

## ***Decomposition of Methyl Orange Color Using a Mixed Catalyst of Iron Oxides in Mesopore Silica with H<sub>2</sub>O<sub>2</sub> Oxidizers***

Steffi Diego Ochtafirma<sup>1</sup>, Hary Sanjaya<sup>1</sup>, Bahrizal<sup>1</sup>, Syamsi Aini<sup>1\*</sup>

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padang State University

Jl. Prof. Hamka, Air Tawar, Padang, West Sumatera, Indonesia

\*Email : [syamsiaini@fmipa.unp.ac.id](mailto:syamsiaini@fmipa.unp.ac.id)

\*\*\*\*\*

### **Abstract:**

Dyes are often used in the textile industry, one of which is methyl orange. Azo dyes are a depiction of a class of organic pollutants that have the potential to be carcinogenic which causes problems with the environment if they are dumped directly into the river without treatment. One method to degrade pollutants in water is the Fenton method with OH radical formation obtained from the reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> ions where these radicals will break down organic compounds into harmless compounds (H<sub>2</sub>O and CO<sub>2</sub>). Previously, it was successfully synthesized the composite catalyst Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> from iron sand and silica sand. To test the catalytic performance of the synthesized Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> of catalyst. The optimum conditions for the degradation of methyl orange with pH 2 by heterogeneous catalyst Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> at 120 minutes, and the amount of catalyst 150 mg. At these optimum conditions degradation efficiency reaches 97%.

**Keywords — Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>, Degradation, and Methyl Orange**

\*\*\*\*\*

### **I. INTRODUCTION**

The increasing textile industry in Indonesia, the more problems that arise. Industry involves coloring in its production [10]. The number of textile industries in Indonesia is not balanced with the processing of liquid waste properly. Textile industry uses synthetic dyes for cheap, durable, easy to obtain and easy to use. The use of synthetic textile dyes raises problems, namely the waste produced is still colored and difficult to degrade. Before being discharged into a water channel, textile coloring waste must be treated first because about 10% to 15% of the coloring agent that has

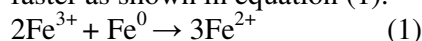
been used cannot be reused and must be disposed of [9].

The dyes often used are the azo group while these dyes have non-biodegradable properties [7]. One composition of the azo group is methyl orange where this compound is often used in the textile industry. Azo dyes are the most commonly found in textile soil, which is around 50% [4]. Dyestuffs are depictions of classes of organic pollutants involving carcinogenic [6].

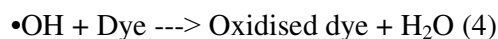
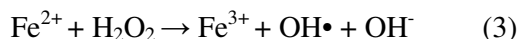
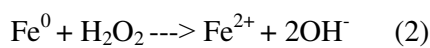
To degrade pollutants in water, many methods are carried out, one of which is the Fenton method, which is one method to degrade organic

compounds by forming OH hydroxide radicals. Furthermore, these free radicals will decompose organic compounds into harmless compounds (H<sub>2</sub>O and CO<sub>2</sub>) [3]. In the classic Fenton process OH hydroxide radicals are obtained from the reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> ions under irradiation conditions with either Ultra Violet (UV) or visible light, which is then called the Fenton Photo process or without irradiation called the Fenton process. In the Fenton hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) method it functions as an oxidizer and iron ion as a catalyst.

In principle Fe<sub>3</sub>O<sub>4</sub> can act as a catalyst due to reduction oxidation reactions of Fe<sup>+2</sup> and Fe<sup>+3</sup> with oxidant H<sub>2</sub>O<sub>2</sub> [7]. Reduction of Fe<sup>3+</sup> becomes Fe<sup>2+</sup> faster as shown in equation (1).



Decomposition of azo-dye requires OH hydroxide radical to break the double bond -N = N-. The formation of radicals OH begins with the oxidant reaction H<sub>2</sub>O<sub>2</sub> with Fe<sup>+2</sup> ions. Fe<sup>0</sup> is easily oxidized to Fe<sup>2+</sup> in the presence of oxidants.



The more hydroxyl radicals formed, the faster the methyl orange decomposition process.

In the previous study methyl orange degradation using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> catalyst with the Fenton method [8], where the optimum time was reached in 150 minutes and the degradation efficiency was less than 95%. Catalysts from different places have different structures and different activities too. Previous experiments have synthesized Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> catalyst composites from iron sand and silica sand with different compositions. To test the catalytic performance of the synthesized Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>, this study was conducted in order to determine the catalytic effectiveness of Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> against methyl orange and the optimum conditions of the degradation process.

## II. METHODS

The materials used are azo methyl orange dye, Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>, distilled water, and aquabides.

### A. Effect Of Time

50 ml of 10 ppm methyl orange solution was put in 100 mL erlenmeyer then set to pH 2 by adding HCl 0,1 M. Then Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> with the amount of catalyst 100 mg and add H<sub>2</sub>O<sub>2</sub> as much as 2 mL. The Erlenmeyer solution is stirred with a magnetic stirrer at certain times 30, 60, 120, 150, and 180 minutes. The catalyst residue was separated using a magnetic field. Pre and post decomposition concentrations were observed using UV-Vis spectrophotometry at a wavelength of 507 nm.

### B. Influence Of The Amount Of Catalyst

50 ml of 10 ppm methyl orange solution was put in 100 mL erlenmeyer then set to pH 2 by adding 0.1 M HCl. Then added Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> with catalysts of 20, 30, 50, 75, 100, 125, and 150 mg and add H<sub>2</sub>O<sub>2</sub> as much as 2 mL. The Erlenmeyer solution is stirred with a magnetic stirrer at the optimum time obtained in the procedure 1. The catalyst residue was separated using a magnetic field. Pre and post decomposition concentrations were observed using UV-Vis spectrophotometry at a wavelength of 507 nm.

The results of the analysis in the form of absorbance values at the measurement wavelengths, are converted to concentration and then calculated efficiency in percent form using the following equation:

$$\%D = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where,

C<sub>0</sub> = Initial dye concentration

C<sub>t</sub> = Final dye concentration

### III. RESULTS AND DISCUSSION

#### A. Effect Of Time

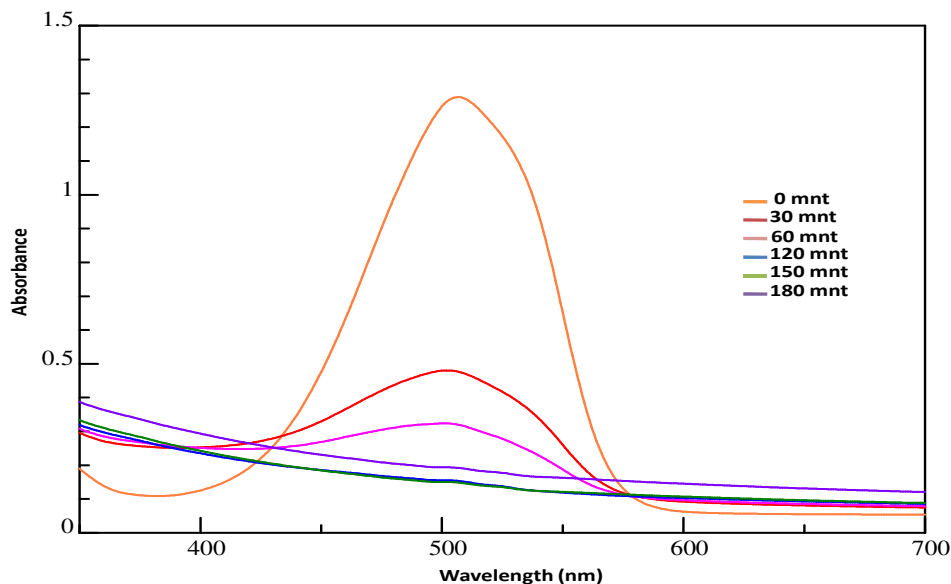


Fig. 1 The absorbance curve of methyl orange degradation in determining the optimal time condition.

Determination of the optimal time in the process of degradation of methyl orange using  $Fe_3O_4/Fe_2O_3@SiO_2$  catalyst is shown in Figure 2.

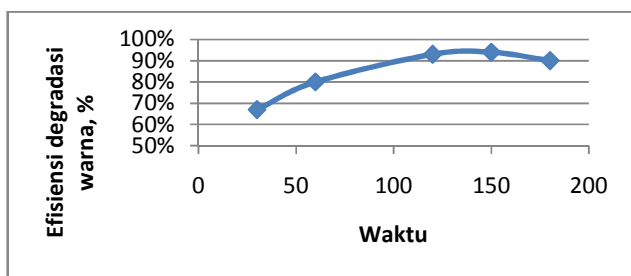


Fig. 2 Effect of time on the percentage of degradation of methyl orange

In an experiment to determine the optimum time of methyl orange solution using a mixture of iron oxide in mesoporous silica carried out at a volume of 50 mL waste solution; amount of 2 mL  $H_2O_2$  amount of  $Fe_3O_4/Fe_2O_3@SiO_2$  100 mg; pH of 2.0 solution. In Figure 2, it is clearly seen the effect of time on the efficiency of degradation of methyl orange. At up to 60 minutes, the degradation efficiency of methyl orange is still low, this is

because the catalyst material used is in the form of powder, so the time needed to form  $Fe^{2+}$  ions is slower [9]. The longer the degradation time, the degradation efficiency increases until an equilibrium state is reached, then the efficiency of the degradation will be constant or it can also decrease degradation efficiency. At 180 minutes there was a decrease due to instability in the multilayer due to the repulsion between the adsorbed molecules, causing the adsorption layer to be released back into the solution (desorption).

Compared with degradation using  $Fe_3O_4@SiO_2$  which breaks down <75% in 60 minutes of methyl orange, decomposition using  $Fe_3O_4/Fe_2O_3@SiO_2$  provides better results with 80% decomposition in 60 minutes and can reduce >95% methyl orange at optimal 120 minutes .

**B. influence of the amount of catalyst**

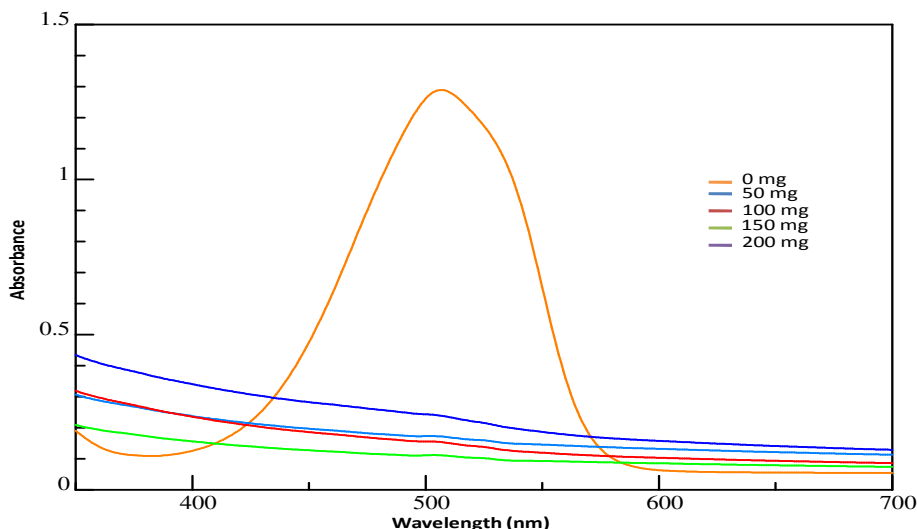


Fig. 1. The absorbance curve of methyl orange degradation in determining the optimum condition of the amount of catalyst.

The amount of catalyst in the Fenton process is very influential, this is evidenced in the results of the experiment of the degradation of orange methyl waste variations in the amount of catalyst shown in Figure 4.

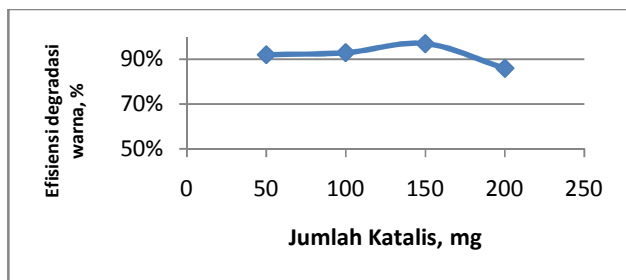


Fig. 5 Freundlich Isotherm

In Figure 2. it can be seen the effect of the amount of catalyst on the absorbance of the degradation of methyl orange waste. The use of  $Fe_3O_4/Fe_2O_3@SiO_2$  catalyst as much as 50 mg obtained a degradation efficiency of 92%, and if the amount of catalyst was increased to 100 mg, the degradation efficiency increased to 93%. Once

further in the use of a 150 mg catalyst, the degradation efficiency increased to 97%. This is because more and more catalysts, more free radicals are formed so that the degradation process is more efficient. However for the use of catalysts above 150 mg, the addition of a catalyst no longer increases the degradation efficiency significantly, even using 200 mg there is a decrease in efficiency. This is because excessive use of the catalyst in the Fenton process will block the incoming light so that the formation of  $OH^\bullet$  free radicals is disrupted, resulting in decreased degradation efficiency [10].

**IV. CONCLUSION**

Based on the research that has been done, it can be concluded that the optimum time for the degradation of methyl orange dyes using  $Fe_3O_4/Fe_2O_3@SiO_2$  at pH 2 is 120 minutes with the amount of catalyst as much as 150 mg. In these conditions degradation efficiency reached 97%.

**ACKNOWLEDGMENT**

The author thank Minister of Research and Technology of Indonesia, and LP2M UNP who have provided research grants, Penelitian Unggulan

Perguruan Tinggi (PUPT) 2019, for Synthesis and characterization of  $\text{Fe}_2\text{O}_3$ , immobilized in mesoporous silica based on green chemistry as a heterogeneous catalyst for Azo-dye decomposition study.

## REFERENCES

- [1] AlOthman, A. Z. 2012. A Review: Fundamental Aspects of Silicate Mesoporous Materials. *Materials* 2012, 5, 2874-2902; doi: 10.3390/ma5122874.
- [2] Blackburn, R.S., dan Burkinshaw, S.M. 2002. *A Greener to Cotton Dyeing With Excellent Wash Fastness*, Green Chemistry, 4, pp. 47-52.
- [3] Gan, N.; X, Du.; Y, Cao.;F, Hu.; T, Li dan Q, Jiang. 2013. An Ultrasensitive Electrochemical Immunesensor For HIV Based On  $\text{Fe}_3\text{O}_4@/\text{SiO}_2$  Nanomagnetic and Nanogold Colloid Labelled Enzyme Antibody Copolymer As SignalTag. *Materials*, 6, 1355-1360.
- [4] Garcia, J., Ruiz, N., Munoz, I., Domenech, X., Garcia-Hortal, J.A., Torrades, F., Peral, J. 2006. *Environmental Assessment Of Different Photo-Fenton Approaches For Commercial Reactive Dye Removal*, J, Hazard, Mater, A138, pp 218–225.
- [5] Rajeshwar, K., Osugi, M.E., Chanmanee, W., Chenthamarakshan, C.R., Zaroni, M.V.B., Kajitvichyanuku, P., and Krishnan-Ayer, R. 2008. Review: Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media, *J. Photochem. Photobiol.*, C.9, pp.15-36.
- [6] Rashed, M.N., El-Amin, A.A. 2007. Photocatalytic Degradation of Methyl Orange in Aqueous  $\text{TiO}_2$  under Different Solar Irradiation Sources, *Internasional Journal of Physical Science*, Vol. 2, No.3, 073-081.
- [7] Ruzicka, O. dan L. Safira. 2014. Aplikasi Fotokatalis  $\text{TiO}_2$  Pada Degradasi Limbah Cair Zat Warna Tekstil, Lomba Karya Ilmiah Sumber Daya Air Tahun 2014.
- [8] Siti Wardiyati, Degradasi Senyawa Organik Menggunakan Metoda Fenton, Disampaikan Pada Seminar Nasional XV Kimia Dalam Pembangunan Di Hotel Phoenix Yogyakarta, 06 September 2012.
- [9] Wardiyati, S., Winatapura, D.S., and Wisnu, A.A, Influence of  $\text{Fe}_3\text{O}_4$  addition in  $\text{TiO}_2$  catalyst on degradation of methylene blue, telah sieminrkan di The 9<sup>th</sup> Seminar on Manetic Material, October 19-21, 2015, Palembang.
- [10] Wijaya, K., Tahir, I., Haryanti, N. 2005. Sintesis  $\text{Fe}_2\text{O}_3$ -Montmorilonit Dan Aplikasinya Sebagai Fotokatalis Untuk Degradasi Zat Pewarna Congo Red, *Indonesian Journal of Chemistry*, 5(1), 41-47.