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LaMnO$_3$ Perovskite Activation of Peroxymonosulfate for Catalytic Palm Oil Mill Secondary Effluent Degradation

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ABSTRACT: The LaMnO$_3$ perovskite catalyst was successfully synthesized using a simple solid-state reaction method. This catalyst was used to activate PMS in the organic content's degradation process in the secondary effluent palm oil mill (POMSE). The organic content in POMSE was equivalent to the COD value; thus the COD value was used as a parameter for the process's success. The catalyst performance test showed that the catalyst effectively reduced COD, and the waste met the maximum threshold allowed by government regulations. The variables that affected the catalyst's effectiveness were the calcination temperature of the catalyst, catalyst loading, PMS concentration, and temperature. The temperature of calcination affects the perovskite crystal formation; the higher the temperature, the more active catalyst obtained. The catalyst loading and PMS concentration variables affect the degradation process of organic levels in POMSE; at low levels, the higher the catalyst loading and PMS concentrations will increase the effectiveness of the degradation process, but at certain levels, the addition of catalysts and PMS reduces the effectiveness of the process. LaMnO$_3$-800°C catalyst presents the highest activity of 92.7% and met the allowable threshold of COD < 300 mg/L. The sequence for removal of COD among the three catalysts with an order of LaMnO$_3$-800°C > LaMnO$_3$-700°C > LaMnO$_3$-600°C. The pseudo-second-order kinetics equation fits the experimental data. The effect of temperature on the kinetics constant follows the Arrhenius equation. Furthermore, the catalyst obtained was stable, with no significant decrease in catalysts activity up to three runs.

Key words: COD reduction, LaMnO$_3$, Palm oil mill secondary effluent, Perovskite, PMS

1. INTRODUCTION

One of Indonesia’s primary commodities is palm oil. Since 2007 Indonesia has become the largest crude palm oil (CPO) producer in the world. Riau is the largest CPO producing province in Indonesia. In 2018, the area of plantations in this province was 2.32 million hectares or nearly 20% of the area of oil palm plantations in Indonesia, with CPO production of 7.14 million tons (BPS, 2019). The processing of fresh palm fruit into CPO generally uses wet extraction [1]. Fresh fruit from the plantations will be sterilized and released from the bunches. Then it is cooked with steam and pressed to remove the oil from the fruit. The oil obtained is refined by decantation, clarification, and centrifugation. The water content in the oil is reduced by the drying process, so the CPO ready to be further processed into its derivative products [2]. In the production of one ton of CPO, it will produce 2.5-3 tons of palm oil mill effluent (POME), the composition of POME is generally of 2% oil, 2-4% suspended solids, and the rest is water [3]. The composition of POME varies depending on the operating unit where POME is produced. For example, COD POME produced from condensate sterilization, sludge separator, and hydro-cyclone wastewater is 47200, 63800, and 14700 [4]. Although POME is not categorized as toxic waste, however, the POME’s high organic content makes it cannot be disposed of directly into the environment. Besides, POME is acidic because there are organic acids in a complex form, and the pH of POME is around 4.5. According to Wong et al. (2008), the content of lignin, hemicellulose, and cellulose in POME is higher than other agriculture wastes. Generally, in palm oil mill, POME processes are carried out using a ponding system. More than 85% of palm
oil processing mills in Indonesia use this system, and the result of wastewater treatment is flown back to the plantation for fertilization [5]. This conventional foundation system is relatively inexpensive and simple, although it requires a large area of land. The main problem with this system is that the wastewater produced does not meet waste disposal standards. Some of the available technologies, such as the use of anaerobic bioreactors or a combination of bioreactor and membrane technologies [6], promise more efficient waste processing and produce energy in the form of biogas [7, 8]. However, this process requires installing new installations and large investments that may affordable for small to medium-sized palm oil mills.

One option that might be applied is a secondary treatment process to obtain wastewater that meets the required quality standards. Wastewater resulting from conventional ponding system processing or palm oil mill secondary effluent (POMSE) has not met quality standards yet is processed again in secondary waste treatment [9, 10]. Thus the company does not need to build a new waste treatment plant but utilizes the existing wastewater treatment and install secondary wastewater treatment. Many conventional methods of POMSE processing have been explored, including using microbes and algae, coagulation, electrocoagulation [9, 11, 12, 13]. According to Saputra et al. [10], conventional methods to degrade organic components are limited because the process is slow and sometimes incompatible with the environment.

Processes that are potentially used for waste degradation are advanced oxidation processes (AOPs). AOPs are a combination of several processes such as ozone, hydrogen peroxide, ultraviolet light, titanium oxide, photocatalysts, sonolysis, electron beam, electrical discharges (plasma), and several other processes to produce hydroxyl radicals [14, 15]. Hydroxyl radical (OH·) is a strong oxidant that can degrade organic substances with a redox potential of 2.8V [16]. In addition to hydroxyl radicals, radical sulfate also shows the ability to degrade organic pollutants equivalent to hydroxyl radicals or even stronger depending on the activation process. Based on the activation process, the redox potential of radical sulfate varies between 2.5 - 3.1 V [17]. In the process of wastewater treatment by AOPs, the system that uses heterogeneous catalysts for PS and PMS activation has the most potential to be further developed because catalyst recovery is easier and more economical [18]. According to Wang et al. [19], one of the challenges of the application of the AOPs process in wastewater treatment using sulfate radicals is finding a synergic combined metal oxide catalyst to activate persulfate (PS) and peroxymonosulfate (PMS). Because each metal oxide has different performance in the PS and PMS activation processes, it is hoped that by using synergically, two metal oxides can increase the catalyst’s ability to activate PS and PMS.

On the other hand, the catalyst’s ability to be used repeatedly is also an essential factor for the economical application of the AOPs process. The ability to reuse the catalyst is closely related to the catalyst’s stability so that the metal oxides present in the catalyst do not dissolve easily into the wastewater. Perovskite is known as a stable mineral form. The combined metal oxides in the perovskite form have high stability due to higher relative acidity and low leaching [20].

In this study, the heterogeneous LaMnO$_3$ perovskite catalyst was synthesized and used to degrade pollutants remaining in POMSE that cannot be removed by conventional waste treatment processes. This paper discusses the effect of calcination temperature on the LaMnO$_3$ perovskite catalyst on the catalyst performance and studies the effect of catalyst loading, PMS loading, and temperature on POMSE COD reduction. Besides, the catalyst’s reusability will also be tested to prove the stability of the catalyst synthesized. The application of the LaMnO$_3$ perovskite catalyst in the AOPs for POMSE treatment is relatively new and has never been reported by previous researchers.

2. METHODS

2.1 Samples and chemicals

The POMSE was obtained from a pound in a palm oil mill wastewater treatment unit in Riau province, Indonesia. The PMS was derived from peroxymonosulfate (oxone®, Dupont’s triple salt: 2KHSO$_5$,KHSO$_4$,K$_2$SO$_4$) obtained from Sigma-Aldrich. The chemical used for catalyst synthesis: La(NO$_3$)$_3$,6H$_2$O, MnSO$_4$,H$_2$O, and Na$_2$CO$_3$,10H$_2$O were purchased from Merck Indonesia. Polyethylene glycol (PEG)-400 and ethanol anhydrate were purchased from Brataco Chem. Indonesia. All the chemicals were used without further purification.

2.2 Catalyst synthesis

The LaMnO$_3$ perovskite catalyst was synthesis via modified a simple solid-state reaction process [21], 35.81g of La(NO$_3$)$_3$,6H$_2$O, 13.98g of MnSO$_4$,H$_2$O, 70.99g of...
3.2 LaMnO$_3$ Characterization

The XRD pattern of three LaMnO$_3$ perovskite catalysts obtained at different calcined temperature is shown in Fig. 2. As can be seen, the XRD pattern of the catalyst obtained at temperatures 600°C, 700°C, and 800°C shows a similar pattern. The XRD pattern of the LaMnO$_3$ perovskite catalyst obtained at a calcined temperature of 800°C shows peak pattern at an angle of 2θ: 23.0397°; 32.7985°; 40.2931°; 46.9562°; 52.8982°; 58.3469°; and 68.8452°, which is identical with JCPDS File No. 50-0297. This peak pattern indicated that the catalyst is rhombohedral LaMnO$_3$ perovskite. The catalyst obtained at a calcined temperature of 600°C and 700°C shows similar characteristics. However, the peaks pattern's intensity is lower, indicating that the crystallinity of the catalyst obtained at a calcined temperature of 800°C is higher than obtained at a lower temperature. Besides the peaks pattern's of LaMnO$_3$, perovskite, all of the catalyst show there is a peaks pattern that indicate of LaO$_2$CO$_3$ existence. According to Wei et al. [21], the precursor La(NO$_3$)$_3$·6H$_2$O and PEG-400 at temperature 75°C will form La$_x$(CO$_3$)$_y$·8H$_2$O with the increasing temperature the La$_x$(CO$_3$)$_y$·8H$_2$O was obliterated, and at 400°C, the monoclinic crystalline La$_2$O$_3$CO$_3$ appeared. As the temperature increases up to 800°C, the La$_2$O$_3$CO$_3$ and MnCO$_3$ will form LaMnO$_3$ perovskite.

![Fig. 2. XRD patterns of the LaMnO$_3$ perovskite catalysts](image)

Table 1 The SSA and the pore volume of LaMnO$_3$ perovskite catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>V (cm$^3$/g)</th>
<th>TOC reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_3$-600°C</td>
<td>2.3</td>
<td>0.037</td>
<td>63.45</td>
</tr>
<tr>
<td>LaMnO$_3$-700°C</td>
<td>1.4</td>
<td>0.039</td>
<td>70.42</td>
</tr>
<tr>
<td>LaMnO$_3$-800°C</td>
<td>6.3</td>
<td>0.035</td>
<td>80.85</td>
</tr>
</tbody>
</table>

The $N_2$ adsorption-desorption isotherm is shown in Fig. 3. The characteristic of $N_2$ adsorption-desorption all catalysts show hysteresis of type H3 loop of IUPAC classification. Type loop H3 indicates that the catalyst consists of aggregates of plate-like particles and slit-shaped pores [25]. The pores size of the catalyst obtained at a calcined temperature of 600°C, 700°C, and 800°C, calculated by the
BJH method, are in the range of 3-11nm; 4-12nm and 1-9 nm respectively, can be classified as mesoporous. The specific surface area (SSA of the catalyst) is shown in Table 1.

Fig. 3. N$_2$ adsorption-desorption isotherms and the inset pore size distribution of LaMnO$_3$ perovskite catalysts. (A) LaMnO$_3$-600 °C, (B) LaMnO$_3$-700 °C, (C) LaMnO$_3$-800 °C.

The LaMnO$_3$ perovskite catalyst obtained at a calcined temperature of 800°C has a significantly higher SSA of 6.3 m$^2$/g than the catalyst obtained at lower calcined temperature. However, the pore volume difference between the catalysts is insignificant.

3.3 Influence of calcined temperature on catalyst activity

In this catalyst performance test, the POMSE degradation process was carried out with the fixed variable: catalyst loading of 0.4g/L, PMS concentration 2g/L, and temperature 30°C. At a predetermined time up to 60min, the sample is taken for the COD analysis. Besides the performance test of the three calcined catalysts obtained at various temperatures, the use of PMS without a catalyst was also tested to find out whether PMS activation was only due to the catalyst or there were other substances in POMSE that could activate PMS. The catalyst obtained at a calcination temperature of 800°C was also tested without PMS to determine the catalyst's ability to reduce COD of the POMSE. The test results can be seen in Fig. 5.

As can be seen, PMS, without being activated, can not degrade organic substances in POMSE. It is seen that there is no reduction in COD in the degradation process for up to 60 min, which proves that PMS is not directly involved in the degradation process of organic substances contained in POMSE. The perovskite LaMnO$_3$ catalyst alone without PMS only decreases COD in the POMSE by less than 10%. This COD reduction process is probably caused by organic substances adsorbed onto the surface of the catalyst. The catalyst SSA is relatively low of 6.3 m$^2$/g, the catalyst’s ability to adsorb organic substances is limited. The significant reduction in COD only occurred in the presence of both catalyst and PMS. It can be concluded that the degradation process of organic substances in POMSE occurs due to the oxidation process by radical sulfate groups derived from PMS, which is activated by the LaMnO$_3$ perovskite catalyst. The mechanism of the reaction of LaMnO$_3$ perovskite catalyst with PMS can proceed as below:

\[
\text{HSO}_5^- + \text{Mn(IV)} \rightarrow \text{Mn(III)} + \text{SO}_4^{2-} + \text{H}^+ \quad (1)
\]

\[
\text{HSO}_5^- + \text{Mn(III)} \rightarrow \text{Mn(IV)} + \text{SO}_4^{2-} + \text{OH}^- \quad (2)
\]

\[
\text{POMSE} + \text{SO}_4^{2-} \rightarrow \text{Intermediate} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{SO}_4^{2-} \quad (3)
\]

In perovskite manganese AMnO$_3$ if the metal A is trivalent like La, then the Mn metal is also trivalent [26]. It means that the more perfect the formation of LaMnO$_3$, the more trivalent Mn will be available so that the PMS activation process by the catalyst will be higher. As shown in Fig. 5, the higher the calcination temperature, the higher the combined catalyst, and PMS’s effectiveness in degrading the organic content in POMSE. The perovskite LaMnO$_3$ catalyst obtained at a calcined temperature of 800°C shows the highest performance with a degradation efficiency of 78.5%.
3.4 Influence of catalyst loading on COD reduction

To study the effect of catalyst loading on the COD of the POMSE reduction process, the fixed variables: PMS concentration 2g/L, temperature 30°C, and time 60min were used, while the catalyst loading was varied 0.2g/L, 0.3g/L, and 0.4g/L. The results of the experiment in this condition are shown in Fig. 6. The catalyst loading affects the efficiency of COD reduction. The more catalyst used, the efficiency of COD reduction in POMSE increases. The reduction in COD obtained when using catalyst loading 0.2g/L, 0.3g/L, and 0.4g/L are 61.2%; 68.7 and 78.5%, respectively. The higher COD reduction due to the increasing number of catalysts used can be caused by the more active Mn metal oxide sites on the perovskite catalyst are available to activate PMS and produce more sulfate radicals to oxidize the organic content in POMSE. The oxidation of organic content in POMSE will decrease the COD value of the POMSE.

Fig. 4. SEM and EDS spectrum (zone indicated by red squares) of LaMnO$_3$ perovskite catalyst obtained at a calcined temperature of (A) 600°C, (B) 700°C, and (C) 800°C.

Fig. 5. Preliminary study of POMSE at various catalysts. Condition of reaction: Initial COD of POMSE = 1700.7 mg/L, catalyst = 0.4 g/L, PMS = 2 g/L, and T = 30°C.

![Graph showing COD removal over time with different catalyst loadings.](image-url)
3.5 Influence of PMS concentration on COD reduction

To study the effect of PMS concentration on organic content degradation in the POMSE, the fixed variables catalyst loading of 0.4 g/L and a temperature of 30 °C was applied. At a predetermined time of up to 60 min, the sample was taken for COD analysis. The PMS concentration varied: 0.8 g/L, 1.2 g/L, 2 g/L, and 2.4 g/L. The effect of PMS concentration on COD reduction in POMSE can be seen in Fig. 7.

As can be seen, an increase in PMS concentration from 0.8 to 2 g/L can increase COD reduction efficiency from 63.54% to 78.85%. However, increasing PMS concentration to 2.4 g/L reduced COD reduction efficiency to around 66.70%. According to Huang et al. [27], excessive PMS use will produce excess sulfate radicals. The excess sulfate radical can attack the catalyst according to the following reaction.

\[
\text{Mn(III)} + \text{SO}_{4}^{2-} \rightarrow \text{Mn(IV)} + \text{SO}_{4}^{2-} \quad (4)
\]

According to Saputra et al. [28, 29], high PMS concentration can reduce the removal of pollutants due to active sulfate radicals (SO\(_{4}^{2-}\)) consumed by PMS, in compliance with the mechanisms as a follow.

\[
\text{HSO}_{5}^- + \text{SO}_4^{2-} \rightarrow \text{SO}_5^{2-} + \text{SO}_4^{2-} + \text{H}^+ \quad (5)
\]

\[
\text{HSO}_5^- + \text{OH}^- \rightarrow \text{SO}_5^{2-} + \text{H}_2\text{O} \quad (6)
\]

Thus, for each catalyst loading used, there is a specific PMS concentration, which will result in the optimum degradation efficiency of organic content in POMSE. The optimum COD reduction efficiency of 78.5% was obtained at a 0.4 g/L catalyst loading and 2 g/L PMS concentration.

3.6 Influence of temperature

The fixed variables applied at the experiment to study the effect of temperature on the COD reduction process from POMSE were catalyst loading of 0.4 g/L and PMS concentration of 2 g/L. The temperature was varied by 30, 40, and 50 °C and every predetermined time, the sample was taken for COD analysis. The rate of degradation of organic content in POMSE is equivalent to the rate of COD reduction, according to the following equation (Gao et al., 2011):

\[
\frac{d(COD)}{dt} = k(COD)^n \quad (7)
\]

The plot of the kinetic equation of 1/COD versus time was linear so that the kinetics followed the pseudo-second-order reaction. Table 2 shows the value of the reaction rate constant, the kinetic equation, and the R\(^2\) coefficient for every temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Kinetic equations (t min)</th>
<th>K (L.mg(^{-1}).min(^{-1}))</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1/COD = 3.86E-05t + 0.0007</td>
<td>3.86E-05</td>
<td>0.99</td>
</tr>
<tr>
<td>40</td>
<td>1/COD = 6.20E-0.5t + 0.0006</td>
<td>6.20E-05</td>
<td>0.99</td>
</tr>
<tr>
<td>50</td>
<td>1/COD = 11.15E-0.5t + 0.0005</td>
<td>11.15E-05</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The experimental data were compared to the model for verifying the kinetic equation obtained, the results depicted in Fig. 8.
Fig. 8 shows that temperature has a significant effect on reducing COD. In the first 30 min, the reaction rate is fast. The decrease of COD at the reaction temperature of 30°C was about 68%, increasing to 76.2% at 40°C, and at 50°C, it increased to 82%. However, the rate reaction slows down after 30 min. The organic substances in POMSE are a matrix of various organic substances from palm oil mill effluent. Every organic substance has a different chemical chain so that sulfate radicals ($SO_4^{\cdot-}$) will more easily degrade organic substances that have a short chemical chain [19]. On the other hand, the concentration of sulfate radicals in the solution has been dramatically reduced. Thus, the COD reduction rate is slow.

Even so, as shown in Table 2 and Fig. 8, the COD reduction data in this experiment can be approximated by a pseudo-second-order kinetics model. The effect of temperature on the reaction rate constant was studied using an Arrhenius plot, as shown in Fig. 9.

Fig. 9. Arrhenius plot of COD reduction using PMS activated by LMnO$_3$ perovskite

Fig. 9 shows that the reaction rate constant is affected by temperature and can be estimated by the Arrhenius equation. The calculated activation energy (Ea) of 46.16 kJ/mol was obtained. This result is lower than the results from Yao et al. [7], which used Mn$_3$O$_4$-reduced graphene oxide hybrid catalyst for PMS activation in aqueous organics degradation process where the Ea of 49.5 kJ/mol was reported. The lower activation energy shows that the LaMnO$_3$ perovskite catalyst is more reactive than that Mn$_3$O$_4$-reduced graphene oxide.

3.7 Catalyst reusability

The stability of the catalyst will largely determine whether the catalyst can be used in practical application. The stable catalyst can be recycled without a significant performance loss will reduce the catalyst’s cost. In this reusability test of the catalyst, the fixed variables: initial COD of POMSE = 1700.7 mg/L, catalyst loading of 0.4g/L, PMS concentration of 2g/L, and the temperature of 30°C were used. The results of the catalyst reusability test can be seen in Fig. 10.

Fig. 10. The reusability test of the LaMnO$_3$ perovskite catalyst

As can be seen, the deactivation of the catalyst until the third cycle was insignificant. This finding indicates that the LaMnO$_3$ perovskite catalyst obtained is stable so that it can be further developed and used in the practical application of POMSE processing.

4. CONCLUSION

The LaMnO$_3$ perovskite catalyst was successfully synthesized via a simple solid-state reaction process at various calcination temperatures. The catalyst obtained at a calcination temperature of 800°C shows the highest activity. The application of the LaMnO$_3$ perovskite catalyst in the POMSE degradation process was influenced by the catalyst loading, PMS concentration, and temperature. The POMSE degradation process's kinetics showed that the degradation reaction followed the pseudo-second-order reaction with an activation energy of 45 kJ/mol. The results of the reusability test showed that up to 3 cycles of catalyst deactivation insignificant. The POMSE degradation process's best conditions were obtained at the catalyst loading of 0.4g/L, PMS concentration of 2g/L, a temperature of 50°C for 60 min, which resulted in a COD reduction efficiency of 92.7%.

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