



## Oxidation Possibility of Manganese Dioxide Under Ambient Conditions

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Fresh manganese dioxide material was prepared by soaking of pyrolusite grains in HCl solution to dissolve Fe(III) and Mn(II) ions to solution, then MnO<sub>2</sub> and FeOOH were relied on oxidation and precipitation reactions to be coating back on the pyrolusite grains surface. The material was used for investigation of methylene blue oxidation process in water solution. In room temperature and at ambient pressure methylene blue was oxidized and decolourized in large range of pH value. The results showed that in acidic solution the manganese dioxide directly oxidize methylene blue and reduced itself into Mn(II) cation. In alkaline solution, manganese dioxide plays the role as an oxidation catalyst to oxidize methylene blue in presence of OH<sup>-</sup> ions and atmospheric oxygen. The mechanism of oxidation processes was also described.

**Keywords:** Manganese Dioxide, Oxidation Mechanism, Catalysis.

### INTRODUCTION

Pollution of organic compounds became worldwide problem, especially volatile organic compounds (VOCs) and persistent organic pollutants that emitted from agricultural and industrial activities, these pollutants affect adversely to atmospheric environment and human health<sup>3</sup>. Therefore, it is very important to eliminate organic pollutants. However, the conventional incineration method requires high temperature (>1000 °C), resulting in high operation cost. Besides, catalytic oxidation of volatile organic compounds, usually occurs at comparatively low temperature (< 500 °C), is one of the most effective methods for destruction of organic pollutants<sup>3</sup>.

Manganese dioxide is relatively common in the nature environment<sup>1</sup>. Manganese dioxide exists in three main mineral types that are birnessite ( $\delta$ -MnO<sub>2</sub>), cryptomelane ( $\alpha$ -MnO<sub>2</sub>) and pyrolusite ( $\beta$ -MnO<sub>2</sub>)<sup>2,10</sup>. In Vietnam, there are many large pyrolusite mines located at Cao Bang, Nghe An and Ha Tinh provinces. Manganese dioxide have been widely used as catalyst for the oxidation not only organic compounds (hydrocarbon<sup>3</sup>, hydroxylamines<sup>7</sup>, alcohols<sup>1</sup>, formaldehyde<sup>10</sup>...) but also inorganic compounds such as carbon monoxide<sup>3,8,9</sup>, Cr(III)<sup>2</sup>, As(III)<sup>5</sup>, Co(II)<sup>6</sup>, etc.

In this paper, oxidation and catalytic oxidation activity of manganese dioxide coating on pyrolusite was investigated through oxidizing process of methylene blue at ambient pressure and room temperature. The paper also determined

oxidation and catalytic oxidation possibility of the material and initially explained mechanism of the oxidation and catalytic oxidation of manganese dioxide in decomposition reaction of methylene blue.

### EXPERIMENTAL

The first material was pyrolusite ore from Cao Bang mine, Vietnam, containing 60 % of MnO<sub>2</sub> by weight, with grains size of 0.5-1.0 mm. This grainy material was symbolized as M<sub>1</sub>. The second one was pyrolusite coated by fresh manganese dioxide prepared from pyrolusite grains by soaking in 5M HCl solution for 12 h. Then Mn(II) was oxidized to Mn(IV) and precipitated together with Fe(III) ions by adding of NaOH solution in presence of H<sub>2</sub>O<sub>2</sub> until pH up to 7. Then the mixture was incubated for 24 h in room conditions in order to settle fresh precipitate on surface of the pyrolusite grains before washing by deionized water and dried at room temperature until humidity of the material was less than 10 %. This material was known as activated material and symbolized as M<sub>2</sub>.

The phase composition of the materials was analyzed by X-ray diffraction method. Transmission electronic microscope was used for determination of MnO<sub>2</sub> particles size in solution. Concentration of Mn(II) and methylene blue in solutions was analyzed by colourimetric absorption method<sup>4</sup>.

**pH influence on oxidation and catalytic oxidation performance:** Investigation procedure was as follows: Portions

of the materials with the same quantity were putted into equal volume of methylene blue solutions with the same concentration, which were adjusted pH values to the range of 4 to 13. The heterogeneous mixtures were then shaken in the good contact with air oxygen for 1 h. The pH value, methylene blue and Mn(II) concentration in the solutions before and after reaction time were determined. The blank samples were made as the same way as that for research samples.

**Catalytic oxidation performance of the materials:** The investigation procedure was similar that described. But pH value of research solutions was adjusted to 13. The mixture was shaken well in presence of air oxygen. The pH value and methylene blue concentration at different time were determined. When pH value as well as methylene blue concentration in the solution almost unchanged, adjust pH to 13 again then continue the experiment for several periods.

## RESULTS AND DISCUSSION

X-ray diffraction spectrum (Fig. 1) of origin pyrolusite shows clearly the presence of two components of MnO<sub>2</sub> and FeOOH. MnO<sub>2</sub> is in tetragonal phase that has specific peak at 2θ angle of 28.8°. FeOOH exists in tetragonal crystal pattern, having specific peak at 2θ angle of 26.9°. XRD spectrum of the M<sub>2</sub> shows that, there were three components and they are MnO<sub>2</sub>, FeOOH and Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O. In this case, MnO<sub>2</sub> and FeOOH have the same specific peaks as those of M<sub>1</sub>. Besides, M<sub>2</sub> contains Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O at the orthorhombic crystal system that has characteristic peak at 2θ angle of 21.3°.

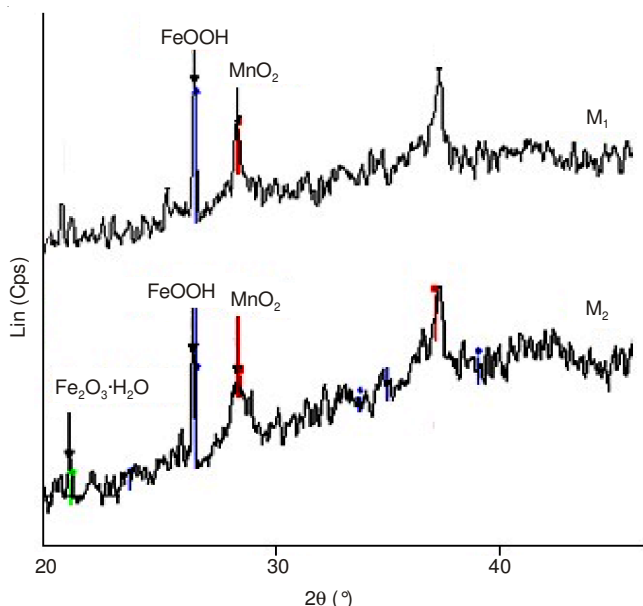


Fig. 1. XRD spectra of M<sub>1</sub> and M<sub>2</sub>

TEM image (Fig. 2) showed that the particles of MnO<sub>2</sub> and FeOOH prepared by precipitation of Mn<sup>2+</sup> and Fe<sup>3+</sup> in solution by NaOH solution in the presence of H<sub>2</sub>O<sub>2</sub> were almost in nano size. The MnO<sub>2</sub> particles were barbed spheres and relatively uniform size in the range of 10-20 nm. FeOOH particles were diamond shapes that interchange with MnO<sub>2</sub> particles. These particles were dispersed or lightly agglomerated in the solution.

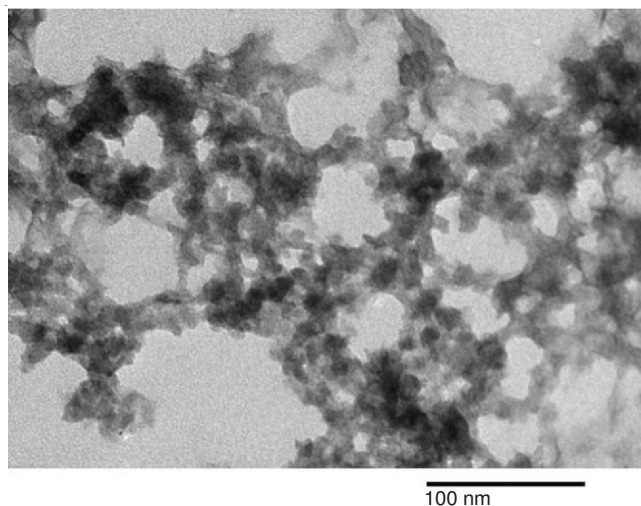


Fig. 2. TEM image of MnO<sub>2</sub> solution

### Oxidation mechanism of the materials

#### Influence of pH on oxidation activity of the material:

Investigation results of oxidation ability of M<sub>1</sub> material at different pH value (from 4 to 13) for methylene blue oxidation showed that, methylene blue was oxidized at every pH in the range, but in different levels. Fig. 3 described the influence of pH on methylene blue oxidized rate by material M<sub>1</sub>. There were appeared three areas. In the area of 4 ≤ pH ≤ 6, almost methylene blue was oxidized, that corresponding to oxidation ability of the material was highest. In the pH area near neutral condition (6 ≤ pH ≤ 9), the oxidation ability was lowest. And in the pH area higher than 9, the oxidation ability was trending to increase with increasing of pH value.

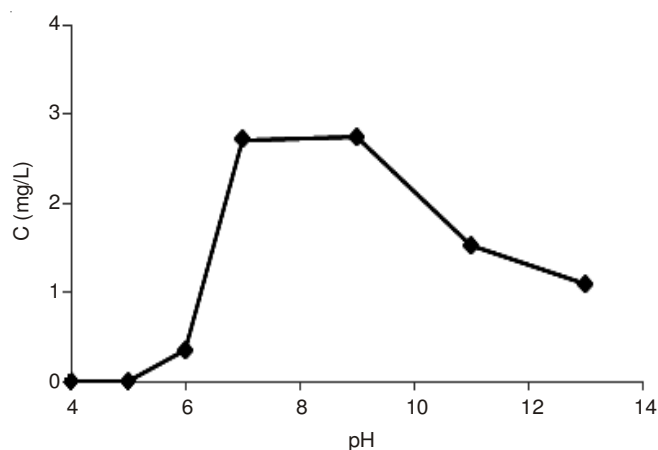


Fig. 3. Methylene blue concentration of solution after treatment at different pH

However, when study UV-visible spectrum of methylene blue and determine Mn<sup>2+</sup> concentration generated after contact of methylene blue and M<sub>1</sub>, the behaviour of oxidation process was partly clear.

UV-visible spectrum of methylene blue has absorption peaks at 610 and 660 nm. In the alkaline condition (Fig. 4), the molecular structure of methylene blue was unchanged after oxidation process, however, its concentration was decreased. But in acidic condition, Fig. 5 showed that the methylene blue was oxidized and changed to another coloured compound having characteristic peaks at 420 and 560 nm. It was clear that

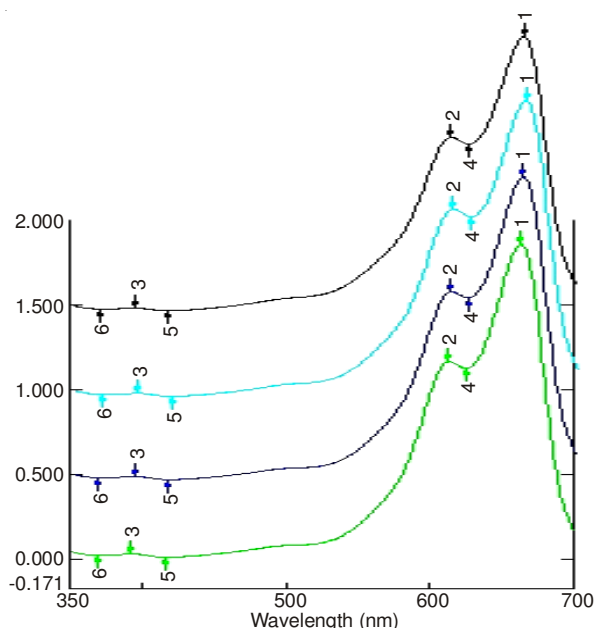


Fig. 4. UV-visible spectra of solution after oxidation in alkaline condition (a) pH = 7, (b) pH = 9, (c) pH = 11, (d) pH = 13

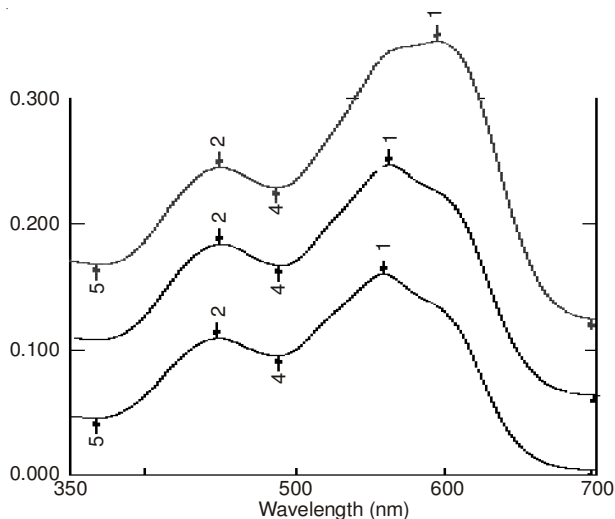


Fig. 5. UV-visible spectra of solution after oxidation in acidic condition (a) pH = 4, (b) pH = 5, (c) pH = 6

in different pH, the way of the oxidizing process occurred in sample solution was different.

**Oxidation mechanism of the materials:** Beside the spectra of methylene blue, the  $Mn^{2+}$  concentration in investigated solutions was analyzed. Fig. 6 showed that in lower pH area,  $Mn^{2+}$  appeared in the solution and its concentration was sharply decreased when pH increased until 7. While in high pH area, the appearance of  $Mn^{2+}$  in solution was almost not discovered. It was clear that in acidic solution, only one oxidation process occurred where  $MnO_2$  directly oxidized methylene blue to form another organic substances and  $MnO_2$  itself reduced into  $Mn^{2+}$ . In the area of  $7 < pH < 9$ , the direct oxidation reaction almost did not happen. The very low (even zero) concentration of  $Mn^{2+}$  in the experimented solution in this pH area was evident to consideration above. In the solution with  $pH \geq 9$ , there was no  $Mn^{2+}$  ion appeared in solution after oxidation process, while methylene blue was completely oxidized. This phenomenon explained that oxidation process in this case

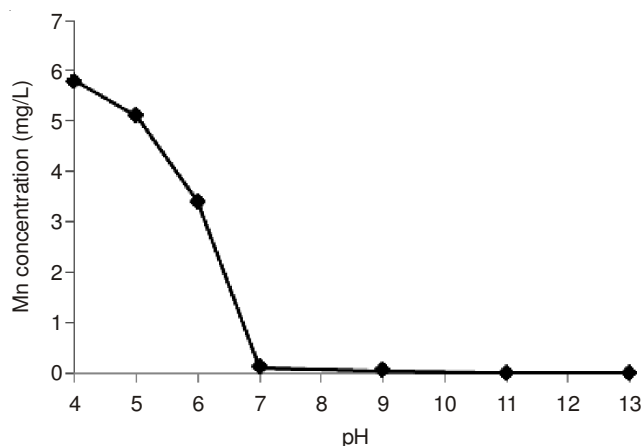
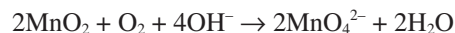
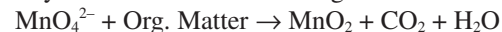


Fig. 6. Influence of pH on releasing concentration of Mn

the  $MnO_2$  played the role as catalyst only. In the solution,  $MnO_2$  reacts with dissolved oxygen and hydroxyl anions to generate manganese compound at higher oxidation level (the most as  $MnO_4^{2-}$ ).



Then,  $MnO_4^{2-}$  itself can oxidize methylene blue or decomposed to  $MnO_4^-$  and  $MnO_2$  and  $MnO_4^-$  oxidized methylene blue similarly  $MnO_4^{2-}$  to obtain  $MnO_2$  again.



**Consumption of  $OH^-$  and reduction of methylene blue concentration:** The experiment was performed as described and results were presented in Figs. 7 and 8.

Fig. 7 shows that in same reaction conditions, the  $OH^-$  consumption was different in quantity as well as consumption rate for  $M_1$  and  $M_2$ .  $M_2$  material possesses fresh  $MnO_2$  layer on its specific surface while  $M_1$  is original pyrolusite mineral only. This is the reason that the catalytic oxidation ability of  $M_2$  was always higher than  $M_1$ . Furthermore, due to high activity of fresh  $MnO_2$  layer, the catalytic oxidation reaction on  $M_2$  occurred until at pH value of 9.5 and that on  $M_1$  only to pH level at 10 in first period and higher than 10.4 for next periods. The pH decreasing rate (or  $OH^-$  consumption rate) in oxidation reaction with  $M_2$  was much higher than that with  $M_1$ .

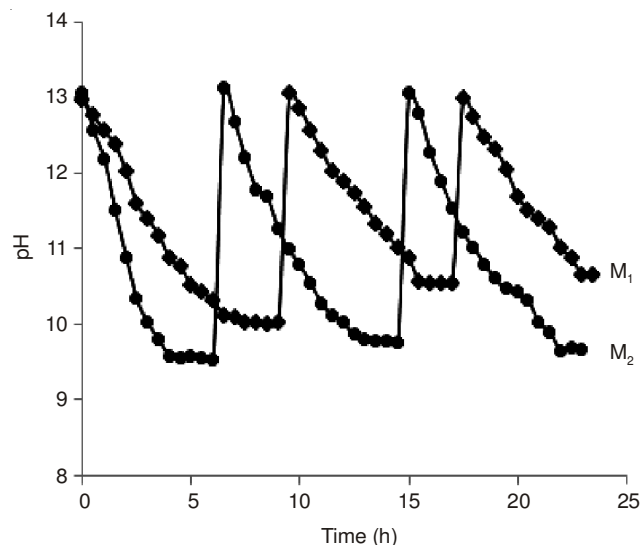


Fig. 7. Consumption of  $OH^-$  in 3 reaction periods

The methylene blue concentration decrease occurred closely with pH decreasing scenario. Fig. 8 showed that the decreasing curve of methylene blue concentration in three consecutive periods. The  $\text{OH}^-$  concentration played decisive role in catalytic oxidation reaction of  $\text{MnO}_2$ . When pH value decreased to 10 and 9.4 corresponding for  $M_1$  and  $M_2$ , the concentration of  $\text{OH}^-$  was not sufficient to oxidation process, the reaction mostly stopped.

Fig. 8 also shows that the oxidation ability of  $M_2$  is higher than that of  $M_1$  in the same experimental conditions. Methylene blue concentration after three consecutive periods reduced to 3.7 and 8.5 mg/L corresponding for  $M_2$  and  $M_1$  from initial concentration of 20 mg/L.

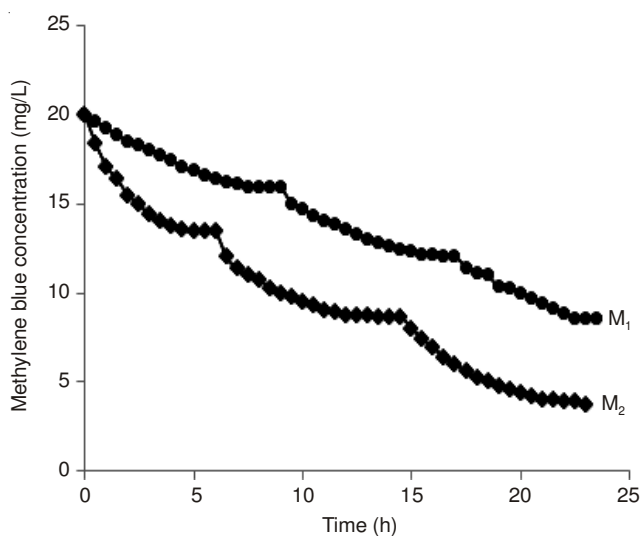


Fig. 8. Reduction of methylene blue concentration through 3 reaction periods

### Conclusion

Both pyrolusite ore and pyrolusite coating fresh nanosize  $\text{MnO}_2$  and  $\text{FeOOH}$  layer were very good oxidation materials

for disintegration of organic matter in water at ambient temperature and pressure in case of methylene blue. The results showed that, there were two different mechanisms of oxidation reaction of  $\text{MnO}_2$  oxidized methylene blue. The first, in the solution with  $\text{pH} \leq 6$ ,  $\text{MnO}_2$  directly oxidized methylene blue to obtain another coloured substance which had different light absorption maxima than original substance and  $\text{Mn(IV)}$  reduced itself into  $\text{Mn}^{2+}$ . The second, in the solution with high  $\text{OH}^-$  concentration ( $\text{pH} \geq 9$ ),  $\text{MnO}_2$  played the role as a catalyst in methylene blue oxidation reaction. This reaction always accompanied with  $\text{OH}^-$  and dissolved oxygen consumption and  $\text{OH}^-$  concentration played as decisive role. The oxidation ability of  $\text{MnO}_2$  at ambient pressure and temperature has high application potential for treatment of organic matter in water environment.

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