



## Synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles and their applications in methylene blue treatment

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### ABSTRACT

In this study, nano Fe<sub>2</sub>O<sub>3</sub> particles were synthesized by the combustion of gel from polyvinyl alcohol (PVA) and tartaric acid (TA) for the degradation of methyl blue (MB) from the aqueous solution by the photocatalytic process. Factors affecting on Fe<sub>2</sub>O<sub>3</sub> formation such as the pH of solution, temperature of gel formation, mole ratio of TA/PVA, temperature of calcination were investigated. The structure, morphology of Fe<sub>2</sub>O<sub>3</sub> particles were characterized by analysis methods such as Differential Thermal Analysis, X- Ray Diffraction and Field Emission Scanning Electron Microscopy. The results showed that single-phase Fe<sub>2</sub>O<sub>3</sub> was smaller than 60 nm of average grain size. When using Fe<sub>2</sub>O<sub>3</sub> to investigate the photocatalytic capacity under the visible light irradiation, the results indicated that Fe<sub>2</sub>O<sub>3</sub> catalysts showed a rather high photocatalytic ability to decompose MB. The intermediates coming from the photocatalytic degradation were identified.

### Introduction

Photochemistry process was proved to be an effective method for treating pollutants in environment [1,2]. There are many catalysts used in photochemistry process including nano iron oxide [3,4]. Iron oxide nanoparticles are cheap, durable, environmentally friendly and proven to be highly effect in pollutant treatment, especially colorant [3,4]. There are many methods to synthesize iron oxide nanoparticles such as hydrothermal [5], sol-gel [3], co-precipitation [6], combustion [7]. The combustion method with the advantage of simplicity, synthesizing a large amount of uniformly sized materials was selected to synthesize iron oxide nanoparticles. With a gel-forming mixture, a mixture of organic acids and polymers increased the ability to make complex with metal ions, therefore they

were dispersed evenly in the polymer net [8,9]. In the photocatalytic process, under the action of light, photochemical electrons and photochemical holes were generated and initiated a series of reactions to convert pollutants into final mineralized products H<sub>2</sub>O and CO<sub>2</sub>. In this research, iron oxide nanoparticles were synthesized by gel mixture TA and PVA and applied to decompose MB. Intermediates formed decomposition process were researched.

### Experimental

Chemicals used Fe(NO<sub>3</sub>)<sub>3</sub>, PVA, TA, NH<sub>4</sub>OH, HNO<sub>3</sub> blue methylene (MB) were analytically pure.

Iron oxide nanoparticles were synthesized by combustion method with a gel-forming agent that was a mixture of TA and PVA. The gel-forming agent was

dissolved in the water until it was dissolved completely at an appropriate temperature.  $\text{Fe}(\text{NO}_3)_3$  was slowly added to above mixture to make homogeneous solution. The parameters affecting synthesis process were changed until the optimum fabrication conditions were selected.

The photocatalytic experiment was carried out in Ace Photochemical UV Power Supply & Mercury Vapor Lamps (USA) at the Inorganic Materials Department - Vietnam Academy of Science and Technology. The reactor volume is 500 ml. A magnetic stirrer was used at a constant rate to create homogeneity in solution during reaction. Mercury lamp (lamp model 7825-34) has an output of 450W, 135 V, and a length 11.4 cm, with a wavelength simulated by sunlight. The photocatalytic experiment of blue methylene was made by initial concentration 10 ppm, catalyst content 0.1 g/L after adsorption equilibrium was set in the dark for 24 hours.

Blue methylene concentration was determined by the UV-Vis spectrophotometer UV - 1800 SHIMADZU at the Institute of Materials Science - Vietnam Academy of Science and Technology. Some intermediate products created by blue methylene degradation were determined by LC-MSD-Trap-SL Agilent 1100 at the Institute of Chemistry, Vietnam Academy of Science and Technology.

## Results and discussion

### Synthesis of $\text{Fe}_2\text{O}_3$ nanoparticles

#### Thermal analysis diagram of gel sample

The sample synthesized with the gel-forming agent was a mixture of tartaric acid and PVA, pH3, the ratio of  $\text{Fe}^{2+}/(\text{TA} + \text{PVA}) = 1:3$ , the ratio of  $\text{TA}/\text{PVA} = 1:1$ , the gel forming temperature  $80^\circ\text{C}$ . The synthetic sample was analyzed by thermal analysis after dried at  $120^\circ\text{C}$ . The result was shown in Figure 1.

On the thermal analysis diagram of the gel sample in Figure 1, a mass reduction effect was 4.40% on the TG line with the temperature range from  $30^\circ\text{C}$  to  $100^\circ\text{C}$ . This mass reduction was due to the water loss on gel sample surface. 74.85% and 10.54% mass reduction effects were followed by corresponding to exothermic peaks at  $178.52^\circ\text{C}$ ;  $196.38^\circ\text{C}$  and  $284.39^\circ\text{C}$  on the DTA line between  $100^\circ\text{C}$  and  $350^\circ\text{C}$ . Peak at  $178.82^\circ\text{C}$  could be tartaric acid decomposition in sample, peak at  $196.38^\circ\text{C}$  was nitrate product decomposition remained in gel process and gel drying at temperature  $120^\circ\text{C}$  and peak at  $284.39^\circ\text{C}$  was PVA burning in sample. When the temperature was increased by more than  $350^\circ\text{C}$ ,

the mass of the sample was almost unchanged. This time could be assigned to the formation of iron oxide nano phase  $\text{Fe}_2\text{O}_3$  needing synthesis.

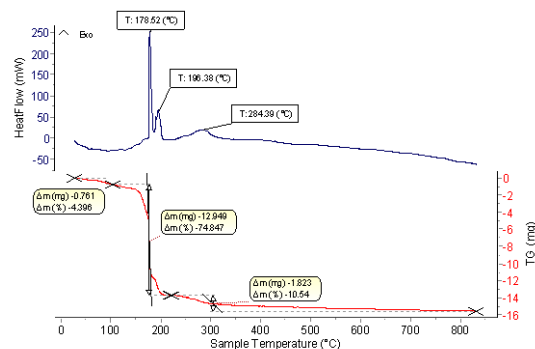


Figure 1: DTA - TGA diagram of gel sample

#### Effect of calcinating temperature to phase formation of iron oxide nanoparticles

Gel sample was synthesized by conditions such as gel forming temperature  $80^\circ\text{C}$ , pH3, ratio of  $\text{TA}/\text{PVA} = 1:1$ , ratio of  $\text{Fe}^{3+}/(\text{TA} + \text{PVA}) = 1:3$  and various calcinating temperatures  $200^\circ\text{C}$ ,  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ . X Ray diffraction diagrams of sample were shown by figure 2.

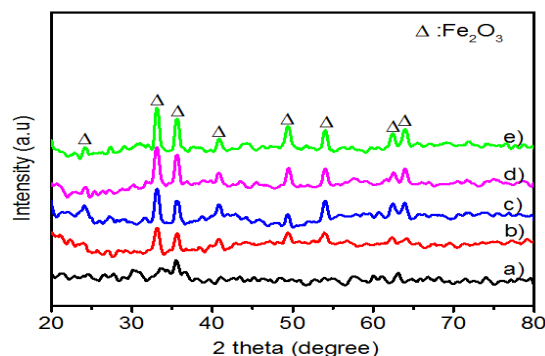


Figure 2: X-Ray diffractions at various calcinating temperatures a)  $200^\circ\text{C}$ , b)  $300^\circ\text{C}$ , c)  $400^\circ\text{C}$ , d)  $500^\circ\text{C}$ , e)  $600^\circ\text{C}$

Figure 2 was shown that at the temperature of  $200^\circ\text{C}$  monophasic formation of iron oxide nano- $\text{Fe}_2\text{O}_3$  was started while the calcinating temperature necessary to form iron oxide nanocrystals was  $600^\circ\text{C}$  [7]. This is explained that the combination of TA and PVA was gel-forming agent, the metal cations were easily complexed with TA, evenly distributed and kept on the structural net of the PVA polymer, phase separation was reduced, the process of calcinating to form products was taken place slowly and the heat was evenly distributed throughout the structure. This result was consistent with previous studies by support effects when synthesizing metal oxide nanoparticles using PVA

and organic acids [8,9]. The temperature in here was greater than 400°C and the single phase of Fe<sub>2</sub>O<sub>3</sub> iron oxide was clearly formed. Therefore, the calcinating temperature 400°C was selected for the next experiments.

#### Effect of pH

Sample was synthesized by pH1, pH2, pH3, pH4 (equal pH = 1, 2, 3, 4 respectively). Other conditions such as gel forming temperature 80°C, ratio of TA/PVA = 1:1, ratio of Fe<sup>3+</sup>/(TA+PVA) = 1:3, calcinating temperature 400 °C. Figure 3 was shown X Ray diffraction diagram.

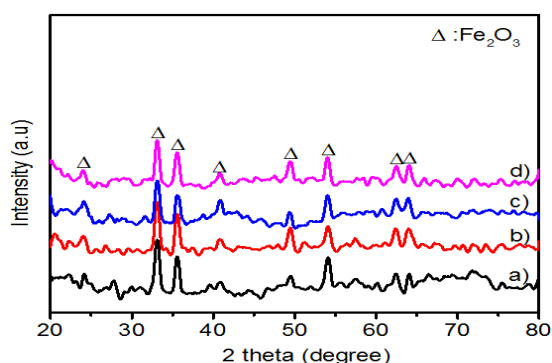


Figure 3: X-Ray diffractions at various pH a) pH1, b) pH2, c) pH3, d) pH4

The results in Figure 3 were shown that at different pH, the single phase of nano Fe<sub>2</sub>O<sub>3</sub> iron oxide was formed. This showed that the pH was little effect on the phase formation of iron oxide Fe<sub>2</sub>O<sub>3</sub>. However, to facilitate further experiments, pH3 was selected for the synthesis of Fe<sub>2</sub>O<sub>3</sub> nanoparticles.

#### Effect of ratio of TA/PVA

The samples were synthesized at fixed values of pH3, gel forming temperature 80°C, ratio of Fe<sup>3+</sup>/(TA + PVA) = 1/3, calcination temperature 400°C and changing the ratio between TA/PVA = 6:1, 3:1, 1:1, 1:3, 1:6. The analysis results of X-ray diffraction diagram were shown by Figure 4.

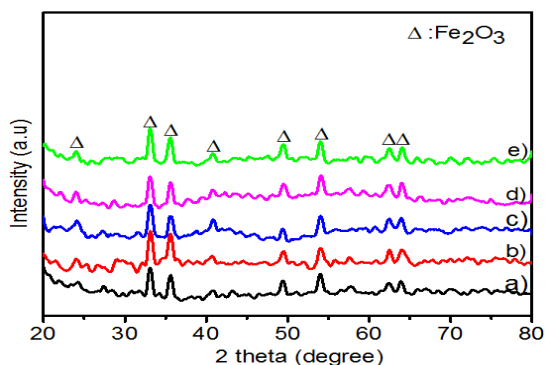


Figure 4: X Ray diffraction at different ratios of TA/PVA a) 6:1, b) 3:1, c) 1:1, d) 1:3, e) 1:6

The results in Figure 4 were shown that at different ratio values of TA/PVA, the single phase peaks of Fe<sub>2</sub>O<sub>3</sub> iron oxide nanoparticles were still formed. However, at the ratio of TA/PVA = 1:1, gel formation had more porous swelling. This could be that amount of TA and PVA was just enough to create metal ion complex and evenly dispersed in the PVA net. Therefore, here the ratio of TA/PVA = 1:1 was selected for the next study.

#### Effect of gel temperature

Samples were synthesized with fixed parameters such as calcinating temperature 400°C, pH3, ratio of TA/PVA = 1:1, ratio of Fe<sup>3+</sup>/(TA+PVA) = 1:3, changing gel forming temperatures 40°C, 60°C, 80°C, 100°C, respectively. The results were shown by figure 5.

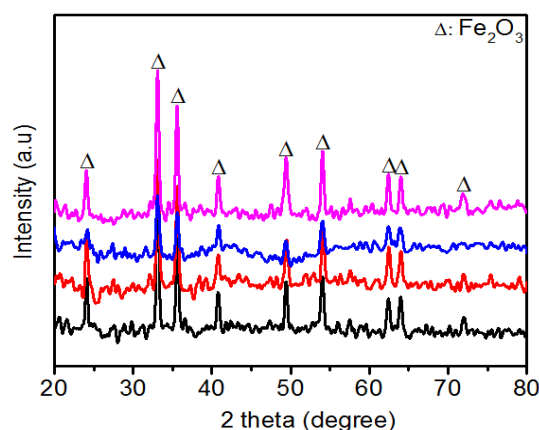


Figure 5: X-Ray diffraction at various temperatures of gel formation a) 40°C, b) 60°C, c) 80°C, d) 100°C

The results of Figure 5 were shown that the gel forming temperature was not effect the phase forming ability of Fe<sub>2</sub>O<sub>3</sub> iron oxide nanoparticles. However, the intensity and width peaks of samples at different temperatures was different. This affected to size of the oxide nanoparticles that were formed. When the gel temperature was increased 100°C, water was evaporated quickly and forming gel was not swelled and porous. At temperatures of 40°C and 60°C, the gel forming time was too long 6-8 hours. Gel forming temperature was selected 80°C with suitable gel forming time during 2 hours.

#### Fe<sub>2</sub>O<sub>3</sub> applications in methylene blue treatment

The optimal parameters were selected at calcinating temperature 400°C, pH3, ratio of TA/PVA = 1:1, ratio of Fe<sup>3+</sup>/(TA + PVA) = 1:3, gel forming temperature 80°C to synthesize sample. Fe<sub>2</sub>O<sub>3</sub> iron oxide particles were rod shape with size about 60 nm (Figure 6).

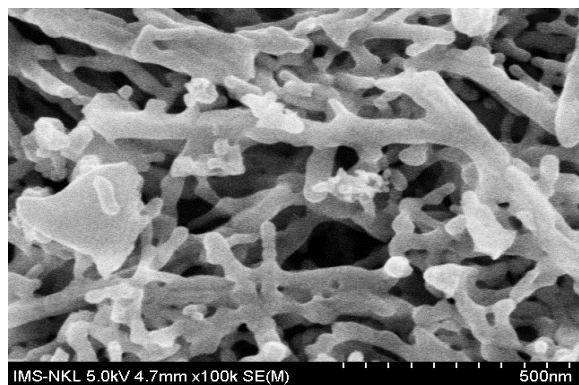


Figure 6: FE-SEM image of the Fe<sub>2</sub>O<sub>3</sub> samples at optimum condition

After successfully synthesizing nano oxide, Fe<sub>2</sub>O<sub>3</sub> was used as catalyst in MB degradation photocatalytic process. The results were shown in Figure 7.

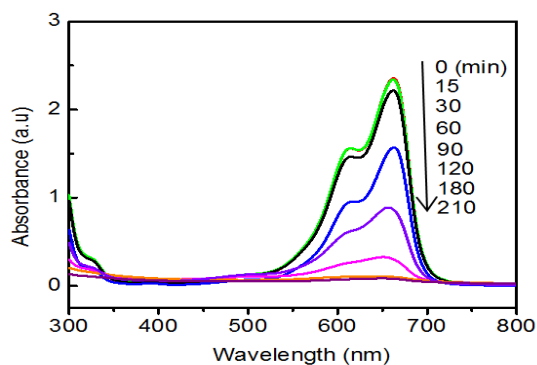


Figure 7: UV-vis absorption spectra of the MB solution during the decomposition reaction

Figure 7 was shown that at 15 minutes of the reaction, no decomposition of MB was happened. However, reaction times were increased from 30, 60, 90, 120, 180 to 210 minutes, efficiency was increased significantly (almost MB was decomposed). Several intermediates were formed during MB photocatalytic decomposition were analyzed. Because of formation of strong oxidizing radicals such as  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ , ... in the photocatalytic process, these strong oxidizing radicals attacked MB pollutant by cutting chain to form free radicals. as well as the process of ring opening,... then these free radicals were combined to form stable substances. The results were shown in Figure 8.

Figure 8 was shown that after reaction time 60 minutes, in addition to characteristic peak at m/z 283.9 (characteristic of MB), peaks at m/z 307, m/z 270, m/z 241, m/z 164.7, ... were formed during the reaction. By electron trap analysis, some intermediates were identified (Figures 9, 10, 11). The parent molecule with m/z 284 lost a methyl group corresponding to m/z 270. The peak of m/z 241 could be continued to lose a

methyl group from m/z 270. The peak of m/z 241 could be created by process of cutting and grafting free radicals. From thence, the MB degradation path to intermediate substances was proposed (Figure 12).

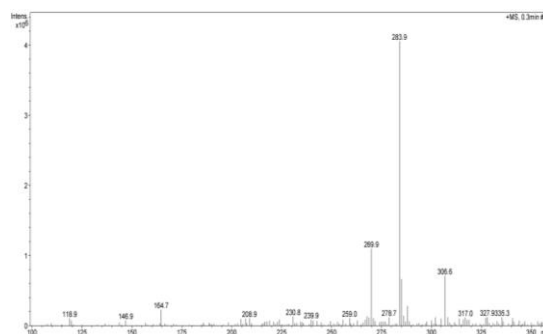


Figure 8: Mass spectrum of degradation products after reaction time 60 minutes

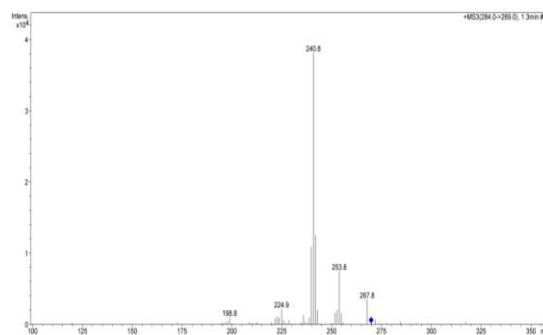


Figure 9: MS/MS of m/z = 270

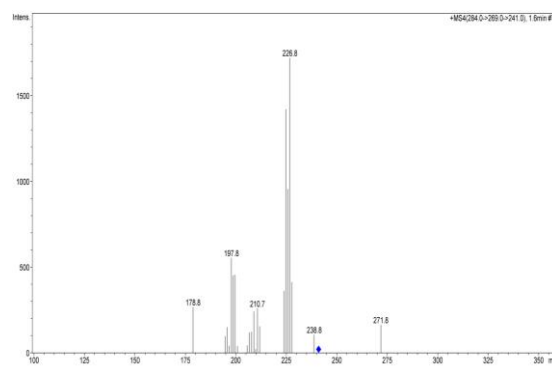


Figure 10: MS/MS of m/z = 241

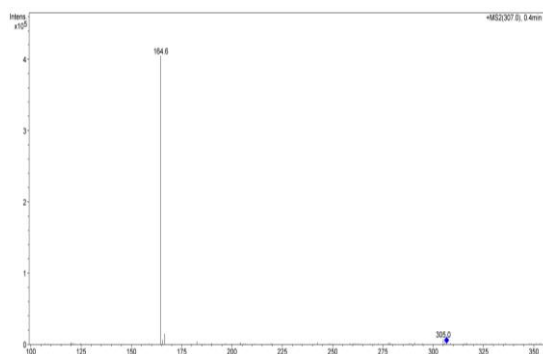


Figure 11: MS/MS of m/z = 307

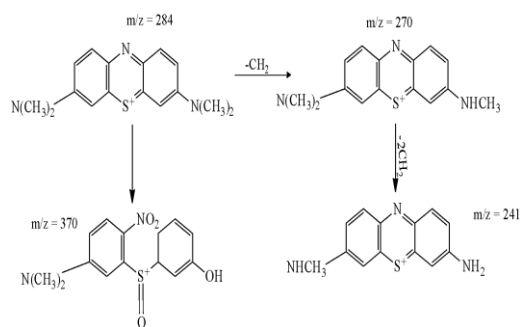


Figure 12: MB degradation path to intermediates

The process of decomposition of organic matter in the sample continued to form simple substances, facilitated to decomposed final products  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ . After reaction time 240 minutes, no organic compound was detected in the sample (figure 13). Therefore, MB was completely decomposed.

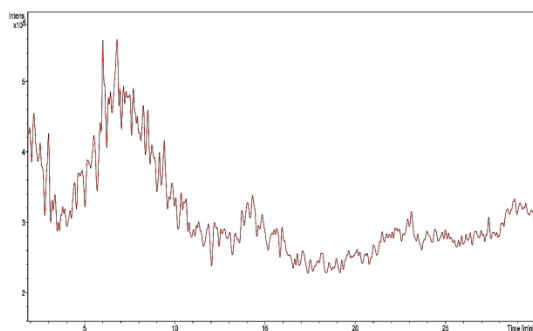


Figure 13: Mass spectrum of sample after reaction time 240 minutes

## Conclusion

$\text{Fe}_2\text{O}_3$  iron oxide nanoparticles were successfully synthesized by combustion method with gel-forming agent which was mixture of TA and PVA. Final product was synthesized by optimum conditions such as calcining temperature  $400^\circ\text{C}$  for 2h, pH3, ratio of TA/PVA = 1/1, ratio of Fe/(AT+PVA) = 1/3, gel forming temperature  $80^\circ\text{C}$ . The calcining temperature to form product was lower than calcining temperature when used PVA agent by equivalent synthetic conditions. The product had a rod-shaped structure with a size of about 16 nm and was used to decompose MB. After the reaction time 240 minute, almost of initial MB content were decomposed completely. Some intermediates formed during the reaction were identified.

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