LaMnO₃ Perovskite Activation of Peroxymonosulfate for Catalytic Palm Oil Mill Secondary Effluent Degradation

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Panca Setia Utama[1] ⓘ, Wahyu Bambang Widayatno[2], Muhammad Rizwan Azhar[3], Hussein Rasool Abid[3,4], Wenchao Peng[5], Oki Muraza[6] ⓘ, Edy Saputra[1,*] ⓘ

[1]Department of Chemical Engineering, Riau University, Pekanbaru 28293, Indonesia
[2]Research Center for Physics, Indonesian Institute of Science (LIPI), Serpong 15314,
[3]School of Engineering, Edith Cowan University, 270 Joondalup Drive, Joondalup, WA, Australia
[4]Chemical Engineering, WA School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Australia
[5]School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China.
[6]Center of Excellence in the Department of Nanotechnology and Chemical Engineering, King Fahd University of Petroleum and Minerals, Dhahran, 31261, Saudi Arabia

ABSTRACT: The LaMnO₃ 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. LaMnO₃-800ºC 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 LaMnO₃-800ºC > LaMnO₃-700ºC > LaMnO₃-600 ºC. 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, LaMnO₃, 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
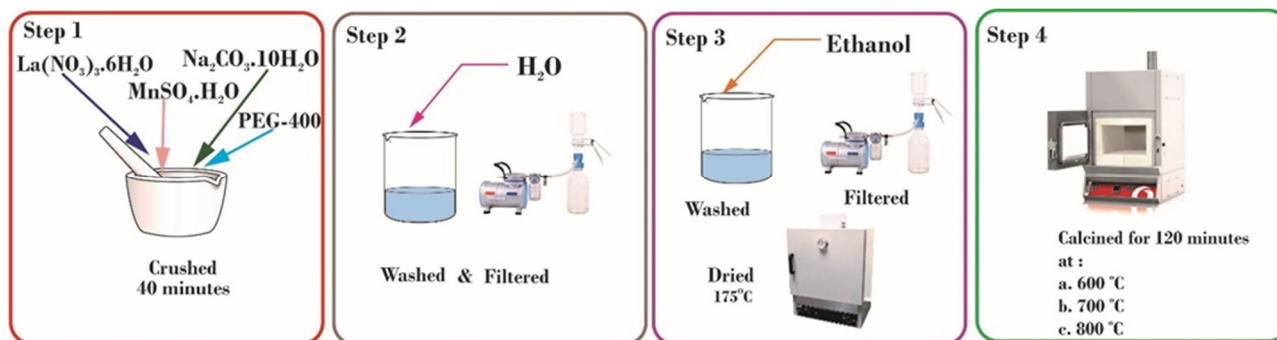
Fig. 1. The diagram of the preparedness for LaMnO₃ catalysts.

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 LaMnO₃ 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 LaMnO₃ 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 LaMnO₃ 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: $2KHSO_5.KHSO_4.K_2SO_4$) obtained from Sigma-Aldrich. The chemical used for catalyst synthesis: $La(NO_3)_3.6H_2O$, $MnSO_4.H_2O$, and $Na_2CO_3.10H_2O$ 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 LaMnO₃ perovskite catalyst was synthesis via modified a simple solid-state reaction process [21], 35.81g of $La(NO_3)_3.6H_2O$, 13.98g of $MnSO_4.H_2O$, 70.99g of

Na$_2$CO$_3$.10H$_2$O, and 3 mL 50% (vol) PEG-400 surfactant were mixed and grounded in a mortar for 40 min and keep at a constant temperature of 30°C for 60 min. Then the mixture was washed using distilled water to remove inorganic salts and then filtered. The solid obtained was then washed with anhydrous ethanol, filtered, and dried at 75°C for 3 hours. The precursor calcined at a predetermined temperature for 2 hours to obtain the LaMnO$_3$ perovskite catalyst. The calcined temperature was varied from 600°C to 800°C to study the effect of calcined temperature on catalyst performance. The schematic of the preparation of LaMnO$_3$ catalysts can be seen in Fig. 1.

2.3 Catalyst performance evaluation on POMSE degradation

The POMSE degradation was performed in a 1000 mL glass reactor equipped with a magnetic stirrer, electric heater, and temperature controller. The performance of the LaMnO$_3$ perovskite catalyst obtained at a calcined temperature of 600, 700, and 800°C was compared to determine the best-calcined temperature. The operating conditions were volume POMSE of 1000mL, stirrer speed of 400 RPM, catalyst loading of 0.4g/L, PMS concentration of 2g/L, and temperature of 25°C for 60 min. For every predetermined time, 5mL of the sample was taken out for COD analysis. COD reactor Hach DRB200, USA, have determined COD removal. For selected POMSE samples, an Analytic Jena AG N6-508/L, Germany was used to determine Total Organic Carbon, TOC. As a comparison, PMS performance alone and LaMnO$_3$ perovskite catalyst in the absence of PMS were also tested under the same conditions. The best catalyst was used to study the effect of catalyst loading, PMS Loading, and temperature on POMSE degradation.

2.4. Analysis and characterization of the catalyst

The POMSE before and after the degradation process was analyzed for the COD parameter according to SNI 6989.73:2009 [22]. The XRD characterization was performed using a Rigaku Miniflex Goniometer at 30 kV and 15 mA, using Cu Kα radiation at a step size of 0.01°. The N$_2$ adsorption-desorption was applied to measure the surface area and pore size of the catalyst, according to the Brunauer-Emmet-Teller (BET) and Barrett, Joyner, and Halenda (BJH) methods using Quantachrome Instruments, Boynton Beach, Florida, USA. The LaMnO$_3$ perovskite morphology was characterized using the scanning electron microscope (SEM) FEI Quanta 400.

3. RESULT AND DISCUSSION

3.1 POMSE Analysis

The POMSE obtained from the land application pool at the palm oil wastewater treatment unit was analyze for its COD. The COD of the POMSE was 1700.7 mg/L higher than the standard from Indonesia regulation, the maximum COD allowed to discharge into water bodies is 350 mg/L [23]. However, the COD in the POMSE is lower than the average COD in the POMSE from biologically treated, which is 2420 mg/L [24].

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 rhombodental 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 is 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$_2$(CO$_3$)$_3$.8H$_2$O with the increasing temperature the La$_2$(CO$_3$)$_3$.8H$_2$O was obliterated, and at 400°C, the monoclinic crystalline LaO$_2$CO$_3$ appeared. As the temperature increases up to 800°C, the LaO$_2$CO$_3$ and MnCO$_3$ will form LaMnO$_3$ perovskite.
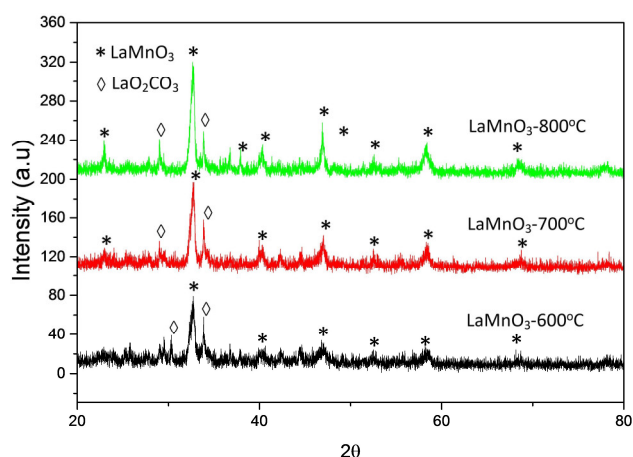

Fig. 2. XRD patterns of the LaMnO$_3$ perovskite catalyst

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

Catalyst	S$_{BET}$ (m^{2}g^{-1})	V (cm^{3}g^{-1})	TOC reduction (%)
LaMnO$_3$-600°C	2.3	0.037	63.45
LaMnO$_3$-700°C	1.4	0.039	70.42
LaMnO$_3$-800°C	6.3	0.035	80.85

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.
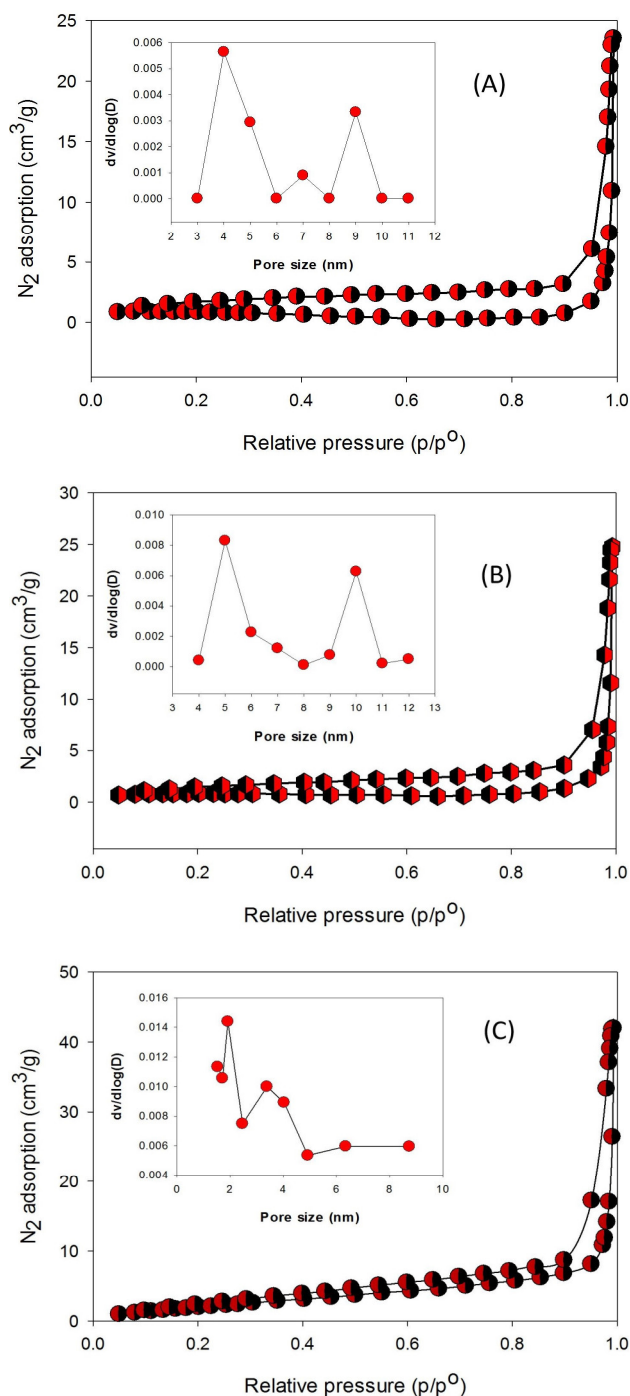

Fig. 3. N_2 adsorption-desorption isotherms and the inset pore size distribution of $LaMnO_3$ perovskite catalysts. (A) $LaMnO_3$-600 °C, (B) $LaMnO_3$-700 °C, (C) $LaMnO_3$-800 °C.
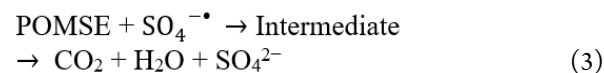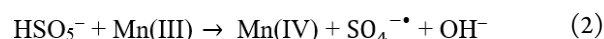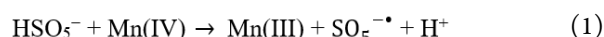
The $LaMnO_3$ perovskite catalyst obtained at a calcined temperature of 800°C has a significantly higher SSA of 6.3 m²/g than the catalyst obtained at lower calcined temperature. However, the pore volume difference between the catalysts is insignificant.

This finding is confirmed by the results of catalyst characterization using SEM. The micrograph of the three catalysts can be seen in Fig. 4. The higher the temperature, the less precursor existence in the catalyst. As can be seen, the precursor existence in the catalyst obtained at 800°C is fewer than others. Thus, at 800°C, the precursor has transformed into the rhombodental crystals, and there is only a few precursors have not reacted.

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 $LaMnO_3$ perovskite 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. Because the catalyst SSA is relatively low of 6.3 m²/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:

$$HSO_5^- + Mn(IV) \rightarrow Mn(III) + SO_5^{-\bullet} + H^+ \tag{1}$$

$$HSO_5^- + Mn(III) \rightarrow Mn(IV) + SO_4^{-\bullet} + OH^- \tag{2}$$

$$POMSE + SO_4^{-\bullet} \rightarrow Intermediate$$
$$\rightarrow CO_2 + H_2O + SO_4^{2-} \tag{3}$$

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 $LaMnO_3$ perovskite catalyst obtained at a calcined temperature of 800°C shows the highest performance with a degradation efficiency of 78.5%.
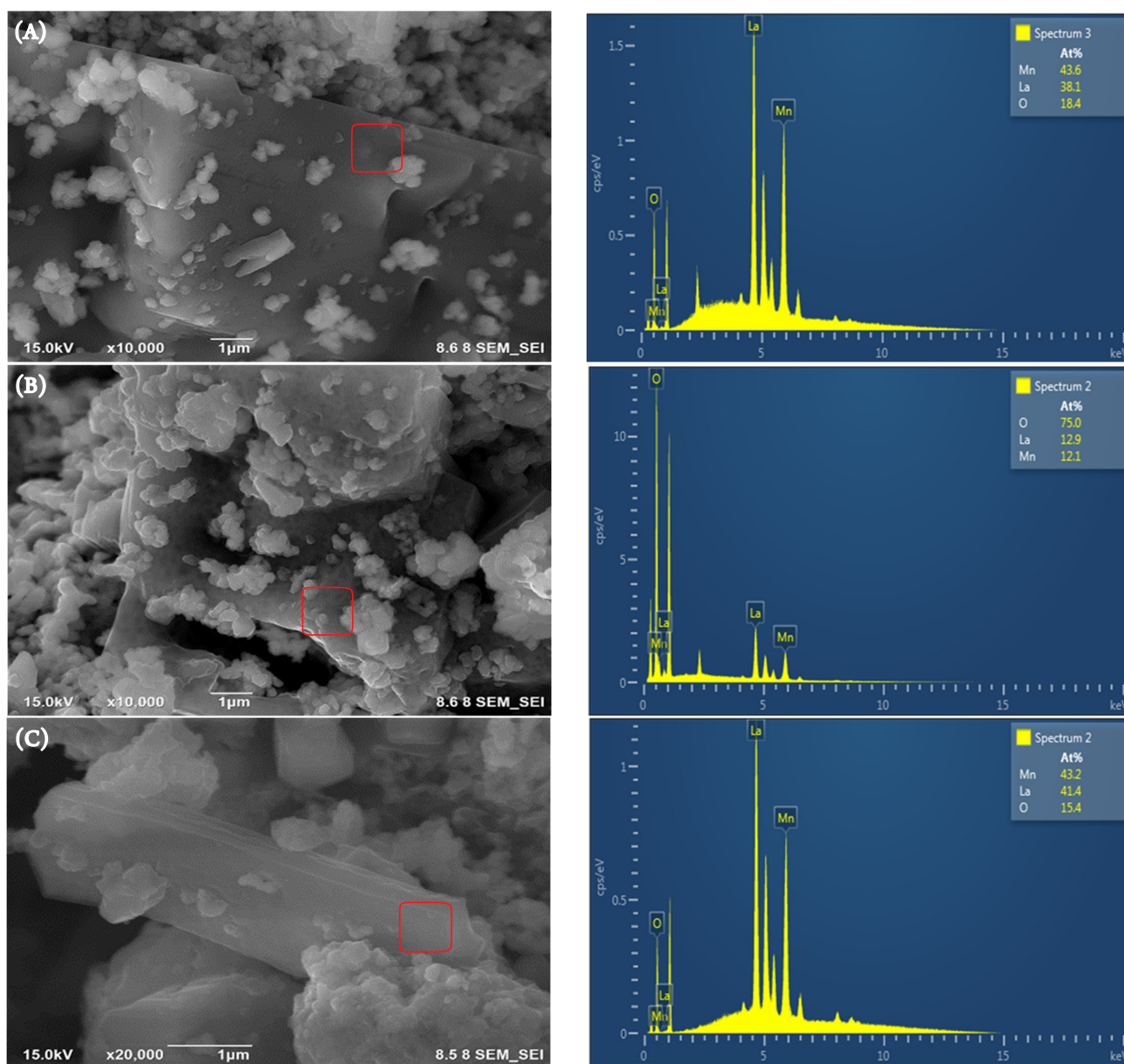
Fig. 4. SEM and EDS spectrum (zone indicated by red squares) of LaMnO$_3$ perovskite catalyst obtained at a calcined temperature of (A) 600°C, (B) 700°C, and (C) 800°C.
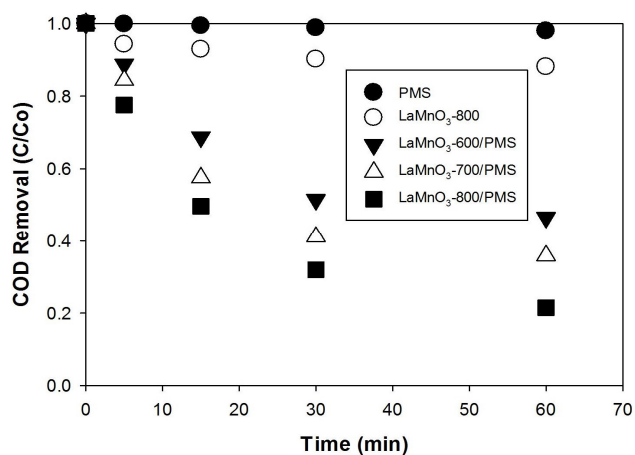

Fig. 5. Preliminary study of POMSE at various catalysts. Condition of reaction: Initial COD of POMSE = 1700.7 mg/L, catalyst = 0.4 g/L, PMS = 2 g/L, and T = 30 ^{o}C

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.
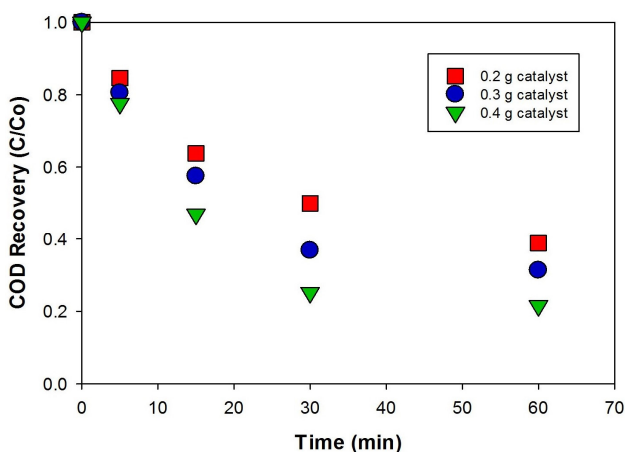
Fig. 6. COD removal on various catalyst loading. Condition of reaction: Initial COD of POMSE = 1700.7 mg/L, PMS = 2 g/L, and T = 30 °C

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 0.4g/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: 0.8g/L, 1.2g/L, 2g/L and 2.4g/L. The effect of PMS concentration on COD reduction in POMSE can be seen in Fig. 7.
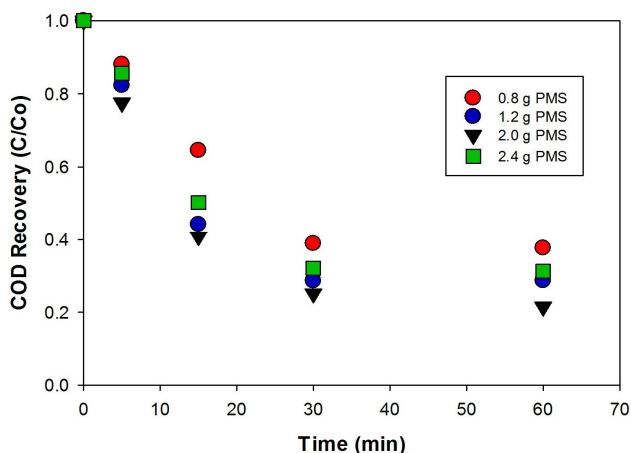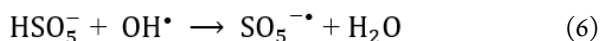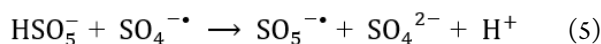

Fig. 7. COD removal on various PMS concentration. Condition of reaction: Initial COD of POMSE = 1700.7 mg/L, catalyst = 0.4 g/L, and T = 30 °C

As can be seen, an increase in PMS concentration from 0.8 to 2g/L can increase COD reduction efficiency from 63.54% to 78.85%. However, increasing PMS concentration to 2.4g/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.

$$Mn(III) + SO_4^{\bullet-} \rightarrow Mn(IV) + SO_4^{2-} \qquad (4)$$
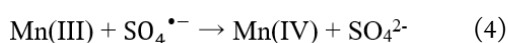
According to Saputra et al. [28, 29], high PMS concentration can reduce the removal of pollutants due to active sulfate radicals ($SO_4^{\bullet-}$) consumed by PMS, in compliance with the mechanisms as a follow.

$$HSO_5^- + SO_4^{-\bullet} \rightarrow SO_5^{-\bullet} + SO_4^{2-} + H^+ \qquad (5)$$

$$HSO_5^- + OH^\bullet \rightarrow SO_5^{-\bullet} + H_2O \qquad (6)$$

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 0.4g/L catalyst loading and 2g/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 0.4g/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):

$$\frac{d(COD)}{dt} = k(COD)^n \qquad (7)$$

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 2 The COD reduction kinetic constant on PMS activated by $LMnO_3$ perovskite

Temperature (°C)	Kinetic equations (t min)	K (L.mg⁻¹.min⁻¹)	R^2
30	1/COD = 3.86E - 05t + 0.0007	3.86E-05	0.99
40	1/COD = 6.20E - 0.5t + 0.0006	6.20E-05	0.99
50	1/COD = 11.15E - 0.5t + 0.0005	11.15E-05	0.99

The experimental data were compared to the model for verifying the kinetic equation obtained, the results depicted in Fig. 8.
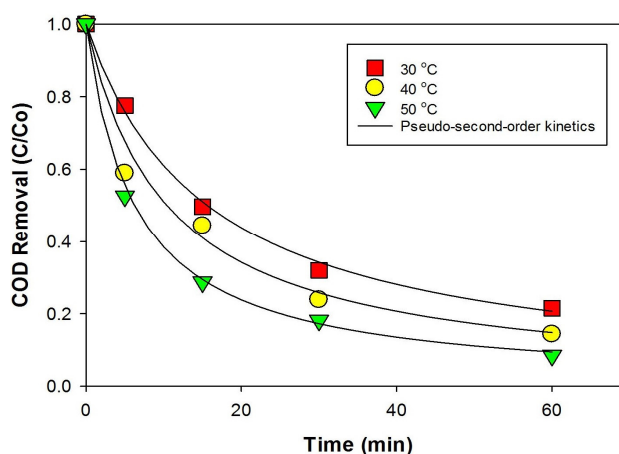

Fig. 8. COD removal on various temperature. Condition of reaction: Initial COD of POMSE = 1700.7 mg/L, catalyst = 0.4 g/L, and PMS = 2 g/L.

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.
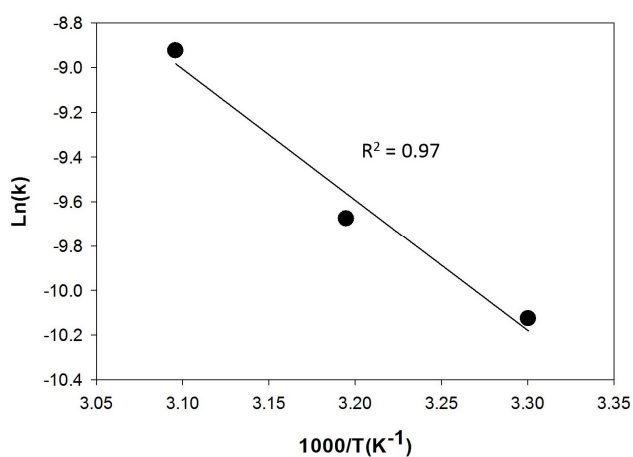

Fig. 9. Arrhenius plot of COD reduction using PMS activated by LMnO$_3$ perovskite

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_3O_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_3O_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.
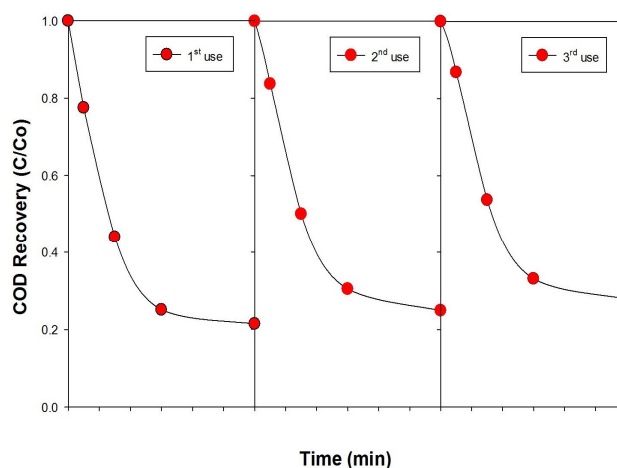

Fig. 10. The reusability test of the LaMnO$_3$ perovskite catalyst

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%.

■   AUTHOR INFORMATION

Corresponding Author
* Email : edysaputra@unri.ac.id

ORCID 🆔
Edy Saputra   : 0000-0001-6430-9072
Oky Muraza   : 0000-0002-8348-8085
Panca Setia Utama : 0000-0002-6829-1321

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