Precursor effect on the Fe-doped cryptomelane (Fe-OMS-2) prepared via one-step sol-gel route as heterogeneous Fenton catalyst for degradation of methylene blue

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Abstract. The pristine cryptomelane (OMS-2) and Fe-OMS-2 (1%, 5%, and 10%) have been successfully synthesized by a one-step sol-gel method and characterized by XRD, SEM, BET surface area and AAS. The incorporation of Fe (III) within the structure of OMS-2 leads to an increase in surface area, pore-volume, and catalytic activity for the degradation of methylene blue (MB) and a decrease in the content of K+ and average of pore diameter. The catalytic test indicated that the catalytic activity of Fe-OMS-2 1% is considerably higher than that of pure OMS-2. The highest degradation of MB is 93.5% achieved using Fe-OMS-2 1% after 120 minutes of degradation time, the initial concentration of MB of 20 ppm, the catalyst concentration of 0.125 mg and the H2O2 volume of 15 mL. The enhanced catalytic activities of Fe-OMS-2 compared to pristine OMS-2 for catalytic degradation of MB are associated with an increase in surface area, pore-volume, and smaller particle size. The results from catalytic studies imply that the metal doping is an effective strategy to enhance the catalytic activities of OMS-2 for degradation of MB.

1. Introduction
Dye pollutions in water have become a major environmental issue worldwide due to the rapid development of textile industries and other related industries that use dyes as their coloring agents. The effluents from these industries contain dyestuffs that are very toxic, mutagenic, and carcinogenic to human and aquatic life. The dyes are unusually resistant to heat, light, and oxidizing agents and must be treated properly before being released into an environment. The chemical structures of most dyes contain aromatic compounds that are highly stable and are very difficult to biodegrade. The presence of a dye in water, even in a small amount, is very visible and undesirable for any use because it could interfere with the ecological balance. Several methods have successfully applied for dye removals such as biological, adsorption, coagulation, membrane filtration, oxidative degradation, and advanced oxidation processes [1,2,3]. Each method has its advantages and limitations for dye removal. Among these, biological treatment is considered to be the most economical. However, the method is time-consuming [4] and can not be applied if the dyes are toxic to the microbes used for dye removal.

The advanced oxidation processes (AOPs) have gained an increased interest for dye removal due to their efficient and environmentally friendly ways compared to other methods. Fenton processes-based advanced oxidation processes are one of the AOPs techniques, gaining more acceptance for treating
wastewater containing dye residues. Fenton processes are characterized by the formation of OH radicals as the main radical, following the reaction between Fenton catalyst (Fe²⁺ ions) and hydrogen peroxides. The radical is the second most powerful oxidant after fluorine, non-selective, and is able to oxidize most of the recalcitrant organic contaminants present in wastewater. Since the catalyst and the substrate being oxidized are the same phases, the separation between them is still challenging and requires further treatments; thus, additional costs are needed. To overcome this, heterogeneous Fenton processes using solid catalysts are introduced and gain extensive interests over the last decades. In this system, the hydrogen peroxide interacts with the surface catalyst, producing OH radicals. Thus, it is required to have a very active solid catalyst with high surface area and ease of electron transfer between the catalyst and hydrogen radical. Several solid catalysts such as clays, zeolite, and other metal oxides have been proposed as heterogeneous Fenton catalysts for the treatment of dye effluent.

Manganese oxide-based Fenton catalysts are known to have high catalytic activities for the degradation of organic contaminants [5,6]. Manganese oxides are ubiquitous in various environmental settings and play an important role in the mobility and the fate of organic contaminants. The oxides are strong oxidant, very stable, have low zero point charge (pHₚₑ), high average oxidation state (AOS), and degrade most recalcitrant organic compounds as well as have high adsorption capacity for heavy metals. The presence of Mn (III) and Mn(II) in the frameworks of either tunnel or layer manganese oxides introduce more defects due to the more oxygen vacancies. The structure of manganese oxides mainly consists of layer and tunnel structures, with the basic structural unit of MnO₆ octahedra. The manganese oxides with tunnel structures are formed through sharing the edge of MnO₆ octahedra, resulting in single, double, and triple chains. These chains are linked together by sharing a corner, creating tunnel sizes of 1x 1 (pyrolusite), 2 x 2 (cryptomelane, OMS-2), and 3 x 3 (todorokite, OMS-1). The layer structures of manganese oxides are generated by stacked sheets of sharing edges of MnO₆ octahedra and are easily found in nature as birnessite minerals. Both cryptomelane and birnessite have been reported to possess high reactivity for catalytic degradation or oxidative degradation of organic molecules. Various factors govern the reactivity of manganese oxides such as morphology, the presence of defects by doping, surface areas, and oxidation potential.

Doping cryptomelane with transition metals (Cu, Co, Ni, Ce, Fe) have been successfully prepared via various synthetic methods such as hydrothermal, reflux, sol-gel, and solid-state. Doping in cryptomelane often introduces more defects and creates strains in the parent molecules and often transforms the cryptomelane into other phases such as birnessite, resulting in higher surface area, different surface morphology, and higher oxidation potential. This, in turn, may result in tremendous improvement of catalytic activities of doped OMS-2 for the degradation of dyes.

In the current study, OMS-2 and Fe-OMS-2 were prepared via the one-step sol-gel method and their catalytic performances were evaluated for the degradation of MB. Fe (III) ion is chosen as the dopant for the OMS-2 due to similar sizes, charges, and coordination tendencies with manganese. The one-step sol-gel synthesis for Fe-OMS-2 is adopted in this study because it is facile to prepare the oxides, cost-effective, requires simple equipment, and moderate synthesis condition.

2. Experimental
2.1. Synthesis
The synthesis procedure of pure OMS-2 and iron doped-OMS-2 were the same as for Cu-doped cryptomelane in our previous work [7] except the CuSO₄·5H₂O was replaced by Fe(NO₃)₃·9H₂O, with the molar ratios of 1%, 5% and 10% to KMnO₄. The obtained materials were named as Fe-OMS-2 1%; Fe-OMS-2 5% and Fe-OMS-2 10%. The properties of these materials were compared with pure OMS-2 that was synthesized using the same procedures except for the absence of dopant.

2.2. Characterization
X-ray diffraction analysis of pure and Fe-dope OMS-2 was carried out on Mini Flex Rigaku Diffractometer using Cu Kα radiation (λ=1.5444nm). The diffractometer was operated with a scanning speed of 2° per min and a scan step of 0.1°. Morpologies of the samples were probed by scanning
electron microscopy (SEM) with a JEOL JSM 6330F microscope. The specific surface area of the samples was measured by N₂ adsorption at 77 K using a BELSORP-max instrument and degassing at 423 K for 2 h. Elemental compositions for potassium, manganese, and iron were analyzed with atomic absorption spectroscopy Shimadzu AA7000.

2.3. Catalytic activity test
Methylene blue (MB) degradation was carried out in a glass Beaker. Briefly, 0.125 g of catalyst powder was loaded into glass Beaker, which contained methylene blue solution (initial MB solution 20 mg/L) and 60 mL deionized water. The suspension was stirred for 30 min and then added 30 wt% H₂O₂ (15 mL). The mixture was pipetted at a given time interval, then placed in an ice bath and centrifuge to remove the catalyst. The remain of MB solution concentration was determined using spectrophotometer Optima SP-300. The activity of the catalyst was calculated on the basis of the Equation (1).

\[ \text{MB degradation} = \frac{C_0-C_t}{C_0} \times 100\% \]  

Where Co and Ct are initial and concentration of methylene blue at any reaction time (t), respectively.

3. Result and discussion

3.1 Characteristic of synthesized OMS-2 and Fe-OMS-2
The pure OMS-2 and Fe-doped cryptomelane (Fe-OMS-2) are synthesized by the sol-gel method using KMnO₄ as oxidant and glucose as a reductant. The Fe-OMS-2 samples are prepared via a one-step sol-gel route by reacting all reactants simultaneously in one container, followed by washing, filtering, and finally calcinating at 450°C for 2 hours. XRD patterns of as-synthesized pure and doped manganese oxide with 1%, 5%, and 10% of Fe(III) are shown in Figure 1. The patterns are in good agreement with the tunnel structure of the octahedral molecular sieve cryptomelane-type manganese oxides (JCPDS (1977) 29-1020). No additional peaks associated with Fe species are detected following the incorporation of Fe into the pure cryptomelane. These results suggested that Fe³⁺ ions are well distributed into the structure of the pure cryptomelane. A similar observation was reported by previous studies, where the XRD patterns of Fe-doped cryptomelane remained unchanged upon doping with Fe(III) [8,9,10,11,12,13]. The Fe-OMS-2 also displays less crystalline materials compared to pristine OMS-2, as indicated by wider peaks and low relative intensities. Thus, the incorporation of Fe³⁺ ions in the structure of OMS-2 introduces more defects, which affect the physicochemical properties of Fe-OMS-2.

Several studies indicated that Fe(III) is replacing Mn(III) in the framework of OMS-2, while others revealed that Fe (III) is substituting K⁺ in the tunnel of OMS-2. However, when OMS-2 is doped with other transition metals such as Cu ion [14], the OMS-2 is transformed into layer birnessite-type manganese oxide at high Cu concentration. Cu ions can be located in a different position, like in the surface, in the framework or in the tunnel, depending on the Cu concentration. Other transition metals such as Ce and Co result in the doped OMS-2 having the less crystalline phase compared to pure OMS-2 [10]. It is likely that the difference in doping strategy results in the formation of Fe³⁺ species either in the surface, framework, or in the tunnel of the cryptomelane. In the current study, the Fe-OMS-2 are prepared by mixing Fe³⁺ ions with KMnO₄ and glucose via mild sol-gel methods, whereas the previous report used the hydrothermal process using high temperature and pressure. The different precursor often leads to the preferential orientation of a certain plane, as reported by Awaluddin et al. [8]. The additional reflection plane (101) of the cryptomelane phase is shown when the citric acid is used as a reducing agent for the preparation of cryptomelane by the sol-gel method [8]. This plane (101) is undetected using other precursors such as glucose [7].

The SEM images of pure cryptomelane and Fe-OMS-2 at different Fe concentrations are shown in Figure 2. The pure OMS-2 manganese oxide consists of the aggregates of particles with different sizes. Upon doping with Fe³⁺ ions, the aggregates became smaller in size and fragmented into small granular particles, especially in the high Fe doping concentration (Figure 2d). The previous studies reported a similar observation upon Fe doping in OMS-2 but using different precursors (citric precursor) [8] and Cu doping into OMS-2 with a similar precursor to the current study [7].
Yin et al. reported the difference in morphology upon the Fe incorporation into OMS-2 [9]. The pure OMS-2 has a needle-like morphology and reduces in length and increases in width upon small Fe doping. Further increase in Fe concentration, Fe-OMS-2 becomes granular particles with aggregations. The same needle-like morphology for pristine OMS-2 was reported by Ma et al. [10], but the
morphology altered into chunky morphology after the Fe addition. The difference in morphology between the current study and the previous reports is likely due to the difference in the preparation method. Ma et al. prepared OMS-2 and Fe-OMS-2 via the hydrothermal method [10], whereas Yin et al. synthesized OMS-2 and Fe-OMS-2 by reflux route [9]. These two previous studies, especially the hydrothermal route, require high temperature and pressure, thus affecting the rate of crystal growth.

Table 1 displays the selected data from BET and BJH measurements, which include BET surface area, total pore-volume, average pore diameter, pore-volume, and pore diameter of peak. The Fe-OMS-2 samples have a higher BET surface area than pure OMS-2. The previous studies also indicated similar trends of an increase in surface areas following the incorporation of dopant into cryptomelane. Similarly, the total pore volume of Fe-OMS-2 increases until 1% Fe doping into OMS-2, then decrease following the addition of 5 % Fe.

Table 1. Textural properties of pure OMS-2 and Fe-OMS-2

| Catalyst type | Surface area (m²/g) | Total pore Volume (cm³/g) | Average pore Diameter (nm) | Pore Volume (cm³/g) | Pore Diameter of Peak (nm) |
|---------------|---------------------|---------------------------|---------------------------|---------------------|---------------------------|
| Pure OMS-2    | 82.916              | 0.4911                    | 23.689                    | 0.4869              | 44.14                     |
| Fe-OMS-2 1%   | 135.4               | 0.6478                    | 19.138                    | 0.6363              | 59.00                     |
| Fe-OMS-2 5%   | 140.33              | 0.4689                    | 13.365                    | 0.4588              | 78.01                     |

Table 2 displays the bulk analysis of pristine OMS-2 and Fe-OMS-2 obtained from atomic absorption spectroscopy (AAS). The content of $K^+$ ions drops significantly the following doping with Fe (III), while the Mn concentration, in general, remain unchanged. The Fe (III) concentration in the OMS-2 as expected increases following the incorporation of Fe (III). These results suggested that Fe$^{3+}$ ions are replacing $K^+$ in the tunnel.

Table 2. Bulk analysis of pure OMS-2 and Fe-OMS-2 using AAS

| Catalyst type | K (mg/L) | M Mn (mmol) | Mn (mg/L) | Mn (mmol) | Fe (mg/L) | Fe (mmol) | K/Mn | Fe/Mn |
|---------------|----------|-------------|-----------|-----------|-----------|-----------|-------|-------|
| Pure OMS-2    | 3.5284   | 0.0902      | 6.0975    | 0.1110    | 0.0000    | 0.0000    | 0.81  | 0.00  |
| Fe-OMS-2 1%   | 1.6244   | 0.0415      | 5.5344    | 0.1007    | 0.6965    | 0.0125    | 0.41  | 0.12  |
| Fe-OMS-2 5%   | 1.4368   | 0.0368      | 6.4849    | 0.1180    | 2.2918    | 0.0410    | 0.31  | 0.35  |
| Fe-OMS-2 10%  | 1.1960   | 0.0306      | 6.639     | 0.1208    | 3.1718    | 0.0568    | 0.25  | 0.47  |

These results suggested that Fe$^{3+}$ ions substitute $K^+$ in the tunnel of OMS-2 instead of Mn in the framework of OMS-2. The small difference in Mn concentrations following the incorporation of Fe$^{3+}$ supports the claim that Fe$^{3+}$ ions are replacing $K^+$ in the tunnel of OMS-2. $K^+$ ions acting as balancing cations play a key role in stabilizing the structure of OMS-2. It is known that OMS-2 consists of mixed valent of Mn, such as Mn (IV), Mn (III), and Mn (II). The presence of Mn (III) or Mn (II) replacing Mn (IV) creates negative charges in the framework of OMS-2, that must be balanced by positive charges like $K^+$ or by removing oxygen atoms. The absence of oxygen (oxygen vacancy) in the OMS-2 structure introduces defects, which may cause a higher catalytic activity of Fe-OMS-2. The relative constant of Mn concentration of Fe-OMS-2 upon Fe doping could be due to the reduction of Mn (IV) into Mn (III).
or Mn (II), also creating more oxygen vacancies (more defects). Several studies indicated that Fe (III) substituted Mn (III) in the framework of Fe-OMS, evidenced by an increase in AOS Mn upon Fe doping and higher Mn (IV) concentration from XPS studies. The different location of transition metals such as Fe and Cu due to different dopant concentration within the structure of OMS-2 has been reported by previous studies [14]. The Cu species are located on the surface of Cu-OMS-2 for low Cu concentration, while for medium and high Cu doping, Cu is located in the tunnel and in framework, respectively.

3.2 Degradation performance of as-synthesized manganese oxide with different Fe concentration

Figure 3 displays the catalytic activities of OMS and Fe-OMS-2 at different Fe concentration. In general, the catalytic activities of Fe-OMS-2 are higher than that of pristine OMS-2. For the 1% Fe-OMS-2, the rate of MB degradation reaches over 72% conversion of MB compared to only 39% conversion for pristine OMS-2 after 10 minutes of degradation time. For 5% and 10% of Fe-OMS-2, the rate of MB degradation (70% and 66%, respectively) is still higher than that of pristine OMS-2, even though lower than that of 1% Fe-OMS-2. The higher degradation rates of Fe-OMS-2 for MB degradation are correlated with the higher BET surface areas, smaller particle sizes, and lower crystallinity. For 1% Fe-OMS-2 with the highest degradation rate, the highest pore volume also play a significant role in the high catalytic activity. Data from bulk analysis also indicated that Mn contents decreased upon Fe incorporation in the 1% Fe-OMS-2, suggesting that some Fe (III) ions are likely to replace Mn (III) in the framework due to their similar size and charge. This, in turn, introduces more defects responsible for high catalytic activity. The effect of Fe doping on the less crystalline of OMS-2 is also responsible for the higher catalytic activity of Fe-OMS-2 compared to pure OMS-2.

![Figure 3](image-url)

**Figure 3.** Degradation performance of as-synthesized manganese oxide with different Fe concentration, [MB] = 20 mg/L; catalyst = 0.125 g; H₂O₂ = 15 mL

Conclusion

The Fe-OMS-2 has been successfully synthesized via a one-step sol-gel route by a redox reaction between KMnO₄ and glucose with Fe³⁺ ions as a dopant. The present of Fe dopant in the crystal structure of OMS-2 increases the surface area and pore volume and reduces the crystallinity and concentrations of K⁺ and Mn. The catalytic activity test indicated that Fe-OMS-2 showed higher catalytic performance than OMS-2. The highest degradation of MB is 93.5% achieved using 1% Fe-OMS-2 catalyst over 120 minutes of degradation times under optimum condition.
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References
[1] Awaluddin A, Agustina M, Aulia R R and Muhdarina 2017 AIP Conf. Proc. 1823 020108
[2] Siregar S S and Awaluddin A 2018 IOP Conf. Ser.: Mater. Sci. Eng. 345 012005
[3] Awaluddin A, Zulfa R, Absus S, Nurhayati, Linggawati A and Siregar SS 2019 IOP Conf. Ser.: Mater. Sci. Eng. 509 012011
[4] Permana I, Awaluddin A and Saryono 2019 Biodiversitas 20 1693
[5] Zulfa R, Absus S, Awaluddin A, Anita S, Siregar S S and Zulfikri 2018 IOP Conf. Ser. J. Phys. 1097 012051
[6] Absus S, Zulfa R, Awaluddin A, Anita S and Siregar S S 2018 AIP Conf. Proc. 2049 020009
[7] Awaluddin A, Astuti L, Linggawati A, Siregar S S and Saputra L 2018 AIP Conf. Proc. 2026 020075
[8] Awaluddin A, Anggraini R, Siregar S S, Muhdarina and Prasetya 2019 MATEC Web Conf. 276 06005
[9] Yin H, Liu F, Feng X, Hu T, Zheng L, Qiu G, Koopal L K and Tan W 2013 Geochim. Cosmochim. Acta 117 1–15
[10] Ma J, Wang C and He H 2017 Applied Catal. B: Environ. 201 503
[11] Gao J, Jia C, Zhang L, Wang H, Yang Y, Hung S F, Hsu Y Y and Liu B J. Catal. 2016 341 82
[12] Stelmachowski P, Videla A H A, Jakubek T, Kotarba A and Specchia S 2018 Electrocatalysis 9 762
[13] Cai J, Liu J, Willis W S and Suib S L 2001 Chem. Mater. 13 2413
[14] Yang Y, Huang J, Zhang S, Wang S, Deng S, Wang B and Yu G 2014 Appl. Catal. B: Environ. 150–151 167