

Photocatalytic degradation of methylene blue dye solution using different amount of ZnO as a photocatalyst

Hartini Ahmad Rafaie^{1*}, Nur Fitrahana Mohd Yusop¹, Nurathira Faqihah Azmi¹,
Nur Syakirah Abdullah¹ and Nurul Infaza Talalah Ramli¹

¹Faculty of Applied Sciences, Universiti Teknologi MARA Pahang, Bandar Tun Abdul Razak Jengka,
Pahang, Malaysia

Corresponding author: hartinirafaie@uitm.edu.my

Received: 16 April 2020; Accepted: 28 July 2020; Published: 5 January 2021

ABSTRACT

Zinc oxide (ZnO) powder was used as a photocatalyst for the photocatalytic degradation of methylene blue (MB) dye solution. In this study, different amount of ZnO (10, 20 and 30 mg) as photocatalyst was used to investigate the performance of photocatalytic degradation of MB dye solution. The morphology and structural properties of ZnO powder were studied by X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FESEM) techniques. The photocatalytic activities of the ZnO powder were investigated by degrading the MB dye solution under UV light irradiation at different amounts of ZnO photocatalyst. The percentage degradation of MB dye solution in the presence of 10 mg ZnO powder was found to be the highest at 96.2 % within 60 min irradiation compared to 20 and 30 mg of ZnO powder. The photodegradation rate constants, k obtained in this study were 0.0661, 0.0558, and 0.0507 min^{-1} for 10, 20, and 30 mg ZnO powder, respectively that follow the pseudo first-order reaction kinetics.

Keywords: *Methylene blue, photocatalytic degradation, photocatalyst, Zinc Oxide*

INTRODUCTION

In recent years, environmental pollution has been identified as one of the greatest problems concerning our society. The vast development of the textile industries has contributed a significant impact to water pollution, which is mainly due to the highly coloured effluents containing organic and inorganic dyes that have been disposed to the water stream [1,2]. Most of these dyes are highly toxic, carcinogenic, harmful to human and aquatic life and due to their complex chemical structure and synthetic nature, they are very stable and highly resistant to degradation [3,4]. There are a lot of ideal ways to treat and eliminate dye pollution from the wastewater such as adsorption, oxidation, filtration, and sedimentation. Photocatalytic degradation is one of the alternative ways that have been demonstrated to effectively degrade and remove the organic pollutants in the presence of photocatalyst [5,6]. Photocatalytic degradation was found to be an effective alternative way compared to the methods mentioned earlier due to using non-toxic photocatalyst, low-cost, and a highly reactive technique [7].

Semiconductor materials such as TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS have been used as photocatalysts. They provide photo-generated holes with high oxidizing power due to their wide bandgap energy. ZnO has been extensively studied to act as an efficient photocatalyst owing to its high photosensitivity, high stability, nontoxicity, widely available, and low cost [8,9]. ZnO is a substantial group II–VI semiconductor with a bandgap energy of 3.37 eV as well as a large exciton binding energy of 60 meV at room temperature [10,11]. ZnO has been suggested as an alternative to TiO_2 photocatalyst due to its ability to absorb a larger fraction of solar spectrum due to higher photon efficiency and also have a larger quantum efficiency compared to TiO_2 [12,13].

The photocatalytic degradation performance is significantly affected by various parameters such as the amount of catalyst loading, initial dye concentration, the surface structure of the catalyst, and pH value. A previous study reported by Nicolas Perciani de Moraes et al. [14] emphasized the catalyst dosage effect on the adsorption of methylene blue dye. It was observed that the amount of absorbed dye was increased when the niobium oxide catalyst dosage was increased from 0.25 to 0.5g. The cause of this increment is associated with the increased surface area and the abundance of available active sites. The effect of catalyst dosage and photocatalyst content on the degradation efficiency [11]. As reported by Vadaei and Faghihian [15], tin tellurium (SnTe) was coupled on the surface of Santa Barbara Amorphous-15 (SBA-15) support as a photocatalyst and the amount of photocatalyst used was varied in the range of 0.001 to 0.01g, to optimize the catalyst dosage. It was found that the degradation efficiency of SnTe@SBA-15 with an optimized dose of 0.006g had diminished twofold compared to the bulk SnTe with an optimized dose of 0.003g. They also observed that a higher dose of a catalyst than the optimized value results in low degradation efficiency due to the incident radiations were partially scattered by the aggregated photocatalyst.

This paper mainly demonstrated the effect of different amounts of ZnO catalyst loading on the photocatalytic degradation of MB dye under UV light irradiation. The mechanism of photodegradation of MB dye is also discussed and provides an important insight into the photocatalytic activity of photocatalyst.

EXPERIMENTAL

Materials and Characterization Methods

In this work, pure ZnO powder (Sigma Aldrich, 99 %) was generally used as a photocatalyst and methylene blue (MB) dye as a pollutant. All reagents were analytically pure and used without further purification. Different amounts of ZnO powder (10, 20, and 30 mg) were used to investigate the effect of different amounts of ZnO loading on the catalytic photodegradation of MB dye under UV light irradiation. The phase and purity of ZnO powder were characterized using XRD (PAN analytical with Cu-K α radiation probe beam of 1.54056 Å wavelength) between range 25-70 °. The size of the particle was estimated by the Scherrer equation on the width half maximum (FWHM) of the ZnO (101) peak. The surface morphology of ZnO powder was examined by field emission scanning electron microscope (FESEM). The optical absorption of the MB degradation at a wavelength of 664 nm was carried out by a UV-visible spectrophotometer (UV-1800, SHIDMADZU).

Photocatalytic degradation measurement

The photocatalytic degradation for ZnO photocatalyst at the different amounts (10, 20, and 30 mg) was measured at room temperature under UV lamp irradiation that predominantly emitted at 365 nm with the power of 12 W, 230 Volts, and 50 Hz frequency. It was employed as a UV source and positioned parallel to the beaker as depicted in Figure 1.

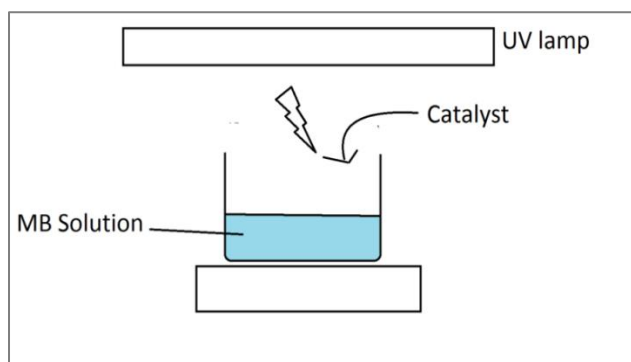


Figure 1: Experimental setup of photocatalytic degradation

The reaction was carried out with 10, 20, and 30 mg of ZnO catalyst dispersed in 100 mL of MB solution (5 mg/L) and irradiated by UV light. Before irradiation, the suspensions were magnetically stirred in the dark for 30 minutes to establish the adsorption-desorption equilibrium of the MB solution. About 4 mL of the sample was withdrawn at an interval of 10 minutes, respectively. The concentration of MB in solution was determined by measuring the absorption at a wavelength of 664 nm using a UV-Vis spectrometer at room temperature and the results were converted into the corresponding concentration (C). The photocatalytic degradation percentage of MB was calculated by using the following equation (Eq. (1)) [2,16,17]:

$$\text{Photocatalytic degradation of MB (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_0 is the initial concentration of the MB solution and C_t is the concentration of the MB solution at irradiation time, t , respectively. Moreover, the photodegradation rate constant, k values for the MB dye degradation at different amount of ZnO catalyst were then calculated using first-order kinetic rate reaction based on the following equation (Eq. (2)) [2,18]:

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

The k was calculated from the graph between $\ln(C/C_0)$ vs irradiation time, where C_0 and C denote the MB dye concentration at the time, $t=0$ and $t=t$ respectively.

RESULTS AND DISCUSSION

Structural and morphological properties

Figure 2 (a) and (b) shows the FESEM images and morphology of ZnO powder at a magnification of 20,000 x and 40,000 x, respectively. It can be observed that the ZnO powder consists of cubic-rod structure particles in the size ranging from 100 -500 nm. Generally, the homogeneity of the surface structure is considered to be more reactive because it offers higher surface area and low coordinating sites.

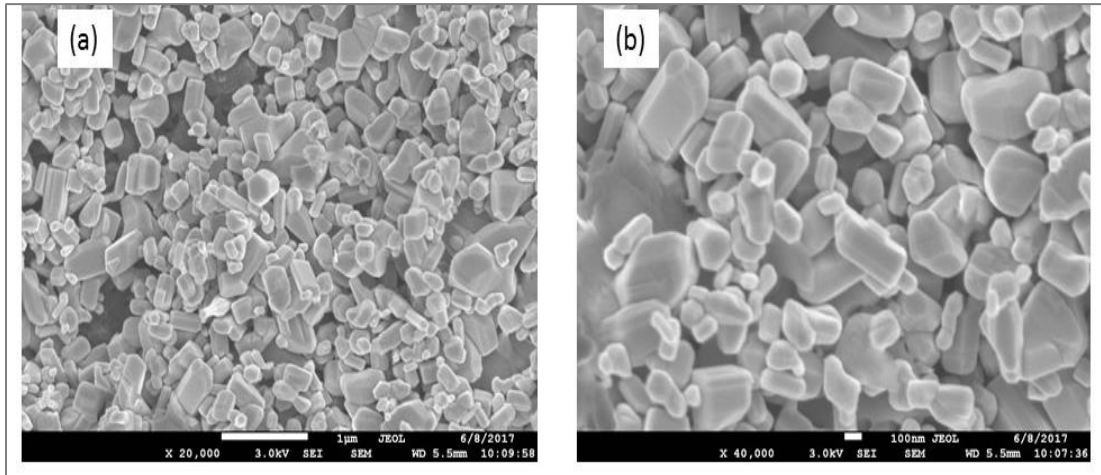


Figure 2: FESEM images of ZnO powder at magnification (a) 20,000 x and (b) 40,000 x

To confirm the crystal structure of the ZnO sample, the X-ray powder diffraction (XRD) analysis was carried out as shown in Figure 3 showing that the ZnO diffraction peak positions and intensities are well-matched with the standard Joint Committee on Powder Diffraction Standards data card No. 36- 1451. The reflections appeared at 31.6 °, 34.4 °, 36.1 °, 47.6 °, 56.7°, 62.9 °, 66.4 °, 68.0 ° and 69.2 ° correspond to the lattice planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively. The observed pattern confirms that ZnO powder possesses a hexagonal wurtzite structure with a space group of P63mc. As seen in Figure 3, the preferred plane of the ZnO is along the (101) direction and the size of the particles has been computed from the width of (101) plane using the Debye Scherrer formula as following equation (Eq. (3))[19,20]:

$$D = K \lambda / \beta \cos \theta \quad (3)$$

Where K is constant, λ is the wavelength of X-rays employed radiation (1.54056 Å), β is corrected full width at half maximum and θ is Bragg angle. The calculated crystallite size of the ZnO powder is about 30 nm.

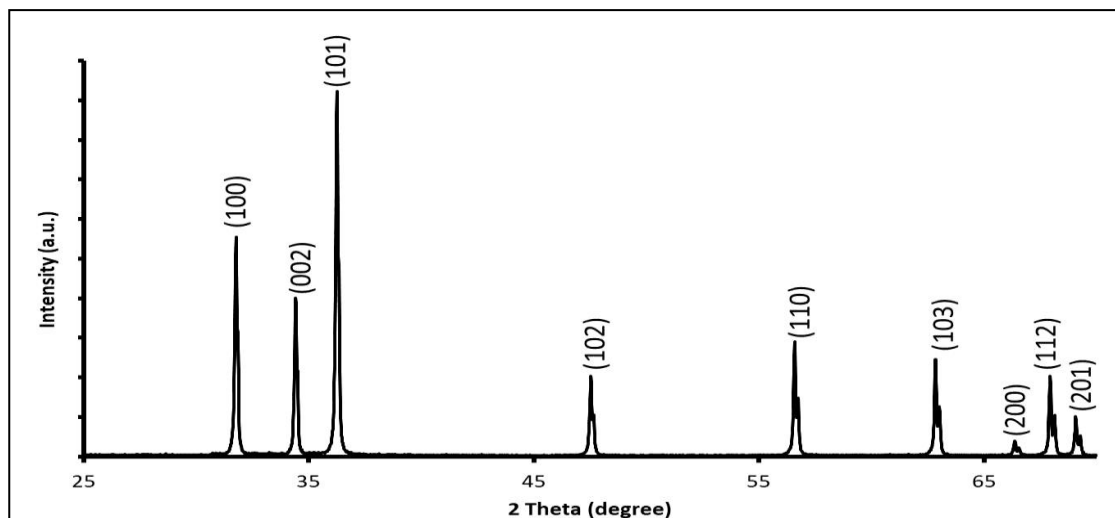


Figure 3: XRD pattern of the ZnO powder

Photocatalytic degradation of MB dye

The amount of catalyst loading is one of the significant parameters for photocatalytic studies. The optimized amount is necessary to be determined to avoid the use of excess catalyst. The amount of catalyst on the photodegradation of MB dye solution was carried out for 10, 20, and 30 mg, respectively. Figure 4 shows the UV–vis absorbance spectra of MB dye with the variation of time during the photodegradation process up to 60 min using ZnO powder catalyst at different amounts of (a) 10 mg, (b) 20 mg, and (c) 30 mg under UV illumination. It can be observed from the spectra that the characteristic absorption intensities of MB dye gradually decreased with time in the presence of ZnO powder at wavelength $\lambda = 664$ nm. The MB dye becomes colorless indicating the degradation of MB dye molecules.

The effect of different amounts of catalyst loading on the photocatalytic degradation percentage was tested and shown in Figure 5. It was found that the percentage of degradation of MB significantly depended on the amount of catalyst loading. The percentage of degradation of MB was decreased from 96.2%, 95.39%, and 92.44% with the increased amount of loading of 10, 20, and 30 mg, respectively. The catalyst loading influenced the amount of active site on the sample and the amount of dye adsorbed by the samples [21]. In this work, ZnO which acts as a catalyst was illuminated with a UV light source, and then the electron-hole pairs are produced with electrons promoted to the conduction band and leaving the positive holes in the valence band [22]. The generated electron-hole pairs induced a complex series of reactions that might result in the complete degradation of the dye pollutant adsorbed on the ZnO surface.

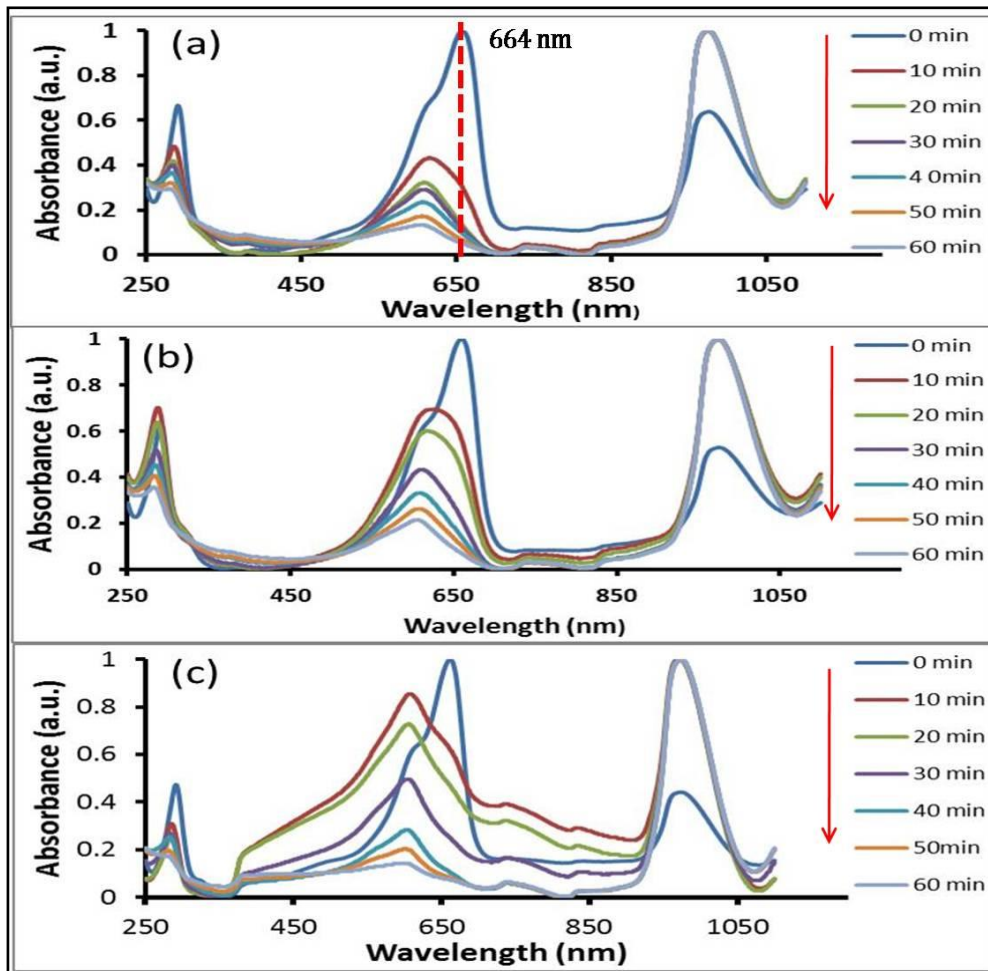


Figure 4: UV-vis absorbance spectra of MB dye as a function of time over ZnO powder at different amount of loading (a) 10 mg, (b) 20 mg, and (c) 30 mg under UV illumination

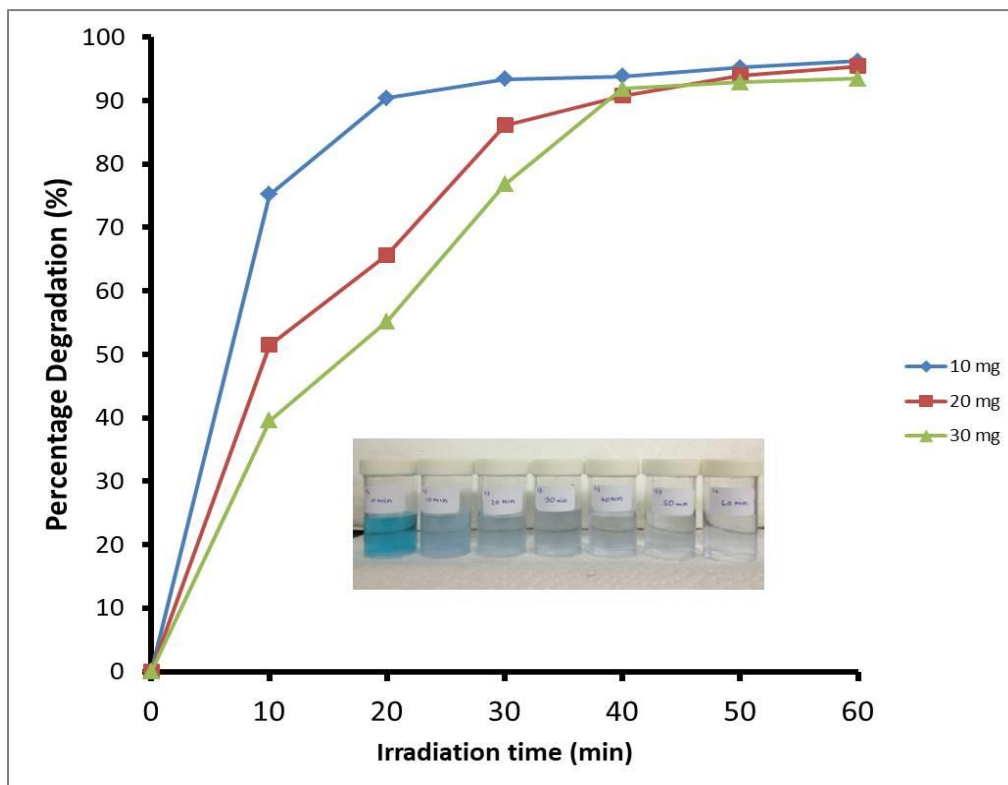


Figure 5: Percentage degradation of MB dye solution using ZnO powder at a different catalyst loading

Further analysis on the photodegradation of MB dye has been carried out by plotting a first-order decay plot of the characteristic MB absorption at peak 664 nm where the photodegradation rate constant, k of ZnO at different amount loading can be evaluated and quantified. Figure 6 represents the photodegradation curves of MB in the form of $\ln(C/C_0)$ versus irradiation time. It can be seen in Figure 6 that the plot represents a straight line which agrees with the Langmuir–Hinshelwood first-order kinetic behavior. The results show that the strongest decomposition of MB dye occurs when 10 mg of the amount of ZnO catalyst with value of degradation rate constant, k of 0.661 min^{-1} was used compared to 0.0558 and 0.0507 min^{-1} value of 20 and 30 mg catalyst loading.

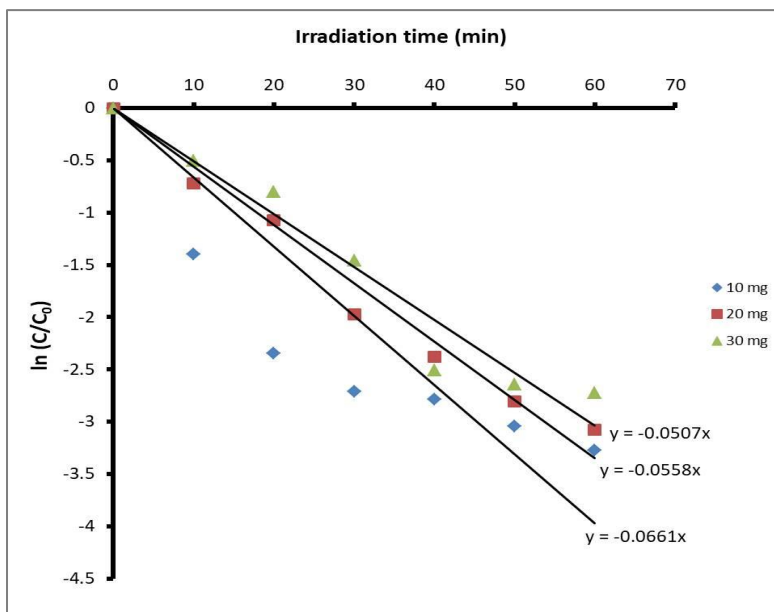
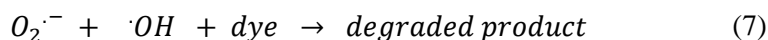
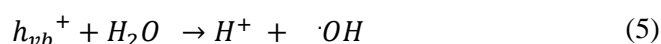


Figure 6: Plot of $\ln(C/C_0)$ vs. irradiation time for the degradation of MB using ZnO powder at a different catalyst loading

The amount of ZnO as a catalyst has a significant effect on the catalytic photodegradation activity as it can be observed with an increase in the amount of catalyst loading, the photodegradation rate constant, k value was decreased. This might be due to the high excess or dosage of the catalyst which results in the deactivation of activated molecules by collision with ground-state molecules [23,24]. Hence, 10 mg amount of catalyst is the optimum catalyst loading that has been observed to degrade the MB solution. Previous literatures have been reported that increasing the amount of photocatalyst will result in extra production of active sites on the photocatalyst surface which then lead to an increased amount of radical formations, consecutively. Hence, a higher dosage of catalyst could improve the degradation efficiency of the MB dye solution. Moreover, the reduction in the rate constant may be due to the reduction in the penetration of light with a surplus amount of ZnO [23,25]. The existing results suggest that the catalytic photodegradation performance was changed by the amount of catalyst loading. Higher catalyst loading is expected to decrease the degradation efficiency because of agglomeration of excess catalyst and thus lowering the photocatalytic activity of the MB dye.

Generally, the degradation of MB solution by ZnO particles could be explained by the mechanism below [16,17,26]. When ZnO photocatalyst is irradiated by light with an energy higher or equal to the bandgap, an electron in the valence band (e_{cb}^-) will be excited to the conduction band and leaving a generation of a hole in the valence band (h_{vb}^+) on the surface of ZnO particles as shown in (Eq. (4)) [16,27]. This excited e_{cb}^- and h_{vb}^+ can recombine and get trapped in metastable surface states or react with electron donors and acceptors adsorbed on the

semiconductor surface. Following that, holes could react with water adhering to the surface of ZnO particles to form a highly reactive hydroxyl radical ($\cdot\text{OH}$) as in (Eq. (5)). Meanwhile, oxygen acted as an electron acceptor by forming a superoxide radical anion ($\text{O}_2^{\cdot-}$) as in (Eq. (6)). MB was fully degraded and removed through direct oxidation by the $\cdot\text{OH}$ radicals and $\text{O}_2^{\cdot-}$ radical as shown in (Eq. (7)).



CONCLUSION

In summary, the amount of catalyst loading is one of the important parameters that need to be considered in the catalytic photodegradation technique for waste-water treatment, particularly in dye removal. It can be observed that 10 mg of ZnO catalyst shows the optimum performance of photocatalytic as it produced a percentage degradation of 96.20 % and photodegradation rate constant, k value of 0.0661 min^{-1} . The mechanism of photodegradation of MB dye is also discussed.

ACKNOWLEDGMENTS

The authors would like to express our gratitude to the Ministry of Higher Education Malaysia (MOHE), Universiti Teknologi MARA (UiTM), Research Management & Innovation Institute (IRMI), FRGS-RACER grants (600-IRMI/FRGS-RACER 5/3 (041/2019)), UiTM Cawangan Pahang, Kampus Jengka and UiTM Shah Alam for providing facilities needed for the study.

REFERENCES

- [1] Saravanan, R., Karthikeyan, N., Gupta, V. K., Thirumal, E., Thangadurai, P., Narayanan, V., & Stephen, A. J. M. S. (2013). ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Materials Science and Engineering: C*, 33(4), 2235-2244.

- [2] Rahman, Q. I., Ahmad, M., Misra, S. K., & Lohani, M. (2013). Effective photocatalytic degradation of rhodamine B dye by ZnO nanoparticles. *Materials Letters*, 91, 170-174.
- [3] Ahmad, M., Ahmed, E., Zhang, Y., Khalid, N. R., Xu, J., Ullah, M., & Hong, Z. (2013). Preparation of highly efficient Al-doped ZnO photocatalyst by combustion synthesis. *Current Applied Physics*, 13(4), 697-704.
- [4] Kumar, R., Kumar, G., & Umar, A. (2013). ZnO nano-mushrooms for photocatalytic degradation of methyl orange. *Materials Letters*, 97, 100-103.
- [5] Al-Hamdi, A. M., Rinner, U., & Sillanpää, M. (2017). Tin dioxide as a photocatalyst for water treatment: a review. *Process Safety and Environmental Protection*, 107, 190-205.
- [6] Akin, M. B., & Oner, M. (2013). Photodegradation of methylene blue with sphere-like ZnO particles prepared via aqueous solution. *Ceramics International*, 39(8), 9759-9762.
- [7] Odling, G., & Robertson, N. (2019). Bridging the gap between laboratory and application in photocatalytic water purification. *Catalysis Science & Technology*, 9(3), 533-545.
- [8] Wu, H. Y., Jian, W. J., Dang, H. F., Zhao, X. F., Zhang, L. Z., & Li, J. H. (2017). Hierarchical Ag-ZnO Microspheres with Enhanced Photocatalytic Degradation Activities. *Polish Journal of Environmental Studies*, 26(2).
- [9] Tian, C., Zhang, Q., Wu, A., Jiang, M., Liang, Z., Jiang, B., & Fu, H. (2012). Cost-effective large-scale synthesis of ZnO photocatalyst with excellent performance for dye photodegradation. *Chemical Communications*, 48(23), 2858-2860.
- [10] Liu, H., Zhong, L., Govindaraju, S., & Yun, K. (2019). ZnO rod decorated with Ag nanoparticles for enhanced photocatalytic degradation of methylene blue. *Journal of Physics and Chemistry of Solids*, 129, 46-53.
- [11] Mao, Y., Li, Y., Zou, Y., Shen, X., Zhu, L., & Liao, G. (2019). Solvothermal synthesis and photocatalytic properties of ZnO micro/nanostructures. *Ceramics International*, 45(2), 1724-1729.
- [12] Hung, S. T., Chang, C. J., & Hsu, M. H. (2011). Improved photocatalytic performance of ZnO nanograss decorated pore-array films by surface texture modification and silver nanoparticle deposition. *Journal of hazardous materials*, 198, 307-316.
- [13] Khayyat, S. A., Akhtar, M. S., & Umar, A. (2012). ZnO nanocapsules for photocatalytic degradation of thionine. *Materials Letters*, 81, 239-241.
- [14] de Moraes, N. P., Silva, F. N., da Silva, M. L. C. P., Campos, T. M. B., Thim, G. P., & Rodrigues, L. A. (2018). Methylene blue photodegradation employing hexagonal prism-shaped niobium oxide as heterogeneous catalyst: Effect of catalyst dosage, dye concentration, and radiation source. *Materials Chemistry and Physics*, 214, 95-106.
- [15] Vadaei, S., & Faghihian, H. (2018). Enhanced visible light photodegradation of pharmaceutical pollutant, warfarin by nano-sized SnTe, effect of supporting, catalyst dose, and scavengers. *Environmental Toxicology and Pharmacology*, 58, 45-53.
- [16] Jawad, A. H., Mubarak, N. S. A., Ishak, M. A. M., Ismail, K., & Nawawi, W. I. (2016). Kinetics of photocatalytic decolorization of cationic dye using porous TiO₂ film. *Journal of Taibah University for Science*, 10(3), 352-362.
- [17] Jawad, A. H., Alkarkhi, A. F., & Mubarak, N. S. A. (2015). Photocatalytic decolorization of methylene blue by an immobilized TiO₂ film under visible light irradiation: optimization

- using response surface methodology (RSM). *Desalination and Water Treatment*, 56(1), 161-172.
- [18] Jain, N., Bhargava, A., & Panwar, J. (2014). Enhanced photocatalytic degradation of methylene blue using biologically synthesized “protein-capped” ZnO nanoparticles. *Chemical Engineering Journal*, 243, 549-555.
- [19] Singha, M. K., & Patra, A. (2020). Highly efficient and Reusable ZnO microflower photocatalyst on stainless steel mesh under UV-Vis and natural sunlight. *Optical Materials*, 110000.
- [20] Aydoghmish, S. M., Hassanzadeh-Tabrizi, S. A., & Saffar-Teluri, A. (2019). Facile synthesis and investigation of NiO-ZnO-Ag nanocomposites as efficient photocatalysts for degradation of methylene blue dye. *Ceramics International*, 45(12), 14934-14942.
- [21] Yunus, N. N., Hamzah, F., So’Aib, M. S., & Krishnan, J. (2017, June). Effect of catalyst loading on photocatalytic degradation of phenol by using N, S Co-doped TiO₂. In *IOP Conf. Ser. Mater. Sci. Eng* (Vol. 206).
- [22] Patil, R. S., Kokate, M. R., Shinde, D. V., Kolekar, S. S., & Han, S. H. (2014). Synthesis and enhancement of photocatalytic activities of ZnO by silver nanoparticles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 122, 113-117.
- [23] Benhebal, H., Chaib, M., Salmon, T., Geens, J., Leonard, A., Lambert, S. D., ... & Heinrichs, B. (2013). Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol-gel process. *Alexandria Engineering Journal*, 52(3), 517-523.
- [24] Rajamanickam, D., & Shanthi, M. (2016). Photocatalytic degradation of an organic pollutant by zinc oxide-solar process. *Arabian Journal of Chemistry*, 9, S1858-S1868.
- [25] 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), 143.
- [26] Isai, K. A., & Shrivastava, V. S. (2019). Photocatalytic degradation of methylene blue using ZnO and 2% Fe-ZnO semiconductor nanomaterials synthesized by sol-gel method: a comparative study. *SN Applied Sciences*, 1(10), 1247.
- [27] Tan, W. K., Razak, K. A., Lockman, Z., Kawamura, G., Muto, H., & Matsuda, A. (2014). Synthesis of ZnO nanorod-nanosheet composite via facile hydrothermal method and their photocatalytic activities under visible-light irradiation. *Journal of Solid State Chemistry*, 211, 146-153.