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Photocatalytic decolorization of methylene blue using zinc oxide supported on mesoporous silica nanoparticles

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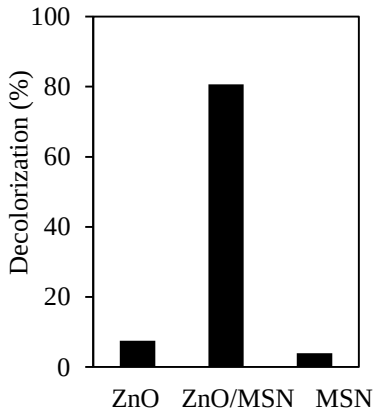
GRAPHICAL ABSTRACT



ABSTRACT

Various dyes that are used in textile, paper, cosmetics and plastics industries may produce harmful effects on the health of living organisms and the environment if not treated properly before being discharged into water bodies. Among many techniques, photocatalytic process is one of the promising treatment for these dyes. Zinc oxide (ZnO) is well-known comparable with TiO_2 due to its unique properties and numerous advantages. While, mesoporous silica nanoparticles (MSN) is an excellent solid support for heterogeneous catalysts due to its high surface area, thermal and mechanical stability, highly uniform pore distribution, tunable pore size, and unique hosting properties. Therefore, in this study, ZnO/MSN (ZM) catalysts were prepared and its physicochemical properties was characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The catalyst was tested on the photodecolorization of methylene blue (MB) dye. The results showed that the interaction between ZnO and MSN support could enhanced the photocatalytic activity. The 0.5 g L^{-1} of 5ZM was found to give the highest degradation (80 %) of 10 mg L^{-1} of MB solution at pH 7 after 3 h under UV light irradiation. The photodecolorization followed the pseudo first-order Langmuir-Hinshelwood kinetic model. This study demonstrated that the prepared 5ZM has a potential to be used in photocatalytic degradation of various dyes as well as organic pollutants.

Keywords: ZnO, MSN, electrochemical, photocatalysis, methylene blue

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1. INTRODUCTION

In recent years, dyes widely used in the textile, paper, cosmetics and plastics industries have led to severe environmental contamination due to the emission of toxic and colored wastewater into water bodies [1-3]. It was found that over 100,000 dyes are commercially available and more than 7 x 10^5 tonnes per year are produced annually [4]. Organic dyes are generally present in the industrial wastewater and cannot be readily degraded because of their stable chemical structures. The discharged of these dyes into water bodies can cause severe problem because of their toxicity, mutagenic and carcinogenic [5-7]. Therefore, many treatment technologies widely used, such as adsorption, coagulation, flocculation, ion exchange and membrane separation [8]. However, these treatments are usually reported as inefficient methods and produce secondary products [9].

Advanced oxidation process (AOP) using heterogeneous semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, CuO, ZrO_2, and CdS as photocatalysts are efficient technique in wastewater treatment because it has capability to convert harmful dyes into non-toxic products, CO_2 and water at ambient temperatures [10,11]. Among them, ZnO is an excellent candidate for applications as photocatalyst because of its unique properties and numerous advantages, such as high photosensitivity and stability in degrading various toxic substances [12]. Even though ZnO has sufficient photocatalytic activity, its poor adsorption properties lead to inefficient photocatalytic activity. Thus, to overcome this shortcoming, an appropriate method need to be exploited in order to improve the adsorption properties of ZnO. Incorporation of ZnO into a mesoporous material support is one of the promising methods which have been discussed by several researchers in recent years [13, 14]. The objective of this study after considering all the factors is to synthesize ZnO/MSN catalysts and study its performance on photocatalytic decolorization of methylene blue (MB).

2. EXPERIMENTS

2.1 Catalyst Preparation

All of the chemical reagents were purchased and used as received without further purification. ZM catalysts were prepared using electrochemical method as reported in previous study [15-19]. Distilled water and NH_4OH were added into TEAP and after electrolysis, MSN was added to the mixture. The mixture was then impregnated and dried before being calcined at 823 K for 3 h.

2.2. Characterization

The crystalline structure of the catalyst was determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of 2θ = 1.5-90°. FT-IR was performed using the KBr method with range of 400-4000 cm^{-1}.

2.3 Photocatalytic testing

The photoactivities of the catalysts were evaluated for the decolorization of MB dye. The photocatalytic activity was performed in a batch reactor fixed with visible lamp and a cooling system. A 0.125 g L-1 catalyst was added to 200 mL MB solution with a desired concentration and stirred for 1 h in the dark to achieve adsorption-desorption equilibrium before being exposed to light radiation for 3 h.

3. RESULTS AND DISCUSSION

3.1 Physicochemical properties of the prepared catalyst

Fig. 1A illustrates a wide-angle XRD pattern of pure ZnO. A series of characteristic peaks were observed at 31.77° (100), 34.42° (002), 36.52° (101), 47.54° (102), 56.60° (110), 62.86° (103), 66.38° (200), 67.96° (112) and 69.10° (201), which can be indexed as a wurtzite phase of ZnO (JCPDS No. 36-1451). The diffraction peaks from other phases of ZnO and impurities could not be observed, suggesting that high-purity of ZnO was obtained [1]. The introducing of ZnO into MSN was also being studied using low-angle XRD pattern in the range of 2θ = 1.5 - 10° (Fig. 1B). Three diffraction peaks were observed at 2θ = 2.39°, 4.05°, and 4.71°, relative to the (100), (110) and (200) reflections, respectively and these peaks represent typical mesostructured silica with hexagonally p6 mm symmetry structure formed by the 2D hexagonal arrays of the mesostructure [19]. Fig. 2 shows the FT-IR spectra of ZnO, MSN and 5ZM catalysts in the region between 4000 and 400 cm^{-1}. Three bands were observed at 466, 810 and 1095 cm^{-1} attributed to the bending vibrations, symmetric stretching and asymmetric stretching of Si-O-Si bonds in MSN, respectively. The band at 975 cm^{-1} was ascribed to Si-OH bending vibrations in MSN. The intensity of all these bands increased when increase ZnO loading, which suggested a possible interaction of Zn on silica framework. Moreover, the intensity of band 975 cm^{-1} was decreased, indicating the replacement of the –OH group by O-metal ions probably occurred. A broad band at 3471 cm^{-1} was observed for all samples, attributed to adsorb H_2O molecules and bands at 1658 cm^{-1} which ascribed to water molecules retained by siliceous materials [20].

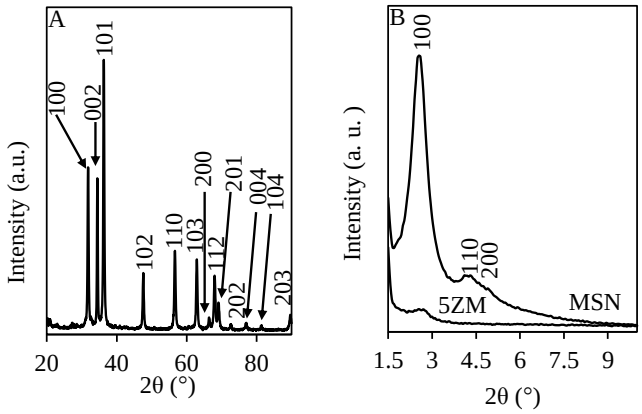

Fig. 1 (A) Wide-angle XRD patterns of ZnO and (B) small-angle XRD patterns

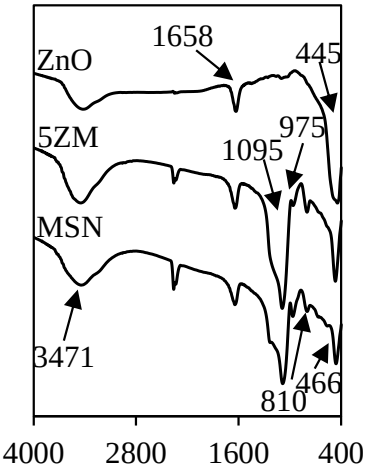

Fig 2 FTIR spectra of the catalysts

3.2 Photocatalytic testing on the decolorization of methylene blue

3.2.1 Performance of the prepared catalyst

The performances of ZnO, MSN and 5ZM catalysts for the decolorization of methylene blue (MB) were examined, and the results are shown in Fig. 3. All catalysts were stirred for 1 h in the dark to achieve adsorption-

desorption equilibrium before being exposed to visible light radiation for 3 h.

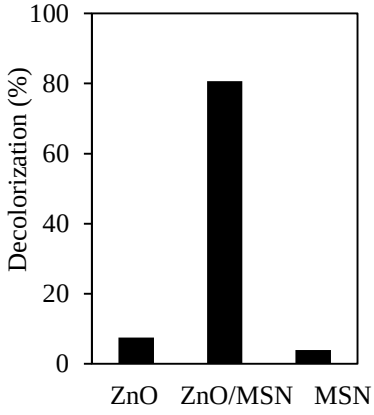

Fig. 3 Catalytic performance of the catalysts

No obvious photodecolorization was observed in the presence of bare MSN. Compared with pure ZnO, the addition of ZnO into MSN resulted a higher decolorization percentage of MB (80 %). This result verified the role of MSN as a support to provide a good dispersion of active site, which led to a faster rate of reaction [21].

3.2.2 Effect of pH and catalyst dosage

The pH solution is one of the significant parameters that influence the rate of photocatalytic activity. In this study, the effect of pH on decolorization of MB by 5ZM was investigated by varying the pH values from 3 to 11, and the results are presented in Fig. 4. The greatest decolorization was obtained at pH 7, with 80 probably due to the neutral condition of the solution which in this pH, more reaction between dye molecules and photocatalyst [1].

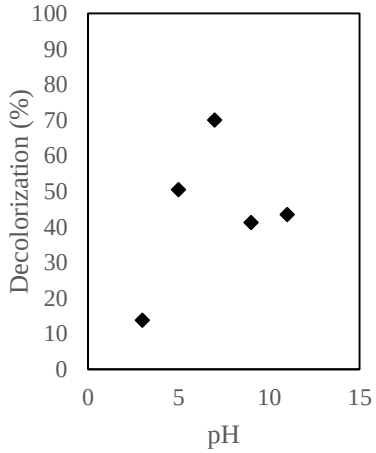

Fig. 4 Effect of pH on decolorization of MB

The effect of 5ZM catalyst dosage was also studied in the range of 0.125-0.750 g L^{-1} and the results are shown in Fig. 5. The decolorization of MB increased with increasing catalyst dosage up to 0.5 g L^{-1}, but further addition of the catalyst seemed to reduce the decolorization. This result could be due to the increase in the number of active sites that could absorb more photons and MB [1]. However, an excess dosage led to the turbidity of the suspension, which reduced the light penetration and inhibits photodecolorization [8].

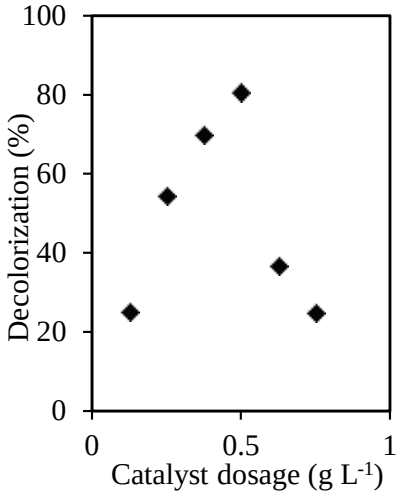

Fig. 5 Effect of catalyst dosage on decolorization of MB

3.2.3 Kinetic studies

Herein, the decolorization rates of MB were also studied using the Langmuir-Hinshelwood (L-H) model [2] over 5ZM catalyst and the linear plot of $\ln(C_0/C_t)$ vs. irradiation time are shown in Fig. 6.

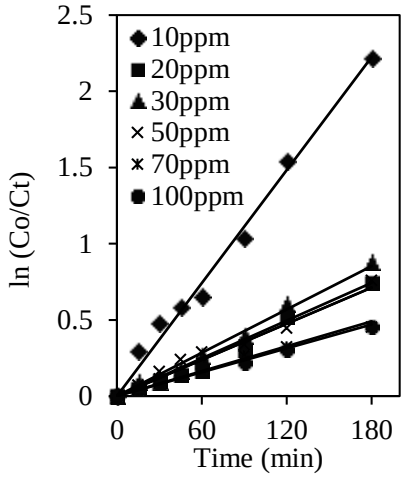

Fig.6 Photodecolorization kinetics of MB using different catalysts

A linear relation was obtained, which indicated that decolorization of MB by ZM followed Langmuir-

Hinshelwood model. The calculated values of k_r and K_{LH} were 0.3413 mg L^{-1} min^{-1} and 0.0028 L mg-1, respectively. The values of k_r was greater than K_{LH}, indicated that a surface reaction, where the dyes were absorbed, was the controlling step of the process [2].

4. CONCLUSION

In conclusion, 5ZM catalyst was prepared via electrochemical method. The physicochemical properties of the prepared catalyst were analyzed using XRD and FT-IR analysis. The results demonstrated that the introduction of ZnO into MSN maintains the structure of MSN and high purity of catalyst. 0.5 g L^{-1} catalyst was found to give the optimum loading, which resulted in 80 % decolorization of MB at pH 7 after 3 h of contact time under visible light irradiation. The kinetics studies showed that the decolorization process followed pseudo first-order and the rate constants determined using Langmuir-Hinsherlwood model were k_r = 0.3413 mg L-1 min^{-1} and K_{LH} = 0.0028 L mg^{-1}. The value of k_r is greater than K_{LH}, indicating that dye adsorption was the controlling step of the process. With the simple process of catalyst synthesizing and the low amount of metal loading required, this system exhibits great potential for improving the quality of wastewater discharged from industries.

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REFERENCES

[1] N.W.C. Jusoh, A.A. Jalil, S. Triwahyono, H.D. Setiabudi, N. Sapawe, M.A.H. Satar, A.H. Karim, N.H.N. Kamarudin, R. Jusoh, N.F. Jaafar, N. Salamun, J. Efendi. Appl. Catal- A: Gen. 468 (2013) 276.
[2] A.A. Jalil, M.A.H. Satar, S. Triwahyono, H.D. Setiabudi, N.H.N. Kamarudin, N.F. Jaafar, N. Sapawe, R. Ahamad. J. Electroanal. Chem. 701 (2013) 50.
[3] A.A. Jalil, S. Triwahyono, N. Sapawe, I.H. Ahmed, M.A.A. Aziz. Desalin Water Treat. (2015).
[4] C.I. Pearce, J.R. Lloyd, J.T. Dyes Pigments. 58 (2003): 179.
[5] E. Brillas, C.A. Martinez-Huitle. Appl. Catal. B: Environ. 166 (2015): 603.
[6] A.H. Karim, A.A. Jalil, S. Triwahyono, S.M. Sidik, N.H.N. Kamarudin, R. Jusoh, N.W.C. Jusoh, B.H. Hameed. J. Colloid. Interf. Sci. 386 (2012): 302
[7] A.H. Karim, A.A. Jalil, S. Triwahyono, N.H.N. Kamarudin, A. Ripin. J. Colloid. Interf. Sci. 421 (2014): 93
[8] N.F. Jaafar, A.A. Jalil, S. Triwahyono, N. Shamsuddin. RSC Adv. 5 (2015): 90991.
[9] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann. Appl. Catal B: Environ. 39 (2002): 75.
[10] U.I. Gaya, A.H. Abdullah. J. Photochem Photobio C. 9 (2008): 1.
[11] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann. Appl Catal B: Environ. 31 (2001): 145.
[12] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan. Sol. Energ. Mat. Sol. C. 77 (2003): 65.
[13] C. Bouvy, W. Marine. B.L. Su. Chem. Phys. Lett. 438 (2007): 67.
[14] L.I. Burova, D.I. Petukhov, A.A. Eliseev, A.V. Lukashin, Y.D. Tretyakov. Superlattice. Microst. 39 (2006): 25.
[15] A.A. Jalil, N. Kurono, M. Tokuda. Synlett 12 (2001): 1944
[16] A.A. Jalil, N. Kurono, M. Tokuda. Tetrahedron. 58 (2002): 7477
[17] A.A. Jalil, N. Kurono, M. Tokuda. Synthesis 18 (2002): 2681
[18] A.A. Jalil, N. Kurono, S. Tagasugi, M. Tokuda. J. IEM. 66 (2005): 1
[19] N.B. Lihitkar, M.K. Abyaneh, V. Samuel, R. Pasricha, S.W. Gosavi, S.K. Kulkarni. J. Colloid. Interf. Sci. 314 (2007): 310.
[20] D.R. Sahu, L.Y. Hong, S.C. Wang, J.L. Huang. Micropor. Mesopor. Mat. 117 (2009): 640.
[21] R. Jusoh, A.A. Jalil, S. Triwahyono, A. Idris, M.Y. Noordin. Sep. Purif. Technol. 149 (2015): 55