Universiti Malaysia Terengganu Journal of Undergraduate Research
Volume 2 Number 2, April 2020: 9-14
eISSN: 2637-1138

SYNTHESIS AND CHARACTERIZATION OF TiO_2/ZnO-EPOXY BEADS AND THEIR PERFORMANCE FOR THE DEGRADATION OF DYE

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Abstract: Semiconductor oxides such as titanium dioxide (TiO_2) and zinc oxide (ZnO) are used as the photocatalyst for removing contaminants. In addition, TiO_2 and ZnO nanoparticles in the suspension form makes it difficult to be recovered and recycled. This study was conducted to investigate the efficiency of immobilizing TiO_2 and ZnO nanoparticles in epoxy beads. The immobilization process using different ratios of photocatalysts TiO_2/ZnO (1:0, 3:1, 1:1, 1:3 and 0:1) fixed on epoxy material. These epoxy beads were used for dye removal in photocatalysis using methylene blue (MB) solution at a concentration of 10mg/L. Besides, epoxy beads also characterized using scanning electron microscope (SEM), attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and thermogravimetric analysis (TGA). The results showed that the highly recommended epoxy bead is 3:1 ratio of TiO_2/ZnO because it has good performance in dye degradation that proved from reducing concentration of MB to 2.4mg/L (76%). However, TiO_2/ZnO characterization of 3:1 by SEM show on the surface the particle are found to be spherical in shape which is relatively high efficiency for the degradation, ATR-FTIR pattern in broad band 4000 cm^{-1} - 400cm^{-1} which correspond to hydroxyl stretching to be adsorbed at peak (474.49 cm^{-1} - 3722.61cm^{-1}) respectively to the optimum for the degradation and TGA rate of change are 5mg to 2.5mg that residue (49.78%) due to decomposition or oxidation from mass loss. These findings are very effective and economical technique to be cost saving and highly efficient photocatalyst.

Keywords: Photocatalysis, titanium dioxide, zinc oxide, immobilization, Epoxy beads

Introduction

Photocatalyst is a process where light and catalyst were concurrently used to support and speed up a chemical reaction. So, photocatalyst was defined as the acceleration of photoreaction by the present of catalyst. Photocatalyst was divided into two categories which are a homogeneous and heterogeneous photocatalytic process (Rehman *et al.,* 2009). Homogeneous photocatalytic process mostly used with metal complete as the catalyst like iron, chromium and copper. In this process under the photon and thermal condition, the higher oxidation stated of metal ion complexes generated hydroxyl radicals. These hydroxyl radicals reacted with organic matter which leads destruction of toxic matters. While the heterogeneous photocatalytic process is a technically gifted method that used for degradation of various organic pollutants in wastewater (Rajeshwar *et al.,* 2008). This process has a few advantages over competing processes which are complete mineralization, no waste disposal problem, low cost and necessity of mild temperature and pressure condition only.

Heterogeneous photocatalysis employing semiconductor catalysts has demonstrated its efficiency in degrading a wide range of organics into readily biodegradable compounds. The ideal photocatalyst should possess the following properties such as nontoxic, costless, photoactive, sustainable towards visible or near UV light and biologically and chemically inert (Khan *et al.,* 2015).

The most effective catalysts were titanium dioxide (TiO_2) and zinc oxide (ZnO) as interesting photocatalyst due to their virtues properties in the organics mineralization. Nevertheless, based on their band gaps, these catalysts will be excited by irradiation of UV light. An artificial light source is ultraviolet-C (UVC). UVC irradiation proved to be most effective, which is most probably due to its capability to induce the directed photocatalysis action on dye methylene blue (MB). In addition, the shorter penetration capability of UVC photons into photocatalyst particle also reduces the probability for electron-hole recombination due to shorter travelled distances leading to greater photocatalytic process (Bayarri *et al.,* 2007).

Many modifications of catalyst are used to treat water effectively. In this regard, the utilization of hybrid TiO_2/ZnO catalyst are reliable since these combinations provides great potential for bacteria disinfection. By immobilizing the TiO_2/ZnO catalyst from powder to bead forms, probably will help their performance to be more effective and contributing to the systems of wastewater treatment. Immobilization of hybrid TiO_2/ZnO catalyst can lower the cost operation of wastewater treatment. However, utilization of single catalyst TiO_2 is less efficiency level than the hybrid catalyst. Compared to the single element of ZnO and TiO_2, hybrid of ZnO/TiO_2 catalyst displays a largely improved photocatalytic activity (Cheng *et al.,* 2014). Furthermore, the systems of wastewater treatment could be disturbed when the suspension-based photocatalysts was very difficult to separate them from treated water after the usage (Byrne, Subramanian, & Pillai, 2018). According to Lei *et al.* (2012), the filtration to eliminate and recycle the powdered TiO_2 suspended in treated water increases the running costs and induces secondary pollution, which has become the main limiting factor for practical application since single catalyst react with less efficiency, the effectiveness of disinfection the bacteria may be difficult to achieve. Besides, the powder form of catalyst clearly shows the higher costs are used during treated the contamination of water.

Therefore, the aim of this work was to investigate the performance hybrid of TiO_2/ZnO as epoxy beads in improving the optical and photochemical performances. TiO_2/ZnO with different ratio contents was synthesized in order to evaluate the effect microstructure of the formed composites.

Materials and Methods

Two types of photocatalyst was used which are TiO_2 (titanium (IV) oxide, 98.0 – 100.5%, Acros) and ZnO (zinc oxide nanopowder, <100nm particle size, Aldrich). TiO_2/ZnO photocatalyst was prepared at different mass ratios of the epoxy beads. TiO_2 nanopowder was mixed with ZnO nanopowder that started with ratio of 1:1, 3:1, 1:1, 1:3 and 0:1 by using of high energy ball milling. Then the mixture was subjected to heat treatment or annealing at 600°C for 2 hours in the furnace. Epoxy resin (Bisphenol A and Butyl glycidyl ether) mixed with the hardener (diethylenetriamine) for 10 minutes on the hot plate stir. The mixture immediately transferred to bead silicone mould and leave to cure in convective oven at 60°C for 24 hours. The beads contained high loading of catalyst since the size was small and easily recovered by physical method. The dried samples were characterized with analytical technique by using Scanning electron microscopy (SEM), Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique and thermogravimetry analysis (TGA).

Photocatalytic performances of the fabricated beads examined by methylene blue photodegradation experiment for 3 hours. UV-Vis (Shimadzu, UV-1800) at 665nm wavelength was used to quantify the concentration of azo dye compounds present in the reactant reservoir during the reaction.

Results and Discussion

Beads Characterisation

SEM was employed to investigate the morphological structure of TiO_2/ZnO after immobilised on epoxy beads. SEM unit operated at 10kV accelerating voltage.

As shown in Table 1, the SEM images, possess a porous network structure formed by a huge number of small spheres. Ratio 3:1 epoxy bead gave the perfect surface of catalyst for photocatalysis process. However, epoxy beads for ratio 1:3 have slightly smooth and flat surface since it was more with plastic or resin than catalyst. Among the calcined samples, those with the highest ratio of ZnO were shown by the smallest particles. It also confirmed with the increased in calcination temperature and combination with accurate of mass ratio with larger particles will be produced. (Siwińska-Stefańska *et al.,* 2018).

Table 1: Result SEM for catalyst with epoxy beads

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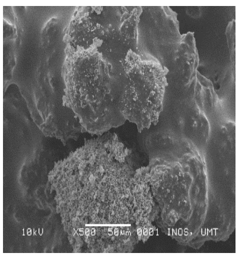
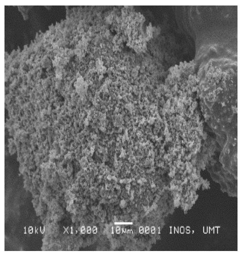
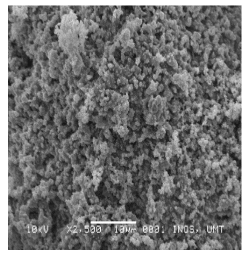
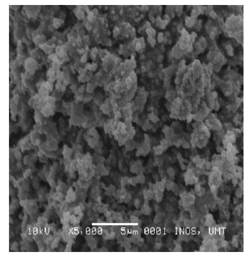
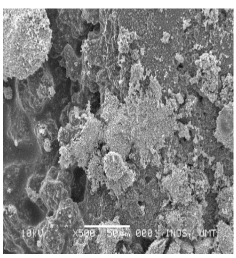
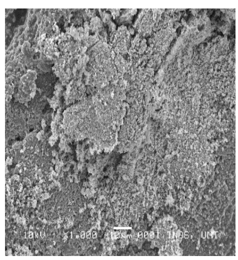
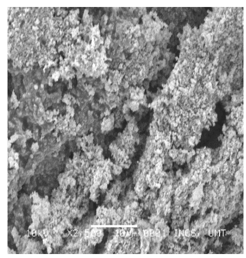
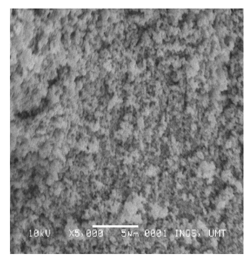
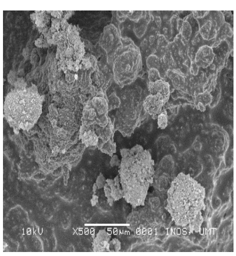
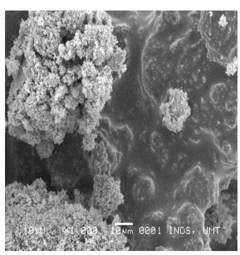
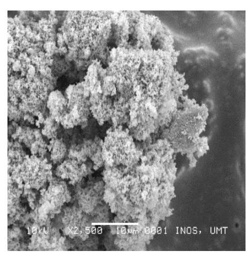
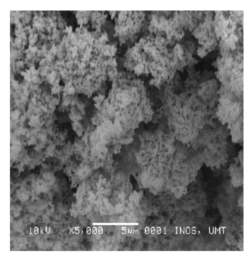
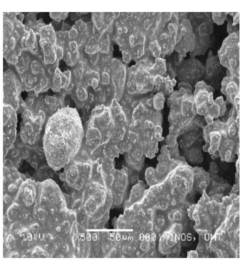
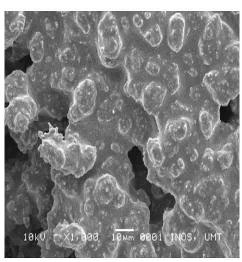
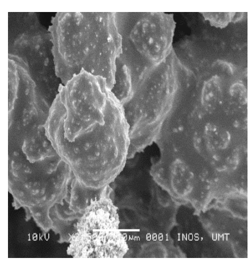
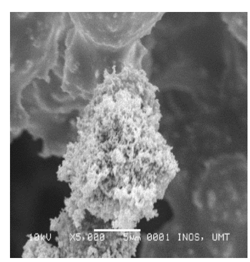
1:0				
3:1				
1:1				
1:3				

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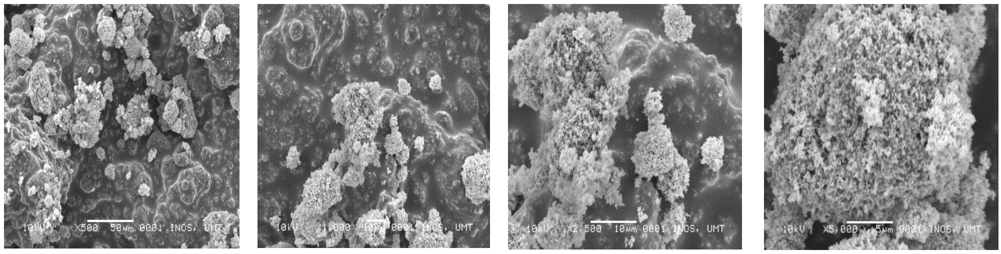

Chemical composition of different ratio of photocatalysts were analysed using FTIR analysis. Figure 1 showed result analysis used ATR-FTIR in the field of photocatalysis was great importance as it provides both qualitative and quantitative molecular insight into interfacial processes that occur in the dark and under UV illumination (adsorption/desorption and chemical reactions).

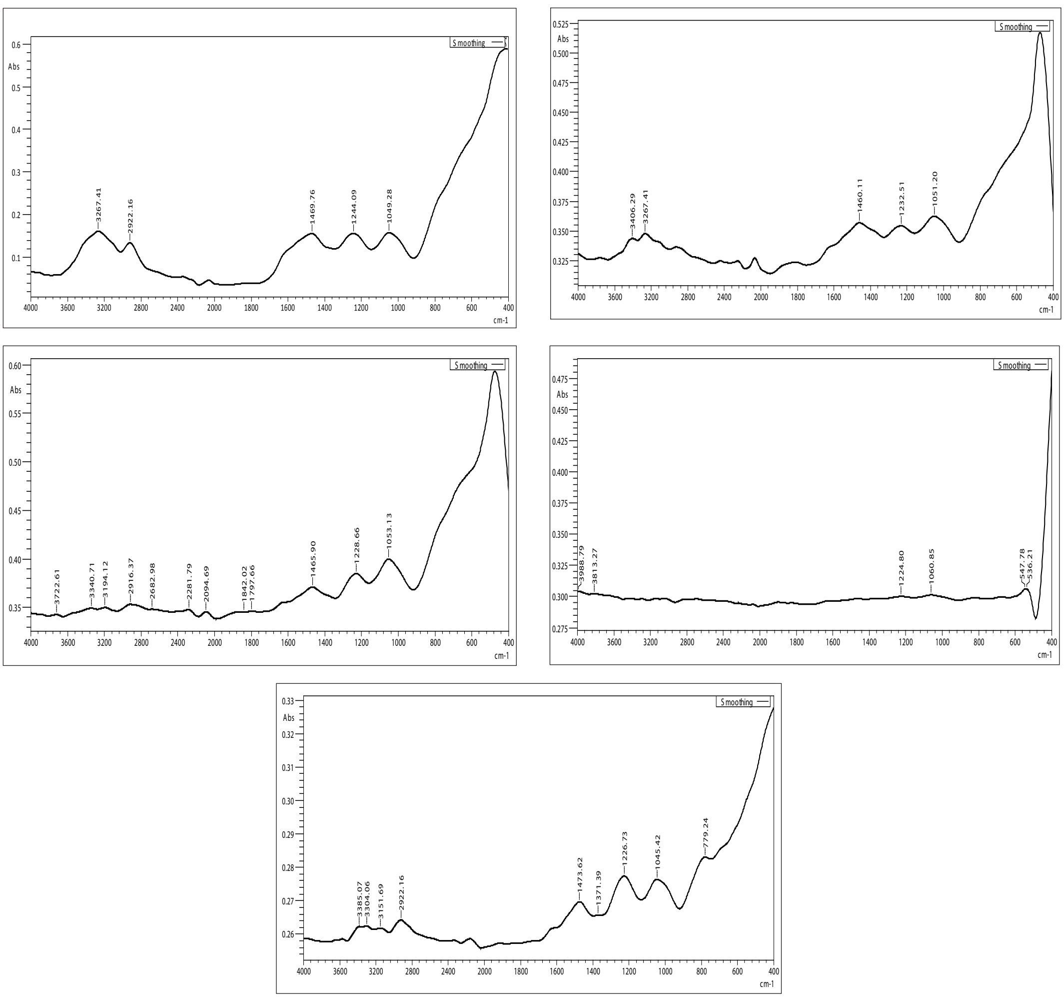

Figure 1: ATR-FTIR spectra of different ratio photocatalysts epoxy (a) 1:0; (b) 3:1; (c) 1:1; (d) 1:3; (e) 0:1

Characteristic IR peaks of bead 1:0 were identified 412.77 – 3267.41 cm^{-1}, the peaks at 474.49 – 3722.6 cm^{-1} for bead 3:1, the peaks at 779.24 – 3385.07 cm^{-1} for bead 1:1, the peaks at 472.56 – 3406.3 cm^{-1} for bead 1:3 and the identified bead 0:1 the peaks at 536.21n-3988.79 cm^{-1}. The most effective interaction in photocatalyst was bead at ratio 3:1 as verified from analysis. The absorption band was assigned around 1600 cm^{-1} to the O – H vibrations in the samples associated with physically adsorbed water (Viswanatha *et al.,* 2012). The two bands can be associated with asymmetric O = C – O vibrations and C = O stretching at 1500 and 1729 cm^{-1} (Yeung et al., 2009). The bands in the region around 1500 cm^{-1} may correspond to the Ti – O – C bond, which may originate from unreacted alcoxy groups (residual carbon after reaction) during the process, indicating the interaction between the organic and inorganic components present in the precursor. In addition, bands ranging from 3346 cm^{-1} to 3700 cm^{-1} were detected, corresponding to the water molecules ‘ symmetric and asymmetric stretching (López et al., 2011).

Thermogravimetric analysis (TGA) used to analyse epoxy beads at different mass ratio of TiO_2/ZnO with the combination of both plastic and resin that used for immobilize. Figure 2 showed the weight loss in the 32-420 °C that residue 2.08 mg (37.74%) for bead 1:0, the weight loss in the 32-560°C that residue 2.69 mg (49.78%) for bead 3:1, the weight loss in the 32-586°C that residue 2.22 mg (37.64%) for bead 1:1, the weight loss in the 31-613°C that residue 2.73 mg (44.08%) for bead 1:3 and the weight loss in the 32-613°C that residue 1.40 mg (27.51%) for bead 0:1. The beads at ratio 3:1 is the most stable for thermal decomposition.

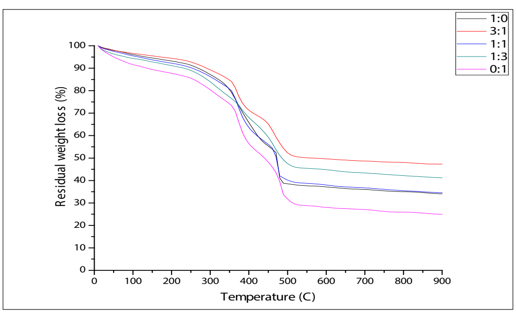

Figure 2: TGA curve of epoxy beads

Photocatalysis degradation of dye

The photocatalytic activity of different ratio TiO_2/ZnO (0:1, 1:1, 1:3, 1:0 and 3:1) were evaluated by the photocatalytic degradation of MB under UV lamp irradiation. Ahmadi, Ghasemi and Rafsanjani (2011) state that the MB decrease with the increase in irradiation time.

As expected, photocatalysis reactions with combination of different photocatalyst degraded MB faster than with single photocatalyst with more than 60% by 180 minutes (Figure 3).

As shown in Figure 3, the degradation rate of MB aqueous solution is the highest up to 76% with TiO_2/ZnO ratio 3:1. The lowest degradation rate of MB aqueous solution is 27.50% at ratio 1:0. He *et al*., (2014) proved that combination of TiO_2/ZnO photocatalyst give synergist for the performances. The improvement related to intrinsic defects and charge separation due to improve interface between TiO_2 and ZnO.

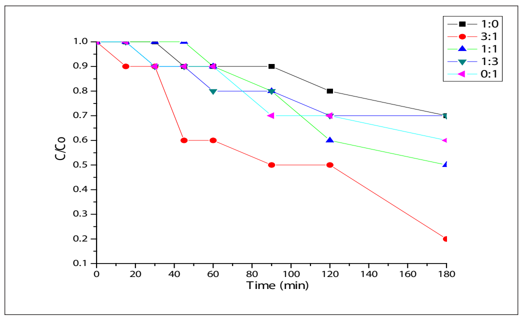

Figure 3: Photocatalytic degradation of dye

Conclusion

TiO_2/ZnO have been successfully immobilised on epoxy beads. The effect of different photocatalysts ratio have been primarily investigated. Results have shown that degradation rate can be optimised through varying the photocatalyst loading ratios. The optimal was found to be at ratio 3:1 from the photocatalyst dye degradation experiment and the bead characterisation. Overall, this work shows that photocatalysts mass loading on beads surface and ratios of TiO_2/ZnO plays an important role in increasing photocatalytic treatment efficiency. It can be concluded that photocatalytic-modified epoxy catalyst beads can be used in environmental technologies especially in self-cleaning surfaces to solar-powered remediation devices for polluted waters.

Acknowledgements

This work was supported by the Talent and Publication Enhancement-Research Grant (TAPE-RG) (55179). The authors would also like to acknowledge Institute of Oceanography and Environment (INOS), UMT for providing the scanning electron microscope (SEM) measurement. School of Fundamental Science for providing Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) instrument. *Makmal Berpusat,* UMT for providing Thermogravimetric analysis (TGA) result. Wastewater Treatment Laboratory for providing their facility, material and apparatus.

References

Ahmadi, M., Ghasemi, M. R, & Rafsanjani, H. H. (2011). Study of Different Parameters in TiO_2 Nanoparticles Formation. *Journal of Materials Science and Engineering*, 5, 87-93.

Bayarri B., Abella´n M.N., Gime´nez J., & Esplugas S. (2007). Study of the wavelength effect in the photolysis and heterogeneous photocatalysis. *Journal of Catalyst*, *129*(1-2), 231–239.

Byrne, C., Subramanian, G., & Pillai, S. C. (2018). Recent advances in photocatalysis for environmental applications. *Journal of Environmental Chemical Engineering*, *6*(3), 3531–3555.

Cheng, C., Amini, A., Zhu, C., Xu, Z., Song, H., & Wang, N. (2014). Enhanced photocatalytic performance of TiO2-ZnO hybrid nanostructures. Scientific Reports, *4*(1).

He, F., Li, J., Li, T. & Li, G. (2014). Solvothermal synthesis of mesoporous TiO_2: The effect of morphology, size and calcination progress on photocatalytic activity in the degradation of gaseous benzene. *Chemical Engineering Journal*, *237,* 312-321.

Khan M.M., Adil S.F., Al-Mayouf A. (2015). Metal oxides as photocatalysts. *Journal of Saudi Chemistry Science, 19*(5), 462–464.

Lei, P., Wang, F., Gao, X., Ding, Y., Zhang, S., Zhao, J., & Yang, M. (2012). Immobilization of TiO2nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants. *Journal of Hazardous Materials*, *227–228*, 185–194.

López, R., Gómez, R., & Oros-Ruiz, S. (2011). Photophysical and photocatalytic properties of TiO2-Cr sol–gel prepared semiconductors. *Catalysis Today, 166*(1), 159-165.

Rajeshwar K., Osugi M.E., Chanmanee W., Chenthamarakshan C.R., Zanoni M., Kajitvichyanukul P., & Krishnan-Ayer R. (2008). Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. *Journal Photochemistry Photobiology, 9*(4), 171–192.

Rehman S., Ullah R., Butt A.M., & Gohar N.D. (2009). Strategies of making TiO2 and ZnO visible light active. *Journal of Hazardous Material* 170(2–3): 560–569.

Siwińska-Stefańska, K., Kubiak, A., Piasecki, A., Goscianska, J., Nowaczyk, G., Jurga, S., & Jesionowski, T. (2018). TiO2-ZnO Binary Oxide Systems: Comprehensive Characterization and Tests of Photocatalytic Activity. *Materials, 11*(5), 841.

Viswanatha, R.; Venkatesh, T.G.; Vidyasagar, C.C. & Nayaka, A. (2012) Preparation and characterization of ZnO and Mg-ZnO nanoparticle. Arch. Appl. Sci. Res., 4, 480–486.

Yeung, K. L., Leung, W. K., Yao, N., & Cao, S. (2009). Reactivity and antimicrobial properties of nanostructured titanium dioxide. *Catalysis Today, 143*(3-4), 218-224.