, O$_2$•‾) to decompose adsorbed organic waste molecules to produce CO$_2$, H$_2$O, or other small molecules (1.5). The small molecules produced from this degradation process are absorbed from the surface of the catalyst in the final stages of degradation [23].

\[
\begin{align*}
\text{Mn (IV)} + \text{H}_2\text{O}_2 & \leftrightarrow \text{Mn (IV)}\cdot\text{H}_2\text{O}_2 \quad (1.1) \\
\text{Mn (IV)•H}_2\text{O}_2 & \rightarrow \text{Mn (II)} + \text{HO}_2• + \text{H} \quad (1.2) \\
\text{Mn (II)} + \text{H}_2\text{O}_2 & \rightarrow \text{Mn (IV)•H}_2\text{O}_2 \quad (1.3) \\
\text{HO}_2• & \leftrightarrow \text{H}^+ + \text{O}_2•^{-} \quad (1.4) \\
\text{HO• (O}_2\text{•‾) + POME (adsorbed)} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \ldots \quad (1.5) \\
2\text{HO•} + 2\text{HO•} & \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad (1.6)
\end{align*}
\]
Conclusion
Birnessite-type manganese oxide has been successfully synthesized through the solvent-free method with variations in reducing agents (citric acid and oxalic acid). Variations of reducing agents produce the same type of manganese oxide but show different levels of crystallinity, diverse morphology, crystal size, and surface area. The results of the degradation POME using manganese oxide-type birnessite shows the potential based on the decrease in the value of COD. The efficiency of decreasing the value of COD was obtained in reaction conditions of H$_2$O$_2$ 17,000 mg/L, catalyst concentration: 400 mg/L and 800 mg/L, respectively for reducing agent of as-synthesized catalyst citric acid and oxalic acid. Citric acid as reducing agents showed better degradation in reducing COD values, although further research is still needed to get the best conditions for degradation of POME using H$_2$O$_2$ and birnessite-type manganese oxide as a catalyst.

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