Proceedings of UNISEL Bestari Research Projects 2016, Ed(s): Setyawan Widyarto, et.al.,
Shah Alam: FIIT-UNISEL Publisher, ISBN: 978-983-3757-29-9

FORMATION OF ZNO-CS HYBRID CATALYST: EFFECT OF WEIGHT RATIO TO DECOLORIZE METHYLENE ORANGE (MO)

Mohd Azam Mohd Adnan[1], Mazian Mohamad[1], Ong Ewe Ling[1] & Nurhidayatullaili Muhd Julkapli[2]

[1]*Faculty of Engineering and Life Sciences, Bestari Jaya Campus, Jalan Timur Tambahan, 45600 Bestari Jaya Selangor, Malaysia Universiti Selangor,Malaysia*
[2] *Nanotechnology and Catalysis Research Center (NANOCAT), Universiti Malaya, Level 3, Block A, IPS Building, 50603 Kuala Lumpur, Malaysia, Universiti Malaya, Malaysia*
E-mail: azam@unisel.edu.my

Abstract

Zinc Oxide (ZnO) is used widely for the photodegradation, application due to its superior photocatalytic oxidation ability, non photocorrosive and non-toxic nature. However, due to their low photons adsorption capability and rapid electron hole pair recombination limits its applications. In here, chitosan (CS) was introduced as a support material to improve photocatalytic activity. ZnO-CS hybrid catalyst was synthesized via simple ex-situ method with different condition. The structural and morphological properties of ZnO/CS hybrid photocatalyst will be further analyzed through X-ray diffractometer (XRD). Meanwhile, the interaction of ZnO to CS matrix is analyzed by FTIR. Furthermore, the photodegradation of methyl orange (MO) as a model of synthetic dyes shown that, the adsorption reached to 85 %, while optimally photocatalytic obtained at 6 g with ZnO in dry feature.

Keywords: Photocatalyst, ZnO-CS, Adsorption

1 INTRODUCTION

Water polluted with dyes is a foremost risk to the environment. The various types of chemical composition used in dyeing industry makes the bio-degradation process of dyes wastewaters more challenging. The contaminants in water must be removed to provide clean water for human consumption. The dyestuffs are utilized in diverse applications such as paper, leather, plastics, printing, cosmetic and drug industries. About 20% of global industrial water pollution occurs from the treatment and dyeing of textiles [1]. Many treatment techniques are upgraded and improve day by day in order to purify this highly toxic waste. However, the dye in wastewater has a slower degradation rate due to their high molecular weight and biochemical stability, therefore, the best ways to clean this dye wastewater is the Advance Oxidation Process (AOP) that performed by photocatalysis, [2]. Photocatalyst produces an oxidation surface to eliminate harmful components in the industrial dye wastewater.

ZnO is renowned for being one of the important photocatalysts with unique advantages, like low cost, high photocatalytic activity, high stability, and non-toxicity. ZnO has attracted a great deal of attention for its use as a catalyst in the photooxidation of organic pollutants. ZnO absorbs UV light through electronic excitation between the valence band and the conduction band then decomposing and mineralizing hazardous organic pollutants to organic compounds of carbon, water vapor and inorganic substances with solar UV [3]. Chitosan (CS), a substance that found in the exoskeleton of marine animals, is an important additive that used to absorb oils, greases, and toxic substances as a part of water treatment process and can remove up to 99% turbidity [4].
In this study, ZnO was immobilized with CS to improve the efficiency of the photocatalyst to degrade MO as a model pollutant. The ZnO-CS hybrid catalyst is designed to satisfy the demands of high adsorption, self- regeneration, easy separation, and cost-effective water treatment. The band gap of ZnO is 3.19 eV and can only be excited by UV light to generate electron, (e-) and holes, (h+) pairs. UV light in sunlight is very defined; the surface modification of ZnO using CS improves the sensitivity to visible light and is capable to perform degradation of synthetic dye, such as MO in the visible light area. The CS extends the absorption edge position; therefore, ZnO-CS is able to perform in the visible region [3].

2 MATERIALS AND METHODOLGY

In this experiment, there are several types of chemicals and raw material employed; ZnO, CS, acetic acid (CH_3COOH), sodium hydroxide (NaOH) and Methylene Orange (MO).

2.1 Formation of ZnO-CS hybrid catalyst

The ZnO-CS hybrid catalyst was formed using the ex-situ sol-gel method. The ZnO and CS were dissolved separately. 2g of ZnO powder was added in 150 ml of (2 %) CH_3COOH and stirred for 1 hour until a clear solution obtained. Then, 2g of Cs flake was added into 100 ml of (2 %) CH_3COOH and stirred for 3 hours until the CS flake totally dissolved. ZnO solution and CS solution is mixed and continue stirred

for 1 hour until a 250 ml homogenous ZnO-CS hybrid solution is formed. The ZnO-CS solution is then form in NaOH solution. It was then allowed to get solidified for 2 hours to turn from transparent to milky white. The beads pH was set to 7 by washing with DI and dried in hot air oven at 60°C for 3 hours to eliminate the DI water on the surface and obtained the dry beads.

2.2 Photodegradation experiments

Photocatalytic decolorization experiments were conducted in the photoreactor consists of single (15 W) tube emitting light in the spectral range between nm wavelength. The beakers of 200 ml capacity were filled up with 100 ml of methyl orange and 2 g, 4 g, and 6 g of ZnO-CS respectively. The generator or pump was continuously aerated to provide oxygen and for completeness mixing of the reaction solution.

The MO was treated with ZnO-CS of different composition ratio and different dosage. All the experiment is to study the effect of important parameters like irradiation time, catalyst weight loading and composition ratio. A small amount of MO is collected for every 15 min after irradiation with UV until 90 min of the irradiation. The reaction solution was stopped for 5 min before the sample collected; to make sure the bead is not wit drawn from MO. The concentration of the dye was measured by SHIDMADZU 29000 U visible spectrometer (UV-Vis). The percentage of adsorption-photodegradation (AP%) was calculated using the following equation:

$$AP\% = \frac{C_o - C_t}{C_o} \times 100\% \qquad 2.1$$

where C_o is the initial concentration of sample before irradiation under UV-light and C_t is the concentration of sample after irradiation under UV-light.

3 RESULT AND DISCUSSION

The ZnO-CS photocatalysts are characterized by FTIR and XRD. The FTIR spectrum provides the molecular absorption and transmission (specific frequency of energy), which is useful for analyzing ZnO-CS beads functional groups, while others are attached to the molecule's functional group, linking the photocatalyst with it. Characterization of FTIR spectra for the formation of ZnO-CS hybrid catalyst with single ZnO and Cs is shown in Figure 1. For pure Cs, the characteristic bands of 3447 cm^{-1} on (I) point, 1079 cm^{-1} on (IV) point and 892 cm^{-1} and (v) point were attributed to the stretching vibration of –OH group of 3'OH, 4'OH and 5'OH groups respectively. The stretching vibration of C=O was assigned the band at (II) point for 1651 cm-1 and the scissoring vibration of NH2 at (III)point for 1555 cm^{-1}[5]. The FTIR spectrum of ZnO exhibits the broad absorption band at 3440 cm^{-1} on (I) point which support the –OH stretching vibrations of adsorbed water on the surface of ZnO. The distinct stretching vibration of ZnO is at the peak 503.91cm^{-1} on (II) point. In the spectrum of ZnO-CS, the band reveals an intriguing characteristic of both CS and ZnO. The strong peak at 3440.12 cm^{-1} is shifted lower wavenumber at 3427 cm^{-1} at (I) point which corresponding to the stretching vibration of –OH and $–NH_2$ that become broader indicating some interaction between these groups and ZnO. The peaks at the point (II) are 1645 cm^{-1} are the bending vibration of the $–NH_2$ and the stretching vibration of C-O groups at the point (III) are 1071 cm^{-1} [3].

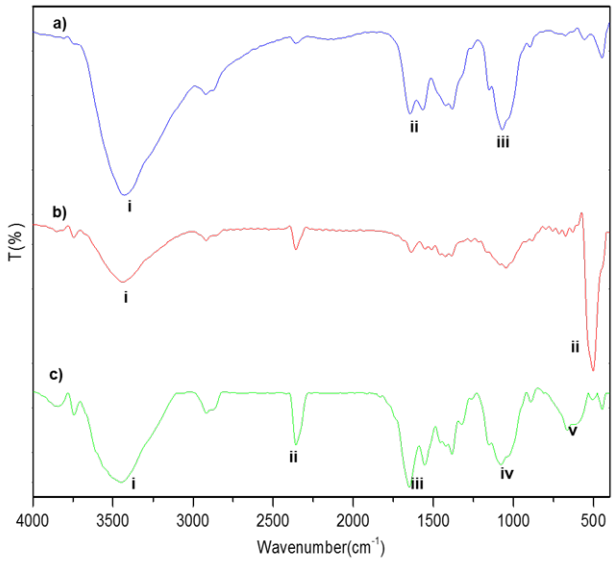


FIGURE 1: FTIR spectra of (a) ZnO-Cs composite with composition 2:1 (b) ZnO (c) pure Cs

The XRD results of both ZnO and ZnO-Cs are shown in Figure 2. The XRD pattern of ZnO shows diffraction peaks at 2Θ =31.98°, 34.62°, 36.42°, 47.42°, 56.76°, 63°, 66.46°, 67.78°, 68.10°, 72.74°, 77.12° which are attributed to the different diffraction peaks for wurtzite form of ZnO [6]. Zno-Cs has well crystalline form with peaks at 2Θ = 23.4°, 31.96°, 32.46°, 34.54°, 36.38°, 47.54°, 56.78°, 63.78°, 68.1°, 69.08°, 77.1°. In XRD profile of ZnO-Cs, there was not much change observed in comparing with ZnO, indicating that the combination of Cs with ZnO did not destroy the characteristic structure of ZnO [3].

Photocatalytic activity

Studying the dependence of decolorization efficiency on the composition of photocatalyst is important. Figure 3 shows the effect of composition on the degradation of 5 ppm MO solution using 6 g of dry ZnO-CS bead. The degradation percentage decreased markedly with the reduction in the amount of ZnO in the composition, particularly after 90 min, the degradation of composition 2:1 (85%), composition 1.5: 1 (58%) and composition 0.5: 1 (51%). This occurs the number of ZnO contain decrease, holes that highly oxidizing will be lesser, the chance for dye molecules to in contact with the holes to perform degradation will be shortened

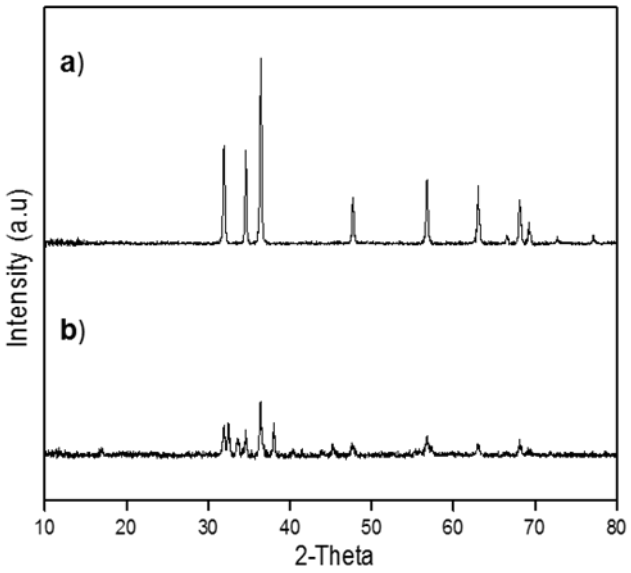
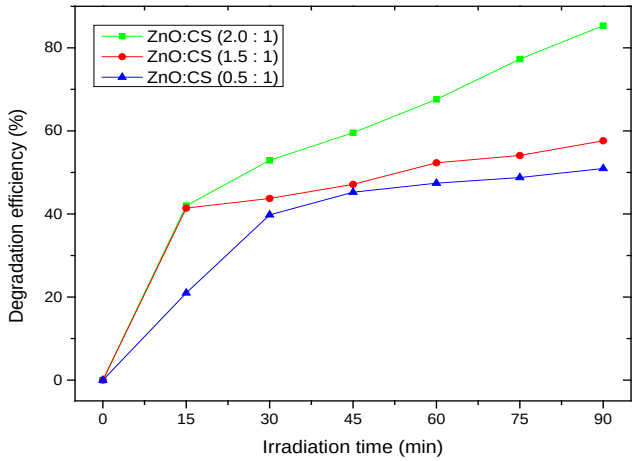


FIGURE 2: XRD spectra of a) ZnO and b) ZnO-Cs



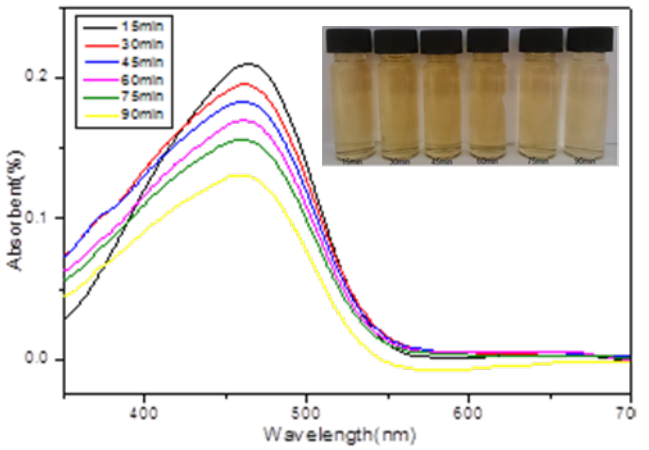


FIGURE 3. Photodegradation efficiency of 5ppm MO solution with 6g of dry ZnO-CS bead after 90min

Effect of Photocatalyst Amount

The photocatalyst amount was another important parameter of dye degradation under UV irradiation. As the catalyst dosage increase from 2g to 4g then 6g, the decolorization increase and reached the maximum of 85%. Degradation efficiency is the highest for amount 6g, this happen to all composition ratios for both hydrogel and dry ZnO-CS bead, this clearly show in Figure 4. The increase of photocatalyst amount increased the number of active sites on the photocatalyst. Consequently, the number of dye molecules and photons absorbed increased [5].

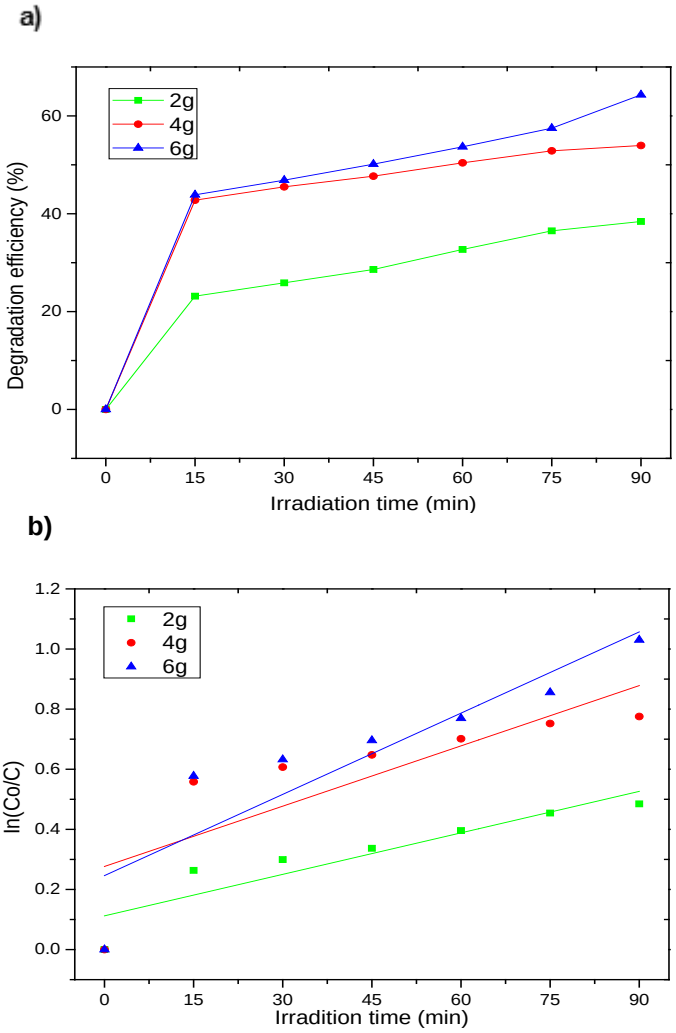


FIGURE 4. (a) Photodegradation efficiency after 90min UV irradiation (b) pseudo first-order kinetic of time evolution by wet ZnO-Cs in composition ratio 2:1

4 CONCLUSION

The photodegradation of MO using ZnO-CS under UV irradiation have been investigated. ZnO is modified with Cs a bio-polymer via a sol-gel method which is very cost-effective and easier synthesizing method. The decolorization percentage of MO using 6 g of dry ZnO-CS with composition ratio of 2:1 was found to be comparatively higher with the degradation efficiency about 85%.

ACKNOWLEDGMENTS

This work is financially supported by the BESTARI Research Grant UNISEL (GPB-UNISEL15/ST-005).

REFERENCES

[1] Rita Kant (2012). Textile dyeing industry an environmental hazard, Journal of Natural Science, 22-26

[2] Sandip Sharma, J.P.Ruparelia and Manish L.Patel (2011). A general review on Advanced Oxidation Processes for waste water treatment, International Conference on Current Treads in Technoogy. December 8-10.

[3 M. Hasmath Farzana and Sankaran Meenakshi(2014). Exploitation of zinc oxide impregnated chitosan beads for thephotocatalytic decolorization of an azo dye, Journal of Biological Macromolecules (72),900-910

[4] Dutta, P. K., Dutta, J., & Tripathi, V. S. (2004). Chitin and Chitosan: Chemistry, Properties and Applications, Journal of Scientific and Industrial Research (63), 20–31

[5] Li-Hua Li, Jian-Cheng Deng, Hui-Ren Deng, Zi-Ling Liu and Ling Xin. Sythesis and characterization of chitosan/ZnO nanoparticle composite membranes, Journal of Carbohydrate Research (345), 994-998

[6] M.A. Habib, M.T. Shahadat, N.M. Bahadur, I.M.I. Ismail, A.J. Mahmood, Int. Nano Lett. 3 (2013) 5,

[7] Huayue Zhu, Ru Jiang, Ling Xiao, Yuhua Chang, Yujiang Guan, Xiaodong Li, Guangming Zeng Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation, Journal of Hazardous Materials (169), 933-940