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Photodegradation of Methyl Orange (MO) Using TiO_2/Zeolite from Coal Fly Ash Waste Under Acidic Conditions and H_2O_2 Addition

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ABSTRACT

This study aims to degrade methyl orange dye by a photocatalytic method using TiO_2/zeolite nanocomposite. The zeolite used is sourced from coal waste fly ash. While the TiO_2/Zeolite nanocomposites were synthesized by the sol-gel method and analyzed using UV-Vis DRS to determine the band gap energy. The band gap energy obtained from calculation results of the Kubelka-Munk formula shows a value of 2.0 eV. This indicates that the working area of methyl orange photodegradation using TiO_2/zeolite is in visible light. Optimization of the methyl orange photodegradation process in this study will be carried out in an acidic environment by varying the nanocomposite dose (0.05; 0.1; 0.2; 0.3; and 0.4 g) and the length of time of irradiation (15; 30; 45; 60; and 75 minutes). This study also conducted a study on the effect of adding H_2O_2. The optimum yield of percent degradation (%D) of methyl orange (MO) obtained was 98.37% from initial concentration 10 mg/L to 0,16 mg/L with varying doses of TiO_2/zeolite 0.1 g and 30 minutes in an acidic environment and the addition of H_2O_2.

Keywords: degradation, photocatalyst, methyl orange, sunlight, TiO_2/Zeolite

1. INTRODUCTION

The development of the industrial sector today has led to an increase in the use of dyes that can pollute the environment [1]. Methyl orange is one of the azo dyes that are often used in the textile industry. Azo compounds are carcinogenic and difficult to degrade, so if discharged into the water system will damage the ecosystem in it.

In addition, the large number of dye molecules in water will interfere with the photosynthesis process [2]. For the problem of dye waste, it needs great attention. The photodegradation method is an effective method because it is known to decompose dye compounds into harmless compounds such as H_2O and CO_2 [3].

This method works by generating highly reactive species, namely hydroxyl radicals (-OH) that can degrade pollutants in wastewater into harmless small molecules. The advantages possessed by this method are relatively low operating costs and environmentally friendly, non-selective to certain pollutants, has high efficiency, relatively cheaper price, non-toxic, and does not produce polluting products [4].

Photodegradation requires a semiconductor catalyst such as titanium dioxide (TiO_2). TiO_2 is a good semiconductor material used for photodegradation activities because it has a large band gap energy of 3.2 eV which can decompose dyes and is temperature stable [2]. This property is the basis for the use of TiO_2 in the photodegradation process.

The use of TiO_2 photocatalysts has limitations including the rapid recombination rate of photogenerated electron-hole pairs, short excitation wavelengths, low selectivity, and difficult to recover [5], [6]. The effectiveness of TiO_2 photocatalysts can be increased by adding a carrier to the catalyst which causes an increase in the surface area of the catalyst. The embodiment used is zeolite. TiO_2 catalysts that are embedded in zeolites are expected to have a dual function, namely as an adsorbent at once [7].

One of these natural resources is coal. Fly ash is one of the wastes from the coal management process that has the potential to pollute the environment. As much as 80-90% of the waste generated from the coal combustion process is fly ash. On the other hand, fly ash contains high amounts of alumina (Al_2O_3) and silica (SiO_2) [8].

The use of TiO_2 impregnated with fly ash zeolite material is a way that can be done to increase the effectiveness of photocatalysis methods in degrading methyl orange compounds, namely inhibiting the rate of recombination of holes and electrons, reducing the potential for agglomeration by maintaining catalyst dispersion, increasing the ability to adsorb pollutants, and making catalyst recovery easier [9]. Based on this description, the use of fly ash TiO_2/zeolite composites has the potential as a photocatalysis material in degrading pollutants in wastewater. Modification of TiO_2 with zeolite from coal fly ash waste as an adsorption-photocatalysis material using the sol gel method has been successfully carried out [10].

2. METHODS

In this study, the material characteristics of TiO_2/zeolite, synthesis of TiO_2/zeolite from fly ash waste of Paiton PLTU were carried out. Characterization of TiO_2/zeolite composite using UV-Vis DRS and testing its ability to degrade methyl orange in various conditions of H_2O_2 addition and without the addition of H_2O_2 8%, TiO_2/zeolite dose variation of 0.1 g and variation of radiation duration of 30 minutes. Data obtained from UV-Vis diffuse reflectance spectroscopy (DRS) test results were calculated using the Kubelka-Munk formula to determine the gap energy and the effect of contact time on methyl orange degradation used to analyze the kinetics of the photocatalyst reaction. The research results are expected to be an alternative method in degrading methyl orange components and as a basis for the utilization of fly ash waste.

2.1. Tools and Materials.

The materials needed are Methyl orange (MO) solution pH 2, Titanium tetra isopropoxide (TTiP) from Merck, Coal fly ash PLTU Paiton, Ethanol pro analysis, TiO_2/zeolite nanocomposite, distilled water, HCl 10% (Merck), NaOH(s) (Merck), and H_2O_2 8% p.a. (Merck).

The tools used are as follows: Centrifuge tube, 1000 mL measuring flask, 500W halogen lamp, mortar, pestle, oven, furnace, hotplate, magnetic stirrer. The instruments used are UV-Vis spectrophotometer and UV-Vis diffuse reflectance spectroscopy.

2.2. Experiment.

Pre-Treatment Fly Ash

Paiton PLTU fly ash was pre-treated by heating the fly ash waste in a furnace for 2 hours at 800°C. Then washed using water: 10% hydrochloric acid in a ratio of 1:5. Fly ash was added to hydrochloric acid in a ratio of 1:5 and then heated in an oven at 140°C for 2 hours. After that, it was washed with water 3 times and filtered. The filtrate obtained was then heated in an oven at 120°C for 6 hours to obtain pure fly ash [10].

Zeolite Synthesis

Pure fly ash was added to NaOH in a ratio of 1:1.6 (b/v) and then ground until smooth. The mixture of fly ash and NaOH was then heated in a furnace for 2 hours at 150 °C. The mixture of fly ash and NaOH was then heated in the furnace for 2 hours at a temperature of 150 °C. Cooled and ground again. 1:5 b/v water was added and put into the oven at 120 °C for 2 hours. After that, washed with water 3 times and filtered. The last step is put into the oven 105 °C for 4 hours [10].

Synthesis of Titanium Oxide (TiO_2)

The process of making Ti(OH)n sol uses TTiP as a precursor. Titanium tetra isopropoxide (TTiP), ethanol pro analysis and water were mixed in the ratio (1:2:5). The mixture was stirred for 4 hours, and the colloid obtained was heated in an oven at 105 °C for 12 hours. Put in a furnace at 350 °C for 1 hour and cool after that crushed until smooth [10].

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Synthesis and Characterization of TiO_2/Zeolite Nanocomposite

TiO_2/zeolite synthesis was carried out using the sol gel method according to our previous study [10]. The band gap energy was calculated using DRS (Analytic Jena). Meanwhile, Fourier transform infrared spectroscopy (FT 1000) was employed to analyze bonds and functional groups.

Maximum Wavelength Scanning (λ_{max})

Scanning maximum wavelength was set from (400 - 700) nm. The test solution used was methyl orange (Merck) standard solution 6.00 mg/L.

Methyl Orange Calibration Curve

Methyl orange working standard series solution namely, (0.00; 1.00; 4.00; 6.00; 8.00; and 10.00) mg/L. The results of the methyl orange standard series absorbance obtained, made the linearity curve equation.

Optimization of Nanocomposite Dosage and Radiation Time in the Photodegradation Process

Photocatalyst effectiveness testing was carried out by observing the performance of TiO_2/zeolite composite of coal fly ash from PLTU Paiton, Malang in reducing the concentration of methyl orange (100 mL, 10.00 mg/L, 2 pH). The first stage of testing was carried out without the addition of 5 mL H_2O_2 8% and with the addition of 8% H_2O_2 with a reaction time of 30 minutes to determine the effect of the addition of H_2O_2 in the photocatalysis reaction. The maximum breakdown of methyl orange under hydrogen peroxide was reported in a prior investigation, which led to the selection of this H_2O_2 concentration [16]. The design of the photocatalysis process reactor can be observed in Figure 1. Testing was carried out in a batch reactor system equipped with a 1000 W halogen lamp as a radiation source. This reactor is made from cube-shaped cardboard.

Figure 1. Batch system reactor design of methyl orange photocatalysis process

The second stage of testing was carried out with variations in the dose of TiO_2/zeolite nanocomposites (0.05; 0.1; 0.2; 0.3; and 0.4) g in a 100 mL methyl orange sample. The third stage of testing was carried out with variations in the length of radiation time (15; 30; 45; 60; and 75) minutes.

Analysis of methyl orange levels before and after the photodegradation process was analyzed using a UV-Vis spectrophotometer by measuring the absorbance value. The methyl orange removal efficiency of the photocatalyst process can be calculated using equation (1) as follows:

$$\text{MO Degradation (\%D)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Co and Ct being the methyl orange (MO) concentration before and after the photocatalyst process, respectively (mg/L).

Reaction Kinetics Analysis

Time variation data of methyl orange degradation process in photocatalysis process is used to analyze the kinetics of photodegradation chemical reaction. The reaction kinetics uses the pseudo-first-order, and pseudo second-order chemical reaction kinetics models with equations (2-3) as follows [11]:

$$LnC_t = InC_o - k_1 t \quad (2)$$

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \quad (3)$$

With Co and Ct are the initial concentration of methyl orange and the concentration of methyl orange at a certain time (mol/L), respectively, t is the photocatalyst reaction time (minutes). The value of ko is the zero-order reaction rate constant (mol/L.min), k_1 is the first-order reaction rate constant (1/s), k_2 is the second-order reaction rate constant (L/mol.s). The values of the constants k_o, k_1, and k_2 were each obtained as the slope of a linear regression of the data Ct vs t, Ln Ct vs t, and 1/Ct vs t. The selection of the kinetic model was determined based on the linear regression results selected with a correlation coefficient (R^2) close to 1.

3. RESULTS AND DISCUSSION

Characterization of TiO_2/Zeolite Composite

The band gap energy of pure TiO_2 is 3.28 eV [12], while the band gap energy of synthesized TiO_2 is 3.07 eV, according to another study [13]. Photocatalyst band gap energy can be determined by managing %R and wavelength data using the Kubelka-Munk equation. The measurement results of the characterization of TiO_2/zeolite fly ash using UV-Vis DRS spectrophotometer are shown in Figure 2.

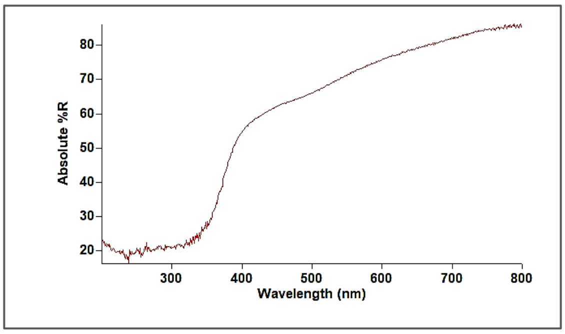

Figure 2. UV-Vis DRS spectra of TiO_2/zeolite fly ash

The band gap energy of TiO_2 photocatalyst can be changed by the addition of zeolite. The band gap value determined by Kubelka-Munk calculation :

$$F(R) = \frac{K}{S} = \frac{(1-R)}{2R} \quad (4)$$

From Figure 3, the band gap energy of the TiO_2/zeolite fly ash photocatalyst is 2.00 eV. The band gap energy is reduced due to localized states near the conduction or valence band of modified TiO_2 [14]. Therefore, TiO_2/fly ash zeolite has a lower band gap energy than TiO_2, making electron excitation simpler and producing -OH radicals, so the photodegradation activity increases [15]. As a result of the reduction in particle size, this result shows a broadening of the valence band and conductance bands, demonstrating the impact of the quantum size effect [16].

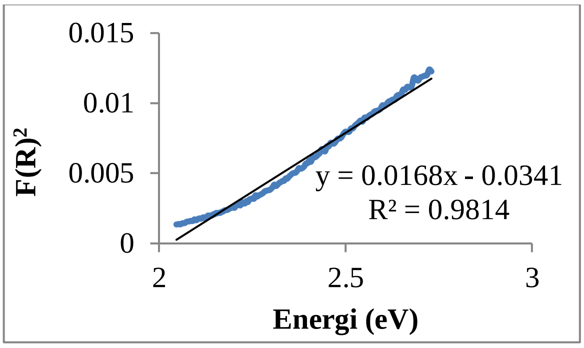

Figure 3. Kubelka-Munk Plot Graph of TiO_2/zeolite coal fly ash

Scanning Maximum wavelength (λ_{max})

The maximum wavelength scanning results at 400 – 700 nm using a standard test solution of 6.00 mg/L long methyl orange were obtained at 520 nm with an absorption value of 0.822.

Effect of H_2O_2 Addition

Based on the effect of the addition of H_2O_2 and without the addition of H_2O_2. Figure 4 shows that the addition of H_2O_2 in methyl orange affects the degradation process. The photodegradation result with the addition of H_2O_2 was 98.37% with a decrease in concentration from 10 mg/L to 0.16 mg/L, while the photodegradation result without the addition of H_2O_2 was 21.44% with a decrease in concentration from 10 mg/L to 7.82 mg/L. Figure 5 is the result of photodegradation with and without the addition of H_2O_2 before and after radiation.

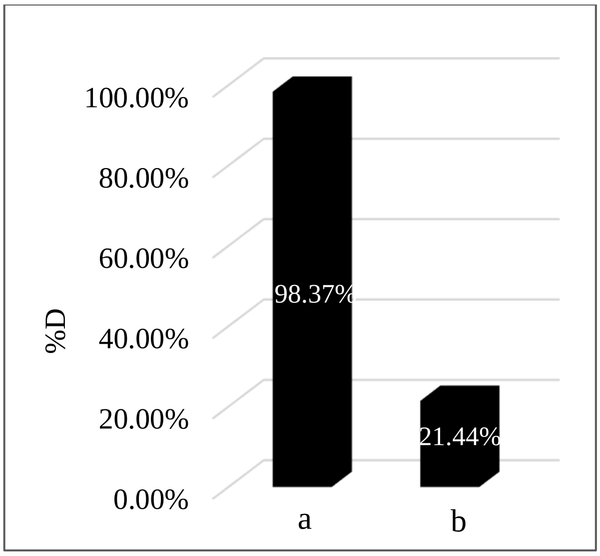

Figure 4. (a) % Degradation of MO with H_2O_2 and (b) % Degradation of MO without H_2O_2

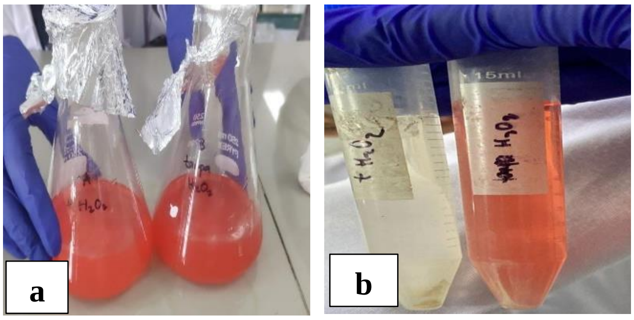

Figure 5. (a) Before irradiation with and without the addition of H_2O_2 and (b) After irradiation with the and without the addition of H_2O_2

In this study, 8% H_2O_2 concentration was used because the optimum H_2O_2 concentration to degrade methyl orange 10 mg/L at pH 2 is 8% with an error rate of 1% [16]. The function of H_2O_2 can increase the effectiveness of photodegradation of TiO_2/zeolite-catalyzed methyl orange dye because with the addition of H_2O_2, more hydroxyl radicals will be produced which function to degrade the dye.

The outcome demonstrates that H_2O_2, which works as an accelerator in the degradation process, is what causes the faster photocatalytic degradation. It causes a greater production of OH radicals. The most potent and significant oxidizing species are OH• radicals, which efficiently converted a variety of organic molecules into CO_2 and H_2O throughout the photodegradation process. By generating OH• radicals, the oxidizing agent plays a major role in the breakdown of these organic molecules, increasing the quantum yield. TiO_2/Zeolite provides an advantage for photocatalytic degradation in the presence of H_2O_2 due to the dissociation of H_2O_2 and OH• radicals [17].

The reaction of the formation of $\bullet HO_2$ is as follows:

$$\bullet OH + H_2O_2 \rightarrow H_2O + \bullet HO_2$$

$$\bullet OH + \bullet HO_2 \rightarrow H_2O + O_2$$

Effect of TiO_2/Zeolite Nanocomposite Dosage

The percentage of photodegradation to the addition of TiO_2/zeolite weight increased to its optimum limit, then continued to decrease as the weight of TiO_2/zeolite increased. According to Liu [18], as the weight of TiO_2/zeolite increases, a shift in blue band adsorption can be observed due to the quantum effect of TiO_2 on the zeolite surface when loading TiO_2. However, with the increase of TiO_2/zeolite, it causes the blue band value to also increase, resulting in a wider band gap and increasing the oxidizing power. On the other hand, when the addition of TiO_2/zeolite is excessive, it will result in increased particle size, decreased dispersibility, and decreased activity so that optimal conditions for the addition of TiO_2/zeolite nanocomposites are needed. From this study, the optimal photodegradation conditions for the addition of TiO_2/zeolite were 0.1 g in 100 ml of sample solution with a percentage of 98.37% (Figure 6).

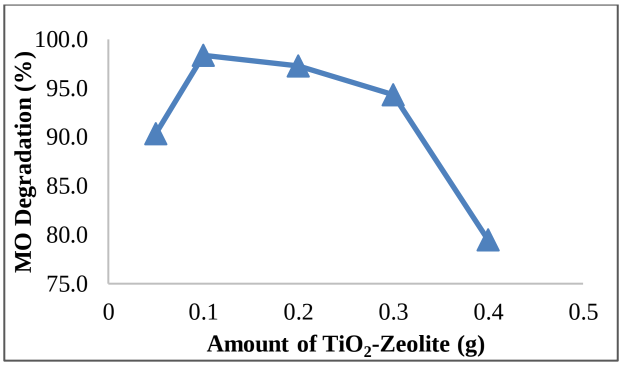

Figure 6. Relationship between TiO_2/zeolite weight and methyl orange photodegradation

Effect of Irradiation Time

The percentage of photodegradation on methyl orange increases with the length of contact time carried out. The interaction between photons, H_2O_2 and TiO_2/zeolite photocatalyst is directly proportional to the length of irradiation. Therefore, the longer the radiation or contact time, it will produce more -OH which can increase the photodegradation process. For methyl orange (MO) concentration of 10 mg/L, the most optimum contact time is 30 minutes with a percentage of 98.37% (Figure 7).

The increase in the percentage of degradation is due to the longer exposure to light, the greater the energy on the photocatalyst, so that the -OH radicals in the photodegradation process are produced more and more active for the process of degradation of dyes [19] [20]. At the beginning of the reaction -OH radicals are formed very quickly and the effect of the availability of large amounts of active side for the adsorption process. After some time, the remaining active side is difficult to fill due to the presence of repulsive forces between molecules on the surface in large numbers. Therefore, the percentage of degradation tends to be constant after some time (after 30 minutes) [16].

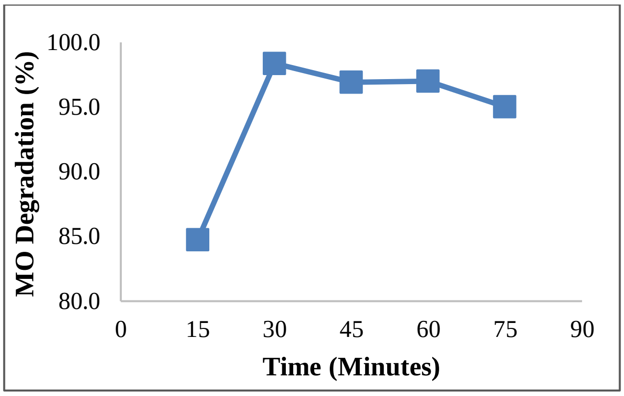

Figure 7. Relationship between irradiation time and methyl orange photodegradation

Kinetics Reaction of Photocatalysis Process

Reaction kinetics analysis was conducted to observe the mechanism of methyl orange photodegradation by TiO_2/zeolite fly ash composite and to determine the reaction rate of the degradation process. The results of the reaction kinetics analysis can be seen in Figure 8.

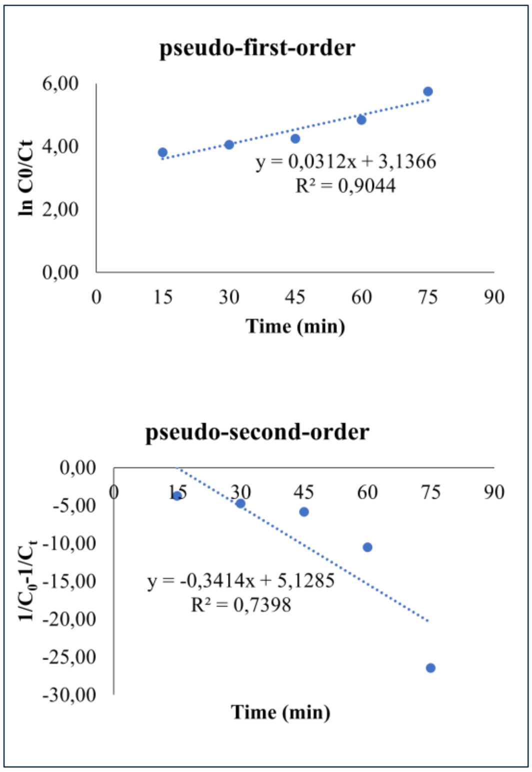

Figure 8. Graphs of zero pseudo-first order and pseudo-second order

The model fits the experimental data well, as evidenced by the rate constants displayed, and the correlation coefficients (R^2) reach as high as 0.9. $R^2 = 0.9044$, a good linear relationship, shows that the photocatalytic degradation of dyes follows first-order reaction kinetics.

4. CONCLUSION

The activity of TiO_2/zeolite photocatalyst can be improved by the addition of H_2O_2, variation of TiO_2/zeolite dosage and radiation time. The optimum methyl orange degradation efficiency was obtained in conditions with the addition of 5 mL H_2O_2 8%, TiO_2/zeolite dosage of 0.1 g/100 mL and irradiation time under halogen light for 30 minutes. This optimum condition reached the highest % degradation of 98.37% from initial conc. 10 mg/L to 0.16 mg/L. Meanwhile, the methyl orange degradation of dyes follows pseudo first-order kinetics reaction.

REFERENCES

[1] Y. C. Chung and C. Y. Chen, 2009, Degradation of azo dye reactive violet 5 by TiO_2 photocatalysis, *Environ Chem Lett*, 7 (4): 347–352.

[2] A. P. L. Batista, H. W. P. Carvalho, G. H. P. Luz, P. F. Q. Martins, M. Gonçalves, and L. C. A. Oliveira, 2010, Preparation of CuO/SiO_2 and photocatalytic activity by degradation of methylene blue, *Environ Chem Lett*, 8 (1): 63–67.

[3] Slamet, S. Bismo, R. Arbianti, and Z. Sari, 2006, Phenol Removal by Combination of Adsorption and Photocatalysis Process Using Activated Carbon and TiO_2, *J Teknologi*, 4: 303–311.

[4] M. Zendehdel, Z. Kalateh, and H. Alikhani, 2011, Efficiency evaluation of NaY zeolite and TiO_2/NaY zeolite in removal of methylene blue dye from aqueous solutions, *Iranian J Environ Health Sci Eng*, 8 (3).

[5] K. Guesh, Á. Mayoral, C. Márquez-Álvarez, Y. Chebude, and I. Díaz, 2016, Enhanced photocatalytic activity of TiO_2 supported on zeolites tested in real wastewaters from the textile industry of Ethiopia, *Microporous and Mesoporous Materials*, 225: 88–97.

[6] P. T. Lum, N. A. Zakaria, and K. Y. Foo, 2017, Eco-Friendly and Visible Light Driven Photocatalytic Nanocomposites, *Symposium on Innovation and Creativity*, 2: 1–4.

[7] K. Wijaya, I. Tahir, and N. Haryanti, 2005, Synthesis Of Fe_2O_3-Montmorillonite And Its Application As A Photocatalyst For Degradation Of Congo Red Dye, *Indo. J. Chem*, 5 (1): 41–47.

[8] N. R. Andarini, S. Wardhani, and M. M. Khunur, 2013, Photodegradation of Methyl Orange Dyestuff Using TiO_2 - Zeolite with the Addition of Inorganic Anion NO_3^-," *student Journal*, 1 (1): 98–104.

[9] V. Gilja, Z. Katancic, L. K. Krehula, V. Mandic, and Z. Hrnjak-Murgic, 2019, Eflciency of TiO_2 catalyst supported by modified waste fly ash during photodegradation of RR45 dye, *IEEE Journal of Selected Topics in Quantum Electronics*, 26 (1): 292–300.

[10] L. J. Kusumawardani, A. Iryani, and E. L. Sinaga, 2023, Modification of Zeolite Made from Coal Fly Ash with TiO_2: Effect of Aging Time on Physical and Optical Properties, *Makara J Sci*, 27 (1).

[11] F. Alakhras, E. Alhajri, R. Haounati, H. Ouachtak, A. A. Addi, and T. A. Saleh, 2020, A comparative study of photocatalytic degradation of Rhodamine B using natural-based zeolite composites, *Surfaces and Interfaces*, 20.

[12] J. Gunlazuardi, 2020, Photoelectrocatalysis for Water Detoxification, *Prosiding*, 1–21.

[13] R. B. Sakti, A. Subagio, and H. Sutanto, 2013, Synthesis of Thin Layer Nanocomposite TiO_2/Cnt Using Sol-Gel Method and Its Application for Photodegradation of Azo Orange 3R Color Substance," *Youngster Physics Journal*, 2 (1): 41–48.

[14] C. Wang, H. Shi, and Y. Li, 2012, Synthesis and characterization of natural zeolite supported Cr-doped TiO_2 photocatalysts, *Appl Surf Sci*, 258 (10): 4328–4333.

[15] S. Wardhani, Moh. F. Farid Rahman, D. Purwonugroho, R. Triandi Tjahjanto, C. Adi Damayanti, and I. Oktavia Wulandari, 2016, Photocatalytic Degradation of Methylene Blue Using TiO_2-Natural Zeolite as A Photocatalyst, *The Journal of Pure and Applied Chemistry Research*, 5 (1): 19–27.

[16] A. P. Aziztyana, S. Wardhani, Y. P. Prananto, D. Purwonugroho, and Darjito, 2019, Optimisation of Methyl Orange Photodegradation Using TiO_2-Zeolite Photocatalyst and H_2O_2 in Acid Condition, in *IOP Conference Series: Materials Science and Engineering*.

[17] S. A. Abo-Farha, 2010, Photocatalytic Degradation of Monoazo and Diazo Dyes in Wastewater on Nanometer-Sized TiO_2, *Journal of American Science*, 6 (11): 130–150.

[18] X. Liu, Y. Liu, S. Lu, W. Guo, and B. Xi, 2018, Performance and mechanism into TiO_2/Zeolite composites for sulfadiazine adsorption and photodegradation, *Chemical Engineering Journal*, 350: 131–147.

[19] R. S. Rini, I. Fajriati, and A. A. Kiswandono, 2019, Effect of Hydrogen Peroxide (H_2O_2) Addition on the Effectiveness of Naphthol Photodegradation Using TiO_2 Photocatalysis, *Analytical and Environmental Chemistry*, 4 (1): 26–40.

[20] L. J. Kusumawardani, A. Iryani, and E. Yulianti, "Photocatalytic Decolorization of Methylene Blue Using TiO_2-Fe Photocatalyst under Visible and Sunlight Irradiation," *AIP Conf. Proc.*, vol. 2638, no. August, 2022, doi: 10.1063/5.0104096.