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Decolorization of Methylene Blue Dye Using ZnO/ZSM-5 Photocatalyst under UV-LED Irradiation

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ABSTRACT. The present research studied about decolorization of methylene blue dye using photocatalyst ZnO/ZSM-5 under UV-LED lamp. ZnO/ZSM-5 was synthesized using the impregnation method by adding two grams ZSM-5 to Zn solution 0.3 M 10 mL. Photocatalyst was characterized using X-ray diffractometer (XRD), Fourier transform infrared (FTIR), field emission scanning electron microscopy-energy dispersive X-Ray (FESEM-EDX), and surface area analyzer (SAA). Analysis using XRD show addition characteristic peaks of ZnO at 2θ 31.60°, 34.21°, 36.08°, 47.35°, 56.50°, 62.73°, 67.83°, that indicates a successful impregnation process. The photocatalysis activity test was done on methylene blue dye 100 mg L^{-1}. ZSM-5 and ZnO activities were tested under UV-LED irradiation and dark conditions. Data showed that percent removal of dye occurred on ZnO/ZSM-5 under 15 minutes irradiation is 78.32%.

INTRODUCTION

The growth of the textile industry has increased significantly every year and comparable to the world population that reaches 7,600,000,000 in 2017 (Department of Economic and Social Affairs, 2017; Gita *et al.*, 2016). Based on data from the Indonesian Ministry of Industry, the number of textile industries in 2013 was 2,916 units. In 2018, Indonesian textile production reached 594,000 tons (Kemenperin, 2018). This amount is proportional to the consumption of dyes as an important part of the textile industry (Ladhe *et al.*, 2011). The majority of dyes used by the textile industry are synthetic ones with the reason that they are cheap, easy to get, durable, and effective to use (Naimah *et al.*, 2014). There are more than 700,000 tons of dyes from 8,000 types of synthetics used annually, which include azo, diazo, acid, alkaline, until anthraquinone dyes (Wang *et al.*, 2018; Sivakumar *et al.*, 2012). During the textile production process, 20% of the dye dissolves into industrial waste so that it can have a negative impact on the environment and health (Babalola *et al.*, 2016). Industrial wastes that still contain dyes are toxic (Babalola *et al.*, 2016), carcinogenic (Stavrinou *et al.*, 2018), and can cause genetic mutations (Aly-Eldeen *et al.*, 2018). One type of synthetic dye used in the textile industry is methylene blue.

Methylene blue is a basic cationic thiazine dye and categorized as an aromatic compound. Methylene blue is a quite stable compound, making it difficult to degraded. Methylene blue that enters the aquatic environment can irritate the eyes, skin, and digestive. Adsorption and coagulation have been used frequently to eliminate waste, but it just converts the phase of dye waste from liquid to solid. Moreover, decolorization using the coagulation method can produce sludge, which requires further processing because it belongs to Hazardous and toxic materials that become a new problem for waste treatment units (Maizatisna, 2007). Therefore, the method of advanced oxidation processes (AOPs) is proposed, which uses oxidizing agents to eliminate waste. The AOPs method was chosen because it has a high degradation efficiency, high reaction rates, and does not produce waste products that require further processing (Ajmal *et al.*, 2014; Chan *et al.*, 2011). Among the AOP methods, photocatalysis is promising due to its simple preparation and commonly can be performed in mild condition. Oxide semiconductors have been used widely as a photocatalyst, for example, TiO_2 (Sharotri *et al.*, 2019), ZnO (Muslim *et al.*, 2017) or NiO (Derikvandi *and* Nezamzadeh-Ejhieh, 2017). Many kinds of research figured out that the application of oxide semiconductors limits with the help of visible light to carry out electron recombination processes. In this research, ZSM-5, as catalyst support, was impregnated with ZnO semiconductor as a photocatalysis agent to degrade

methylene blue dyes. ZSM-5 can act as a catalyst support which allows the formation of large particle catalysts with small crystals separated from each other. In addition, it is more resistant to heating at high temperatures than its catalytic species (active side) (Derikvandi *et al.*, 2017).

EXPERIMENTAL

In this research, the synthesis of ZnO/ZSM-5 was done by an impregnation method with ZSM-5 as catalyst support. The samples were characterized using XRD, FTIR, FESEM-EDX, and N_2 adsorption-desorption techniques. Furthermore, the photocatalysis activity test was done on methylene blue dyes 100 mg L^{-1} 25 mL. The ZSM-5 and ZnO/ZSM-5 activities were tested under UV-LED irradiation and dark conditions.

Materials

The chemicals used in this research were $Zn(CH_3COO)_2{\cdot}2H_2O$ (Merck 99.50%), Zeolite ZSM-5 SA-12-50 with aging variation 12 hours 50 °C that was synthesized from kaolin Bangka Belitung, Indonesia (Hamid, 2015), ZnO (Synthesized from $Zn(CH_3COO)_2{\cdot}2H_2O$ with precipitation method) (Subagyo, 2019), methylene blue, demineralization water (Otsuka), and aluminum foil.

Synthesis of ZnO/ZSM-5

Zeolite ZSM-5 SA-12-50 was calcined at temperature 550 °C gradually. The calcination process at this temperature aims to activate and eliminate organic templates (Wei *et al.*, 2017). ZnO/ZSM-5 synthesis method was adopted from the research done by Derikvandi and Nezamzadeh-Ejhieh (Derikvandi *and* Nezamzadeh-Ejhieh, 2017). Powder $Zn(CH_3COO)_2{\cdot}2H_2O$ 3.2927 g dissolved in a 50 mL volumetric flask using demineralization water to produce 0.3 M solution. The synthesis process of ZnO/ZSM-5 was done by mixing two grams ZSM-5 with 0.3 M 10 mL Zn solution. The mixture was stirred using a magnetic stirrer for 8 hours at 30 °C then heated at 110 °C in the oven for 12 hours. Then, it was calcined at 550 °C for 4 hours.

Characterization

The characterization of ZSM-5 and ZnO/ZSM-5 crystal structures was done by X-Ray Diffractometer (XRD). The ZSM-5 and ZnO/ZSM-5 were placed on the sample holder that has been cleaned before. Data retrieval using XRD instruments used CuKα radiation sources (λ = 1.54 Å) and measuring angles 2θ at 5° until 90° with increments 0.05°. Characterization of chemical bonds from ZSM-5 and ZnO/ZSM-5 was determined by FTIR spectrophotometer instruments. ZSM-5 and ZnO/ZSM-5 were mixed with KBr using a ratio of 1 : 9 on mortar to homogenize it. The mixture was pressed into pellets. The pellets were analyzed with infrared radiation (IR) at 4000 to 400 cm^{-1} wavenumbers. Surface morphology characterization of ZSM-5 and ZnO/ZSM-5 was analyzed by Field Emission scanning electron microscopy (FESEM) instruments. Both samples were prepared by placing them on carbon tape on the sample holder. Data retrieval with the FESEM instrument uses secondary electron signals with a 20 kV accelerator voltage. The surface area and pore diameter of the ZSM-5 and ZnO/ZSM-5 was analyzed using the Brunauer-Emmett-Teller (BET) method to determine the specific area (SBET). Pore distribution was investigated with the Barrett-Joyner- Halenda (BJH) method on the results of N_2 physisorption.

Photocatalytic Activity Test

The absorbance of methylene blue in dark conditions and under irradiation of UV-LED lamps is measured at a maximum wavelength of 665 nm. The absorbance was then used in the calibration curve to get concentration. The photocatalysis activity test for methylene blue begins with adding 0.0200 g of ZnO/ZSM-5 in the beaker. Furthermore, 100 mg L^{-1} methylene blue was made from 500 mg L^{-1} stock solutions in a volumetric flask. Then, the decolorization process was done under UV-LED irradiation and dark condition for 15 minutes.

RESULT AND DISCUSSION

Synthesis of ZnO/ZSM-5

ZSM-5 was calcined at 550 °C gradually to activate the sample and eliminate organic templates. ZSM-5 sample after the calcination process has white color, as shown in Figure 1. The ZnO/ZSM-5 synthesis method was adopted from the research done by Derikvandi and Nezamzadeh-Ejhieh (Derikvandi *and* Nezamzadeh-Ejhieh, 2017). The synthesis of ZnO/ZSM-5 in this research was done by the impregnation method by adding metal material. Metal solutions inserted into the structure were not filtered but dried slowly to remove impurities that are

still left inside.

Figure 1. ZSM-5 Sample after calcination process 550 °C.

Powder $Zn(CH_3COO)_2 \cdot 2H_2O$ 3,2927 g dissolved in a 50 mL volumetric flask using aquademin to produce 0.3 M solution. The ZSM-5 preparation results were weighed as much as 2 g. The synthesis process of ZnO/ZSM-5 made by mixing two grams ZSM-5 with 0.3 M 10 mL Zn solution. The mixture is stirred using a magnetic stirrer for 8 hours at 30 °C. The stirring process aims to homogenize particle size, followed by heating at 110 °C in the oven for 12 hours to dry and remove impurities that are still present in the pore. The oven samples were calcined at 550 °C for 4 hours to decompose CH_3COOH. The final product of the synthesis is ZnO/ZSM-5 white solids.

Characterization

X-Ray Diffractometer (XRD). ZSM-5 and ZnO/ZSM-5 obtained were characterized using an X-Ray Diffractometer (XRD) to compare the crystal structure and crystallinity. The expected XRD results from this research were the addition of a new peak on the ZnO/ZSM-5 diffractogram, which is indicating the impregnation process of Zn with the supported catalyst ZSM-5 successfully done. Catalyst support ZSM-5 is a zeolite with MFI structure that has some characteristic peaks. In this research, the ZSM-5 has some characteristic peaks at 2θ 7.76°, 8.64°, 22.81°, 23.66°, 26.74°, which is corresponding to the ZSM-5 with MFI structure in Treacy's research and marked with (*) in Figure 2(a) (Treacy *et al.*, 2001).

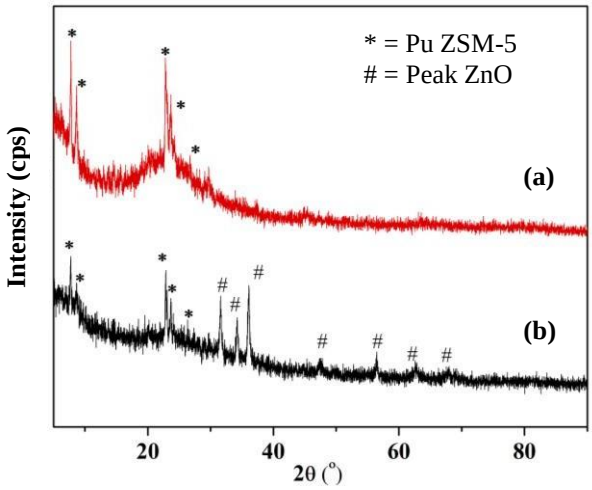

Figure 2. The diffractogram of (a) ZSM-5 (b) ZnO/ZSM-5.

Catalyst support ZSM-5 that have been modified with ZnO semiconductor have new characteristic peaks at 2θ 31.60°, 34.21°, 36.08°, 47.35°, 56.50°, 62.73°, 67.83°, which is indicating the impregnation process was successfully done (Marked with # in Figure 2(b)). This can be confirmed through the peak characteristic of ZnO on JCPDS No. 36-145 with 2θ 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86°, 66.37°, 67.96°. Intensity decreases in the diffractogram after the addition of semiconductor ZnO indicates the process of Zn distribution on the surface of the catalyst support ZSM-5 (Rianto *et al.*, 2012). In principle, the main diffractogram peaks of the ZSM-5 and ZnO/ZSM-5 appear at the same 2θ. Figure 2 shows a different pattern between (a) and (b). It is not proper to claim that there is no structural change based on the previous sentence. The structural change can be claimed only after conducting diffraction data refinement. The similarity of the diffractogram pattern indicates that the addition of Zn to the zeolite ZSM-5 does not change the MFI structure. This fact is corresponding with research done by Wang because the addition of Zn replaces Al from the zeolite framework in the calcination process (Wang *et al.*, 2015).

Fourier Transform Infrared (FTIR). The analysis using Fourier Transform Infrared (FTIR) aims to find out information on the types of functional groups and bonds of samples of ZSM-5 and ZnO/ZSM-5. The samples analyzed are usually in the form of solid, liquid, or gas. The analysis in this research used KBr as a solid solvent in samples with a ratio of 1 : 9 (Sample : KBr). The FTIR spectra of ZSM-5 sample shown in Figure 3(a) shows

some characteristic peaks at wavenumber 1226; 1087.89; 796.63; 551.66; 459.07 cm^{-1}. Peak 1226 cm^{-1} in number **(3)** indicates the asymmetric TO_4 external stretching vibrations, where T indicates Al or Si. The peak at 796.63 cm^{-1} in number **(5)** is an internal sensitive or external sensitive tetrahedron vibration (internal symmetrical stretching vibration), which is typical for materials containing silica. The peak at 551.66 cm^{-1} in number **(6)** indicates the pentacle ring of ZSM-5. The peak at 459.07 cm^{-1} in number **(7)** indicates a T-O bending vibration of the sensitive internal tetrahedron structure. The peak matches with Hamid's research, regarding the formation of ZSM-5 from kaolin with sample IR spectra having a wavenumber range of 1400 – 400 cm^{-1} and characteristic peaks around 1226, 1087, 794, 551, and 459 cm^{-1} (Hamid, 2015). Wavenumber 1226 cm^{-1} is an asymmetric external stretching vibration for TO_4 bond. The area of 1226 cm^{-1} is a peak that is sensitive to changes in the atomic position in the length and angle of bonds with neighboring units on the Si-O-Si oxygen bridge and (Mozgawa *et al.*, 2004). The appearance of absorption bands in the area of 1100 cm^{-1} is a model of asymmetric stretching vibration TO_4. The characteristic peak at 794 cm^{-1} indicates the vibrations related to sensitive internal tetrahedron structures or sensitive external tetrahedral structures (external symmetrical stretching vibrations). The sensitive peak at 551 cm^{-1} indicates the five pentacle ring for ZSM-5 and indicated characteristic zeolite type of MFI. The structure of the peaks in the area of 459 cm^{-1} indicates the vibration of T-O bending for internal tetrahedron structures.

The addition of Zn gave a new peak in the area number **(1)** at 1633.76 cm^{-1}, which indicated the presence of vibration stretching and ZnO. This data also indicates the addition of ZnO semiconductors through impregnation successfully done. The widening of the peak in the area of 3450.77 cm^{-1} shows the stretching vibration of O-H bonds due to the presence of water that is still present in the molecule due to the humid environment (Shah *et al.*, 2018).

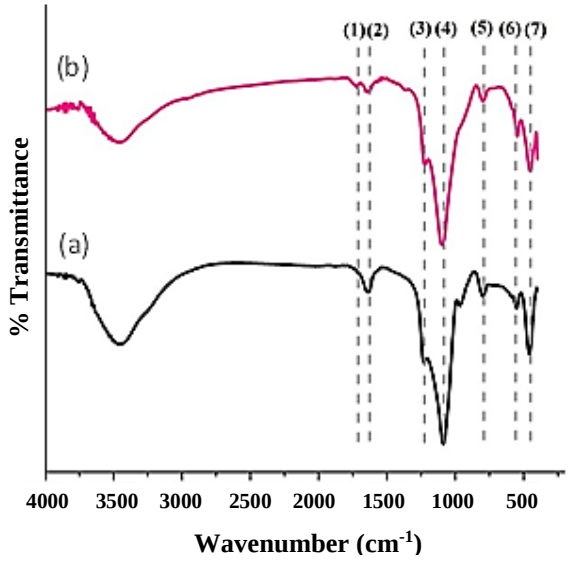

Figure 3. Spectra (a) ZSM-5 (b) ZSM-5/ZnO.

Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray (FESEM-EDX). The samples characterized using FESEM-EDX in this research were ZnO/ZSM-5. Figure 4 shows the crystal morphology of beam-shaped ZSM-5. Besides that, it also shows crystals that form aggregates (clustered particles) with certain pore channels. The aggregate is due to the addition of Zn shown in Figure 5. FESEM instruments equipped with EDX can be used to determine the composition of ZnO/ZSM-5 elements in the section that was analyzed. EDX measures x-ray emission during electron firing at FESEM to find out the chemical composition on a micro and nanoscale with specific peaks.

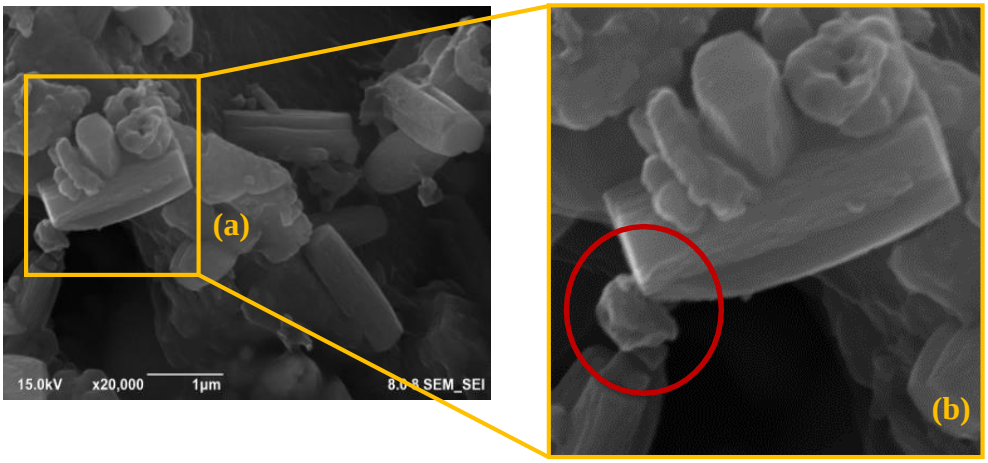

Figure 4. The FESEM imaging of ZnO/ZSM-5 with 20,000 times magnification (a) and the catalyst section tested by EDX (b).

The results of the distribution of elements and the spectrum of ZnO/ZSM-5 using FESEM-EDX instruments are shown in Figure 4 and 5, which consists of the constituent elements of the sample, namely Si, Al, O, and Zn. The results of FESEM-EDX characterization from the sample indicate that the impregnation process was successfully done with the presence of Zn.

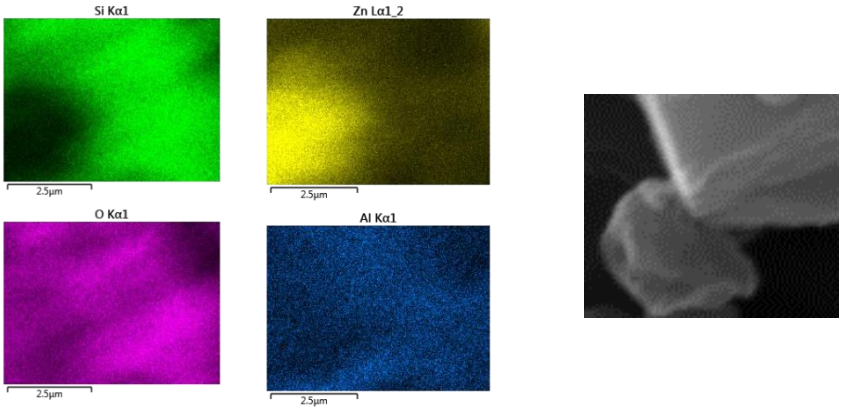

Figure 5. EDX mapping analysis of ZnO/ZSM-5 along with the FESEM area correspond to the EDX mapping.

Surface Area Characterization Using Adsorption-Desorption Nitrogen. The surface area and pore diameter distribution of the ZSM-5 and ZnO/ZSM-5 research were analyzed using N_2 adsorption-desorption. The specific surface area can be determined through the BET (SBET) method, while the pore size distribution is known by the BJH method. The N_2 adsorption-desorption isotherm of zeolite ZSM-5 samples is shown in Figure 6.

Figure 6 (a) and (b) shows ZSM-5 and ZnO/ZSM-5 samples by adsorption of N_2 molecules in low amounts at a relative pressure P/P_0 from zero to 0.25 and 0.30. The area of relative pressure P/P_0 0.25 and 0.3 shows the surface of the solid sample covered by N_2 molecules, resulting in the formation of a monolayer. At P/P_0 0.25 until 0.45 (Figure 6a) and 0.3 until 0.45 (Figure 6b) shows the increase of volume N_2 molecules adsorbed and indicates mesoporous filling. Pores on the surface of the solid can have the effect of limiting the number of layers of adsorbate, resulting in a capillary condensation process. Capillary condensation result in the appearance of a hysteresis loop in the area of relative pressure of 0.45 until 1 both on ZSM-5 and ZnO/ZSM-5. The hysteresis loop occurs because of the difference in the number of nitrogen molecules which are desorped and adsorbed at the same relative pressure. It can be seen that the ZSM-5 and ZnO/ZSM-5 in Figure 6 has a type IV isotherm profile that shows characteristic of solids with mesopores of size 2 – 50 nm with H4 type hysteresis loops. Hysteresis loop H4 can be associated with porous materials with narrow gaps (Rownaghi *et al.*, 2012). The SBET of the ZSM-5 is 686.37 m^2/g, and ZnO/ZSM-5 is 533.89 m^2/g.

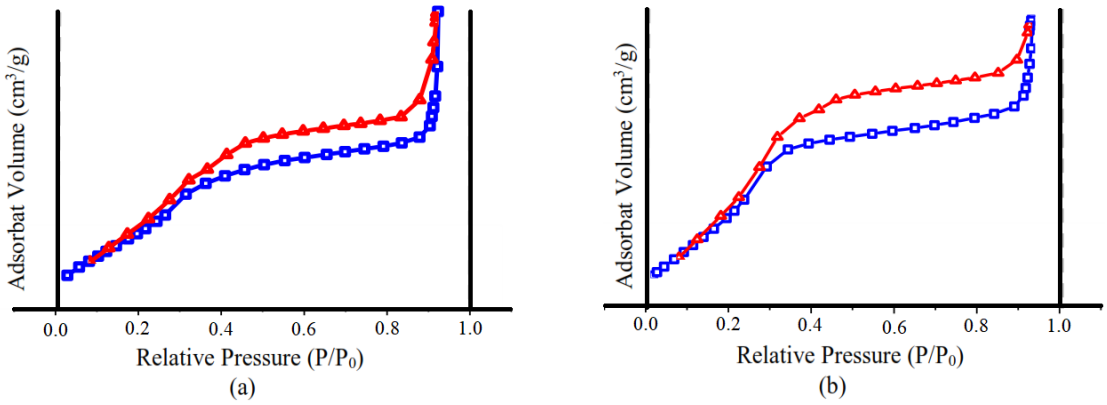

Figure 6. Mesoporous N_2 adsorption-desorption isotherm graph (a) ZSM-5 (b) ZnO/ZSM-5.

The pore distribution of the sample can be known through the BJH method (Barrett, Joiner, Halenda) in Figure 7. This method is used to determine the meso-sized pore distribution. Figure 7 indicates the presence of meso-sized pores on the ZSM-5 and ZnO/ZSM-5 with a pore distribution in pore diameters of around 2 – 5 nm.

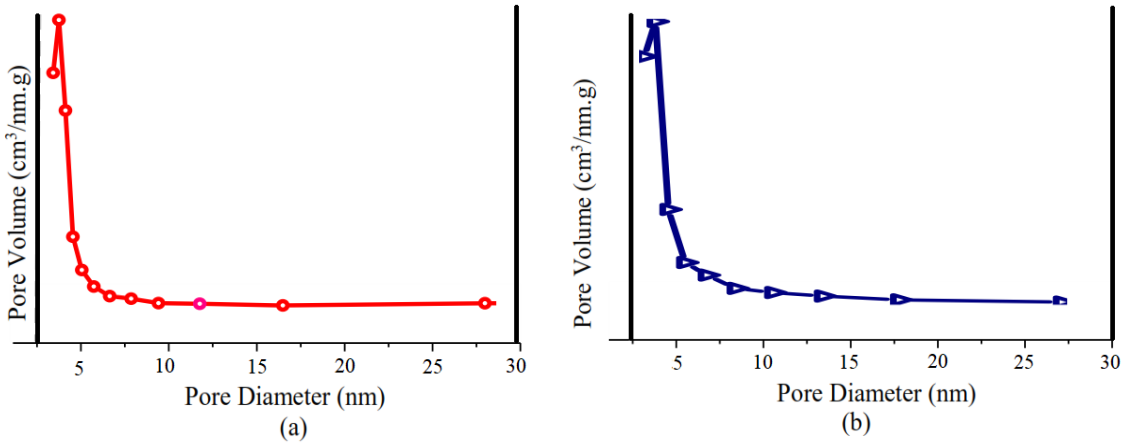

Figure 7. ZSM-5 Pore size distribution with BJH method.

Photocatalysis Activity Test

The photocatalysis activity test for color decolorization was done by adding 0.02 g of ZSM-5 and ZnO/ZSM-5 in the beaker. Next, a stock solution of 500 mg L^{-1} is made and diluted to 100 mg L^{-1}. The maximum absorbance of methylene blue 100 mg L^{-1} occurs at a wavelength of 665 nm. The absorbance of the color reduction photocatalyst activity test was triple measured using UV-Vis instruments in this wavelength in dark conditions and under irradiation of UV-LED lights for 15 minutes. The adsorption process was done at the same time duration, which is 15 minutes. The absorbance data after the photocatalysis process were presented in Table 1.

Data on Table 1 shows that methylene blue color reduction using ZSM-5 are better than ZnO semiconductors, indicating from the lower absorbance value (Table 1) and the high of percent removal (see Table 1) of methylene blue color after photocatalysis with ZSM-5 compared to ZnO 0.02 g and 12.20% (0.0034 g). The results of the methylene blue color reduction using ZSM-5 under UV-LED irradiation and dark conditions have almost the same percent removal value (ZSM-5 uses higher irradiation of 2.18% compared to dark conditions). Photocatalysis using ZnO semiconductors impregnated with ZSM-5 catalyst support has a better result than ZnO and ZSM-5 only. In this research, ZnO/ZSM-5 has higher percent removal (Figure 8) than ZSM-5 and ZnO with a mass of 0.02 g and ZnO 12.20% (0.0034 g). This phenomenon is because the photocatalysis process using impregnated catalyst support and semiconductor with the irradiation process in neutral pH of methylene blue can optimize the process. Irradiation using UV-LED lights with greater energy than the band gap (E_g) semiconductors can cause electron-hole formation (e^- h^+) due to the excitation of electrons from the valence band to the conduction band, thereby increasing the percent removal of methylene blue color reduction. The hole in the valence band acts as a strong

oxidant to produce hydroxyl radicals, which can reduce the methylene blue color (Zouzelka *et al.*, 2016). ZnO/ZSM-5 with UV-LED irradiation has the highest percent removal of 78.32%. ZSM-5 as a porous material with a large surface area, has increased photocatalyst activity due to the addition of ZnO semiconductors through the impregnation process. In this research, the adsorption was more dominant than the photocatalysis effect, estimated from the differences of percent removal ZnO/ZSM-5 and ZnO semiconductors under irradiation using UV-LED lamps is 74.01%. In addition, the percent removal of methylene blue adsorption using ZnO/ZSM-5 photocatalysts in dark conditions is 51.19% greater than ZnO.

Table 1. Absorbance data, final concentration, and percent removal.

Treatment	Notation	Average of Absorption	Average Final Concentration	Percent Removal
ZnO 12.2% No UV-LED	A	0.18	97.86	1.18
ZnO 12.2% UV-LED	B	0.17	95.13	4.31
ZnO 0.0200 g No LED	C	0.17	92.60	6.67
ZnO 0.0200 g UV-LED	D	0.15	82.27	16.59
ZSM 0.0200 g No UV- LED	E	0.12	64.15	35.47
ZSM-5 0.0200 g UV-LED	F	0.12	61.62	37.65
ZnO/ZSM-5 0.0200 g No UV-LED	G	0.09	46.04	52.36
ZnO/ZSM-5 0.0200 g UV-LED	H	0.05	21.68	78.32

CONCLUSIONS

The impregnation of ZnO semiconductors to catalyst support ZSM-5 can increase photocatalyst activity under UV-LED light irradiation. The photocatalysis process in the methylene blue degradation results in an increasing percent removal of methylene blue dyes using ZnO/ZSM-5 that reaches to 78.32%.

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REFERENCES

World Population Prospects: The 2017 Revision, 2017. Department of Economic and Social Affairs, Population Division. New York.

Gita, S., Hussan, A., and Choudhury, T.G., 2016. Impact of Textile Dyes Waste on Aquatic Environments and Its Treatment. *Journal of Environment Ecology* 35(3) 2349–2353. ISSN 0970-0420.

Kementrian Perindustrian, 2018. *Prospect of Textile Industry*. Kemenperin, Indonesia.

Ladhe, U.V., Wankhede, S.K., Patil, V.T., and Patil, P.R., 2011. Removal of Erichrome Black T from Synthetic Wastewater by Cotton Waste. *E- Journal of Chemistry* 8. 2, 803–808. doi: 10.1155/2011/178607.

Naimah, S., Ardhanie, S., Jati, B.N., Aidha, N.N., and Arianita, A., 2014. Color Degradation in Textile Industrial Waste Water with Photocatalytic Method Using Nanocomposites TiO_2-Zeolit. *Journal of Chemistry and Package* 36, 225–236, 2014. doi: 10.24817/jkk.v36i2.1889.

Wang, X., Jiang, C., Hou, B., Wang, Y., Hao, C., and Wu, J., 2018. Carbon Composite Lignin-Based Adsorbents for the Adsorption of Dyes. *Journal of Chemosphere* 206, 587–596. doi: 10.1016/j.chemosphere.2018.04.183.

Sivakumar, V., Asaithambi, M., and Sivakumar, P., 2012. Physico-Chemical and Adsorption Studies of Activated Carbon from Agricultural Wastes. *Advances in Applied Science Research* 3, 219–226. ISSN: 0976-8610.

Babalola, J.O., Koiki, B.A., Eniayewu, Y., Salimonu, A., Olowoyo, J.O., Oninla, V.O., Alabi, H.A., Ofomaja, A.E., and Omorogie, M.O., 2016. Adsorption Efficacy of *Cedrela Odorata* Seed Waste for Dyes: Non Linear Fractal Kinetics and Non Linear Equilibrium Studies. *Journal of Environment Chemistry Engineer* 4, 3527–3536. doi: 10.1016/j.jece.2016.07.027.

Stavrinou, A., Aggelopoulos, C.A., and Tsakiroglou, C.D., 2018. Exploring the Adsorption Mechanisms of Cationic and Anionic Dyes on to Agricultural Waste Peels of Banana, Cucumber and Potato: Adsorption Kinetics and Equilibrium Isotherms as a Tool. *Journal of Environment Chemical Engineering* 6, 6958–6970. Doi: 0.1016/j.jece.2018.10.063.

Aly-Eldeen, M.A., El-Sayed, A.A.M., Salem, D.M.S.A., and El Zokm, G.M., 2018. The Uptake of Eriochrome

Black T Dyefrom Aqueous Solutions Utilizing Waste Activated Sludge: Adsorption Process Optimization Using Factorial Design. *Egyptian Journal of Aquatic Research* 44, 179–186. doi: 10.1016/j.ejar.2018.09.001.

Maizatisna, 2007. Degradation of Naphtol Blue Black Dyes by Sonolysis and Photolysis with the Addition of TiO_2 Anatase. Skripsi Universitas Andalas.

Ajmal, A., Majeed, I., Malik, R.N., Idriss, H., and Nadeem, M.A., 2014. Principles and Mechanisms of Photocatalytic Dye Degradation on TiO_2 Based Photocatalysts: A Comparative Overview. *Journal of RSC Adv* 4, 37003–37026. doi: 10.1039/C4RA06658H.

Chan, S.H.S., Yeong Wu, T., Juan, J.C., and Teh, C.Y., 2011. Recent Developments of Metal Oxide Semiconductors as Photocatalysts in Advanced Oxidation Processes (AOPs) for Treatment of Dye Waste-Water. *Journal of Chemistry Technology Biotechnol*. 86, 1130–1158. doi: 10.1002/jctb.2636.

Muslim, Z.R., Aadim, K.A., and Kadhim, R.F., 2017. Preparation of ZnO for Photocatalytic Activity of Methylene Blue Dye. *International Journal of Basic and Applied Science*. 6, 1–7. E-ISSN: 2301-4458.

Derikvandi, H., and Nezamzadeh-Ejhieh, A., 2017. Increased Photocatalytic Activity of NiO and ZnO in Photodegradation of a Model Drug Aqueous Solution: Effect of Coupling, Supporting, Particles Size, and Calcination Temperature. *Journal of Hazardous Material*. 321, 629–638. doi: 10.1016/j.jhazmat.2016.09.056.

Hamid, A., 2015. Synthesis of Mesoporous ZSM-5 from Kaolin and Colloidal Silica with Two Step Crystallization: Influence of Temperature and Aging Time. *Tesis Kimia Fakultas Sains Institut Teknologi Sepuluh Nopemper*, 99.

Subagyo, R., Kusumawati, Y., and Widayatno, W. B. 2020. Kinetic Study of Methylene Blue Photocatalytic Decolorization Using Zinc Oxide Under UV-LED Irradiation. *AIP Conferences Proceeding*, 2237, 020001.

Wei, Z., Chen, L., Cao, Q., Wen, Z., Zhou, Z., Xu, Y., and Zhu, X., 2017. Steamed Zn/ZSM-5 Catalysts for Improved Methanol Aromatization with High Stability. *Journal of Fuel Processing Technology.* 162, 66–77. doi: 10.1016/j.fuproc.2017.03.026.

Treacy, M.M.J., Higgins, J.B., and Von Balloms, R., 2001. *Collection of Simulated XRD Powder Patterns for Zeolite, 4th edition. ed*. Elsevier, Amsterdam.

Rianto, L.B., Amalia, N. S., and Khalifah, S.N., 2012. The Effect of Titanium Metal Impregnation on Natural Zeolite Malang to its Surface Area. *Alchemy* 2, 58–67. ISSN 2086-1710.

Wang, X., Gao, X., Dong, M., Zhao, H., and Huang, W., 2015. Production of Gasoline Range Hydrocarbons from Methanol on Hierarchical ZSM-5 and Zn/ZSM-5 Catalyst Prepared with Soft Second Template. *Journal of Energy Chemistry*, 24, 490–496. doi: 10.1016/j.jechem.2015.06.009.

Mozgawa, W., Handke, M., and Jastrzębski, W., 2004. Vibrational Spectra of Aluminosilicate Structural Clusters. *Journal of Molecular Structure*. 704, 247–257. doi: 10.1016/j.molstruc.2004.01.059.

Shah, J., Jan, M.R., and Khitab, F., 2018. Sonophotocatalytic Degradation of Textile Dyes Over Cu Impregnated ZnO Catalyst in Aqueous Solution. *Journal of Process Safety Environmental Protection*. 116, 149–158. doi: 10.1016/j.psep.2019.05.054.

Rownaghi, A.A., Rezaei, F., and Hedlund, J., 2012. Uniform Mesoporous ZSM-5 Single Crystals Catalyst with High Resistance to Coke Formation for Methanol Deoxygenation. *Journal of Microporous Mesoporous Material*. 151, 26–33. doi: 10.1016/j.micromeso.2011.11.020.

Zouzelka, R., Kusumawati, Y., Remzova, M., Rathousky, J., and Pauporté, T., 2016. Photocatalytic Activity of Porous Multiwalled Carbon Nanotube-TiO_2 Composite Layers for Pollutant Degradation. *Journal Hazardous Material*. 317, 52–59. doi: 10.1016/j.jhazmat.2016.05.056.