Photocatalytic performance of ZnO-Rhizophora mucronata biochar catalyst for methylene blue degradation

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Abstract

ZnO-*Rhizophora mucronata* biochar (ZRB) catalyst was synthesized by a simple solvothermal method. The as-obtained catalysts were characterized by energy dispersive X-ray spectroscopy (EDX) and scanning electron microscope (SEM). The photocatalytic performance of catalysts were tested by the oxidation of methylene blue (MB) under visible light irradiation. The optimum conditions including visible light irradiation time, catalyst dosage and visible light intensity were 20 min, 0.04 g/L and 60W, respectively. The ZRB catalyst can be applied as a highly effective photocatalyst for dye pollutants.

Keywords: ZnO-*Rhizophora mucronata* biochar catalyst; Photocatalytic degradation; Organic dye

Introduction

Various Dyes are used in various industries to make precise colors in manufactured products and in biological laboratories for analytical purposes or as biological stains.[1] The discharge of dyes into the aquatic environment results in wastewaters with high toxicity and low transparency. These dyes can be competently eliminated by advanced oxidation processes (AOPs) without generating any toxic intermediates in its aqueous media.[2] Recently, photocatalysts are regarded as one of the most promising classes of semiconductor materials, due to their well-defined electrochemistry, easy protonation reversibility, excellent redox recyclability, good environmental stability, and a variety of nanostructured morphologies,

conforming to the needs of sustainable development.[3] Therefore, we attempted to prepare ZnO-*Rhizophora mucronata* biochar (ZRB) photocatalyst via a simple solvothermal approach in order to obtain synergistic effect towards the effective degradation of MB. The optimum conditions; visible light irradiation time, photocatalyst dosage and visible light irradiation intensity were investigated.

Experimental

Synthesis of *Rhizophora mucronata* biochar (RB)

Rhizophora mucronata woods were collected from a nearby Nakhon Si Thammarat Rajabhat University and then cut into small pieces, followed by washing with water for removal of dust adhere to it. Then it was dried in the sunlight for 15-20 days. Dried materials were kept inside the furnace at 200°C for 12 hours for removal of moisture and other volatile impurities. Samples of biochar were crushed and sieved through a 50 mesh size sieve before applying in next step.

Synthesis of ZnO-*Rhizophora mucronata* biochar (ZRB) catalyst

To synthesize ZRB photocatalyst, 5.0 g of *Rhizophora mucronata* biochar (RB) and 250 mL of 0.1 mol/L $Zn(NO_3)_2$ were mixed. Then, the mixture was ultra-sonicated for 2 h and stirred for 5 h at 90˚C. After removal of the solvent at 100˚C, the solid samples were heat-treated in a furnace at 600˚C for 2 h The final product is ZRB photocatalyst.

Photocatalytic degradation of methylene blue

The photocatalytic degradation of the ZRB catalysts were performed by the decomposition of MB with visible light irradiations. The specified quantity of ZRB catalyst was suspended in 100 mL of dye solution (of varying concentrations) in a glass vessel. Before visible light, the suspensions were magnetically stirred in the dark for 2 h to ensure the establishing of an adsorption/desorption equilibrium among the photocatalyst, dye and atmospheric oxygen, which was hereafter considered as the initial concentration (Co).[4-5] For optimal photocatalytic degradation conditions, various experimental parameters were studied, including visible light irradiation time, catalyst dosage and visible light intensity. The sample solution was withdrawn regularly (3 mL each time) from the glass reactor. The supernatants were analyzed using a UV-vis spectrophotometer at λ_{max} of 665 nm.

Results and Discussion

Photocatalyst Characterization

To determine the major elements of ZRB catalyst. The synthesized sample was analysed by EDX. From Fig. 1 (a), the spectrum shows the presence of both C and O, as major elements, with strong Zn peaks; indicating that the *Rhizophora mucronata* biochar was successfully anchored with ZnO. The contents of C, O and Zn in the synthesized ZRB catalyst were 4.4, 15.6 and 80.0 % weight, respectively. Fig. 1(b) shows a SEM image of ZRB. It can be seen that the ZRB surface had spherical shape.

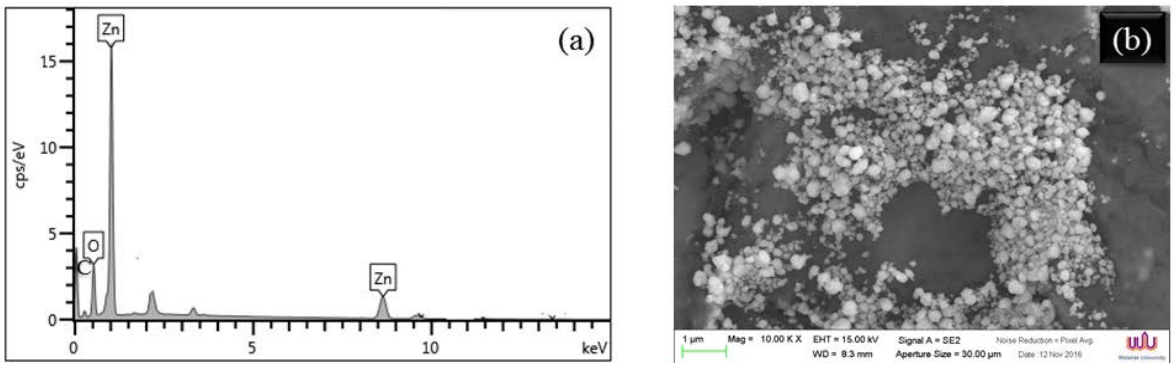

Fig. 1. (a) EDX spectrum and (b) SEM image of ZRB photocatalyst

Optimum conditions for MB degradation

The data from optimum conditions studied are showed in Fig. 2. Figure 2(a) shows the effect of visible light irradiation time. The results showed that the ratio of Ct/Co drastically decreases at the initial period of the irradiation time and gradually slows down with time. Figure 2(b) shows the effect of catalyst dosage. It can be well seen that the percent degradation of MB drastically increases with an increase of ZRB catalyst dose. The optimal loading of ZRB catalyst is obtained at 0.04 g/L. Figure 2(c) shows the effect of visible light intensity. It can be seen that the MB degradation efficiency increased with visible light intensity. Therefore, the optimum conditions for MB degradation by using ZRB as catalyst were 20 min, 0.04 g/L and 60W for visible light irradiation time, catalyst dosage and visible light intensity, respectively.

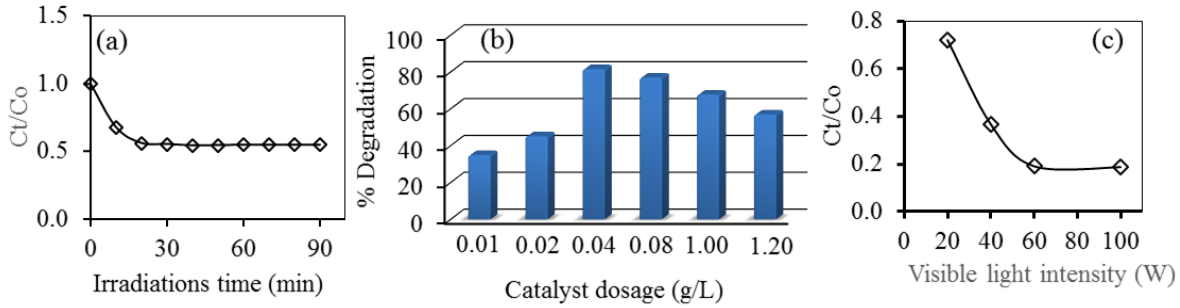

Fig. 2. Effects of (a) visible light irradiation time, (b) catalyst dosage and (c) visible light intensity

The activity of ZRB photocatalyst

The photocatalytic activity of ZRB photocatalyst was evaluated using MB under the following optimal conditions. From the results shown in Fig. 3(a), we can see that the degradation ratio *(Ct/Co)* of ZRB is much high indicating that ZRB is active under ultrasonic irradiation. The kinetics of the degradation can be expressed as $-ln(Ct/Co) = k_{appt}$, where k_{app} is the apparent rate constant, *Co* and *Ct* are the concentration of MB before visible light irradiation and after time t, respectively. The kinetic plot and the obtained apparent rate constant (k_{app}) are presented in Fig. 3(b). ZRB photocatalyst exhibits the high photocatalytic activity (k_{app} = 6.68x10^{-2} min^{-1}), indicating that the photocatalyst can produce a significant synergetic effect.[5]

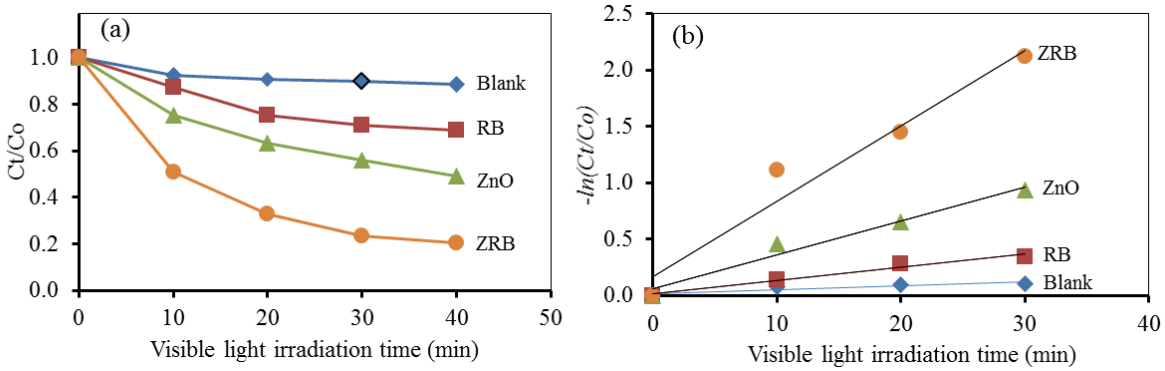

Fig. 3. (a) The photocatalytic degradation and (b) Kinetic plots for the photocatalytic degradation of MB under visible light over the ZRB photocatalyst.

Conclusion

A ZRB photocatalyst was successfully synthesized by the solvothermal method. The photocatalytic activity of the synthesized ZRB displayed high performance. The optimum conditions including visible light time, catalyst dosage and visible light intensity were 20 min, 0.04 g/L and 60W, respectively. Therefore, our results confirm that the ZRB catalyst could be an excellent photocatalyst for further developments in the photocatalytic degradation of dye pollutants and can be a suitable candidate for eco-friendly environmental applications.

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References

1. P. Nuengmatcha, S. Chanthai, R. Mahachai, W.C. Oh. Visible light-driven photoca talytic degradation of rhodamine B and industrial dyes (texbrite BAC-L and texbrite NFW-L) by ZnO- graphene-TiO_2 composite. *J. Environ. Chem. Eng.* 2016, 2170-217 7.

2. S. Sajjadi, A. Khataee, M. Kamali, Sonocatalytic degradation of methylene blue by a novel graphene quantum dots anchored CdSe nanocatalyst. *Ultrason. Sonochem*. 2 017, 676-685.

3. Q. Wang, L. Zheng, Y. Chen, J. Fan, H. Huang, B. Su. Synthesis and characteriz ation of novel PPy/$Bi_2O_2CO_3$ composite with improved photocatalytic activity for deg radation of Rhodamine-B. *J. Alloys Compd.* 2015, 127-132.

4. S. Yi, J. Cui, S. Li, L. Zhang, D. Wang, Y. Lin. Enhanced visible-light photocata lytic activity of Fe/ZnO for rhodamine B degradation and its photogenerated char ge transfer properties. *Appl. Surf. Sci.* 2014, 230-236.

5. S. Rabieh, K. Nassimi, M. Bagheri, Synthesis of hierarchical ZnO-reduced graphene

oxide nanocomposites with enhanced adsorption-photocatalytic performance, Mater. L ett. 2016, 28-31.