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THE EFFECT OF ANNEALING TEMPERATURE GROWTH ON Fe-TiO_2 THIN FILM PHOTOACTIVITY IN METHYLENE BLUE

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Abstract: *The purpose of this study is to determine the effect of annealing temperature growth on Fe-TiO_2 thin film photoactivity. This was made by mixing TTIP, AcAc, ethanol, and Iron Nitrate Nanohydrate, after which the obtained mixture was sprayed and annealed on the substrate for two hours using the coating method. The temperature was increased to 500°C, 550°C, and 600°C, with the thin film photoactivity determined in methylene blue using UV light for 5 hours with decreasing values of COD, BOD, and absorbance. The results show annealing temperature growth increased photoactivity of the thin film. The highest photoactivity at 600°C in degrading methylene blue with decreasing values of COD, BOD, and absorbance was 19.56%, 35.84%, and 66.70%, respectively.*

Keywords: *annealing temperature, Fe-TiO_2, methylene blue, photoactivity*

INTRODUCTION

Titanium dioxide (TiO_2) in the form of powder and thin films is widely known to have good photoactivity (Jami, Dillert, Suo, Bahnemann, & Wark, 2018; Alhaji et al, 2017) and has been used to overcome various environmental problems (Haider, Anbari, Corre, & Ferrão, 2017). This compound has been used to degrade pesticides (Abdennouri et al., 2016), cosmetic liquid waste (Pulicharla et al., 2014), municipal wastewater (Kanakaraju, Glass, & Oelgemoller, 2014), textile waste (Naimah, Ardhanie, Jati, Aidha, & Arianita, 2014), and methylene blue which happens to be one of the most commonly used dyes in the textile industry (Ibrahim, 2017).

Its use causes textile waste contaminated with a threshold concentration of around 5-10 mg/L in permitted waters (Hadayani, Riwayati, & Ratnani, 2015). The textile waste contains dyestuffs around 20-30 mg/L, which disrupts water ecosystems (Huda & Yulitaningtyas, 2018).

The ability of a compound to degrade a solution with the aid of light is called photoactivity. Several factors affect the photoactivity rate of TiO_2, such as surface area, crystal structure, and size, thickness and energy gap (Kaltsum, Kurniawan, Nurhasanah, & Priyono, 2016). One way to increase it is by adding a dopant that plays a role in minimizing the energy gap (Karim, Pardoyo, & Subagiyo, 2016). These could be metals such as Fe, Ag, Al, Mn, Cu, Y, Ga (Pradana, Sutanto, & Hidayanto, 2017) or non-metals such as N, S, C, B, P, I, F (Durri & Sutanto, 2015). Another way to enhance the photoactivity of thin films is the formation of crystal structures, which is affected by the annealing temperature. The sequence of phases is based on the ability of three crystal structures namely rutile, anatase, and brookite. However, to produce the brookite phase is technically more difficult than anatase and rutile (Di Paola, Bellardita, & Palmisano, 2013). In this study, a thin film of anatase phase will be created. The phase which begins to form at 500°C, creates varying annealing temperatures of 500°C, 550°C, and 600°C. Therefore, in this study, a thin film of TiO_2 with dopant Fe (Fe-TiO_2) will be created, with the annealing temperature varied to determine its photoactivity in methylene blue.

Photoactivity of TiO_2 thin film with dopants given in methylene blue has been studied (Kumar, Rashid, & Barakat, 2015). The more the dose of Ag/TiO_2, the more significant the decrease in absorbance. In previous studies (Kaltsum & Saefan, 2017), thin films of TiO_2 and Fe-TiO_2 succeeded in degrading peroxide value (PV) and free fatty acid (FFA) in cooking oil. The degradation produced by Fe-TiO_2 thin film is greater than TiO_2. The use of Fe-TiO_2 thin film created by the sol-gel method at a temperature of 500°C successfully degraded methylene blue by visible light sources for 3 hours. The parameters used to determine the degradation are concentration differences of methylene blue before and after irradiation (Anwar & Mulyadi, 2015). In this study, the thin film of Fe-TiO_2 was created by the spray coating method, UV light source, irradiation time for 5 hours, variation in annealing temperature, and degradation parameters of COD, BOD, and absorbance. The use of a UV light source and 5 hours irradiation time is to keep the light intensity constant with a significant decrease in the degradation parameter value.

METHOD

This research includes the creation, characteristics, and photoactivity of Fe-TiO_2 thin films testings using methods similar to the previous study (Kaltsum & Saefan, 2017). In the previous study, Fe-TiO_2 thin film was annealed at 500°C and applied to degrade the PV and FFA contents in used cooking oil. In this study, the thin annealing temperature was varied and applied to degrade methylene blue. The precursor solution is a mixture of Titanium tetraisopropoxide (TTIP), Acetylacetone (AcAc), ethanol, and Iron Nitrate Nanohydrate. The sprayed substrate is annealed at a temperature of 500°C, 550°C, and 600°C.

The formed thin film is tested for its characteristics (morphology, crystal structure, and optics) and photoactivity. These characteristics are sequentially tested by scanning the electron microscope (SEM), x-ray diffractometer (XRD), and UV-vis spectrometer. Photoactivity of the thin film was certified on methylene blue 5 ppm solution using UV light 10 watts Sankyo Denki brand type G10T8 for 5 hours. The *methylene blue* solution before and after irradiation was used to measure the chemical oxygen demand (COD), biochemical oxygen demand (BOD), and absorbance .

Methylene blue ($C_{16}H_{18}N_3C_lS$), one of the chemical dyes widely used in the textile industry, has an aromatic hydrocarbon structure with very strong adsorption power (Hadayani et al., 2015). This compound is toxic to the environment and humans. Thus its presence needs to be degraded.

RESULTS AND DISCUSSION

The characteristics of the thin film

The results of testing the thin film characteristic include morphology, crystal structure, and optical character. The morphology of the thin film is the surface image and thickness, the crystal structure comprises of its type and grain size, while the optical character is the absorbance and energy gap.

The morphology of the thin film

The morphological test results of the three thin films are shown in Figures 1 and 2. The thin film annealed at 500°C has rather large, tenuous and uneven grains with an average thickness of 0.049 μm. At

550^oC it is tight, with smaller grains, and an average thickness of 0.060 μm. However, at 600^oC it has tiny and tight grains, with an average thickness of 0.049 μm. The thickness of the same thin film at the annealing temperature of 500^oC and 600^oC illustrates the number of grains formed at a temperature of 600^oC is greater, despite its smaller size. The results of this morphology test show that an increase in the annealing temperature of the thin film minimizes the size of the grain because it was accompanied by the creation of grains (Sutanto & Wibowo, 2015). The increase in annealing temperature does not show a linear relationship with thickness. However, increasing it from 500^oC to 550^oC enhances the thickness of the thin film, while an increase from 550^oC to 600^oC decreases the thickness. Increased thickness with an increase in annealing temperature is also shown by Vidhya, R., Sankareswari, M., Neyvasagam in the Cu-TiO_2 layer (Vidhya, Sankareswari, & Neyvasagam, 2016). The decrease in thickness occurs because increasing the annealing temperature grows the grain responsible for enhancing the densification process followed by the shrinking of the film thickness (Sinaga, 2009).

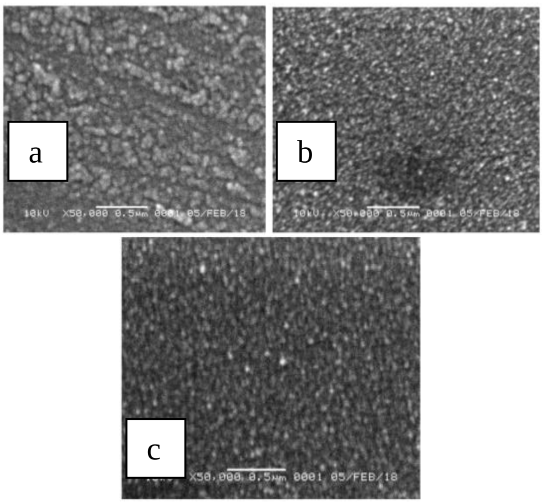

Figure 1. Surface image of Fe-TiO_2 thin film at annealing temperature (a) 500^oC, (b) 550^oC, and (c) 600^oC

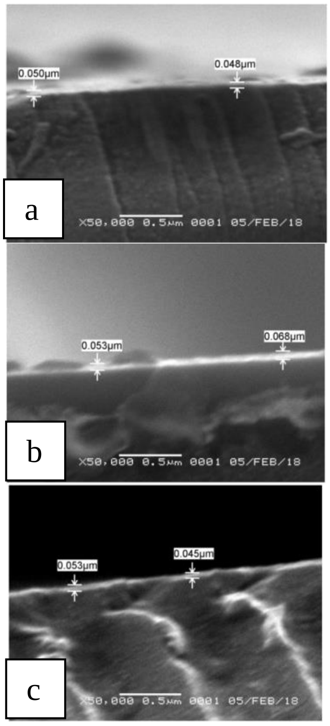

Figure 2. The cross section of the Fe-TiO_2 thin film at annealing temperature (a) 500 ^0C , (b) 550 ^0C, and (c) 600 ^0C

The optical characteristic

The results of the absorbance test of the three thin films are shown in Figure 3. Fe-TiO_2 thin film annealed at 500^oC and 600^oC has the same absorbance spectrum, while annealed Fe-TiO_2 at 550^oC has a small spectrum. The size of the absorbance spectrum is affected by the thickness and surface of the thin film. The thicker the thin film, the more light absorbed. The annealed thin film at 500^oC and 600^oC is thicker with a large absorbance value than the thin film annealed at 550^oC because both have a smaller thickness.

Uneven and non-homogeneous films will scatter more light than a flat and homogeneous film. The annealed film at 600^oC has a more homogeneous surface. The surface order of the thin film also affects absorbance.

The absorbance spectrum data is used to determine the energy gap by the Touch plot method using equation (1).

$$ahv = A(hv\text{-}E_g)^{\frac{1}{2}} \qquad (1)$$

A is constant, a denotes the *absorbance* coefficient, hv the energy of the photon and E_g energy gap. The results of the energy gap calculations of the three thin films are shown in Table 1.

Table 1. Energy gap Value in Fe-TiO_2 Thin Film

Thin Film Fe-TiO_2	Energy gap (Eg)
500 ^{0}C	3,58 eV
550 ^{0}C	4,04 eV
600 ^{0}C	3,52 eV

The value of the energy gap is influenced by absorbance. A large absorbance value causes more energy to be absorbed, thereby, decreasing the energy gap (Sutanto & Wibowo, 2015). The value of the energy gap of Fe-TiO_2 annealed at temperatures of 500ºC and 600ºC is small owing to their large absorbance.

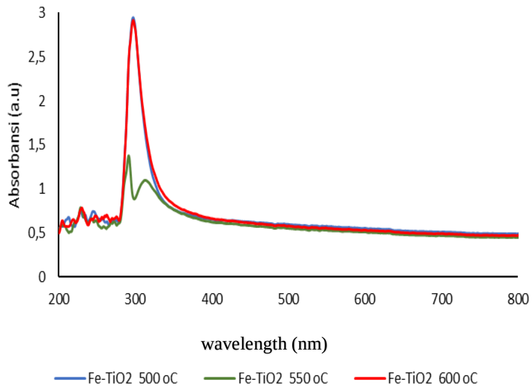

Figure 3. The absorbance spectrum of Fe-TiO_2 thin film at an annealing temperature of 500ºC, 550ºC, and 600ºC

The Crystal structures

The crystal structure of the three thin films is shown in the graph of the diffraction pattern of intensity vs. angle (2ϴ) in Figure 4-6. In the Fe-TiO_2 thin film, the annealing temperature of 500ºC was obtained at two peaks at angles 27.84º and 33.3º which corresponds to the plane (110) of the rutile TiO_2 and anatase (104) TiO_2 plane, respectively. In the second thin film, Fe-TiO_2 annealing temperature of 550ºC found three peaks of intensity at angles 24,68º, 28,62º and 37,7º which corresponded sequentially to anatase (101), (006), and (110) TiO_2 planes. Unlike the other two thin films, that of Fe-TiO_2 600^{0}C annealed temperature did not find prominent peak intensity correspond to TiO_2. This might be because at 600ºC, the crystal phase changes from anatase to rutile.

XRD diffraction pattern data can also be used to determine the size of the grain using the *Scherrer* equation (2),

$$D = \frac{K\lambda}{B\cos\Theta} \tag{2}$$

D denotes the size of the grain, K the material constant, the λ wavelength of the light source, B the *Full Width at Half Maximum* (FWHM), and ϴ the angle twisted. The results of the calculation of grain size are presented in Table 2. It is the average size of each grain. This result indicates an increase in the annealing temperature required to reduce the size of the grain in accordance with the appearance of morphology obtained from the SEM test results.

Table 2. The grain size of Fe-TiO_2 thin film

Thin film Fe-TiO_2	Grain size (nm)
500 ^{0}C	3,590
550 ^{0}C	2,605
600 ^{0}C	2,530

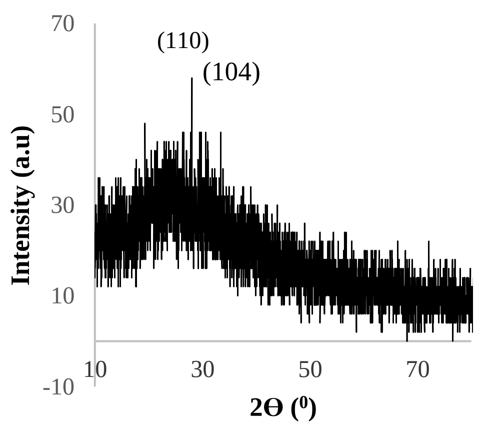

Figure 4. The diffraction pattern of Fe-TiO_2 thin film at an annealing temperature of 500^{0}C

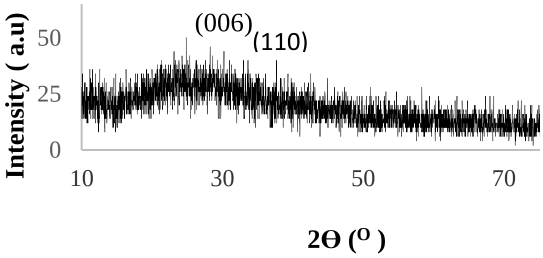

Figure 5. The diffraction pattern of Fe-TiO_2 thin film at the annealing temperature of 550^0C

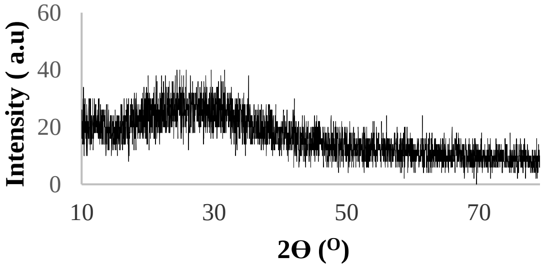

Figure 6. The diffraction pattern of Fe-TiO_2 thin film at an annealing temperature of 600^0C

Photoactivity of Thin Film

Photoactivity of Fe-TiO_2 thin films is tested on methylene blue using UV light for 5 hours. The parameters used are the degradation of COD, BOD, and absorbance as presented in Table 3. It analyzed that the ability to degrade them in sequence from the highest is Fe-TiO_2 thin film annealing temperatures of 600^0C, 550^0C, and 500^0C. The degradation of COD, BOD, and absorbance in Fe-TiO_2 thin films of 600^0C annealing temperature was 19.56%, 35.84%, and 66.70%, respectively. These results show that increasing annealing temperature enhances the photoactivity of thin films. Another study showed that Fe-TiO_2 thin films successfully degraded 99.5% methylene blue (pH 10) with concentration parameters (Anwar & Mulyadi, 2015). The concentration value is proportional to absorbance. The study difference is in the method used to create thin films, irradiation time, light sources, degradation parameters, and pH of methylene blue samples. The pH of the blue methylene in this study was 3. The difference in the results of a considerable decrease in absorbance might be due to differences in the pH of the methylene blue sample including pH 3 (acidic conditions) and pH 10 (alkaline conditions). A large decrease in alkaline absorbance is due to the ease of OH* radical formation on the surface of the TiO_2 photocatalyst (Anwar & Mulyadi, 2015). In this study, the degradation parameters used were not only absorbance but also COD and BOD contents.

Photoactivity of the thin film is influenced by thickness, grain size, crystal structure, absorbance, and energy gap (Kaltsum et al., 2016). The thin film of Fe-TiO_2 600^0C annealing temperature has the smallest grain size, large absorbance, and small energy gap. The smaller the size of the grain, the greater its total surface area. Thus, more and more methylene blue molecules interact with thin film and degraded. Large absorbance shows a thin film capable of absorbing the light that hits it in large quantities (Kaltsum, Kurniawan, Priyono, & Nurhasanah, 2017). The more light (photons) absorbed, the higher the number of radicals produced with the capability to degrade methylene blue. A small energy gap provides the opportunity for small energy photons to raise electrons from the valence to the conduction band producing radicals capable of degrading methylene blue.

The photocatalyst process is when a thin film in methylene blue is illuminated with light consisting of several steps. First, thin films subject to light (photons/ hν) will produce conduction electrons in the conduction band (e^-_{CB}) and holes in the valence band (h^+_{vb}) (equation 3). Hole interacts with water molecules (OH^- and H_2O) to produce hydroxide radicals (OH*) (equation 4-5), while interaction with conduction electrons produces superoxide radicals ($O_2{}^{*-}$) (equation 6). Finally, these two radicals (OH* and O_2*) interact with methylene blue ($C_{16}H_{18}N_3SCl$) to produce CO_2 and H_2O (equation 7-8) (Andari &

Wardhani, 2014). From all these processes it can be concluded that the photocatalyst process of $Fe\text{-}TiO_2$ thin film in methylene blue will convert it to simpler compounds, such as water (H_2O) and CO_2 (Yuningrat, Oviantari, & Gunamantha, 2015). Thus, the molecule of methylene blue is degraded and the solution becomes clearer.

$$Fe\text{-}TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb} \quad (3)$$
$$h^+_{vb} + OH^- \longrightarrow OH^* \quad (4)$$
$$h^+_{vb} + H_2O \longrightarrow OH^* + H^+ \quad (5)$$
$$e^-_{cb} + O_2 \longrightarrow O_2^{*-} \quad (6)$$
$$C_{16}H_{18}N_3SCl + 108OH^* + 6e^- \longrightarrow Cl^- + SO_4^{2-} + 3NO_3^- + 16CO_2 + 63H_2O \quad (7)$$
$$C_{16}H_{18}N_3SCl + \frac{51}{2} O_2^{*-} \longrightarrow HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \quad (8)$$

The characteristic of the methylene blue compound also affects the photo-activity occurred. This cationic (positive) compound easily interacts with the hydroxide and superoxide radicals in thin films which tend to be negative. Increasing the annealing temperature enlarges the surface area of the grain. Thus, more methylene blue compounds interact and degrade.

Table 3. The degradation presentation of COD, BOD, and absorbance by a thin film of $Fe\text{-}TiO_2$

Thin Film	Degradation (%)		
	COD	BOD	Absorbance
$Fe\text{-}TiO_2$ annealing temperature 500 C	11,09	19,53	49,30
$Fe\text{-}TiO_2$ annealing temperature 550 C	14,65	27,41	62,70
$Fe\text{-}TiO_2$ annealing temperature 600 C	19,56	35,84	66,70

CONCLUSION AND SUGGESTION

The growth of annealing temperature increases the photoactivity of $Fe\text{-}TiO_2$ thin films in methylene blue. At 600^0C, the thin film has the highest photo-activity, capable of degrading COD by 19.56%, BOD by 35,84%, and absorbance by 66.70%. High phot-activity in the thin film of $Fe\text{-}TiO_2$ 600^0C annealing temperature is affected by small grain size, large absorbance, and small energy gap. The characteristic of methylene blue with high absorption and cationic effect also affects the photoactivity of thin films.

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REFERENCES

Abdennouri, M., Baalala, M., Galadi, A., El Makhfouk, M., Bensitel, M., Nohair, K., Barka, N. (2016). Photocatalytic degradation of pesticides by titanium dioxide and titanium pillared purified clays. *Arabian Journal of Chemistry*, *9*, 313–318. https://doi.org/https://doi.org/10.1016/j.arabjc.2011.04.005.

Alhaji, M., Sanaullah, K., Khan, A., Hamza, A., Muhammad, A., Ishola, M., Bhawani, S. A. (2017). Recent developments in immobilizing titanium dioxide on supports for degradation of organic pollutants in wastewater- A review. *International Journal of Environmental Science and Technology*, *14*(9), 2039–2052. https://doi.org/https://doi.org/10.1007/s13762-017-1349-4.

Andari, N. ., & Wardhani, S. (2014). Fotokatalis TiO2-Zeolit untuk Degradasi Metilen Biru. *Chemistry Progress*, *7*(1), 9–14.

Anwar, D. I., & Mulyadi, D. (2015). Synthesis of Fe-TiO 2 Composite as a Photocatalyst for Degradation of Methylene Blue. *Procedia Chemistry*, *17*, 49–54. https://doi.org/https://doi.org/10.101

6/j.proche.2015.12.131.

Di Paola, A., Bellardita, M., & Palmisano, L. (2013). Brookite, the Least Known TiO2 Photocatalyst. *Catalysts*, *3*(1), 36–73. https://doi.org/https://doi.org/10.3390/catal3010036.

Durri, S., & Sutanto, H. (2015). Karakterisasi Sifat Optik Lapisan Tipis ZnO Doping Al yang di Deposisi diatas Kaca dengan Metode Sol-Gel Teknik Spray-Coating. *Jurnal Fisika Indonesia*, *19*(55), 38–40.

Hadayani, L. ., Riwayati, I., & Ratnani, R. (2015). Adsorpsi Pewarna Metilen Biru Menggunakan Senyawa Xanthat Pulpa Kopi. *Momentum*, *11*(1), 19–23.

Haider, J., Anbari, A., Corre, O. Le, & Ferrão, P. (2017). ScienceDirect ScienceDirect ScienceDirect Exploring potential Environmental applications of TiO2 Nanoparticles Assessing the feasibility of using the heat demand-outdoor temperature function for a long-term district heat demand forecast. *Energy Procedia*, *119*, 332–345. https://doi.org/https://doi.org/10.1016/j.egypro.2017.07.117.

Huda, T., & Yulitaningtyas, T. (2018). Kajian Adsorpsi Methylene Blue Menggunakan Selulosa dari Alang-Alang. *Indonesian Journal of Chemical Analysis*, *1*(1), 9–19.

Ibrahim, H. M. M. (2017). Photocatalytic degradation of methylene blue and inactivation of pathogenic bacteria using silver nanoparticles modified titanium dioxide thin films. *World Journal of Microbiology and Biotechnology*, *31*(7), 1049–1060. https://doi.org/https://doi.org/10.1007/s11274-015-1855-9.

Jami, M., Dillert, R., Suo, Y., Bahnemann, D. W., & Wark, M. (2018). Photoactivity of Titanium Dioxide Foams. *International Journal of Photoenergy*, *2018*, 1–9.

Kaltsum, U., Kurniawan, A. ., Priyono, P., & Nurhasanah, I. (2017). Pengujian Sifat Fotokatalis Lapisan Tipis TiO2 pada Produk Degradasi Jelantah Menggunakan Elektrooptis. *Jurnal Penelitian Fisika Dan Aplikasinya*, *7*(2), 61–67. https://doi.org/https://doi.org/10.26740/jpfa.v7n2.

Kaltsum, U., Kurniawan, A. F., Nurhasanah, I., & Priyono, P. (2016). Reduction of Peroxide Value and Free Fatty Acid Value of Used Frying Oil Using TiO 2 Thin Film Photocatalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, *11*(3), 369–375. https://doi.org/https://doi.org/10.9767/bcrec.11.3.577.369-375.

Kaltsum, U., & Saefan, J. (2017). Pengaruh Doping Fe pada Lapisan Tipis TiO2 terhadap Sifat Optis dan Fotoaktivitas dalam Jelantah. In *Seminar Nasional Hasil Penelitian (SNHP)-VII*, 1–5. Semarang.

Kanakaraju, D., Glass, B. ., & Oelgemoller, M. (2014). Titanium Dioxide Photocatalysis for Pharmaceutical Wastewater Treatment. *Environmental Chemistry Letters*, *12*(1), 27–47. https://doi.org/https://doi.org/10.1007/s10311-013-0428-0.

Karim, S., Pardoyo, & Subagiyo, A. (2016). Sintesis dan Karakterisasi TiO 2 Terdoping Nitrogen (N-Doped TiO2) dengan Metode Sol–Gel. *Jurnal Kimia Sains Dan Aplikasi*, *19*(2), 63–67.

Kumar, R., Rashid, J., & Barakat, M. (2015). Zero Valent Ag Deposited TiO2 for the Efficient Photocatalysis of Methylene Blue under UV-C Light Irradiation. *Colloids and Interface Science Communications*, *5*, 1–4.

Naimah, S., Ardhanie, S., Jati, B. ., Aidha, N. ., & Arianita, A. (2014). Degradasi Zat Warna pada Limbah Cair Industri

Tekstil dengan Metode Fotokatalitik Menggunakan Nanokomposit TiO2 – Zeolit. *Jurnal Kimia Dan Kemasan*, *36*(2), 225–236.

Pradana, A., Sutanto, H., & Hidayanto, E. (2017). Deposisi, karakterisasi sifat optik dan uji degradasi Db71 pada lapisan tipis Zno : Co konsentrasi tinggi. *Youngster Physics Journal*, *6*(3), 242–248.

Pulicharla, R., Zolfaghari, M., Brar, S. ., Cledon, M., Drogui, P., & Surampalli, R. (2014). Cosmetic Nanomaterials in Wastewater : Titanium Dioxide and Fullerenes Cosmetic Nanomaterials in Wastewater : Titanium Dioxide and Fullerenes. *Journal of Hazardous, Toxic, and Radioactive Waste*, *20*(1), 1–12. https://doi.org/https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000261

Sinaga, P. (2009). Pengaruh Temperatur Annealing terhadap Struktur Mikro, Sifat Listrik dan Sifat Optik dari Film Tipis Oksida Konduktif Transparan ZnO:Al yang Dibuat dengan Teknik Screen Printing. *Jurnal Pengajaran MIPA*, *14*(2), 51–59.

Sutanto, H., & Wibowo, S. (2015). *Semikonduktor Fotokatalis Seng Oksida dan Titania (Sintesis , Deposisi dan Aplikasi)*. Semarang: Telescope.

Vidhya, R., Sankareswari, M., & Neyvasagam, K. (2016). Effect of Annealing Temperature on Structural and Optical Properties of Cu-TiO2 Thin Film. *International Journal of Technical Research and Applications*, *37*, 42–46.

Yuningrat, N. ., Oviantari, M. ., & Gunamantha, I. (2015). Fotodegradasi Senyawa Organik dalam Lindi dengan Menggunakan Katalis TiO2 Terimobilisasi. *Jurnal Sains Dan Teknologi*, *4*(2), 647–660.