pH-Control of Oxidative Degradation of Methylene Blue Over Octahedral Molecular Sieve Cryptomelane-Type Manganese Oxide (OMS-2) and Fe-OMS-2

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Abstract. The octahedral molecular sieve cryptomelane-type manganese oxide (OMS-2) and Fe-doped OMS-2 (1%, 5%, 10%) were successfully synthesized by the redox reaction between KMnO$_4$ and citric acid using the sol-gel method. The sol products were heated at 120°C and followed by calcination at 600°C. The as-synthesized pristine manganese oxide and Fe-OMS-2 were then characterized by XRD to determine their crystallinity and phase structure. The XRD results indicated that both the pristine and Fe-doped manganese oxides produced tunnel cryptomelane-type manganese oxides. No other peaks due to other phases are detected, indicating that Fe ions are well distributed in the framework of cryptomelane. The oxidative activities, either the pristine and Fe-OMS-2, were evaluated for degradation of methylene blue (MB) at pH ranges 2-6 by the addition of HCl solution. The oxidative tests showed that the oxidative degradation of methylene blue greatly increase with a decrease in solution pH and decrease with an increase in concentration Fe species in Fe-OMS-2 compared to pristine cryptomelane.

1. Introduction
The synthetic dyes are widely used for coloring materials in the textile, paper, printing, and plastic industries. One of the most used synthetic dyes is methylene blue, which belongs to a cationic thiazine dye. According to the decree of the Indonesian environment minister, number: Kep51/MENLH/10/1995, the permissible threshold value of the concentration of methylene blue in the water is around 5 to 10 mg/L. It is known that more than 10-25 % of methylene blue is lost during the dyeing process and about 2-20% is discharged into waterways without proper treatment. This compound is stable to heat, light and oxidizing agents and difficult to biodegrade. The adverse effects of methylene blue to human include headache, vomiting, fever, and high blood pressure. The dye is also harmful to the environment if discharged without treatment.

Several methods have been proposed to deal with dye effluents such advanced oxidation processes (AOP), adsorption, coagulation membrane filtration, biodegradation, and heterogeneous catalytic degradation. The heterogeneous catalytic degradation has been studied intensively because the method is simple and efficient to degrade many synthetic dyes. Therefore, the availability of very active catalyst is very important and pre-requisite before applied to real wastewater containing dye residues. Nowadays, the research on the synthesis of solid catalysts for the degradation of organic contaminants
is gaining a lot of attention. Many research groups have focused on finding a very active catalyst with a simple and cost-effective method.

Many metal oxides have been proposed as heterogeneous catalysts to degrade synthetic dyes. Among them, manganese oxides have gained considerable attention due to their unique crystal structure and physicochemical properties. Manganese oxide has been widely used in various applications, namely as a cathode material in lithium batteries because of its ability to exchange cations [1]. In addition, the oxide is also used as an adsorbent [2] and as a catalyst to oxidize CO [3]. The activity of manganese oxide can be improved further in various ways. Doping is one way to improve catalytic activities of manganese oxides by replacement of Mn metal in MnO₂ with other metals in small quantities [4,5]. Doping can modify the interaction between Mn and O in MnO₂ so that the catalytic activity changes.

The manganese oxides are known to have a tunnel and layer structure with a basic structural unit of MnO₆ octahedral. Different tunnel sizes may be obtained, such as 1x1 tunnel (pyrolusite), 2x2 tunnel (cryptomelane) and 3x3 tunnel (todorokite). The layer structure of manganese oxide occurs in nature such as birnessite, which is formed by stacked sheets of edge-sharing MnO₆ octahedral. Either layer or tunnel structure of manganese oxide has been successfully synthesized. Different synthetic strategies often produce different catalytic activities due to the difference in the crystal structure and physical properties.

Manganese oxide synthesized by solvent-free [6], sol-gel [7], and precipitation methods [8-10] shows good results for the degradation of methylene blue using hydrogen peroxide as an oxidant. Only limited studies have focused on the oxidative degradation of dyes. Layer (birnessite) and tunnel manganese oxides (cryptomelane) are powerful oxidant and can oxidize many organic contaminants. Cui et al. were synthesized three crystal phases of manganese oxides via reflux method and conducted studies of the effects of crystal types and pH solutions on the oxidative degradation of RhB [11]. The results showed that the decolorization efficiencies of RhB for the three manganese oxides all increase with decreasing pH solution. Cryptomelane (α-MnO₂) exhibited the highest activity and could efficiently degrade RhB at pH 2–6, pyrolusite (β-MnO₂) and birnessite (δ-MnO₂) only showed high oxidative activities at pH 2.

In the current research, pristine OMS-2 and Fe-OMS-2 were prepared by sol-gel method and their oxidative performances were evaluated for oxidative degradation of MB in aqueous solution. The effect of solution pH and Fe-dopant concentration on oxidative degradation of MB was also studied.

2. Experimental Method

2.1. Synthesis of cryptomelane-type manganese oxide
A total of 15.804 g (0.1 moles) of potassium permanganate (KMnO₄) was dissolved in 1000 mL DDW while stirring. Then mixed with citric acid as much as 6.934 g (0.033 moles) to form a solution with a ratio of KMnO₄ and citric acid 3:1. After ± 3 minutes added dopant Fe(NO₃)₃·9H₂O as much as 4.04 g (10% dopant) then after 10 minutes a sol will be formed which will turn into a gel. After one hour later, the formed gel was filtered and washed with 250 mL DDW 4 times (rinse before calcination), then dried at 110°C for 12 hours. The xerogel was calcined at 700°C for 5 hours. The formed product is mashed, washed 3 times each with 10 mL HCl 0.1 M and 10 mL DDW. The product is dried at 110°C to be characterized. In the synthesis process, the modification by adding Fe³⁺ with the molar ratio 1%, 5%, and 10%. The products were denoted as Cry (no addition of Fe³⁺); Fe 1%; Fe 5%; and Fe 10%.

2.2. Characterization of as-synthesized manganese oxide
As-synthesized manganese oxides were characterized by powder X-ray diffraction using a powder XRD miniFlex Rigaku Instrument. The diffraction patterns were recorded using Cu Kα (λ = 1.5444 nm) radiation at a scanning speed of 2°/min and a scan step of 0.1° in the range of 2θ = 10-80°.
Elemental analysis (K, Mn, and Fe) was determined by Atomic Absorption Spectroscopy (AAS) (Shimadzu AA 7000).

2.3. Decolorization of MB dye by as-synthesized manganese oxide
Methylene blue solution was prepared using 10 ppm methylene blue, 50 mg manganese oxide and variation of pH (2, 3, 4, 5, and 6). The solution was stirred at 360 rpm and was centrifuged. The absorbance of the methylene blue solution was measured with time variations of 10, 20, 30, 40, 50, 60, 90, and 120 minutes. Samples that have been separated according to time variations are then separated using a centrifuge for 15 minutes and then absorbance is measured. Decolorization of methylene blue for Fe doped was used at pH 2.

3. Results and Discussion

3.1. Characterizations of as-synthesized manganese oxide
The XRD patterns of the as-synthesized manganese oxides and Fe-doped manganese oxides were shown in figure 1. The peaks match well with the cryptomelane phase (OMS-2) of MnO₂ (JCPDS 29-1020), with the diffraction peaks at 2θ values of 12.66°; 17.98°; 28.72°; 37.52°; 49.92°; 60.06°. The Fe-OMS-2 samples display similar diffraction patterns with the pristine OMS-2. This results indicated that either Fe ions are well distributed into the framework of OMS-2, replacing Mn in the framework of the pristine OMS-2. The similar results are also observed by previous studies [4,5], which showed the same diffraction pattern upon doping.

![XRD pattern of the as-synthesized manganese oxide](image)

**Figure 1.** XRD pattern of the as-synthesized manganese oxide.

Table 1 displayed the elemental analysis of OMS-2 and Fe-OMS-2. The K⁺ concentrations decrease upon doping with 5% of Fe. This results suggested that Fe ions are replaced by K⁺ ions in the tunnel of OMS-2. The replacement of K⁺ by Fe ions resulted in the doped samples with similar crystallinity with pristine OMS-2 reported by previous studies [4].
Table 1. The result of elemental analysis

| Samples | K (mmole) | Mn (mmole) | Fe (mmole) | K/Mn | Fe/Mn |
|---------|-----------|------------|------------|------|-------|
| Cry     | 0.081     | 0.121      | -          | 0.672| -     |
| Fe 1%   | 0.075     | 0.094      | 0.002      | 0.797| 0.022 |
| Fe 5%   | 0.050     | 0.110      | 0.023      | 0.456| 0.213 |
| Fe 10%  | 0.056     | 0.102      | 0.009      | 0.547| 0.090 |

3.2. Decolorization of MB dye by as-synthesized manganese oxide

Figures 2-3 displayed the effect of solution pH on the degradation of MB using pristine OMS-2 and Fe-OMS-2. The effect of solution pH on the MB degradation is very significant for the pristine OMS-2. For OMS-2 at pH 2, the percentage of decolorization MB is 99.07%, pH 3 is 28.13%, pH 4 is 28.22%, pH 5 is 40.88%, and at pH 6 is 39.72%. It is apparent that the increase in pH solution gives negative effects on MB degradation. It is reported that OMS-2 is unstable in the acidic condition, thus providing easy electron transfer from the catalyst to MB, which results in the high oxidative activity in the acidic condition. Doping OMS-2 with Fe proves to be ineffective for MB degradation, as shown in figures 3-4. It is likely that the resulting Fe-OMS-2 has higher stability that that OMS-2, thus inhibiting easy electron transfer from Fe-OMS-2 to the MB. These results are consistent with a decrease in K⁺ concentrations of Fe-OMS-2 compared to pristine OMS-2. The incorporation of the dopant into the OMS-2 framework probably replacing K⁺ provide less defects in the doped samples, which in turn, affecting the oxidizing power of doped samples compared to pristine samples.

![Figure 2. The effect of pH on decolorization of MB using pristine OMS-2](image-url)
Figure 3. The effect of Fe-OMS-2 on decolorization of MB at pH 2

4. Conclusion
The cryptomelane type manganese oxide (OMS-2) and Fe-OMS-2 are successfully prepared by the redox reaction between KMnO₄ and citric acid using the sol-gel method. The Fe-OMS-2 was synthesized using one-step synthesis by reacting all reactants simultaneously. The oxidative activities of OMS-2 and Fe-OMS-2 samples are tested for the oxidative degradation of MB. The acidic pH solution gives a positive impact on the MB degradation. The highest degradation of MB over OMS-2 occurs at pH 2 with more than 92% of MB degradation within 40 minutes of reaction times. The Fe-OMS-2 gives a negative effect on the oxidative degradation of MB.

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References
[1] Al-Attar L and Dyer A 2007 Land Contam. Reclamat. 15 3017-3024
[2] Chakrabarti S, Dutta B K and Apak R 2009 Water Sci. Technol. 60 427-436
[3] Matsuda E, Tanaka S, Koike K, Tanaka A, Sano M and Miyake T 2007 Res. Chem. Intermed. 34 535-549
[4] Awaluddin A, Anggraini R, Siregar S S, Muhdarina and Prasetya 2019 MATEC Web Conf. 276 06005
[5] Awaluddin A, Astuti L, Linggawati A, Siregar S S, Prasetya P and Saputra L 2018 AIP Conf. Proc. 2026 020075
[6] Siregar S S and Awaluddin A 2018 IOP Conf. Ser., Mater. Sci. Eng. 345 012005
[7] Awaluddin A, Agustina M, Aulia R R and Muhdarina 2017 AIP Conf. Proc. 1823 020108
[8] Absus S, Zulfa R, Awaluddin A, Anita S, Siregar S S and Prasetya 2018 AIP Conf. Proc. 2049 020009
[9] Awaluddin A, Zulfa R, Absus S, Nurhayati, Linggawati A and Siregar SS 2019 IOP Conf. Ser. Mater. Sci. Eng. 509 012011
[10] Zulfa R, Absus S, Awaluddin A, Anita S, Siregar S and Zulfikri 2018 J. Phys. Conf. Ser. 1097 012051
[11] Cuì H J, Huang H Z, Yuan B and Fu M L 2015 Geochem. Trans. 16 1-8