Journal of Fundamental Sciences Vol.7, No.2 (2011) 137-139.

ISSN 1823-626X

Journal of Fundamental Sciences

available online at http://jfs.ibnusina.utm.my

Photodecomposition of methylene blue over $EGZrO_2$/HY in aqueous alkaline solution

N. Sapawe[1], A.A. Jalil[1 *], S. Triwahyono[2,3]

[1]Institute of Hydrogen Economy, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, MALAYSIA
[2]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, MALAYSIA
[3]Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, MALAYSIA

Received 29 June 2011, Revised 30 August 2011, Accepted 7 October 2011, Available online 10 December 2011

ABSTRACT

The photodecomposition of methylene blue (MB) in an aqueous alkaline solution over $EGZrO_2$/HY catalyst was investigated. The prepared catalyst was examined using X–ray diffraction (XRD) and transmission electron microscopy (TEM). The MB was completely decolorized under visible light at pH 11 after 432 h over 1 wt% $EGZrO_2$/HY photocatalyst. Photolysis almost did not occurs even the MB was kept for the same reaction time but when the system was kept under dark condition in the absence of catalyst the MB converted into methylene violet (MV) after 30 h of reaction.

| Decomposition | photocatalyst | 1 wt% $EGZrO_2$/HY | methylene blue | methylene violet |

http://dx.doi.org/10.11113/mjfas.v7n2.253

1. INTRODUCTION

Dimethylaminophenazo thionium chloride, generally known as methylene blue (MB), is one of the basic dyes with the structure of heterocyclic aromatic chemical compound. These dyes were commonly used initially for dyeing of silk, leather, plastic, paper, as well as in manufacturing of paints and printing inks [1]. MB is not considered as an acutely toxic, mutagenic, and hazardous; but it has harmful effects [2]. It can give rise to short periods of rapid or difficult breathing once inhales, while ingestion of MB may cause nausea, vomiting, diarrhea, and gastritis. Large doses could cause abdominal and chest pain, headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia [3].

Approximately 1–15% of dyes are discharged during dying process of textile industries [4,5]. MB is one of the main sources of aquatic pollution with coloured compound and most practical dye for aqueous use; the presence of the sulfur seems to stabilize the molecule [6]. There have been reports of various complex patterns in MB catalyzed systems in alkaline solution during the past few decades [7–12]. MB forms dimers and may form also higher aggregates in the aqueous solution [13,14]. In addition, it is also can be decompose slowly in aqueous solution of pH>9.

Recently, advanced oxidation processes (AOPs) using semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, etc. as photocatalyst have become more popular among the researchers because the AOPs can convert a wide range of harmful dyes into non–toxic products, CO_2, and water at ambient temperature [15–17]. The use of support materials such as zeolite also became the focus of intensive study because it can lead to an efficient photoactivity, as a result of the synergistic effect given by both metal oxide and support [15,16,18].

Therefore, the aim of this study is to focus attention on the decomposition of MB over $EGZrO_2$/HY photocatalyst in aqueous alkaline solution. The reactions were conducted under dark and visible light illumination, in the presence and absence of the photocatalyst. The photocatalyst was subjected to X–ray diffraction (XRD) and transmission electron microscopy (TEM), while the changes on the decomposition of MB were observed as well.

2. EXPERIMENTAL

2.1 Materials

The HY zeolite had a Si/Al ratio of 80 and was purchased from the Zeolyst International. *N*,*N*–dimethylformamide (DMF) was purchased from Merck and naphthalene was obtained from Fluka. Sodium hydroxide, hydrochloric acid, and methylene blue (C.I. 52015 for microscopy) were obtained from QReC^{TM}. The platinum (Pt) and zirconia (Zr) plate cells were obtained from Nilaco Metal, Japan. All reagents were of analytical grade and were used as received. Deionized water was used for the

---

Corresponding author at :
Institute of Hydrogen Economy, Faculty of Chemical Engineering,
Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, MALAYSIA.
Email: aishah@cheme.utm.my (A.A. Jalil)

preparation of the pH solution and adjustments to the pH were performed using a 0.1M HCl and NaOH solution.

2.2 Catalyst preparation

The 1 wt% $EGZrO_2/HY$ catalyst was prepared using a DMF solution (10 mL) which containing of 0.1 M TEAP, electrolyzed in the presence of a naphthalene mediator (6 mmol) and HY zeolite (1.5 g) in a normal one–compartment cell fitted with a Pt plate cathode (2 × 2 cm^2) and Zr plate anode (2 × 2 cm^2) at a constant current density of 120 mA/cm^2 under a nitrogen atmosphere at 273 K [17–19]. After electrolysis, the mixture was impregnated, oven dried overnight at 378 K, and calcined at 823 K for 3 h to yield a white powder (1 wt% $EGZrO_2/HY$), therefore ready for characterization and photocatalytic testing. The required weight percent of the $EGZrO_2$ supported on HY and the time required for complete electrolysis was calculated based on Faraday's law of electrolysis,

$$t = \left(\frac{F}{I}\right)(z \times n) \tag{1}$$

where t = total time for the constant current applied (s); F = 96486 C mol^{-1}, which is the Faraday constant; I = the electric current applied; z = the valency number of ions of substances (electrons transferred per ion); and n = the amount of substance (no of moles, liberated n = m/M).

2.3 Characterization

The crystalline structures of the photocatalyst were studied by XRD recorded on a D8 ADVANCE Bruker X–ray diffractometer using Cu K_α radiation at a 2θ angle ranging from 3° to 90°, while the morphological properties of 1 wt% $EGZrO_2/HY$ photocatalyst were examined by TEM (JEOL JEM–2100F).

2.4 Reaction testing

The decomposition of MB was tested under dark and fluorescent light, with or without presence of photocatalyst, and the reaction was conducted for 18 days (432 h). A 0.075 g of the photocatalyst was used and dispersed in 200 mL of 10 mg L^{-1} MB aqueous solution at pH 11. At specific time intervals, 2.5 mL of the sample solution was withdrawn and centrifuged prior measurements for the remaining MB concentration by a UV–vis spectrophotometer (Agilent Technologies Cary 60 UV–vis) using the characteristic adsorption band at 664 nm, 612 nm, and 590 nm. The decolorization percentage was calculated as follows,

$$Decolorization\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where C_o represents the initial concentration and C_t denotes a variable concentration.

3. RESULTS & DISCUSSION

The XRD pattern of the prepared $EGZrO_2/HY$ photocatalyst was compared with $EGZrO_2$ and bare HY, and the results are shown in Fig. 1. The peak intensity of HY decreased as the $EGZrO_2$ was loaded because the presence of foreign substances affected the morphology of the supported HY fingerprint. A series of characteristic peaks were observed for $EGZrO_2$ which are consistent with the tetragonal and monoclinic phase of ZrO_2 (JCPDS 36–1541), with no other diffraction peaks were detected indicated the purity of the prepared $EGZrO_2$ [20].

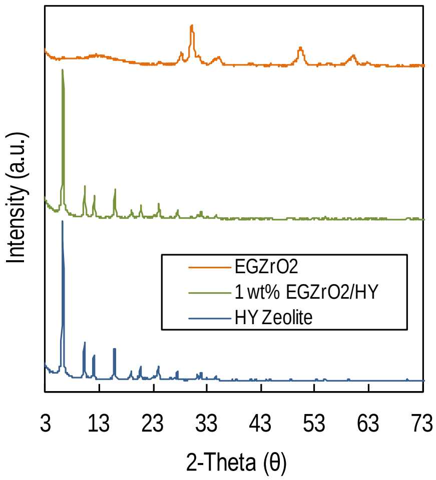

Fig. 1 XRD patterns of photocatalysts for full range 3–73°.

The morphological properties of the $EGZrO_2/HY$ photocatalyst were examined by transmission electron microscopy (TEM), and the image is presented in Fig. 2. The inset figures correspond to the fast Fourier transform patterns (FFT), and indicated that the material is crystalline phase. The existence of black spot confirms that the $EGZrO_2$ nanoparticles were well dispersed on the HY support.

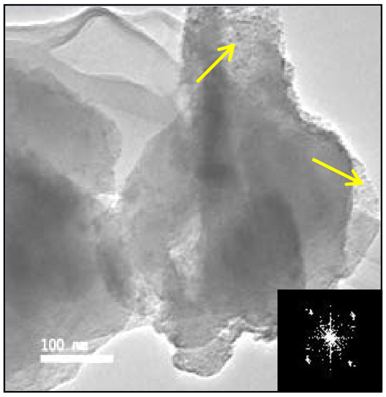

Fig. 2 TEM micrographs of 1 wt% $EGZrO_2/HY$ photocatalyst, and the inset is its corresponding FFT.

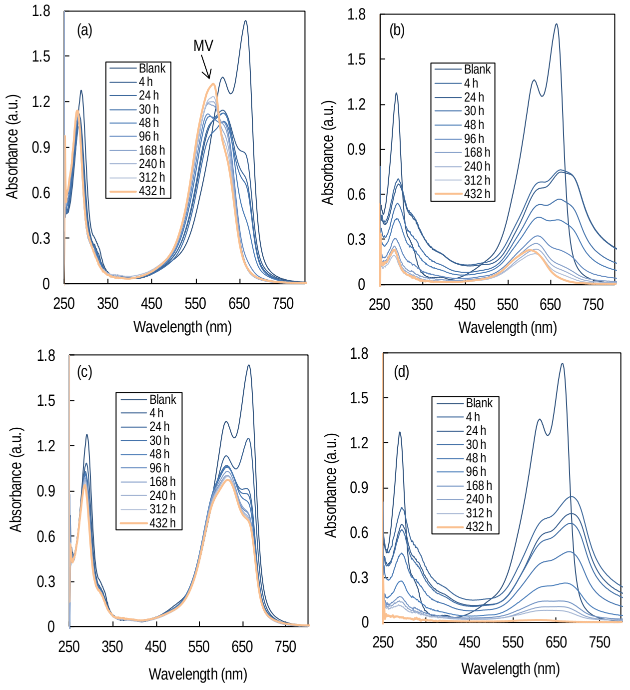

Fig. 3 Absorption spectra of a solution of MB under dark condition (a) without (b) with photocatalyst, and under fluorescent light (c) without (d) with photocatalyst.

The absorption spectra of MB in alkaline solution at zero time (blank) are demonstrated at 664 nm (α–band) and 612 nm (β–band) (Figs. 3a–3d). These two peaks are assigned to the absorption bands of the monomeric and dimeric forms [6]. Under dark conditions, in the absence of $EGZrO_2/HY$ photocatalyst, both α– and β–bands are decreasing, while a new peak at 590 nm was appears after kept for 30 h, indicating the formation of methyl violet (MV) (Fig. 3a). However, in presence of photocatalyst, the MB was partially diminished, but after 312 h, the absorption band seems to starts shifted to 590 nm (Fig. 3b). From this observation, it could be dictated that under strong alkaline conditions (pH 11) under dark condition, the MB is slowly converted into MV by hydrolysis of a dimethylamino group [6,21].

The photolysis study of MB (Fig. 3c) was also conducted under visible light, and it shows that less significant of MB decolorization was occurred. However, in the presence of $EGZrO_2/HY$ photocatalyst (Fig. 3d), both α– and β–bands were reduced utterly with no formation of MV, showing the complete decolorization of MB after 432 h of contact time.

4. CONCLUSIONS

In this study, 1 wt% $EGZrO_2/HY$ photocatalyst was prepared by a simple electrochemical method. The physicochemical properties of the prepared photocatalyst were studied by XRD and TEM. The MB is slowly converted to MV when the reaction is carried out under dark and strong alkaline conditions (pH 11) during 30 h of contact time. However, in the presence of catalyst and under fluorescent light, the MB was completely decolorized without formation of MV.

ACKNOWLEDGEMENT

The authors are grateful for the financial support by the Research University Grant from Universiti Teknologi Malaysia (Grant No. 01H59), the awards of UTM Zamalah Scholarship (Norzahir Sapawe) and the Hitachi Scholarship Foundation for their support.

REFERENCES

[1] H. Berneth, A.G. Bayer, (2003). Ullmann's Encyclopedia of Industrial Chemistry. Germany: Willey–VCH Press.
[2] K.V. Kumar, A. Kumaran, Biochem. Eng. J. 27 (2005) 83–93.
[3] O. Hamdaoui, M. Chiha, Acta Chim. Slov. 54 (2007) 407–418.
[4] T. Sauer, G.C. Neto, H.J. Jose, R.F.P.M. Moreira, J. Photochem. Photobiol. A: Chem. 149 (2002) 147–154.
[5] E.A. El–Sharkawy, A.Y. Soliman, K.M. Al–Amer, J. Colloid Interface Sci. 310 (2007) 498–508.
[6] L. Adamcikova, K. Pavlikova, P. Sevcik, React. Kinet. Catal. Lett. 69 (2000) 91–94.
[7] M. Burger, R.J. Field, Nature 307 (1984) 720–721.
[8] P. Resch, R.J. Field, F.W. Schneider, J. Phvs. Chem. 93 (1989) 2783–2791.
[9] P. Resch, R.J. Field, F.W. Schneider, M. Burger, J. Phys. Chem. 93 (1989) 8181–8186.
[10] M. Watzel, A.F. Munster, Chern. Phvs. Lett. 242 (1995) 273–278.
[11] P. Sevcik, H.B. Dunford, J. Phys. Chem. 95 (1991) 2411–2415.
[12] L. Adamcikova, P. Sevcik, Z. Naturforsch., A: Phys. Sci. 52 (1997) 650.
[13] P.J. Hillson, R.B. McKay, Trans. Faraday Soc. 61 (1965) 374–382.
[14] M. Schubert, A. Levine, J. Am. Chem. Soc. 77 (1955) 4197–4201.
[15] N. Sapawe, N.F. Jaafar, N.H.H. Hairom, M.A.H. Satar, M.N. Ariffin, S. Triwahyono, A.A. Jalil, J. Fundamental Sci. 7 (2011) 19–23.
[16] S. Triwahyono, A.A. Jalil, M. Musthofa, Appl. Catal. A: Gen. 372 (2010) 90–93.
[17] A.A. Jalil, N. Kurono, M. Tokuda, Synlett. 12 (2001) 1944–1946.
[18] A.A. Jalil, N. Kurono, M. Tokuda, Tetrahedron 58 (2002) 7477–7484.
[19] A.A. Jalil, N. Kurono, M. Tokuda, Synthesis 18 (2002) 2681–2686.
[20] Q. Chang, J.E. Zhou, Y. Wang, G. Meng, Adv. Powder Technol. 20 (2009) 371–374.
[21] G. Oster, N. Wotherspoon, J. Am. Chern. Soc. 79 (1957) 4836–4838.