The Novel Synthesis of CaMnO$_3$ Perovskite Type-Oxide and its Catalytic Activity for Degradation of Dye

N Dewi, W Setyarini, R Anggraini, S S Siregar and A Awaluddin*
Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Riau, Kampus BinaWidya, Km 12.5 Simpang Baru, Pekanbaru, Riau, Indonesia 28293
amirawaluddin01@gmail.com

Abstract. The CaMnO$_3$ perovskite type-oxide has been synthesized using a citrate sol-gel method using two different MnO$_2$ precursors and calcium carbonate. The cryptomelane-type manganese oxide precursor produced well-crystalline CaMnO$_3$ perovskite, whereas pyrolusite-type manganese oxide (commercial) generated mixtures of CaMnO$_3$ perovskite and un-reacted MnO$_2$ using the same CaCO$_3$ as other precursor. The CaCO$_3$/MnO$_2$ mole ratio seems to play a crucial role to obtain high purity of the CaMnO$_3$ perovskite. The CaMnO$_3$ perovskite proves to have high catalytic activity for the degradation of methylene blue (MB) using hydrogen peroxide as an oxidant. This Fenton catalyst is able to degrade 98.5% of MB within 20 minutes of degradation times at pH 2.

1. Introduction
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. The various strategies have been proposed for handling the dye wastes, which are mainly classified into three categories, namely biological [1], physical and chemical treatments. The chemical treatments based on advanced oxidation processes (AOPs) are advantageous due to their effectiveness for degradation of organic contamination. The Fenton or Fenton-like process, which is one of AOPs, using a metal oxide as a heterogeneous catalyst and hydrogen peroxide (H$_2$O$_2$) as an oxidant are gaining a lot of attention lately due to their effectiveness to degrade dye contamination.

Metal oxides based on manganese oxides have been successfully applied as heterogeneous Fenton catalyst for degradation of organic pollutions [2-4]. These oxides have been synthesized with a wide range of techniques and doped with several transition metals to improve their catalytic activity [5-6]. Other approach applied to enhance their catalytic activity is to modify their surface with acid or base treatments. In addition, manganese oxides are also could be converted into perovskite type-oxide. The perovskite is a typically mixed metal oxide with general formula ABO$_3$, where A is a rare earth metal or alkaline earth metal and B a transition metal [8]. This oxide has a well-defined structure with high thermal and hydrothermal stability, thus can be used in gas and solid reactions occurring at high temperature or liquid reactions at low temperature. The oxide has also been reported to possess high framework oxygen mobility with the possibility of forming oxygen vacancies. The presence of oxygen vacancies and transition metal B with several oxidation states make them reox-active that leads to the application in a wide variety of fields such as solid oxide fuel cells [9-10], magnetic material [10], oxidation catalysts and etc.
The application of perovskite as a catalyst in advanced oxidation processes (AOPs) in particular as heterogeneous Fenton or Fenton-like reaction is promising and has attracted several researchers. In the Fenton or Fenton-like reaction, the reaction between a catalyst with H₂O₂ will generate highly reactive radicals such as •OH, which then attack and react non-selectively with organic compounds producing intermediate compounds or carbon dioxide and water for complete mineralization [11-14]. Currently, Calcium containing mixed oxides, such as Ca₂Fe₂O₅, CaMnO₃, CaTiO₃ and CaZrO₃ with perovskite have attracted considerable interest due to their wide application such as fuel cells [9-10], magnetic materials, and chemical sensors and heterogeneous catalysts due to the high mobility of framework oxygen and presence of transition metal in their structure.

In the present work, perovskite type-oxide CaMnO₃ was synthesized by a novel synthesis method from cryptomelane type-manganese oxide and CaCO₃ via citrate sol-gel method. The oxide was then applied as a heterogeneous Fenton-like catalyst for degradation of dye.

2. Methodology

2.1. Powder CaCO₃, KMnO₄, Glucose, Citric acid, HNO₃, MnO₂ commercial, and methylene blue were all analytical grade and used without further purification. All the chemical reagents were purchased from Merck (Germany).

2.2. Synthesis

2.2.1. Synthesis of cryptomelane type-manganese oxide (α-MnO₂)

α-MnO₂ was synthesized with a sol-gel method from KMnO₄ and glucose [5] where 15.804 g KMnO₄ (in 1000 ml deionized water) and 5.940 g glucose are mixed, generating gel and the product was dried at 100°C overnight. Finally, xerogel was calcined in a furnace at 700°C for 2 h.

2.2.2. Synthesis of CaMnO₃ perovskite

CaMnO₃ perovskite was prepared via citrate sol-gel method using different mole ratios of MnO₂/CaCO₃ (1:1 and 3:4) was dissolved in nitrate acid 0.5 M. Citric acid was added into the nitrate precursors as the chelating agent. After stirring for 17 h, the solution was heated at 100°C in open air under constant stirring to achieve a viscous mixture, which was dried at 105°C for 24 hours and well ground. Finally, the obtained solids were calcined in a muffle furnace at 270°C for 2 h firstly and then at 700°C for 7 h, respectively.

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 (λ = 1.5406 Å). The data were collected with scan speed 2° per minute in 2θ, from 2θ = 5° to 90°.

The crystallite size of as-synthesized catalysts was estimated using Scherrer’s equation:

\[
D = \frac{(0.941 \lambda)}{\beta \cos \theta}
\]

where D was the average grain size, λ was the X-ray wavelength (0.15406), θ and β were the diffraction angles and Full-Width at Half-Maximum (FWHM, in radian) of an observed peak, respectively.

2.4. Catalytic activity

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 50 mg catalyst. The suspension was continuously stirred magnetically for 30 min to achieve adsorption/desorption equilibrium. Following adding 15 mL of 30 wt% H₂O₂ solution, the mixture was allowed to react at room temperature. At given time intervals, 5 mL of the mixture was pipetted into a volumetric flask, quickly diluted with distilled water to 25 mL, and placed in the iced bath. For optical absorption measurements, the diluted solution was immediately centrifuged at 2000 rpm for 10 min to separate the catalyst particles. Then the centrifuged dye solution put into a quartz cell, and the changes of absorptions at 660 nm were taken to
identify the concentrations of MB, using an Optima Sp-300 UV-vis spectrophotometer. The amount of MB degradation was determined using the equation:

\[
\% \text{ decrease MB} = \frac{C_o - C_t}{C_o} \times 100
\]  

Where \( C_o \) and \( C_t \) are the initial and final concentration of MB, respectively.

3. Results and Discussion

X-ray diffraction (XRD) is a typical characterization technique used to determine crystal structure, purity, crystallinity and crystal size of a material under investigation. The XRD patterns of as-synthesized samples are shown in figures 1 and 2. Figure 1 displays the XRD patterns of the cryptomelane, as-synthesized perovskite (the mole ratio CaCO/MnO\(_2\) of 1:1) and as-synthesized perovskite (the mole ratio CaCO/MnO\(_2\) of 3:4) using the cryptomelane as the starting material. The peaks at 2θ (figure 1 for the mole ratio CaCO/MnO\(_2\) of 3:4) at 20.98°, 29.36°, 33.18°, 33.94°, 37.30°, 48.48°, 54.54°, and 65.18° are corresponding to (020), (310), (310), (112), (022), (411), (141) and (521) diffraction planes of orthorhombic structure of CaMnO\(_3\) perovskite (JCPDS 50-1746), respectively. When the mole ratio CaCO/MnO\(_2\) of 1:1, no CaMnO\(_3\) perovskite phase was generated, indicating that the mole ratio play a crucial role in the formation of the CaMnO\(_3\) perovskite phase. In other word, an excess amount of MnO\(_2\) is needed to react with CaCO\(_3\) for the formation of the CaMnO\(_3\) perovskite. Nurhaziqahet et al (2020) used calcium acetate and manganese acetate with a mole ratio of 1:2 as starting materials, indicating that more manganese precursor is also needed for the formation of the CaMnO\(_3\) perovskite phase [14]. Gagrani et al (2019) used the different precursors, namely CaSO\(_4\) and MnSO\(_4\) with the two mole ratios CaSO\(_4\)/MnSO\(_4\) of 1:2 and 1:1, respectively. The CaMnO\(_3\) perovskite was obtained with the CaSO\(_4\)/MnSO\(_4\) mole ratio of 1:2, whereas the 1:1 mole ratio produced CaMn\(_2\)O\(_4\) [15]. This latter synthesis also used more amount manganese precursor to produce the CaMnO\(_3\) precursor. As a comparison, the MnO\(_2\) commercial (pyrolusite) was also used as a reactant for the synthesis of the CaMnO\(_3\) perovskite using CaCO\(_3\) as the other precursors as shown in figure 2. Using the similar mole ratios of 1:1 and 3:4, the CaCO\(_3\)/MnO\(_2\) mole ratio of 3:4 generated the mixtures of perovskite and un-reacted MnO\(_2\) and CaCO\(_3\), whereas with the ratio of 1:1 no perovskite phase was produced.

![Figure 1. XRD patterns of perovskite synthesized by citrate method with the variation of ratios mol CaCO\(_3\): \( \alpha-MnO_2 \) [3:4 (blue) and 3:4(red)] and \( \alpha-MnO_2 \) (black)](image-url)
Figure 2. XRD patterns of perovskite synthesized by citrate method with the variation of ratios mol CaCO$_3$: MnO$_2$ commercial [3:4 (blue) and 1:1 (red)] and MnO$_2$ commercial (black)

Table 1. The crystal size of catalyst

| No | Catalyst | Crystal size (nm) |
|----|----------|------------------|
| 1  | Cryptomelane  
Perovskite 1:1 from cryptomelane | 13.676 |
| 2  | cryptomelane  
Perovskite 3:4 from cryptomelane | 22.265 |
| 3  | cryptomelane | 16.811 |
| 4  | Pyrolusite | 25.687 |
| 5  | Perovskite 1:1 from pyrolusite | 2408.369 |
| 6  | Perovskite 3:4 from pyrolusite | 347.952 |

Table 1 presents the crystal sizes of cryptomelane, pyrolusite and the corresponding perovskite-type oxides prepared from cryptomelane and pyrolusite with the different mol ratios. The pure CaMnO$_3$ perovskite prepared from cryptomelane source has the lowest crystal size compared to the other prepared calcium manganese oxides.

The as-synthesized CaMnO$_3$ perovskite (CaCO$_3$/MnO$_2$ mole ratio of 3:4) and (CaCO$_3$/MnO$_2$ mole ratio of 1:1) prepared from the cryptomelane source were then tested for the degradation of methylene blue (MB) using H$_2$O$_2$ as an oxidant as shown in the figures 3 and 4. It is very obvious from figures 3 and 4 that the as-synthesized CaMnO$_3$ perovskites showed very active heterogeneous Fenton catalyst for the degradation of MB at pH 2 compared to the cryptomelane, reaching 98.5% of MB degradation at 20 minutes of degradation time.
Figure 3. The amount of MB degradation using perovskite 1:1 with pH= 2; 5.5 and 9.3, [MB] = 50 ppm, catalyst weight = 50 mg, volume $\text{H}_2\text{O}_2$ = 15 mL at room temperature.

Figure 4. The amount of MB degradation using perovskite 3:4 with pH= 2; 5.5 and 9.3, [MB] = 50 ppm, catalyst weight = 50 mg, volume $\text{H}_2\text{O}_2$ = 15 mL at room temperature.

4. Conclusion
The CaMnO$_3$ pure perovskite type-oxide has been successfully synthesized using cryptomelane-type manganese oxide and calcium carbonate as starting material. The mole ratio of CaCO$_3$/MnO$_2$ and the type of MnO$_2$ are dominant factors for generating pure crystalline of the CaMnO$_3$ perovskite. The oxide proves to be very active heterogeneous Fenton catalyst for the degradation of MB.

Acknowledgment
This study was funded by The Ministry of Education and Culture, under the scheme of “Tesis Magister” with the contract no. 443/UN.19.5.1.3/PT.01.03/2020 on behalf of Prof. Dr. Amir Awaluddin, M.Sc.
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