PERFORMANCE OF EGZrO$_2$-EGFe$_2$O$_3$/HY AS PHOTOCATALYST AND ITS EFFICACY IN DECOLORIZATION OF DYE-CONTAMINANTS

(Keupayaan EGZrO$_2$-EGFe$_2$O$_3$/HY sebagai Fotomangkin dan Keberkesanannya Dalam Penyahwarnaan Bahan Cemar Pewarna)

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Received: 17 August 2015; Accepted: 13 June 2016

Abstract
The performance of electrogenerated metals supported on HY zeolite (EGZrO$_2$-EGFe$_2$O$_3$/HY) was studied under sunlight irradiation for the decolorization of methylene blue (MB) and Congo red (CR) in aqueous solutions. The prepared photocatalysts were examined using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller surface area analysis (BET). An amount of 0.375 g L$^{-1}$ EGZrO$_2$-EGFe$_2$O$_3$/HY was found to be the optimum dosage for 10 mg L$^{-1}$ dyes, which gave almost complete photodecolorization of both MB and CR dye after 2 hours of contact time at pH 9 and pH 7, respectively. In addition, a control experiment was also conducted under similar conditions to confirm the efficacy of the prepared photocatalyst. The simple preparation of the photocatalyst and low amount of metal loading required, with simultaneously existence of synergistic effect from both metal oxides exhibits the great potential of the system that could be applied in textile or other industries wastewater treatment.

Keywords: photocatalyst, dyes, decolorization, sunlight

Abstrak
Keupayaan logam elektrogenerasi disokong pada zeolit HY (EGZrO$_2$-EGFe$_2$O$_3$/HY) telah dijalankan di bawah sinar matahari untuk penyahwarnaan metilena biru (MB) dan Congo merah (CR) dalam larutan akues. Fotomangkin telah dikaji menggunakan pembelauan sinar X-ray (XRD), mikroskopi elektron transmisii (TEM), dan analisis luas permukaan Brunauer-Emmett-Teller (BET). Sejumlah 0.375 g L$^{-1}$ EGZrO$_2$-EGFe$_2$O$_3$/HY telah didapati sebagai dos optimum untuk 10 mg L$^{-1}$ larutan pewarna, yang memberikan penyahwarnaan hampir lengkap bagi kedua-dua pewarna MB dan CR selepas 2 jam tindak balas pada pH 9 dan pH 7. Di samping itu, satu eksperimen kawalan juga telah dijalankan pada keadaan yang sama untuk mengesahkan keberkesanan fotomangkin yang disediakan. Penyediaan yang mudah untuk fotomangkin dan jumlah muatan logam sedikit yang diperlukan, pada masa yang sama dengan kewujudan kesan sinergi dari kedua-dua oksida logam mempamerkan potensi besar untuk sistem ini digunakan dalam industri tekstil atau industri rawatan air sisa yang lain.

Kata kunci: fotomangkin, pewarna, peyahwarnaan, sinar matahari

Introduction
Over the decades, an environmental problems distress on soil and water pollution has become an important issue. In accordance, the major pollutants in wastewater such as organic dyes were produced, wherein about 15% of total
world production of dyes is lost during dyeing processes and is released in textile effluents [1-3]. In Malaysia, about 97% of the dye effluents are mainly come from three industrial classes, which are food, chemical and textiles industry [3]. Among this, about 22% of the total volume of these industrial wastewater is from the textile industry, commonly use basic dyes, such as crystal violet, rhodamine B, methyl violet, methylene blue and etc., to add colour for their final products of wool, silk, cotton, linen and modified acrylic fibres [3-4]. Though, most of the unspent dyes generate undesirable effluents and usually discharged to the environment with or without further treatment [1,5-7]. These effluents run into water bodies and can cause severe problems if not being treated properly as they are toxic, mutagenic and carcinogenic to human life as well as prohibit the photosynthesis of aquatic life even as small quantities as 1 ppm [3, 4]. To overcome this problems, several methods have been reported for the removal of such dyes including chemical and biological oxidation, adsorption, electrochemical oxidation, coagulation and flocculation, ion exchange, and membrane separation [5, 6, 8-10]. However, those methods have their own limitations for example time-consuming, generation of secondary wastes, expensive, and commercially unattractive.

Advanced oxidation processes (AOPs) particularly using semiconductors such as TiO₂, ZnO, WO₃, Fe₂O₃, CuO, ZrO₂, CdS, In₂O₃, SnO₂, etc. as photocatalysts has became attractive and accorded great importance due to its potential to destroy and transform a wide range of harmful dyes at ambient temperature to the simplest form of non-toxic products, CO₂ and water [2-4]. Zeolite is considered to be an important support owing to their high surface area, high thermal stability, eco-friendly nature, and also have reported to provide specific photophysical properties such as control charge transfer and electron transfer processes [3,4]. A review of recent research revealed that some of the successful examples of metal oxides supported zeolite are TiO₂-HZSM-5, Co-ZSM-5, CuO-X zeolite and Fe-exchange zeolite [3,4,11-13]. Most of the popular one are TiO₂ and ZnO but the report on the ZrO₂ supported zeolite photocatalyst is quite rare. ZrO₂, which have specific optical and electrical properties, possessing both acid-base and redox function, thermal stability, and strong mechanical strength is believed to exhibit a great performance when support on zeolite [3].

Recently, we have reported a new preparation method for an α-Fe₂O₃ and EGZrO₂ supported HY catalyst by a simple and rapid electrochemical process, which possesses high photoactivity in the decolorization of methylene blue [3,14]. The nanosized metal oxides as well as the synergistic interaction between the metal and the support were found to play important roles in the enhancement of the reaction [4]. Further study on the property of that zinc metal oxide showed that it was nanoparticle in size, which showed promising photoactivity in the removal of methyl orange from aqueous solution [15]. Thus, by the corresponding method, we have succeeded to generate a very fine particles metal with higher reactivity.

Herein, as an extension of our study, we attempted to prepared nanoparticles electrogenerated ZrO₂–Fe₂O₃ supported HY zeolite (EGZrO₂–EGFe₂O₃/HY) by using the corresponding novel preparation method which is fast, simple and efficient than other methods with the aim to reduce amount of metal oxide used and tested its photoactivity on the decolorization of methylene blue (MB) and Congo red (CR) towards a green environment. The prepared catalyst was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller of surface area analysis (BET). The performance of photoactivity decolorization was investigated to obtain the optimum conditions.

Materials and Methods

Materials
The HY zeolite had a Si/Al ratio of 80 and was purchased from Zeolyst International. The N,N-dimethylformamide (DMF) was purchased from Merck and the naphthalene was obtained from Fluka. The sodium hydroxide (NaOH), hydrochloric acid (HCl), and methylene blue (C.I. 52015 for microscopy) were obtained from QReC™. The platinum (Pt), zirconia (Zr), and iron (Fe) plate cells were obtained from Nilaco Metal, Japan. All of the reagents were analytical grade and were used as received. Deionized water was used for the preparation of the pH solution and adjustments to the pH were performed using a 0.1 M HCl and NaOH solution.

Catalyst preparation
The 1 wt.% EGZrO₂–1 wt.% EGFe₂O₃/HY was prepared following a previously reported protocol [3,4]. A DMF solution (10 mL) containing 0.1 M tetraethylammonium perchlorate was 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 x 2 cm²) and Zr plate anode (2 x 2 cm²), then switched to Fe plate anode, at a constant current density of 120 mA/cm² under a nitrogen atmosphere at 273 K. Naphthalene was used as a mediator in the system to produce radical anions, which then reduced the metal cations from the anode to give metal nanoparticles. 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 (EGZrO₂−EGFe₂O₃/HY), and finally ready for characterization and photocatalytic testing. Furthermore, the EGZrO₂ and EGFe₂O₃ photocatalyst was prepared by the same procedure except for the addition of the HY zeolite (1.5 g) prior to electrolysis, and a white powder was obtained as the final product. The required weight percent of the EGZrO₂ and EGFe₂O₃ supported on HY was calculated based on Faraday’s law of electrolysis as expressed in equation 1:

\[
t = \left( \frac{F}{I} \right) (z \times n)
\]

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 (mA); \( z \) = the valency number of ions of substance (electrons transferred per ion); and \( n \) = the number of moles of substance (number of moles, liberated \( n = m/M \)) [3,4].

### Characterization

The crystalline structures of the photocatalyst were studied by X-ray diffraction (XRD) recorded on a D8 Advanced Bruker X-ray diffractometer using Cu Kα radiation at a 2θ angle ranging from 3 to 90°. The phases were identified with the aid of the Joint Committee on Powder Diffraction Standards (JCPDS) files. The morphological properties of the EGZrO₂−EGFe₂O₃/HY photocatalyst were examined by transmission electron microscopy (TEM) (JEOL JEM-2100F). The textural properties (i.e. specific surface area, pore volume and pore diameter) were determined from nitrogen adsorption-desorption isotherms at liquid nitrogen temperature using a Micromeritics ASAP 2010 instrument. The surface area was calculated with the Brunauer-Emmett-Teller (BET) method, and the pore distributions were determined by the Barrett-Joyner-Halender (BJH) method. Prior to measurement, all of the samples were degassed at 110 °C to 0.1 Pa.

### Reaction testing

The photocatalytic activity of the prepared EGZrO₂−EGFe₂O₃/HY photocatalyst was tested for the decolorization of MB and CR. A 0.075 mg sample of the photocatalyst was dispersed in 200 mL of 10 mg L⁻¹ MB aqueous solution. The adsorption-desorption equilibrium was achieved under dark conditions after 30 min, and the mixture was irradiated for 120 min with constant stirring under sunlight (January to March 2015, between 12 NN until 3 PM with an average intensity 1.315 × 10⁵ Lux unit). However, during the illumination time, no volatility of the solvent was observed. At specific time intervals, 2.5 mL of the sample solution was withdrawn and centrifuged prior measurements of the MB and CR concentration by a UV-vis spectrophotometer (Agilent Technologies Cary 60 UV-vis) using the characteristic adsorption band at 664 nm and 496 nm. The decolorization percentage was calculated as follows (equation 2):

\[
Decolorization \% \ = \ \left( \frac{C_0 - C_f}{C_0} \right) \times 100
\]

where \( C_0 \) represents the initial concentration, and \( C_f \) denotes a variable concentration.

### Results and Discussion

The XRD pattern of 1 wt.% EGZrO₂−1 wt.% EGFe₂O₃/HY photocatalysts were compared with bare HY, and the results are shown in Fig. 1a. The peak intensity of HY was decreased as the addition of EGZrO₂ and EGFe₂O₃ due to the presence of foreign substances that could affected the morphology of the HY fingerprint. A series of characteristic peaks were observed for EGZrO₂ at 30.2° (101), 35.2° (110), 50.3° (112), and 60.2° (211), which are consistent with the tetragonal \((t)\) phase of ZrO₂, and in agreement with JCPDS file PDF No 01-072-2743 (Fig. 1b) [3,14]. Characteristic peaks were observed at 2θ equal to 28.2°, 31.5°, and 34.5° and corresponded to the diffraction patterns of (-111), (111), and (002) of the monoclinic \((m)\) phase of ZrO₂, (Fig. 1b) [3,14]. Next, the XRD peaks of EGFe₂O₃ (Fig. 1b) were observed at 2θ = 24.1° (012), 33.1° (104), 35.6° (110), 40.7° (113), 49.4° (024), 54.1°...
(116), 62.5° (214) and 64.2° (300). These peaks can be indexed to pure rhombohedral symmetry of Fe$_2$O$_3$ indicating the crystalline hematite phase (JCPDS file PDF No 00-024-0072) [3,14]. Hence, there is no other diffraction peaks were detected which indicated the purity of the prepared EGZrO$_2$ and EGFe$_2$O$_3$.

The morphological properties of the 1 wt.% EGZrO$_2$–1 wt.% EGFe$_2$O$_3$/HY photocatalyst were observed by the transmission electron microscopy (TEM), and the images are presented in Fig. 2, respectively. The value of the interplanar distance ($d$-spacing) of the lattice fringes was estimated from this image was consistent with the value of lattice spacing of EGZrO$_2$ and EGFe$_2$O$_3$ obtained from the XRD analysis. This agreement confirms that the EGZrO$_2$ and EGFe$_2$O$_3$ nanoparticles were well dispersed on the HY support.

The surface area analysis data obtained from the BET method as well as the pore volume and pore diameter determined by the Barret-Joyner-Halenda (BJH) desorption isotherms method was tabulated in Table 1. The
addition of EGZrO$_2$ and EGFe$_2$O$_3$ onto HY decreases the surface area and pore volume, but increases the pore diameter. The decrease in the pore volume may be a reflection of the uneven particle sizes of the catalyst [16-18].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m$^2$g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HY zeolite</td>
<td>557</td>
<td>2.70</td>
<td>0.376</td>
</tr>
<tr>
<td>EGZrO$_2$/HY</td>
<td>505</td>
<td>1.83</td>
<td>0.323</td>
</tr>
<tr>
<td>EGFe$_2$O$_3$/HY</td>
<td>496</td>
<td>1.79</td>
<td>0.222</td>
</tr>
<tr>
<td>EGZrO$_2$–EGFe$_2$O$_3$/HY</td>
<td>536</td>
<td>1.87</td>
<td>0.250</td>
</tr>
</tbody>
</table>

The performance of the prepared 1 wt.% EGZrO$_2$–1 wt.% EGFe$_2$O$_3$/HY photocatalyst for the decolorization of MB and CR was examined, and the results are shown in Fig. 3. A controlled experiment was conducted for both MB and CR, under six different conditions including photolysis and reaction in the presence of the bare HY, EGZrO$_2$, EGFe$_2$O$_3$, EGZrO$_2$–EGFe$_2$O$_3$, and 1 wt.% EGZrO$_2$–1 wt.% EGFe$_2$O$_3$/HY catalysts. Each experiment was performed under both dark and sunlight conditions. The experiments under dark conditions removed less than 22% of the MB after 2 hours of contact time, which indicated the importance of sunlight in this study. Under photolysis conditions, 2% MB was decolorized because of the degradation of the substance after long exposure to sunlight. No significant effect was observed using bare HY under dark and UV–light conditions where 22% and 27% MB was removed, respectively. The use of EGZrO$_2$, EGFe$_2$O$_3$, EGZrO$_2$–EGFe$_2$O$_3$ under sunlight resulted in 32%, 40%, and 67% decolorization of MB, in respectively, which is higher than the same reaction under dark conditions. Indeed, the removal percentage was increased up to 99.8% by using 1 wt.% EGZrO$_2$–1 wt.% EGFe$_2$O$_3$/HY.

Furthermore, for CR dye, less than 17% of the CR was adsorbed under dark conditions after 2 hours of contact time, and no photolysis was occurring after long exposure to sunlight. About 15% and 20% of CR was removed using bare HY under dark and sunlight conditions, respectively. The EGZrO$_2$, EGFe$_2$O$_3$, EGZrO$_2$–EGFe$_2$O$_3$ was resulted in 27%, 34%, and 63% decolorization of CR under sunlight, respectively, indicates the significance the use of sunlight in this study. The 1 wt.% EGZrO$_2$–1 wt.% EGFe$_2$O$_3$/HY shows the highest removal percentage which accounted 98% decolorization. Based on all above, we can conclude that the porosity of the catalyst surface may play an important role in adsorption, as previously reported in liquid–gas adsorption systems for wastewater.
treatment. Good distribution of the EGZrO₂ and EGFe₂O₃ nanoparticles on the surface of the HY might facilitate their surface contact with sunlight and lead to higher efficiency of the reaction. The synergistic effect from both EGZrO₂–EGFe₂O₃ and HY were also found to play an important role in enhancing the photodecolorization reaction. This result reveals that EGZrO₂–EGFe₂O₃/HY is a potential photocatalyst semiconductor.

Conclusion
In this study, the 1 wt.% EGZrO₂–1 wt.% EGFe₂O₃/HY photocatalyst with enhanced photoactivity was prepared by a simple electrochemical method. The physicochemical properties of the prepared photocatalyst were studied by XRD, TEM, BET surface area analysis. The photocatalyst were evaluated for the decolorization of 10 mg L⁻¹ of MB and CR under different pH, at pH 9 and pH 7, using an amount of 0.375 g L⁻¹ 1 wt.% EGZrO₂–1 wt.% EGFe₂O₃/HY after 2 hours of contact time, hence gave removal percentage of 99.8% and 98.0%, in respectively. This system exhibits great potential for improving the quality of the wastewater discharged from textile industry and other industries because of the simple preparation of the photocatalyst and the low amount of metal loading required. It was believed to be extendable to the synthesis of other catalysts with different characteristics and be used in various applications. Furthermore, more technologies and instrument were needed in order to examine and investigate the mechanism pathways of the synthesis of catalyst using this electrolysis system. In addition, it also provides new findings to explore the new structural model of the catalyst.

Acknowledgement
The authors are grateful for the financial support by the Short Term Research Grant (STRG) from Universiti Kuala Lumpur (Grant No. 15047) and Majlis Amanah Rakyat (MARA) Malaysia, and also the Section of Technical Foundation – Malaysian Institute of Chemical and Bioengineering Technology Universiti Kuala Lumpur for their support.

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