The Preparation of Cu-Modified Cryptomelane Type-Manganese Oxide Catalysts by one Step sol-gel Synthesis for Decomposition of Methylene Blue

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Abstract. The cryptomelane manganese oxide octahedral molecular sieve (OMS-2) and Cu-modified cryptomelane octahedral molecular sieve (Cu-OMS-2) with different Cu concentrations (1, 5, 10%) were successfully prepared by one-step sol-gel synthesis. The XRD patterns of OMS-2 and Cu-OMS-2 remain unchanged, indicating the Cu ions are well incorporated within OMS-2, except the peak due to (101) plane appears and grows significantly until 5% Cu incorporation. The SEM images revealed that the additions of Cu ions in the OMS-2 have a remarkable impact on the Cu-OMS-2 morphologies, especially for 10% Cu incorporation. The bulk analysis by AAS showed the steady decreases in K⁺ and Mn concentrations, and increase in Cu concentrations, suggesting that some Cu²⁺ ions are replacing K⁺ in the tunnel and Mn in the framework of OMS-2. The catalytic tests for the degradation methylene blue (MB) by heterogeneous Fenton processes revealed that the catalytic performance of Cu-OMS-2 increases remarkably with the increased concentrations of Cu doping. The increased catalytic activities for Cu-OMS-2 are associated with the smaller particles sizes are revealed by SEM results.

1. Introduction
Manganese oxides have been known as versatile materials, having application in various areas such as adsorbent [1], rechargeable batteries [2], supercapacitor [3,4], and catalyst [5,6]. The naturally occurring oxides are ubiquitous in a wide range of environmental settings, like the ocean floor, freshwater bodies, soils, sediments, and desert. The oxides are powerful oxidants, able to transform a wide range of organic compounds. The structures of manganese oxides are basically divided into layer and tunnel structures, which consist of basic structural units of MnO₆ octahedra. These units are arranged together by sharing edges or corner to form a layer or tunnel structure. Both tunnel and layer structures exist in nature such as layer birmessite, 1x1 tunnel structure (pyrolusite), 2x2 tunnel structure (cryptomelane), 3x3 tunnel structure (todorokite), etc.

The synthetic manganese oxides have gained increased interests since the physicochemical properties, phase structures, microstructures, and morphologies could be controlled with proper synthetic strategies [7]. The oxides have been synthesized by many synthetic methods such as sol-gel [8], solid-state [9], hydrothermal [10], precipitation [11], and reflux [12]. The different reducing agents like glucose, citric acid, and oxalic acid have also been used to synthesized manganese oxides, which produce oxides with different properties [8,13]. Lately, the different mixing strategies of reactants were also reported to generate manganese oxides with the controllable properties [14].
One of the increased applications for manganese oxides is used as a heterogeneous Fenton catalyst for remediation of wastewater containing organic pollutants. Organic pollutants such as dyes are considered as severe environmental problems. Dyes are colored organic compounds that absorb light in the visible region and attach strongly to a fiber with physical or chemical bonding. Most dyes are highly structured polymers that are difficult to treat with conventional methods such as biodegradation. Even though the biodegradation is the most economical way to treat organic pollutants in wastewater, the processes are time-consuming, and cannot be applied to the most dye effluents due to the toxicity of the dye constituents to the microbes used for the dye removal. Dyes are also unusually resistant to light, heat and oxidizing agent. They are often toxic to human and aquatic life even in the small concentration (< 1 ppm) due to the presence of metals, chlorides, etc. The presence of dye is highly visible and undesirable in water for any use. Therefore, it is required to overcome these recalcitrant dye effluents with effective and environmentally friendly way. The Fenton process-based advanced oxidation processes are one of the most efficient, easy, acceptable, and environmentally friendly methods for dye removal. Fenton processes are characterized by the formation of OH radicals as the main radical from the reaction between H$_2$O$_2$ with a catalyst. In heterogeneous Fenton process, a solid catalyst is applied for generation of OH radicals with ease separation between the catalyst with the products.

The manganese oxides have been considered as the very active Fenton catalysts for wastewater remediation. In the current research, the OMS-2 and Cu-OMS-2 were successfully synthesized by one-step synthesis using a sol-gel method. The strategy for the synthesis of Cu-OMS-2 was considered to be simple and cost-effective and few studies have reported this method. Both OMS-2 and Cu-OMS-2 are used as heterogeneous Fenton catalysts for the degradation of methylene blue.

2. Experimental Section

2.1. Synthesis
The as-synthesized manganese oxide was prepared via a sol-gel method where 0.1 mole KMnO$_4$ were dissolved in 1000 ml deionized water to form a homogenous solution. Then 0.033 mole citric acid was added slowly into a KMnO$_4$ solution. The mixtures were allowed to react for 3 minutes before the addition of the different mole ratio of Cu$^{2+}$ (CuSO$_4$·5H$_2$O), which was described in our previous work [15]. The final powder product was collected for characterization. In the synthesis process, the CuSO$_4$·5H$_2$O was added with the molar ratios of 0%, 1%, 5% and 10% to KMnO$_4$. The products were denoted as OMS-2, Cu 1%, Cu 5%, and Cu 10%), respectively.

2.2. Characterization
The as-synthesized products were characterized by XRD MiniFlex Rigaku Instrument using Cu Kα radiation (λ = 1.5406 Å) as the X-ray source at a scanning speed of 2º/min and a scan step of 0.1º. The morphology of the products was observed by SEM JEOL JSM 6330F. The elemental analysis of potassium, manganese, and copper of the product was determined by Shimadzu AA 7000.

2.3. Catalytic activity
The experiment was carried out in glass Beaker filled with 25 mL MB dye solution (60 mg/L), 60 mL deionized water, and 50 mg catalyst. The Beaker was placed in a hotplate stirrer and suspension was continuously stirred magnetically for 30 min to achieve adsorption/desorption equilibrium and added 15 mL of 30 wt% H$_2$O$_2$. The mixture was allowed to react at room temperature with continuous stirring. At given time intervals, the mixture was pipetted into a volumetric flask and placed in an ice bath. The diluted solution was immediately centrifuged at 3000 rpm to remove the catalyst particle. The changes of absorptions were monitored by taken filtered samples from the reaction mixture at selected time intervals and measured using spectrophotometer (Optima SP-300).
3. Result and Discussion
The OMS-2 (cryptomelane) and Cu-OMS-2 were synthesized by one-step sol-gel method using KMnO$_4$ and citric acid with Cu$^{2+}$ ion as the dopant at atmospheric pressure. The one-step synthesis is more simple, easy and cost-effective method compared to two-step method for the preparation Cu-doped OMS-2 [14] and other Cu-doped manganese oxides as reported by Yang et al. [16], other studies are applying the hydrothermal method for one-step synthesis of transition metal-doped OMS-2. The method is costly and requires high pressure and high temperature and special container (autoclave) that need to be handled with care. The XRD results for OMS-2 and Cu-OMS-2 are presented in figure 1, which indicate that the patterns remain unchanged with doping Cu, except the diffraction plane (101) that grows in intensity upon the increase in dopant concentrations until 5% Cu. The increase in intensity for Fe-OMS-2 is also observed with citric acid precursor using the similar doping method [15].

![Figure 1. XRD patterns of the samples doped with the different Cu concentrations](image)

The plane (101) is undetected for Cu-OMS-2 prepared using the similar method with glucose precursor [17], Cu-OMS-2 prepared by the one-step and two-step hydrothermal method and transition metal (Ce, Co, Fe ) doped OMS-2 synthesized by the hydrothermal method [18]. The XRD patterns of Cu-OMS-2 also show no broader and additional peaks associated with compounds of Cu doping, suggesting the crystalline nature of Cu-OMS-2 remain the same as that of pristine OMS-2 [16]. However, Yang et al. observed the broader diffraction peaks of Cu-OMS-2 after the small and medium the molar ratio of Cu/Mn [16]. The Cu-OMS-2 crystal phases are then transformed into the layer birnessite-type octahedral layer manganese oxide after the incorporation of high Cu doping. Yang et al. also reported that the locations of Cu within OMS-2 are dependent upon the Cu/Mn molar ratio, in which Cu is located in the external surface of OMS-2 for low doping, in the framework and tunnel of OMS-2 for medium and in the framework and layer of birnessite-type manganese oxides [16]. The crystalline natures of transition metal-doped OMS-2 are correlated with the type of dopants [18]. The Ce-doped OMS-2 resulted in poor crystalline materials, whereas Fe-OMS-2 led to a higher crystalline phase with bare changes in crystalline nature for the Co-OMS-2 compared to the pristine OMS-2.

The SEM images for OMS-2 and Cu-OMS-2 are displayed in figures 2 (a)-(c), which indicated that the morphology of OMS-2 (figure 2 (a)) is altered upon Cu doping. The irregular sizes of smooth aggregates are transformed into small, regular sizes of particles upon Cu doping. The smaller particles probably resulted in more surface areas, especially for 5% and 10% of Cu doping.
Figure 2. SEM images of the samples doped with the different Cu concentrations 
(a) OMS-2 (b) Cu 1% (c) Cu 5% (d) Cu 10% (mag. of 5,000 x)

The bulk chemical compositions of OMS-2 and Cu-OMS-2 are presented in table 1. There is a steady decrease in K and Mn concentration at higher dopant concentrations, suggesting that the Cu ions are substituting K in the tunnel and is replacing Mn in the framework of OMS-2.

Table 1. Elemental analysis of OMS-2 and Cu-OMS-2 and MB degradation after 120 minutes

| Sample Code | K  (mg/L) | K (mole) | Mn (mg/L) | Mn (mole) | Cu (mg/L) | Cu (mole) | K/Mn | Cu/Mn | MB Degradation (%) |
|-------------|-----------|----------|-----------|-----------|-----------|-----------|------|-------|-------------------|
| OMS-2       | 3.185     | 0.081    | 6.662     | 0.121     | 0.000     | 0.000     | 0.672| 0.000| 54.82             |
| Cu 1%       | 2.770     | 0.071    | 6.685     | 0.122     | 0.328     | 0.005     | 0.582| 0.042| 76.78             |
| Cu 5%       | 2.241     | 0.057    | 6.327     | 0.115     | 1.024     | 0.016     | 0.498| 0.140| 87.45             |
| Cu 10%      | 2.126     | 0.054    | 4.829     | 0.088     | 2.127     | 0.033     | 0.619| 0.381| 95.70             |

The catalytic tests of OMS-2 and Cu-OMS-2 for MB degradation using heterogeneous Fenton process are shown in figure 3. It is noticeable from the figure that the high Cu-OMS-2 concentration results in remarkable increases for MB degradation, especially for 10% Cu doping. The MB degradation reaches over 85% conversion at 10 minutes of reaction time for 10% Cu doping compared to only 30% conversion for pristine OMS-2. The highest MB degradation is almost 96% conversion achieved after 120 minutes of reaction times using 10% Cu doping. The Similar MB degradation (94%) is reported by Awaluddin et al. using Cu-OMS-2, but using glucose as a reducing agent for the synthesis of OMS-2 [17]. The data from SEM are in good agreement with the results of MB degradation, that is, 10% Cu-OMS-2 has the smallest particle sizes compared to pristine and other Cu-
OMS-2. Smaller particle sizes are, in general, have higher surface areas, resulting in more active sites on the surface of a solid catalyst.

### Figure 3. Degradation performances of the OMS-2 and Cu-OMS-2 with the different Cu concentrations

#### 4. Conclusion

The OMS-2 and Cu-OMS-2 are successfully synthesized by one-step synthesis via sol-gel method. The Cu ions are probably situated within the framework and in the tunnel of Cu-OMS-2 as revealed by bulk analysis. The incorporation of Cu as dopant within Cu-OMS-2 resulted in much higher degradation rates and could be attributed with smaller particle-sized as evidenced by SEM results. The MB degradation reaches over 85% conversion using 10% Cu-OMS-2 at 10 minute reaction times, tremendously higher conversion compared to pristine OMS-2.

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