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# A comparative study on the photodegradation of methyl orange, methylene blue using $Fe_2O_3$, $Mn_2O_3$, and $Fe_2O_3 – Mn_2O_3$ nanomaterials

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ABSTRACT

In this study, photocatalysis was applied to degrade methyl orange (MO) and methylene blue (MB) pollutants using nanoparticles (i.e., $Fe_2O_3$, $Mn_2O_3$, $Fe_2O_3 – Mn_2O_3$). The results were shown that MB was relatively easier to decompose than MO. At the same initial concentration of 10 ppm, all nanomaterials need 120 min to degrade MB from 74.4%-96.5%, while after 180 min, MO is only degraded by 50%-95%. For both pollutants, the mixed nano-oxides of $Fe_2O_3$-$Mn_2O_3$ presented a superior treatment efficiency compared to the two single oxides (i.e., $Fe_2O_3$ and $Mn_2O_3$). The degradation efficiency was recorded with the order $Fe_2O_3$-$Mn_2O_3$ > $Fe_2O_3$ > $Mn_2O_3$. During photodecomposition, formed intermediates due to the incomplete reaction of pollutions and hydroxyl radical were investigated using the ions trap technique.

## Introduction

Photocatalysis is the degradation of pollutants into less toxic/non-toxic substances that occur under the action of a catalyst and light. The recombination of the electron-hole pair generated by the reaction process greatly affects photocatalytic efficiency.

Many studies have also shown that the photocatalytic efficiency is significantly increased when using a mixture of oxide nanoparticles compared with the photocatalyst efficiency of single oxides. For example, Ag/$TiO_2$-g-$C_3N_4$[1], $TiO_2$/$Fe_2O_3$ [2], CuO/α-$Fe_2O_3$ [3], $TiO_2$/$CeO_2$ [4] significantly improved the catalytic activity compared to the original components such as ZnO, $TiO_2$, CuO. In the many catalysts, nano-oxide $Fe_2O_3$, $Mn_2O_3$, $Fe_2O_3$-$Mn_2O_3$ have been used to treat pollutants in the environment such as MO, MB, phenol, pesticides, and given high decomposition efficiency [5-7]. This study showed that the efficiency of pollutant

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removal when the used mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$ was higher than that of when compared with single nano-oxide synthesized under the same conditions.

## Experimental

Oxide nanoparticles were synthesized by combustion method under optimal conditions, with $Fe_2O_3$ synthesized by ref. [8], $Mn_2O_3$ synthesized by ref. [9], $Fe_2O_3$ – $Mn_2O_3$ synthesized by ref. [10]. The chemicals of MO, MB are of analytical quality.

The photocatalysis process of MO, MB decomposition was carried out in a photocatalyst system consisting of the main components: reaction vessel, lamp, and cooling system. With a reaction vessel volume of 500 mL, a magnetic stirrer was used at a constant speed throughout the reaction to create homogeneity in the solution. Mercury lamp (lamp symbol 7825-34) had a capacity of 450W, 135 V, length of 11.4 cm, with wavelengths stimulated by sunlight. The luminous intensity at the surface of the lamp was 1.04 W/cm$^2$; at the surface of the reactor 0.37 W/cm$^2$. The distance from the center of the lamp to the surface of the solution d (cm) could be varied. In this study, this distance was kept the same. The cooling water system was continuously flowed through the equipment system to maintain a stable temperature during the reaction and ensure that the system was not affected by the temperature factor. In addition, the system was cooled by ambient air. To limit ultraviolet radiation from affecting the eyes, the system was protected in a steel cabinet.

First, a volume of a solution of a contaminant and the catalyst with a defined concentration was added to the reactor system. The catalyst content was the same with different contaminants (MO: 0.1 g/L; MB: 0.1 g/L). The reaction was carried out after the adsorption equilibrium was established.

MO and MB concentrations were measured by UV–Vis spectrophotometer, SHIMADZU in Institute of Materials Science – Vietnam Academy of Science and Technology.

Intermediates that appeared by decomposition were measured by LC-MSD-Trap-SL Agilent 1100 in the Institute of Chemistry - Vietnam Academy of Science and Technology.

First, the LC-MSD-Trap-SL Agilent 1100 enables researchers to select doubly charged ions for fragmentation preferentially. The LC conditions for LC-MSD-Trap-SL are shown in Table 1:

Table 1: LC conditions for LC-MSD-Trap-SL

| LC conditions | |
|---|---|
| Column | ZORBAX SB-C18, 4.6 x 150 mm, 5 µm (860975-902) |
| Column temperature | 40 °C |
| Flow rate | 0.4 mL/min |
| Injection volume | 10 µL |
| Mobile phase | A = water + 0.1% formic acid |
| | B= acetonitrile |

Based on the literature review, we proposed a possible degradation pathway for MO and MB. Next, by using the LC-MSD-Trap-SL, we selected specifically charged ions from the proposed pathway and confirmed it by the MS spectrum.

## Results and discussion

### *Study, comparison of MO decomposition by nano oxides of $Fe_2O_3$, $Mn_2O_3$, and $Fe_2O_3$ – $Mn_2O_3$*

The initial concentration of MO to perform MO decomposition was 10 ppm. After different reaction times, the MO concentrations were determined. The results are shown in figure 1.

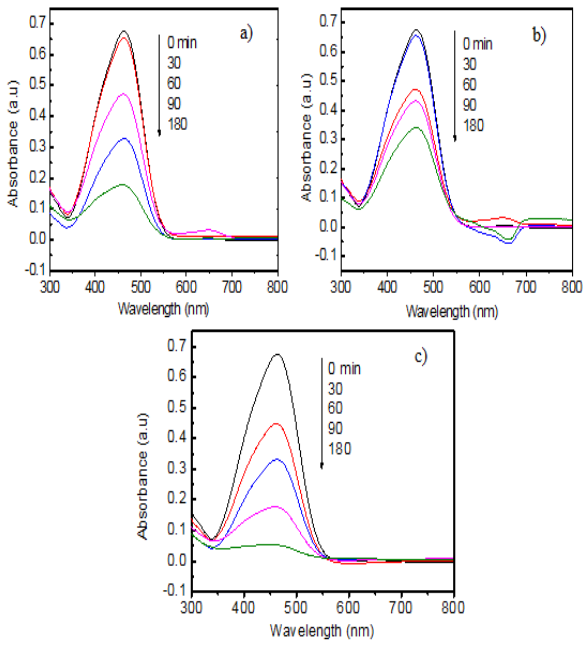


Figure 1: MO decomposition when used by different photocatalyst materials a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$

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Figure 1 was shown that, when used different catalysts, the MO decomposition efficiency was different. The MO removal efficiency used $Fe_2O_3$ catalyst (Figure 1a) was more than 75%, $Mn_2O_3$ (Figure 1b) near 50% for 180 minutes. Meanwhile, at 180 minutes, the mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$ showed a significant increase in treatment efficiency. Nearly 95% of MO pollutants were decomposed. This showed the high decomposition efficiency of the photocatalysis process used mixture of nano-oxide $Fe_2O_3$–$Mn_2O_3$.

The intermediates formed during MO decomposition by photocatalysis process used $Fe_2O_3$, $Mn_2O_3$, $Fe_2O_3$–$Mn_2O_3$ catalysts were also identified. The results are shown in Figure 2.

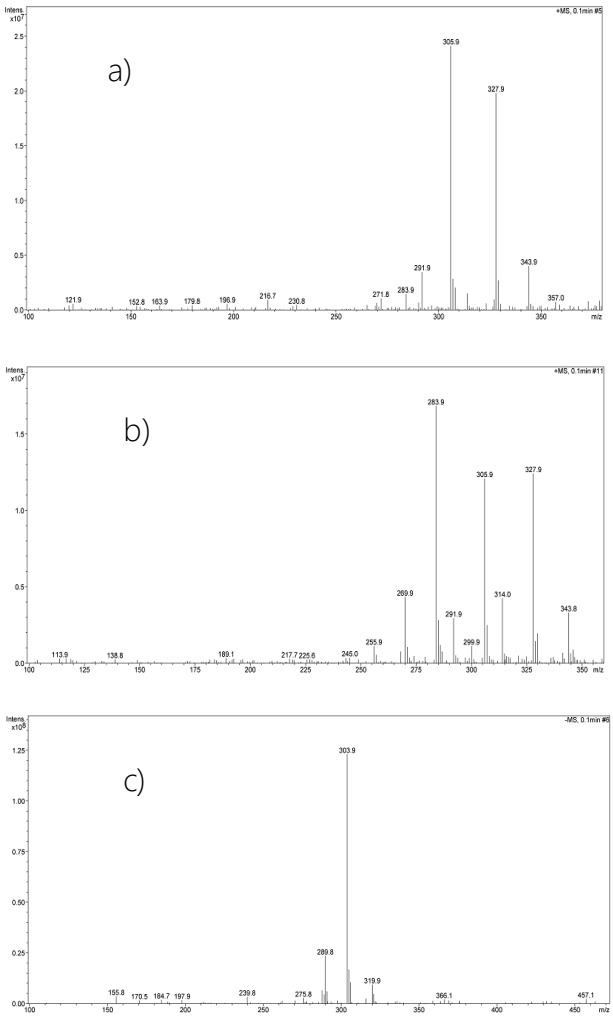



Figure 2: Mass spectrum of samples at a reaction time of 60 min *a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$*

The intermediates formed during MO decomposition by photocatalysis using $Fe_2O_3$, $Mn_2O_3$, $Fe_2O_3$–$Mn_2O_3$ catalysts were also identified by using electron traps, several intermediate compounds were detected at m/z 306, m/z 328 (figure 2a) for $Fe_2O_3$, m/z 306, m/z 328, m/z 292, m/z 314 (figure 2b) for $Mn_2O_3$, m/z 320, m/z 276, m/z 290 (figure 2c) for $Fe_2O_3$–$Mn_2O_3$.

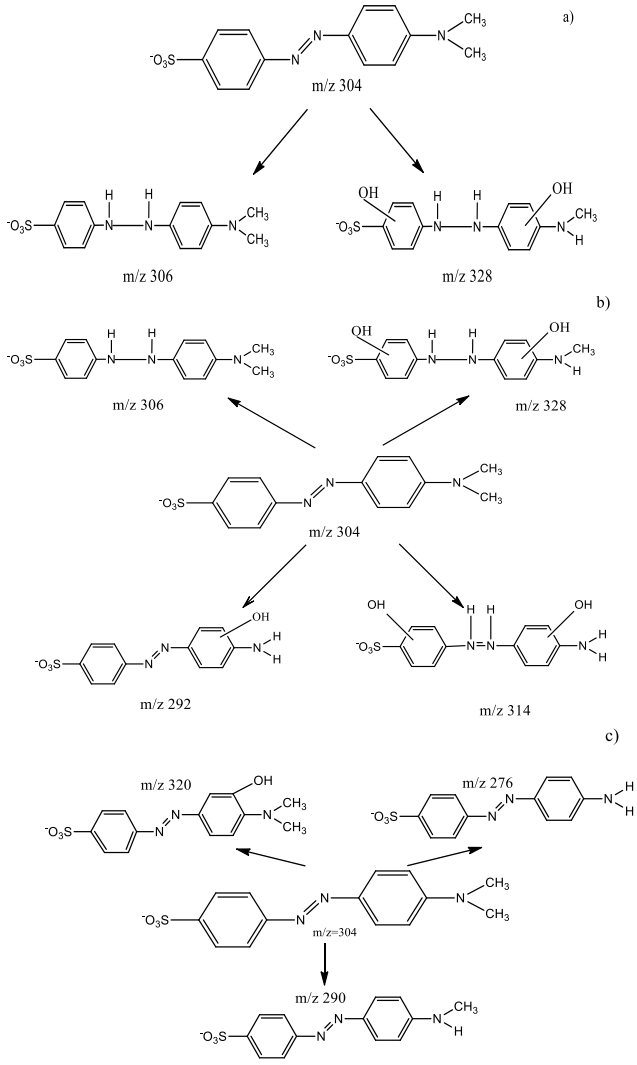



Figure 3: Some intermediates were formed during the photocatalyst process by different catalysts a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$

The results in Figure 3 showed that the intermediates formed during the reaction process by different catalysts were different. Here, the cutting and joining were taken place to form intermediate products from free radicals and organic radicals generated by the decomposition process.

### *Study, comparison of MB decomposition by nano oxides $Fe_2O_3$, $Mn_2O_3$, and $Fe_2O_3$–$Mn_2O_3$*

The initial concentration of MB to perform MB decomposition was 10 ppm. The reaction time was 150 minutes. The results were shown in Figure 4.

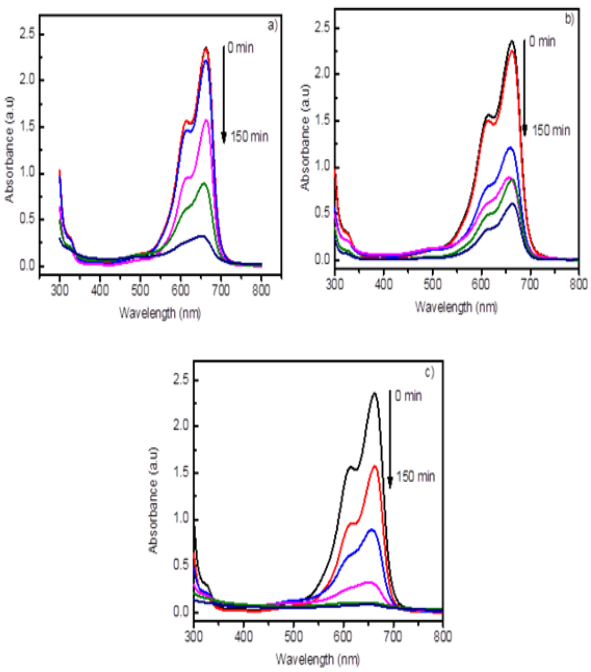
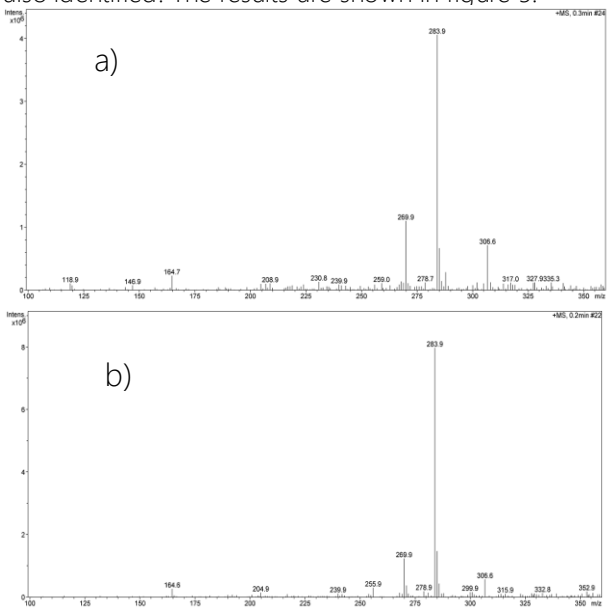



Figure 4: MB decomposition when used by different photocatalyst materials a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$

Figure 4 shows that the MB decomposition efficiency when used mixture of catalyst nano-oxide $Fe_2O_3$–$Mn_2O_3$ was higher than that when used single catalyst nano-oxides of $Fe_2O_3$, $Mn_2O_3$ at the same reaction time. At 150 minutes, the MB removal efficiency of the $Fe_2O_3$–$Mn_2O_3$ catalyst was 96.5% (87.1% and 74.4% of $Fe_2O_3$, $Mn_2O_3$, respectively).

The intermediates formed during MB decomposition by photocatalysis process used different catalysts were also identified. The results are shown in figure 5.



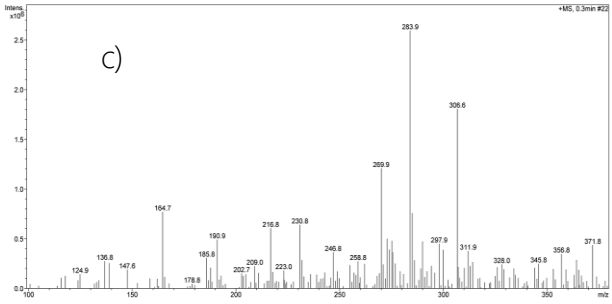




Figure 5: Mass spectrum of samples at a reaction time of 60 min *a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$*

Figure 6 was shown the formation of different intermediates from reactions using different catalysts. When used catalyst mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$, the cutting and coupling process formed new substances with simpler structures than the original MB, and intermediates were formed by catalyst process using single nano-oxides $Fe_2O_3$ and $Mn_2O_3$.

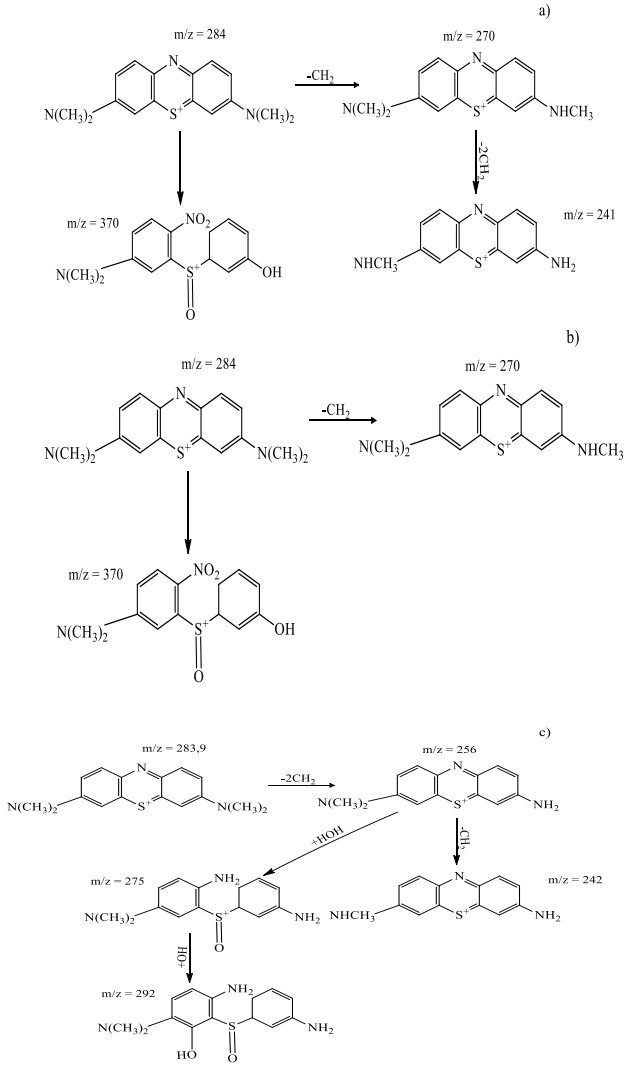



Figure 6: The decomposition route of MB used catalyst nano-oxides *a) $Fe_2O_3$, b) $Mn_2O_3$, c) $Fe_2O_3$–$Mn_2O_3$*

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Thus, the photocatalytic ability of a mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$ was compared to single nano-oxides $Fe_2O_3$ and $Mn_2O_3$ for both MO and MB pollutants: under the same condition of the reactor system, reaction temperature, initial concentration of the pollutant, the pH, and the catalyst content. It was shown that the decomposition efficiency of the mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$ was higher than that of single nano-oxides under selected conditions. This was consistent with many studies.[2,11,12] It could be caused by the same radii of $Mn^{3+}$ and $Fe^{3+}$ ions.[13,14] Therefore, $Mn^{3+}$ ion easily replaced a part of $Fe^{3+}$ ion in $Fe_2O_3$ crystal lattice. It could be that the increase of energy level of the conduction band ($e_{CB}$ was negative) made the increase of reduction capacity of $e_{CB}$ as well as the photocatalytic ability of a mixture of nano-oxide. On the other hand, because the electron configuration of $Mn^{3+}$ ($3d^4$) is short an electron compared to $Fe^{3+}$($3d^5$), it can easily transfer an electron from $Fe_2O_3$ to $Mn_2O_3$. This reduced the recombination ability between photogenerated electron and photogenerated hole, which hold to increase the photocatalytic ability of a mixture of nano-oxide compared with that of single nano-oxides. More detailed explanations about the characteristics of nano-mixed oxides $Fe_2O_3$-$Mn_2O_3$ were previously observed by V.N.M Nguyen et al.[15]

## Conclusion

Single nano-oxides of $Fe_2O_3$, $Mn_2O_3$, and a mixture of nano-oxide $Fe_2O_3$-$Mn_2O_3$ used to decompose MO and MB by photocatalysis process were studied. The removal efficiency of MO decomposition used $Fe_2O_3$ catalyst was more than 75%, $Mn_2O_3$ near 50%, $Fe_2O_3$-$Mn_2O_3$ near 95% for 180 minutes. With MB, during 150 min, the decomposition efficiency of $Fe_2O_3$–$Mn_2O_3$ was 96.5% (87.1%, 74.4% of $Fe_2O_3$ and $Mn_2O_3$, respectively).

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