Synthetize of Nano Particles α-Fe₂O₃ Material from Waste Magnetic Filter Ceramic Tile Industry Prepare by Calcination Method as Photocatalyst Degradation of Methylene Blue

Anggi Ayuningtiyas¹, Eko Prabowo Hadisantoso¹, Kristanto Wahyudi²
¹ State Islamic University of Sunan Gunung Jati (UIN, Bandung)
² Center For Ceramic (Balai Besar Keramik, Bandung)

E-mail: anggianggi585@gmail.com

Abstract. Recently, there has been a lot of research on the synthesis of hematite nanoparticles, due to its properties and application in renewable energy and environmental remediation. Hematite is suitable for photocatalyst material since the advantages of its properties which is stable under ambient conditions, resistance to corrosion, cheapest and have narrow band gap. However, the potential raw material which rich of iron oxide can be supplied from waste magnetic filter in ceramic tile industries. In this paper, synthetize nano particles hematite was studied using calcination method. Raw materials originated from waste magnetic filter one of ceramic manufacturer in West Java. Raw material was calcined at temperature 800 °C and 900 °C then applied as photodegradation of methylene blue. The XRD analysis showed that nanoparticles hematite was formed gradually according to calcination temperature. The best photodegradation results were obtained by 0,11 g mass nanoparticles hematite, during 3 hours under irradiation visible light.

1. Introduction
Nowadays, Indonesia is the seventh largest ceramic tile producer in the world [1]. Most of the manufacture spread on Java and produce red ceramic tile from local raw materials such as clay and feldspar. Both raw material rich iron oxide particles including wustite (FeO), hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄) mineral. Those iron oxide particles can cause black core which reduce quality of ceramic tile surface visually. Magnetic filtering is used to remove iron oxide particle in the raw material preparation process [2]. The result of this filtering process is solid waste which richly iron oxide. Currently, the utilization of magnetite filter waste still rarely done. One of potentials is to utilize that waste into nanoparticles hematite (α-Fe₂O₃) as photocatalyst material.

Hematite is suitable for photocatalyst material since the advantages of its properties which is stable under ambient conditions and in most aqueous solutions (pH > 3), resistance to corrosion and the cheapest n-type semiconductor which its properties has a narrow band gap of approximately 2.0–2.2 eV. make it efficient absorption light up to 600 nm and collect up to 40% of the solar spectrum energy [3-7]. Photocatalysis process is initiate and boost up chemical reaction that involve the absorption of light by a catalyst [8]. Photocatalysis by hematite has been used to degrade organic pollutants such as aromatics, dyes because it can convert pollutants into harmless organic, at ambient condition, low cost and high efficiency using UV and visible light [8-10]

There are various methods to synthetize nano particles hematite including precipitation [4], hydrothermal [5,6], solvothermal methods, ionic liquid assisted synthesis, combustion methods,
thermal decomposition, polymeric precursor [6], sol-gel and calcination [3]. The advantages of calcination method are controlled the particles size and mineral shape, no chemical materials usage, simple and large quantity production.

The purpose of this study is focused on synthetize nano particles $\alpha$-Fe$_2$O$_3$ by calcination method by magnetic filtering waste precursor. Microstructure and photocatalytic properties of nano particles $\alpha$-Fe$_2$O$_3$ were investigated.

2. Experimental
2.1. Materials Preparation
Magnetic filter waste material was obtained from one of ceramic tile manufacture in West Java. Waste material was milled for 24 hours then proceed decantation to separate clay and iron particle masses. Decantation process resulted 33% deposition of black mass contain iron oxide particles. The mass of deposition then dried to 19 hours at 110 $^\circ$C. The deposition masses were calcined in the electric furnace at temperature rate 2.5 $^\circ$C/minute and held 1 hour at designed temperature 800 $^\circ$C and 900 $^\circ$C to produce nano particles $\alpha$-Fe$_2$O$_3$.

The organic dye used was methylene blue. Before measuring the intensity reduction in the sample, a calibration curve was made as a standard, see Fig. 1. This curve was made by measuring the absorbance of the standard solution of methylene blue with concentrations of 1, 2, 3, 4, and 5 ppm using a UV-Vis spectrophotometer at the maximum wavelength. Determination of the maximum wavelength was done by measuring the standard solution of methylene blue 1 ppm. The result of maximum length was 664 nm. The regression equation with $y = 0.2114x - 0.0038$ would be used to calculate the concentration of the methylene blue solution after photodegradation.

![Figure 1. Calibration curve of methylene blue](image)

2.2. Method and Characterization
Photodegradation of concentration of 10 ppm was observed for variation of $\alpha$-Fe$_2$O$_3$ mass for 0.01 g, 0.03 g, 0.05 g, 0.07 g, 0.09 g and 0.11 g and irradiation time of UV light and visible light for 3 hours. Next photodegradation was observed for 0.11 gr $\alpha$-Fe$_2$O$_3$ mass and variation of UV light and visible light irradiation time for 1 – 3 hours by interval 0.5 hour.

The identification of crystal phases was carried out by X-ray powder diffraction (XRD) technique. X-ray analysis was used to examine the present phases, the degree of crystallinity and crystallites size of hydroxyapatite. Phases identification was assessed by comparing the diffraction pattern with ICDD-PDF2 standards. Degree of crystallinity ($X_c$) was studied by equation below:

$$X_c = \frac{I_{300} - V_{112/300}}{I_{300}} \times 100 \%$$

(1)
where $I_{300}$ was intensity of (300) peak and $V_{112/300}$ hollow intensity between peak 112 and 300. The size of crystallites was calculated using following Scherrer’s equation:

$$D = \frac{K\lambda}{\beta\cos(\theta)}$$  \hspace{1cm} (2)

where $K$ was crystals constant, $\lambda$ was radiation wavelength, $\beta$ was full width of peak from the intensity distribution pattern measured at half of the maximum intensity value, and $\theta$ was the Bragg angle in degree.

3. Results and discussions

3.1. Mineralogical characterization of calcination results

It could be seen that both 2θ of calcination at 800 °C and 900 °C had similarities to 2θ standard of $\alpha$-Fe$_2$O$_3$ based on ICSD 98-002-2505. These results indicated that $\alpha$-Fe$_2$O$_3$ was successfully synthesized by calcination method at temperatures of 800 °C and 900 °C, see Fig. 2.

![XRD Pattern](image)

**Figure.** 2 XRD Pattern F0 (non-calcination), F8 (calcination at 800 °C) and F9 (calcination at 900 °C)

According to Table 1. Crystallinity based on equation (1) reported 46.09% for calcined 800 °C and 37.84% for calcined 900 °C. Crystallites size based on Debye-Scherer equation (2) calculated 18.45 nm for calcined 800 °C and 19.87 nm for calcined 900 °C. The differences of crystallites sizes might come from agglomeration process of $\alpha$-Fe$_2$O$_3$.

| $2\theta$ of $\alpha$-Fe$_2$O$_3$ standards, F0, F8 and F9 |
|----------------------------------------------------------|
| $\alpha$-Fe$_2$O$_3$ standards | F0 | F8 | F9 |
| 24.15 | - | 24.17 | 24.02 |
| 33.16 | 33.04 | 33.18 | 33.26 |
| 35.64 | 35.52 | 35.62 | 35.70 |
| 40.87 | - | 40.92 | 40.92 |
| 49.47 | 49.19 | 49.48 | 49.58 |
| 54.08 | 53.61 | 54.08 | 54.18 |
| 62.45 | 62.47 | 62.47 | 62.56 |
| 64.02 | - | 64.06 | 64.08 |

3.2. Photocatalytic Degradation of Methylene Blue
The rate of photodegradation of methylene blue solution using α-Fe₂O₃ 800 °C and 900 °C for different mass under irradiation UV and visible light are displayed in Fig. 3(a) and (b), respectively. Under UV light and visible light for 3 hours, the photodegradation rates of α-Fe₂O₃ 800 °C and 900 °C rise up accordance increasing of mass nanoparticles with maximum 50.62%. In Fig. 3(c) and (d), the photodegradation of methylene blue solution will increase since time lapse of irradiation for 1 to 3 hours. There were differences photodegradation results between irradiation by UV light and visible light. Irradiation visible light showed superiority than irradiation UV light. The higher result was 70.07% of photo degradation.

All results show that increasing mass, the greater the% value of the degradation of methylene blue. This was caused the more α-Fe₂O₃, the more hydroxyl radicals (*OH) were produced, thereby enhancing the degradation of methylene blue. The amount of degraded methylene blue showed the higher activity of α-Fe₂O₃ photocatalyst. Nano particles α-Fe₂O₃ would receive energy by the irradiation of light, then electrons from the valence band would be excited to the conduction band which results in a hole (h+) in the valence band. The hole then accepted electrons from the water and formed a hydroxyl radical (*OH). While the electrons in the valence band would be negatively charged which reduced oxygen and produced super oxide anions (O²⁻). This super oxide anion and hydroxyl radical would degrade methylene blue compounds into CO₂ and H₂O which safe for the environment.

![Figure 3. Photocatalyst degradation of methylene blue](image-url)
The rays used in this research are UV light and visible light. UV light has a wavelength of 200-400 nm while visible light has a wavelength of 400-700 nm. According to Max Planck's law, energy is inversely proportional to wavelength. The larger the wavelength, the less energy produced. Therefore, in the photocatalyst, light is very important because it determines the energy absorbed by the catalyst. In a photocatalyst in order for the semiconductor to excite, the energy absorbed by the semiconductor must be equal to or greater than the semiconductor's bandgap [18].

Based on XRD diffractogram pattern nanoparticles α-Fe₂O₃ can be obtained by calcination method at temperature 800 °C and 900 °C. Increasing temperature calcined caused decreasing of crystallinity of nanoparticles α-Fe₂O₃ from 46.09% to 37.84% and the size of crystallite increase from 18.45 nm to 19.87 nm. Photocatalyst perform that degradation of methylene blue occur significantly for both calcination temperature and both light irradiations. Enhancement of mass and irradiation time can increase photodegradation. The most photodegradation is 70.07% which is achieved by 0.11 g nanoparticles α-Fe₂O₃ calcined 800 °C under irradiations of visible light.

4. Conclusion
In this study, nanoparticles α-Fe₂O₃ has been produced by calcination method from magnetic filter waste from ceramic tile industry. Photocatalyst properties of α-Fe₂O₃ has successfully degraded methylene blue. The largest photodegradation is showed by nanoparticles α-Fe₂O₃ calcined 800 °C under irradiations of visible light.

Acknowledgments
This research was supported by Center for Ceramic (Balai Besar Keramik), Ministry of Industry.

References
[1] Luca Baraldi 2017 World Production And Consumption Of Ceramic Tiles MECS - Machinery Economics Studies by ACIMAC
[2] Juliana Costa Silva 2019 Carina Ulsen, Mauricio Guimarães Bergherman, Daniela Gomes Horta Reduction Of Fe₂O₃ Content Of Foyaite By Flotation And Magnetic Separation For Ceramics Production Journal Material Research And Technology 8(5) 4915–4923
[3] Kazeminezhad and S. Mosivand 2014 Phase Transition of Electrooxidized Fe₃O₄ to γ and α-Fe₂O₃ Nanoparticles Using Sintering Treatment I. Acta Physica Polonica A 125 1210-1214
[4] Jimmy Alexander Morales-Morales 2017 Synthesis Of Hematite α-Fe₂O₃ Nano Powders By The Controlled Precipitation Method Ciencia en Desarrollo 8(1) 99-107
[5] A. Lassoed, M.S. Lassoed, B. Dhkhl, S. Ammar, A. Gadri Synthesis 2018 Photoluminescence And Magnetic Properties Of Iron Oxide (α-Fe₂O₃) Nanoparticles Through Precipitation Or Hydrothermal Methods Physica E: Low-dimensional Systems and Nanostructures
[6] M. Mishra, D.-M. Chun 2015 alpha-Fe₂O₃ As a Photocatalytic material: A Review Applied Catalysis A, General
[7] Muhamad Muhajir, Poppy Puspitasari, Jeefferie Abdul Razak 2019 Synthesis And Applications Of Hematite α-Fe₂O₃: a Review Journal of Mechanical Engineering Science and Technology 3(2) 51-58
[8] C.N.C. Hitam, A.A. Jalil 2020 A Review On Exploration Of Fe₂O₃ Photocatalyst Towards Degradation Of Dyes And Organic Contaminants Journal of Environmental Management 258 110050
[9] Surya Lubis, Ilham Maulana and Masyithah 2018 Synthesis And Characterization Of TiO₂/α-Fe₂O₃ Composite Using Hematite From Iron Sand For Photodegradation Removal Of Dye Journal Natural 18(1)
[10] Nick Joaquin Rapadas and Mary Donnabelle L. Balela Hydrothermal 2017 Synthesis Of Hierarchical Hematite (α-Fe₂O₃) Microstructures for Photocatalytic Degradation of Methyl Orange Philippine Journal of Science 146 (4) 395-402
[11] Rong Li, Yuefa Jia, Naijing Bu, Jun Wu, Qiang Zhen 2015 Photocatalytic Degradation Of
Methyl Blue Using Fe₂O₃/TiO₂ Composite Ceramics *Journal of Alloys and Compounds* **643** 88–93

[12] Esmaeel Darezereshki, Fereshteh Bakhtiari, Mostafa Alizadeh, Ali Behradvakylabad, Mohammad Ranjbar 2012 Direct Thermal Decomposition Synthesis And Characterization Of Hematite (α-Fe₂O₃) Nanoparticles *Materials Science in Semiconductor Processing* **15** 91–97

[13] Yan Wang, Weiping Du, and Yiming Xu 2009 Effect of Sintering Temperature on the Photocatalytic Activities and Stabilities of Hematite and Silica-Dispersed Hematite Particles for Organic Degradation in Aqueous Suspensions *Langmuir* **25**(5)

[14] Marta Valášková, Jonáš Tokarský, Jirí Pavlovský, Tomáš Prostejovský and Kamila Koci 2019 α-Fe₂O₃ Nanoparticles/Vermiculite Clay Material: Structural, Optical And Photocatalytic Properties *Materials* **12** 1880

[15] Ibrahim Abdulkadir, Hafiz M.I. Abdallah Sreekantha B. Jonnalagadda and Bice S. Martincigh 2018 The Effect Of Synthesis Method On The Structure, And Magnetic And Photocatalytic Properties Of Hematite (α-Fe₂O₃) Nanoparticles *South African Journal of Chemistry* **71** 68–78

[16] S Lubis, Sheilatina and Murisna 2018 Synthesis Characterization and Photocatalytic Activity of α-Fe₂O₃ /Bentonite Composite Prepared by Mechanical Milling *SEMIRATA- International Conference on Science and Technology Series: Journal of Physics: Conf. Series* **1116**

[17] F.B. Li, X.Z. Li, C.S. Liu, T.X. Liu 2007 Effect Of Alumina On Photocatalytic Activity Of Iron Oxides For Bisphenol A Degradation *Journal of Hazardous Materials* **149** 199–207

[18] M. Imran, A. Abutaleb, M. A. Ali, T. Ahamad, A. R. Ansari, M. Shariq, D. Lolla dan A. Khan 2020 UV Light Enabled Photocatalytic Activity Of A-Fe₂O₃ Nanoparticles Synthesized Via Phase Transformation *Materials Letters* **258** 1-4