Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 11(2), 156-162, 2023

Characterization and Kinetic Study of Methylene Blue Photocatalytic on ZnO/ZSM-5

Hellna Tehubijuluw[1*], Fensia Analda Souhoka[1], Yuly Kusumawati[2], Didik Prasetyoko[2], Riki Subagyo[2], Reva Edra Nugraha[3], Aishah Abdul Jalil[4]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Pattimura University, Jalan Ir. M. Putuhena, Kampus Poka, Ambon, 97233, Indonesia
[2]Department of Chemistry, Faculty of Sciences and Data Analytics, Institut Teknologi Sepuluh Nopember, Keputih Sukolilo, Surabaya 60111, Indonesia
[3]Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya, East Java, 60294, Indonesia
[4]Department of Chemical Engineering, Faculty of Chemical and Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, Johor, Malaysia

[*] *Corresponding Author: hellnatehubijuluw@gmail.com*

Received: July 2023
Received in revised: August 2023
Accepted: September 2023
Available online: September 2023

Abstract

Photodegradation of organic pollutants depends significantly on the structure of metal oxide-based semiconductor photocatalysts. ZnO/ZSM-5 has shown the potential to significantly improve its photocatalytic efficiency for removing waterborne pollutants. ZnO/ZSM-5 has been reported to be an active catalyst for degrading methylene blue. These methods commonly involve various catalytic reactions, with the Langmuir-Hinshelwood process being used to describe the reaction kinetics. A kinetic study on the photocatalytic degradation of methylene blue using ZnO/ZSM-5 was conducted under UV-LED lamp irradiation. ZnO/ZSM-5 was characterized using XRD, SEM, and N_2 adsorption-desorption, and it was prepared via the impregnation method. The interaction between ZnO/ZSM-5 and methylene blue solutions over a period of 30 to 180 minutes was monitored using a UV-Vis spectrophotometer. The photocatalytic degradation of methylene blue followed first-order rate kinetics. The Langmuir-Hinshelwood (L-H) kinetic analysis revealed that the photocatalytic reaction constant (kc) was 4.207 L.mg^{-1}.menit^{-1}, and the Langmuir-Hinshelwood constant (K) was 261.509 L.mg^{-1}.

Keywords: Photodegradation, semiconductor, *kinetic study, methylene blue, photocatalytic, ZnO/ZSM-5*

INTRODUCTION

The textile industry in Indonesia is rapidly developing and expanding. This development has both positive and negative environmental consequences and can cause genetic alterations and interfere with the reproduction of living creatures. Methylene blue (MB) has the chemical formula $C_{16}H_{18}ClN_3S$ which is classified as a toxic aromatic hydrocarbon chemical and cationic dyes with a high adsorption capability. This substance is a dark green crystal that creates a blue solution when dissolved in water or alcohol, with a molecular weight of 319.86 g/mol, a melting point of 180 °C, and a water solubility of 35.5 g/L (Miclescu & Wiklund, 2010, Susanti et al., 2022). The use of MB can cause various side effects, including digestive system irritation and skin irritation if breathed (Moghazy, 2019, Baunsele et al., 2022). MB pollutants not only degrade water quality, but also have a significant impact on human health due to their toxicity, carcinogenic, mutagenic, or teratogenic properties (Bhatti et al., 2012, Ngapa & Ika, 2020).

There are various methods to overcome the environmental problems caused by waste, especially waste containing synthetic dyes, one of which is the photocatalyst method. Light is used to activate the catalyst, which then reacts with chemical molecules in the photocatalytic process. ZnO is the most commonly used semiconductor because compared to TiO_2, the ZnO particle preparation technique is easier to do. (Chen et al., 2017, Pirhashemi et al., 2018, Kusumawati et al., 2017), TiO_2 (Wang et al., 2018), WO_3 (Song et al., 2017), (Zhang et al., 2017), Fe_2O_3 (Dutta et al., 2014, Tian et al., 2014), and CdS (Heiba et al., 2015). Different materials based on ZnO have been used for the degradation of MB photocatalysts using Ag-ZnO/graphene (Ahmad et al., 2013). ZnO/Clay (Akkari et al., 2016), ZnO/Carbon Nano

(Micheal et al., 2020), and ZnO/Carbon Fiber (Luo et al., 2020).

Subagyo et al., (2022) studied the synthesis of ZSM-5 material from red mud (RM) impregnated with TiO_2. In this work, it was found that the use of ZSM-5 as a supporting material can reduce the color of MB by 90%. RM was used as a catalyst to produce ZnO/ZSM-5 composites, which were used in the kinetics analysis of methylene blue photocatalysis. The previous studies have carried out pH studies with removal at pH 11 of 98.38 %. The aim of this study is to develop a kinetic model of MB photocatalysis using UV-LED lamps and ZnO/ZSM-5 composites.

METHODOLOGY

Materials and Instrumentals

All reagents bought from Merck. Deionized water was used for all solutions. The reagents used on this observe are zinc (II) acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$ merck), ethanol (C_2H_5OH, 99.5 %) 0.1 M HCl . The elements used are sodium hydroxide (NaOH 99%, Merck), colloidal silica (Ludox 30%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 40 % w/v solution in water, Merck), cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, Aldrich) and methylene blue ($C_{16}H_{18}ClN_3S$, Merck Millipore). The red mud from Bintan Island, Indonesia. The intstrumen used are X-ray diffraction (XRD, X-pert Philips) with Cu Kα radiation, Scanning electron microscope (SEM, Flexsem 1000 Hitachi), N_2 adsorption-desorption (Quantachrome Nova), UV-Vis spectrophotometer (GENESYSTM 10S UV-Vis), UV-LED (EPILEDS, 12 Watt)

Synthesis of ZSM-5

ZSM-5 was synthesized using red mud (RM) as silica and alumina source with a hydrothermal method. Alkaline fusion method was used to mixed RM and NaOH in the initial stage at 450 °C for 2 h, observed with the continuous distilled water addition and stirring for 24 h. The filtrate was separated and dried at 105 °C for 24 h. The molar composition of SiO_2: Al_2O_3: TPA and H_2O ratio was 0.2:0.004:0.04:3.6 respectively. Ludox was added to the solution and stirred for 8 h. TPAOH was added to the mixture and heated at 80 °C for 6 h. After finishing the 6 h reaction, CTAB (SiO_2/CTAB = 3.85) was added and stirred for 1 h. The resulting gel was then heated in an autoclave at 150 °C for 24 h. The white gel was filtered, washed with distilled water till the pH became neutral, and then dried. The end product of white ZSM-5 powder was used as a support catalyst for ZnO impregnation. The ZSM-5 was characterized using X-ray diffraction.

Synthesis of ZnO/ZSM-5

The moist impregnation method was used to synthesize ZnO/ZSM-5 (Akkari et al., 2016). In 10 mL of aqua demineralized, $Zn(CH_3COO)_2H_2O$ (10% w/w) and ZSM-5 (0.3424 g) have been introduced. The aggregate was then stirred for 3 h at 90 °C with a magnetic stirrer, dried for 3 h at 110 °C, and calcined for 6 h at 550 °C (heating rate 2 °C/min) for 1 h in N_2 surroundings and endured for 6 h in air surroundings. The ZnO/ZSM-5 have been characterized using X-ray diffraction, SEM and N_2 adsorption-desorption.

Photocatalytic Activity Test

The photocatalytic activity test of ZnO/ZSM-5 was investigated with the aid of using photocatalytic of methylene blue with the usage of UV-LED as an irradiation supply with a wavelength of 365 nm. The UV-LED mild was located within the middle of the reactor, 20 cm away from the sample. Photocatalysis was accomplished with a variation of time from 30 to 180 min. The concentrations of methylene blue used have been 80, 90, and 100 mg/L. The concentrations of methylene blue used have been 80, 90, and 100 mg/L. The filtrate was separated with the aid of centrifugation and analyzed the usage of a UV-Vis spectrophotometer. The variation of pH and initial concentration of methylene blue have been additionally evaluated.

RESULTS AND DISCUSSION

Characterization and Properties ZnO/ZSM-5

The results of the ZnO/ZSM-5 synthesis were characterized using X-ray diffraction, emission scanning electron microscope, and N_2 adsorption-desorption to determine the crystal structure, morphology, and textural properties of ZnO/ZSM-5. XRD was used to determine the crystal structure of ZSM-5 and ZnO/ZSM-5 composites. The diffractogram patterns of ZSM-5 and ZnO/ZSM-5 composites are shown in Figure 1. According to JCPDS data no. 36-1451, ZnO peaks with wurtzite ZnO structure appear at 2q = 31.75, 34.41, 36.24, and 47.52°.

The surface morphology of ZnO and ZnO/ZSM-5 was determined using SEM. The SEM analysis of ZnO and ZnO/ZSM-5 is shown in Figure 2. Cube-like objects with irregular sizes indicate that ZnO is well deposited on the surface of ZSM-5 and the morphology of ZSM-5 is not affected.

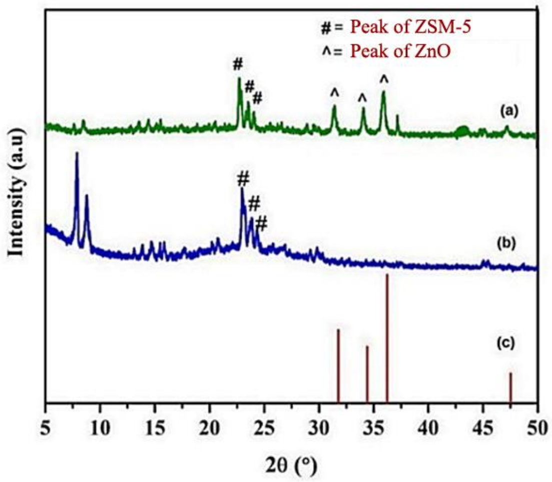
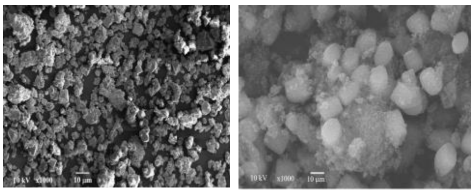


Figure 1. Diffraction pattern of (a) ZnO/ZSM-5, (b) ZSM-5, (c) JCPDS No. 36-1451

The specific surface area of ZnO/ZSM-5 was determined directly by the adsorption-desorption N_2, the pore volume of ZnO and that of ZnO/ZSM-5 was measured by the BJH (Barrett-Joiner-Halenda) method. Figure 3 shows the N_2 adsorption-desorption isotherm of the ZnO and ZnO/ZSM-5. Zinc oxide (ZnO) follows a type III isothermal curve, which means that zinc oxide (ZnO) undergoes multilayer adsorption.



(a) (b)

Figure 2. SEM image of (a) ZnO, (b) ZnO/ZSM-5

The figure shows that the synthesized zinc oxide (ZnO) has mesopores (Prasetyoko et al., 2023) . The increase in N_2 adsorption ZnO/ZSM-5 at relatively high pressures (P/P_o) = 0.3 – 0.5 and the formation of hysteresis loop at relatively high pressures (P/P_o) = 0.9 -1.0 are correlated with the characteristics of mesoporous materials (Type-IV isotherm). The specific surface area of ZnO/ZSM-5 is 277.55 m^2/g.

Photocatalytic Activity Test

Photocatalytic activity tests were performed at different concentrations of methylene blue solution. Figure 4 shows the photocatalytic activity of ZnO/ZSM-5 at MB concentrations of 80, 90, and 100 mg/L with UV-LED lamps. The comparison of the concentrations of MB at 90 mg/L and 100 mg/L, the concentration of MB at 100 mg/L have a good photocatalytic activity as shown in Figure 4. The results show that the higher the amount of MB, the lower the photocatalytic activity (Sacco et al., 2018). Also, increasing the amount of MB is sensitive to UV light in ZnO/ZSM-5 because if less UV light is absorbed in the sample, the photon energy in the sample decreases, which may result in a lower ability of electrons to excite.

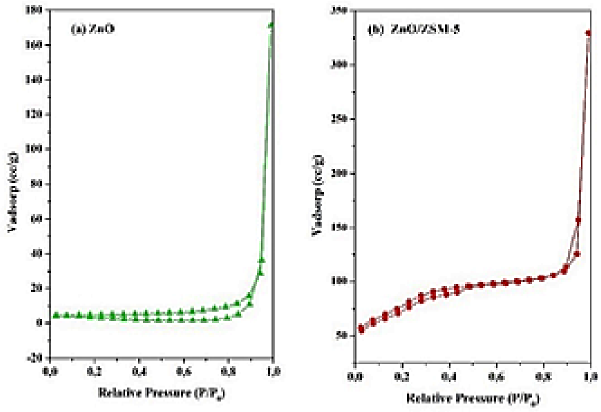


Figure 3. N_2 adsorption desorption isotherm of (a) ZnO and (b) ZnO/ZSM-5

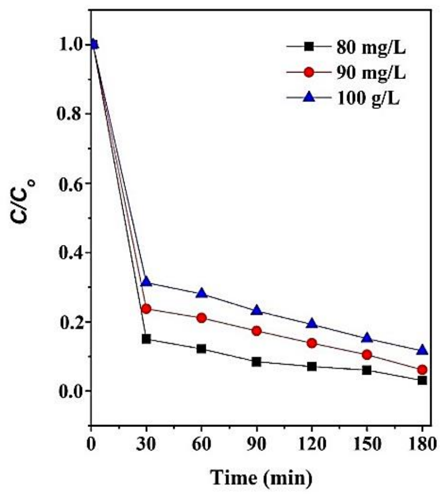


Figure 4. Photocatalytic activity of ZnO/ZSM-5 for degradation of MB using varying MB concentration (a) 80 mg/L; (b) 90 mg/L; (c) 100 mg/L in photocatalytic activity

Figure 5 illustrates the impact of pH on the removal percentage efficiency of the methylene blue solution. The adsorption of methylene blue increased with increasing pH, reaching a maximum of 98.38% at pH 11 solution.

This is because methylene blue is a cationic dye (positively charged). This means that under alkaline pH conditions, there is an enhancement in photocatalysis, which can be attributed to the electrostatic interactions between the negatively charged catalyst surface and the cationic species of methylene blue (Abdollahi et al., 2012); (Cheng et al., 2015).

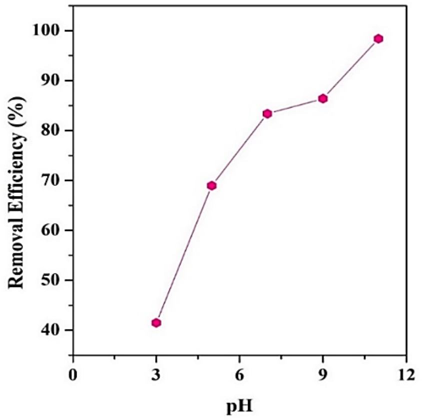


Figure 5. Photocatalytic removal efficiency of MB using ZnO/ZSM-5 with varying pH

Furthermore, the concentration of hydroxyl ions (OH^-) increases with rising pH levels. The quantity of hydroxyl radicals (*OH) generated during the oxidation of OH- ions at the hole (h+) also increases significantly when there is a substantial production of OH^- ions. Additionally, the greater the number of hydroxyl radicals formed, the more efficient the photocatalysis of methylene blue (MB) becomes. (Eljiedi & Kamari, 2017); (El-Kemary et al., 2010). The lowest reduction of methylene blue occurred at acidic pH due to the competition of H^+ ions with dye cations. Additionally, the cationic dye methylene blue produce cationic molecules (C^+) and degrades ions (CH^+) (Jia et al., 2018).

Kinetic Study Analysis

The study of the kinetics of the photocatalytic reaction in MB was discussed according to the theory of Langmuir Hinshelwood. In this study, the concentrations of MB used were 80, 90, and 100 mg/L using a UV-LED lamp (ZnO/ZSM-5 = 10 mg/20 mL). By plotting ln *(C_o/C)* on the y-axis and time (t) on the x-axis, the first-order kinetics model is applied as shown in Figure 6a (Equation 1). Plotting ln(C_o/C) against time (t) will produce a straight line with slope= k. Additionally, the second order is calculated by plotting *1/C - 1/C_o* against time on the y-axis (t) (Equation 2) in Figure 6b. Reaction determinations follow first-order kinetics (1) and second-order kinetics (2).

$$ln \frac{C_0}{C} = kt \quad (1)$$

$$^1/_C - ^1/_{C_o} = kt \quad (2)$$

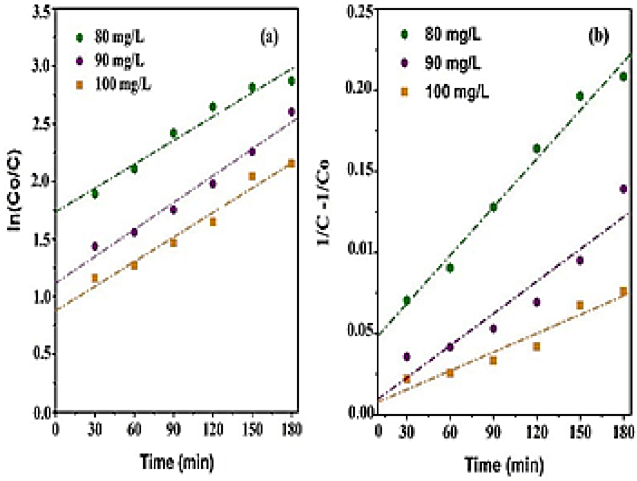


Figure 6. (a) Linear plot of ln (C_o/Ct) versus time (b) Linear plot of 1/C–1/C_o versus time for photocatalytic methylene blue degradation by ZnO/ZSM-5 with varying MB concentration.

The correlation of the coefficients (R_1^2 and R^2_2) is shown in Table 1. Also, the second order is determined by plotting *1/C - 1/C_o* as a function of time on the y-axis (t). The value of the correlation coefficient is a good parameter for determining photocatalytic kinetics (Umpuch & Sakaew, 2013). (Irani et al., 2016) has also reported values for the correlation coefficient values using methylene blue. The results show that the photocatalytic methylene blue by ZnO/ZSM-5 follows the first-order kinetic. The correlation coefficient of the second-order kinetics is in Table 1.

Table 1. The correlation coefficient of first-order and second-order kinetics

The concentration of methylene blue (mg/L)	$R^2{}_1$	$R^2{}_2$
80	0.964	0.984
90	0.969	0.899
100	0.974	0.929

The relationship between the initial photocatalysis rate (*r_o*) and (*C_o*) for the heterogeneous photocatalytic process is given by the L-H model to Equations 3 and 4 (Hitkari et al., 2018); (Gupta et al., 2006); (Kumar et al., 2008).

Table 2. Comparison of the photocatalytic degradation of dyes methylene blue using various photocatalysts

Catalyst	Time	Dose	% R	Lamp	Reference
GC^a -TiO_2	400 min	25 g/L	60	Mercury, 230 W	(Wang et al., 2014)
SiO_2 nanoparticle	90 s	10 g/L	83.5	Mercury	(Aly & Abd-Elhamid, 2018)
$MRGO^b$ -BiOBr	2 h	50 g/L	95.2	UV-Lamp,15 W	(Janani et al., 2016)
CdS-Ag_3PO_4	30 min	0.5 g/L	94	Wolfram, 40 W	(Mirsalari & Nezamzadeh-Ejhieh, 2021)
WO_3/TiO_2	120 min	10 g/L	96	UV-radiation	(Ernawati et al., 2019)
ZnO/ZSM-5	180 min	20 g/L	98.9	UV-LED[c],12 W	This work

Note: [a] graphene-carbon nanotubes [b] magnetically reduced graphene oxide [c] Ultraviolet-light emitting diode

$$r_{0} = k_c((K(C_0))/ 1+K(C_0)) = k_{r0}1(C_0) \quad (3)$$

$$\frac{1}{k_{r01}} = \frac{1}{k_c K} + (C_0)/k_c \quad (4)$$

where K and kc are the equilibrium constants of L-H adsorption and the kinetic rate constant reaction on the surface which obtained by plotting $1/r_o$ vs (C_o). The flow of $1/kr_o^1$ to (C_o) is linear with a correlation coefficient of R^2 = 0.989 as shown in Figure 7.

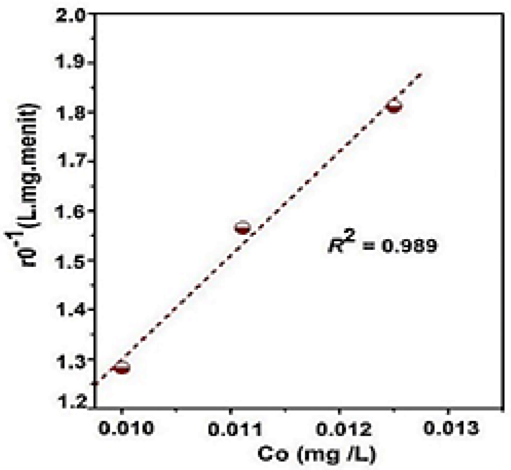


Figure 7. Plot of r_o versus C_o for the photocatalytic degradation

The Langmuir-Hinshelwood kinetic model parameters calculated by intercept and gradient obtained the photocatalytic reaction constant (kc) of 4.207 $L.mg^{-1}.min^{-1}$ and the value of the Langmuir-Hinshelwood constant (K) 261.509 $L.mg^{-1}$.
This demonstrates that the photocatalysis of methylene blue (MB) on ZnO/ZSM-5 follows the Langmuir-Hinshelwood (L-H) kinetic model. It is intriguing to compare the system investigated in this study with other reported photocatalyst systems, as indicated in Table 2. The methods employed aim to offer a high-quality stop service and achieve a high regression value.

CONCLUSION

ZnO/ZSM-5 was successfully synthesized by the wet impregnation method. Specific surface area (S_{BET}) 277.55 m^2/g. The pH 11 solution had the highest removal effectiveness, at 98.38 %. ZnO/ZSM-5 photocatalytic kinetics conforms to a first-order model with R^2 > 0.957. MB photocatalysis on ZnO/ZSM-5 followed the Langmuir-Hinshelwood (L-H) kinetic model with R^2 value of 0.989. The Langmuir-Hishelwood kinetic study revealed that the photocatalytic reaction constant and the Langmuir-Hinshelwood constant were 4.207 $L.mg^{-1}.min^{-1}$ and 261.509 $L.mg^{-1}$, respectively.

ACKNOWLEDGMENT

The authors thank the Chemistry Department Faculty of Sciences and Data Analytics Institut Teknologi Sepuluh Nopember for their financial support and the Chemical Materials and Energy Laboratory, and the Research and Development Assistant of the Ministry of Research and Technology of the Republic of Indonesia for studies funding. Faculty of Mathematics and Natural Sciences, Pattimura University for PNBP grand scheme number: 13.10.6H/SPK-PJ/UN13-PPK/FMIPA/2022.

REFERENCE

Abdollahi, Y., Abdullah, A. H., Zainal, Z., & Yusof, N. A. (2012). Photocatalytic degradation Of P-Cresol by Zinc Oxide Under UV Irradiation. *International Journal of Molecular Sciences*, *13*(1), 302-315.

Ahmad, M., Ahmed, E., Hong, Z. L., Khalid, N. R., Ahmed, W., & Elhissi, A. (2013). Graphene-Ag/ZnO Nanocomposites as High Performance Photocatalysts Under Visible Light Irradiation. *Journal of Alloys and Compounds*, *577*, 717-727.

Akkari, M., Aranda, P., Ben Rhaiem, H., Ben Haj Amara, A., & Ruiz-Hitzky, E. (2016). ZnO/clay Nanoarchitectures: Synthesis, Characterization and Evaluation as Photocatalysts. *Applied Clay Science*, *131*, 131-139.

Aly, H. F., & Abd-Elhamid, A. I. (2018). Photocatalytic Degradation of Methylene Blue Dye Using Silica Oxide Nanoparticles as a Catalyst. *Water Environment Research*, *90*(9), 807-817.

Baunsele, A., Boelan, E., Kopon, A., Rahayu, R., & Siswanta, D. (2022). Kinetic Study of Blue Methylene Adsorption Using Coconut Husk Base Activated. *Indonesian Journal of Chemical Research*, *10*(2 SE-Research articles).

Bhatti, H. N., Akhtar, N., & Saleem, N. (2012). Adsorptive Removal of Methylene Blue by Low-Cost Citrus sinensis Bagasse: Equilibrium, Kinetic and Thermodynamic Characterization. *Arabian Journal for Science and Engineering*, *37*(1), 9-18.

Chen, X., Wu, Z., Liu, D., & Gao, Z. (2017). Preparation of ZnO Photocatalyst for the Efficient and Rapid Photocatalytic Degradation of Azo Dyes. *Nanoscale Research Letters*, *12*(1), 4-13.

Cheng, M., Zeng, G., Huang, D., Lai, C., Wei, Z., Li, N., Xu, P., Zhang, C., Zhu, Y., & He, X. (2015). Combined Biological Removal of Methylene Blue from Aqueous Solutions Using Rice Straw and Phanerochaete Chrysosporium. *Applied Microbiology and Biotechnology*, *99*(12), 5247-5256.

Dutta, A. K., Maji, S. K., & Adhikary, B. (2014). γ-Fe_2O_3 Nanoparticles: An Easily Recoverable Effective Photo-Catalyst for The Degradation of Rose Bengal and Methylene Blue Dyes in The Waste-Water Treatment Plant. *Materials Research Bulletin*, *49*(1), 28-34.

El-Kemary, M., El-Shamy, H., & El-Mehasseb, I. (2010). Photocatalytic Degradation of Ciprofloxacin Drug in Water Using ZnO Nanoparticles. *Journal of Luminescence*, *130*(12), 2327-2331.

Eljiedi, A. A. A., & Kamari, A. (2017). Removal of Methyl Orange and Methylene Blue Dyes from Aqueous Solution Using Lala Clam (Orbicularia Orbiculata) Shell. *AIP Conference Proceedings*, *1847*.

Ernawati, L., Wahyuono, R. A., Muhammad, A. A., Nurislam Sutanto, A. R., Maharsih, I. K., Widiastuti, N., & Widiyandari, H. (2019). Mesoporous WO_3/TiO_2 Nanocomposites Photocatalyst For Rapid Degradation Of Methylene Blue in Aqueous Medium. *International Journal of Engineering, Transactions A: Basics*, *32*(10), 1345-1352.

Gupta, A. K., Pal, A., & Sahoo, C. (2006). Photocatalytic Degradation of A Mixture of Crystal Violet (Basic Violet 3) and Methyl Red Dye in Aqueous Suspensions Using Ag^+ Doped TiO_2. *Dyes and Pigments*, *69*(3), 224-232.

Heiba, Z. K., Mohamed, M. B., & Imam, N. G. (2015). Biphasic Quantum Dots of Cubic and Hexagonal Mn doped CdS; Necessity of Rietveld Analysis. *Journal of Alloys and Compounds*, *618*, 280-286.

Hitkari, G., Singh, S., & Pandey, G. (2018). Photoluminescence Behavior and Visible Light Photocatalytic Activity of ZnO, ZnO/ZnS and ZnO/ZnS/α-Fe_2O_3 nanocomposites. *Transactions of Nonferrous Metals Society of China (English Edition)*, *28*(7), 1386-1396.

Irani, M., Mohammadi, T., Mohebbi, S., Irani, M., Mohammadi, T., & Mohebbi, S. (2016). Photocatalytic Degradation of Methylene Blue with ZnO Nanoparticles; a Joint Experimental and Theoretical Study. *Journal of the Mexican Chemical Society*, *60*(4), 218-225.

Janani, S., Sudha Rani, K. S., Ellappan, P., & Miranda, L. R. (2016). Photodegradation of Methylene Blue Using Magnetically Reduced Graphene Oxide Bismuth Oxybromide Composite. *Journal of Environmental Chemical Engineering*, *4*(1), 534-541.

Jia, P., Tan, H., Liu, K., & Gao, W. (2018). Synthesis, Characterization and Photocatalytic Property of Novel ZnO/bone Char Composite. *Materials Research Bulletin*, *102*(February), 45-50.

Kumar, K. V., Porkodi, K., & Rocha, F. (2008). Langmuir-Hinshelwood Kinetics-A Theoretical Study. *Catalysis Communications*, *9*(1), 82-84.

Kusumawati, Y., Massin, J., Olivier, C., Toupance, T., Ivansyah, A. L., Martoprawiro, M. A., Prijamboedi, B., Radiman, C. L., & Pauporté, T. (2017). Combined Computational and Experimental Study of Carbazole Dyes for Iodide and Cobalt-Based ZnO DSSCs. *Journal of Photochemistry and Photobiology A: Chemistry*, *341*, 69-77.

Luo, S., Liu, C., Zhou, S., Li, W., Ma, C., Liu, S., Yin, W., Heeres, H. J., Zheng, W., Seshan, K., & He, S. (2020). ZnO Nanorod Arrays Assembled On Activated Carbon Fibers For Photocatalytic Degradation:Characteristics and Synergistic Effects. *Chemosphere*, *261*, 127731.

Micheal, K., Ayeshamariam, A., Devanesan, S., & ... (2020). Environmental Friendly Synthesis of Carbon Nanoplates Supported Zno Nanorods For Enhanced Degradation of Dyes and Organic

Pollutants with Visible Light Driven Photocatalytic Performance. *Journal of King Saud University - Science, 32*(2020) 1081-1087.

Miclescu, A., & Wiklund, L. (2010). Methylene blue, an old drug with new indications?. *Jurnalul Român de Anestezie Terapie intensivã*. *17*(1) 5-41.

Mirsalari, S. A., & Nezamzadeh-Ejhieh, A. (2021). CdS–Ag_3PO_4 Nano-Catalyst: A Brief Characterization and Kinetic Study Towards Methylene Blue Photodegradation. *Materials Science in Semiconductor Processing*, *122*(September 2020), 105455.

Moghazy, R. M. (2019). Activated Biomass of The Green Microalga Chlamydomonas Variabilis as an Efficient Biosorbent to Remove Methylene Blue Dye from Aqueous Solutions. *Water SA*, *45*(1), 20-28.

Ngapa, Y. D., & Ika, Y. E. (2020). Optimasi Adsorpsi Kompetitif Pewarna Biru Metilena dan Metil Oranye Menggunakan Adsorben Zeolit Alam Ende - Nusa Tenggara Timur (NTT). *Indonesian Journal of Chemical Research*, *8*(2), 151-159.

Pirhashemi, M., Habibi-Yangjeh, A., & Rahim Pouran, S. (2018). Review On The Criteria Anticipated for The Fabrication of Highly Efficient ZnO-Based Visible-Light-Driven Photocatalysts. *Journal of Industrial and Engineering Chemistry*, *62*, 1-25.

Prasetyoko, D., Sholeha, N. A., Subagyo, R., Ulfa, M., Bahruji, H., Holilah, H., Pradipta, M. F., & Jalil, A. A. (2023). Mesoporous ZnO Nanoparticles Using Gelatin-Pluronic F127 as A Double Colloidal System for Methylene Blue Photodegradation. *Korean Journal of Chemical Engineering*, *40*(1), 112-123.

Sacco, O., Vaiano, V., & Matarangolo, M. (2018). ZnO Supported on Zeolite Pellets as Efficient Catalytic System for The Removal of Caffeine by Adsorption and Photocatalysis. *Separation and Purification Technology*, *193*(October 2017), 303-310.

Song, B., Wang, T., Sun, H., Shao, Q., Zhao, J., Song, K., Hao, L., Wang, L., & Guo, Z. (2017). Two-Step Hydrothermally Synthesized Carbon Nanodots/WO_3 Photocatalysts with Enhanced Photocatalytic Performance. *Dalton Transactions*, *46*(45), 15769-15777.

Subagyo, R., Tehubijuluw, H., Prasetyo Utomo, W., Dwi Rizqi, H., Kusumawati, Y., Bahruji, H., & Prasetyoko, D. (2022). Converting Red Mud Wastes Into Mesoporous ZSM-5 Decorated with TiO_2 as An Eco-Friendly and Efficient Adsorbent-Photocatalyst for Dyes Removal. *Arabian Journal of Chemistry*, 103754. 1-16

Susanti, I., Iqbal, R. M., Sholeha, N. A., & Putri, K. F. (2022). The Ecofriendly Biosorbent of Methylene Blue Using Banana Peels Waste. *Indonesian Journal of Chemical Research*, *10*(2), 93-96.

Tian, B., Wang, T., Dong, R., Bao, S., Yang, F., & Zhang, J. (2014). Core-Shell Structured γ-Fe_2O_3@SiO_2@AgBr:Ag Composite with High Magnetic Separation Efficiency and Excellent Visible Light Activity for Acid Orange 7 Degradation. *Applied Catalysis B: Environmental*, *147*, 22-28.

Umpuch, C., & Sakaew, S. (2013). Removal of Methyl Orange from Aqueous Solutions by Adsorption Using Chitosan Intercalated Montmorillonite. *Songklanakarin Journal of Science and Technology*, *35*(4), 451-459.

Wang, C., Cao, M., Wang, P., Ao, Y., Hou, J., & Qian, J. (2014). Preparation of Graphene-Carbon Nanotube-TiO_2 Composites with Enhanced Photocatalytic Activity for The Removal of Dye And Cr (VI). *Applied Catalysis A: General*, *473*, 83-89.

Wang, L., Zhao, J., Liu, H., & Huang, J. (2018). Design, Modification and Application of Semiconductor Photocatalysts. *Journal of the Taiwan Institute of Chemical Engineers*, *0*, 1–13.

Zhang, L., Qin, M., Yu, W., Zhang, Q., Xie, H., Sun, Z., Shao, Q., Guo, X., Hao, L., Zheng, Y., & Guo, Z. (2017). Heterostructured TiO_2/WO_3 Nanocomposites for Photocatalytic Degradation of Toluene under Visible Light . *Journal of The Electrochemical Society*, *164*(14), H1086-H1090.