

ELECTRODEPOSITED ZnO/Zn PHOTOCATALYSTS FOR THE DEGRADATION OF BENZENE-TOLUENE-XYLENE MIXTURE IN AQUEOUS PHASE

(Fotomangkin ZnO/Zn Electroendapan bagi Degradasi Campuran Benzena-Toluena-Xilena dalam Fasa Aqueus)

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Abstract

The recognition of the ability of volatile organic compounds, (VOCs) to pollute the ground water is now well documented. VOCs such as benzene, toluene and xylene from the petroleum industries processed water leaked through the underground old piping system into the soils and groundwater during its transportation to the wastewater plant. Photocatalysis have been used as a potential system in the degradation of VOCs in the wastewater. However, the powdered form photocatalysts that were used in various studies are difficult to be separated from the aqueous solution at the end of the treatment. Therefore, the main objective of this research is to prepare the electrodeposited photocatalysts for the degradation of aromatic hydrocarbon mixture, benzene-toluene-xylene (BTX) solution under UV light (354 nm). The concentrations of electrolyte and electrodeposition voltages used to prepare the photocatalysts were studied for their efficiency in the degradation. From the research, ZnO/Zn prepared in 0.8 M NaOH and under 12 V possessed the best catalytic degradation performance by degrading 32.37% of BTX in the solution. The ZnO/Zn photocatalyst was characterized using X-ray Diffraction Techniques (XRD) which illustrated high crystallinity of Zn species and reasonably high amorphous phase of ZnO species.

Keywords: Electrodeposited photocatalyst, benzene-toluene-xylene, UV-light, zinc oxide

Abstrak

Implikasi pencemaran air bawah tanah oleh Sebatian Organik Meruap telah didokumentasikan dengan baik. Sebatian Organik Meruap seperti benzena, toluena, dan xilena daripada air yang telah diproses oleh industri petroleum meresap dari sistem pempaipaan bawah tanah lama yang bocor ke dalam tanah dan air bawah tanah semasa pengangkutan ke loji fasa aqueus. Fotopemangkinan merupakan suatu kaedah yang berpotensi dalam degradasi sebatian organik dalam fasa aqueus. Walau bagaimanapun, fotomangkin berbentuk serbuk sukar dipisahkan daripada larutan aqueus selepas rawatan. Oleh itu, matlamat utama penyelidikan ini ialah menyediakan fotomangkin elektro endapan bagi mendegradasi sebatian hidrokarbon aromatik, iaitu benzena-toluena-xilena (BTX) dengan kehadiran sinaran UV (354 nm). Kepekatan elektrolit dan arus elektro endapan yang digunakan dalam penyediaan fotomangkin dikenalpasti keberkesananannya dalam proses degradasi. Daripada penyelidikan ini, ZnO/Zn yang disediakan dengan menggunakan 0.8 M NaOH dan bawah arus elektro 12 V merupakan mangkin terbaik yang dapat mendegradasikan 32.37% BTX dalam larutan. Fotomangkin yang paling baik dianalisis menggunakan Teknik Pembelaan Sinar-X (XRD) dan menunjukkan kehabluran tinggi bagi spesis Zn dan bersifat amorfus bagi spesis ZnO.

Kata kunci: elektroendapan, fotomangkin, sebatian benzena-toluena-xilena, sinaran UV, zink oksida

Introduction

Benzene, toluene and xylene (BTX) are volatile organic compounds (VOCs) which exist as a common constituent in petroleum processing industries. It may be found in the processed water which will then be transported into the wastewater treatment plant. The soils and the groundwater contamination by volatile organic petroleum hydrocarbons were in a deep concerned in the last decades. The VOCs were escaped into the soils and underground water through continuous leaking of old piping systems. According to world health organization, BTX are

considered as among the most hazardous pollutants. BTX is considering as priority pollutants due to their low water solubility and their acute toxicity and genotoxicity [1, 2].

BTX degradation by photocatalytic degradation possesses several advantages over conventional methods [3, 4, 5, 6]. Conventional methods such as precipitation, adsorption and flocculation have been tested but they were less efficient due to time consuming destruction into harmless compounds. Therefore, photocatalytic process has been explored recently and is the most promising technique to be applied as it shows high efficiency in treating organic pollutants in the industrial wastewater. However, most of the photocatalysts prepared are in powdered form which will then caused problem in separation of powdered form photocatalysts from the treated organic wastewater and cannot be recycled. But, a more promising photocatalyst that is the electrodeposited photocatalyst do not cause such problems. Although the electrodeposited photocatalysts have been studied in terms of their physicochemical properties, yet the application of the electrodeposited photocatalysts have not been studied widely.

ZnO photocatalysts have been explored extensively due to its high efficiency in photocatalytic reaction. ZnO is a potential photocatalyst as it has lower band gap energy. Hence, it is believed that electrodeposited zinc oxide photocatalysts which are still under investigation will give better results in photocatalysis reaction. In this study, electrodeposited zinc oxide photocatalysts will be studied in terms of their physicochemical properties and photocatalytic efficiency.

Materials and Methods

Preparation of ZnO/Zn Photocatalysts

ZnO/Zn photocatalysts were prepared by anodic electrodeposition. Firstly, the preparation of ZnO/Zn photocatalysts were started with scrubbing a zinc sheet (50 x 60 x 0.38 mm) with sand paper, etched in 0.1 M NaOH and washing in distilled water. In the ZnO/Zn preparation, different concentrations of NaOH (0.4 M, 0.8 M, 1.2 M) aqueous solution were used as the electrolyte. A DC voltage (12 V) was applied for 20 min using a constant voltage power supply of PL Regulated 303 DC.

Photocatalytic Degradation Procedure

The photocatalytic activities of the prepared ZnO/Zn catalyst were determined for the photodegradation of BTX. 200 mL of BTX solution (1000 ppm) was pipetted into a pyrex glass reactor and the reactor was sealed with inert rubber stopper. Ultra Violet Lamp (6 W, 354 nm) was used as light source in this experiment. 3-4 mL of sample solution was taken out before UV irradiation and referred as t_0 . Second sample solutions were taken out after 30 minutes of UV irradiation time. The sample solution was taken out at every 30 minutes. All sample solution was analyzed using UV-Vis spectrophotometer Shimadzu 2510PC at λ range 220-300 nm. For catalytic degradation study, the same procedures as photolysis study was repeated but the UV lamp was switched off and ZnO/Zn plate prepared using 0.8 M NaOH solution was placed in the square glass reactor. For photocatalytic degradation study, the same procedure was repeated in the presence of both UV lamp and photocatalysts.

The degree of photodegradation (X) as a function of time is given by Equation 1:

$$X = \frac{A_o - A_t}{A_o} \times 100\% \quad (1)$$

where,

A_o = initial absorbance at time, t_0

A_t = absorbance at certain time, t

ZnO/Zn Film Characterization Using XRD

The crystallographic structure of the ZnO/Zn plates were identified using X-ray Diffraction (XRD) (Bruker Advance D8 with Siemens 5000 diffractometer) equipped with Cu- K_α radiation operates at 40 kV and 40 mA with $\lambda = 1.5418 \text{ \AA}$. The samples were cut into 15 mm \times 15 mm small plate to be fitted in the sample holder in a 40 \times 33 \times 2

mm glass plate. Data were collected over the 2θ range from 10° to 80° . Scan was performed at step scan of 0.05° with step mode of 1 second/step. Diffractograms were compared with the PDF data of the Joint Committee on Powder Diffraction Standards (JCPDS) which comes with the software called Diffrac Plus.

Results and Discussion

Control Test on BTX Degradation

Figure 1 shows that in the presence of UV light without the existence of ZnO/Zn photocatalyst, only 5.02% degradation of BTX was observed after 4 hours of irradiation. Photoirradiation or direct photolysis on the BTX solution gave only a small amount of BTX degradation. This is in agreement with the research conducted by Huang *et al.* (2007) where negligible effect was observed on the degradation of monochlorobenzene in the presence of only UV light [7]. Meanwhile, lowest degradation efficiency of 1.40% of BTX at 240 mins has been observed in the figure indicating that a negligible amount of BTX has been adsorbed onto the ZnO/Zn plate in the dark. In the presence of ZnO/Zn photocatalyst alone, excitation of electrons over the band gap energy does not occur in the absence of UV light as such less than 2% of BTX removal was detected and this is probably due to adsorption phenomenon.

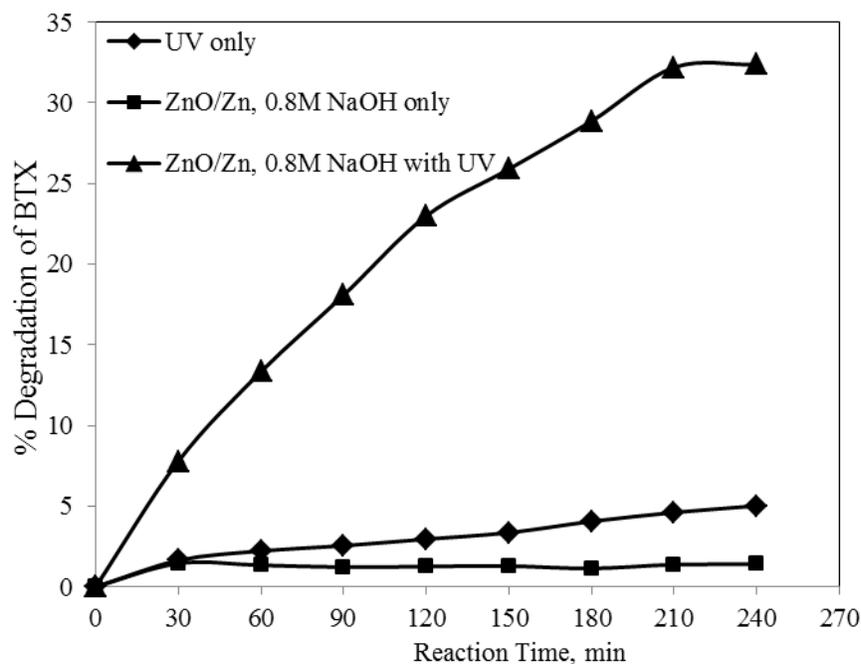


Figure 1. Effect of different systems on degradation of BTX

Meanwhile, the system with the presence of both UV light and ZnO/Zn photocatalyst gave the high degradation of 32.20% at 210 minutes of irradiation. From Figure 1, it can be proven that photocatalytic degradation occurred when both ZnO/Zn photocatalyst and UV light are present in the system. Therefore, it can be claimed that oxidative degradation of the BTX solution by ZnO/Zn photocatalyst had occurred [8]. It has been well established that when the semiconductor was photoexcited with an energy equals to or higher than its energy band gap, an electron would be excited from the valence band to the conduction band followed by leaving a hole at the valence band thus an electron-hole pair was created on the surface of the catalyst [9]. The hole ($h_{\nu B}^+$) which is highly oxidative enabled the BTX directly oxidized to reactive intermediates or mineralized into simple compounds such as CO_2 and H_2O .

Effect of Electrolyte Concentrations on ZnO/Zn Plate Preparation

Different electrolyte concentrations of NaOH (0.4 M, 0.8 M and 1.2 M) used to prepare ZnO/Zn plates have been tested for their performances on the degradation of BTX (Figure 2). Among these concentrations, 0.8 M NaOH was the best concentration used to prepare ZnO/Zn plate within 20 mins and under 12 V as it gave 32.37% of BTX degradation after 4 hours. As the concentrations used to prepare ZnO/Zn plates were higher, the amount of the ZnO nanoparticles formed on the surface of the Zn plate also increased. The photocatalytic activity of ZnO was related to the porosity of oxide film formed during the anodic oxidation process. The porous surface will possibly give high surface area and therefore the higher porosity of the oxide film will lead to higher photocatalytic activity. When the electrolyte concentration used to prepare ZnO/Zn plate was increased to 1.2 M NaOH, the performance of the catalyst in BTX degradation decreased due to less ZnO particle formed on the Zn plate. Since the ZnO plate that has been formed was corroded by the highly alkaline bath, the active sites of the ZnO decreased. Particle aggregation in the high concentration of NaOH electrolyte during the electrodeposition process might also contributed to less oxide particles formed on the surface of the photocatalyst which leads to low photocatalytic activity [10].

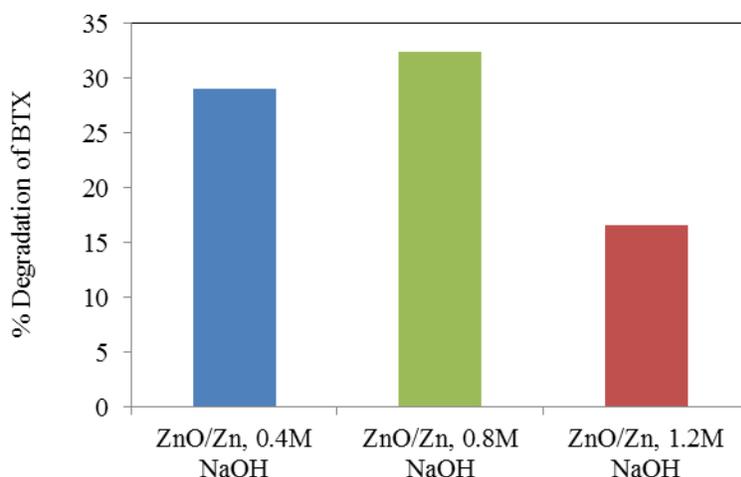


Figure 2. Percentage photodegradation of BTX after 240 minutes using three different electrolytes of NaOH for the preparation of ZnO/Zn photocatalysts

Optimization of Applied Voltage in ZnO/Zn Preparation

The applied voltage for the preparation of ZnO/Zn photocatalyst will affect its photocatalytic activity in UV-induced degradation of BTX. The order of increasing percentage of BTX degradation is in the order of: 8V<10V<12V as displays in Figure 3.

All photocatalysts were prepared by anodic electrodeposition within 20 minutes. ZnO/Zn prepared by applied voltage of 8V gave 23.58% degradation of BTX. Meanwhile, ZnO/Zn prepared by applied voltage of 10 V gave higher percentage degradation of 28.71%. When voltage of 12V was applied, 32.37% degradation of BTX was recorded. Thus, 12 V is considered as the best applied voltage for the preparation of ZnO/Zn (0.8M NaOH) photocatalyst. This might be due to higher voltage contributing to higher rate of anodic electrodeposition, hence more ZnO layer form at the Zn plate at a faster rate. This event will contribute to an increase in the photocatalyst pore size and the porous surface area on the ZnO/Zn plate which resulted in enhancement of degradation activity.

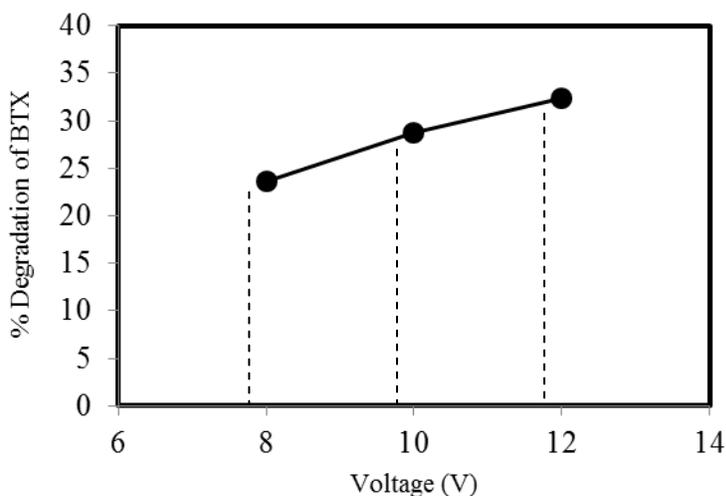


Figure 3. Percentage of BTX degradation using ZnO/Zn (0.8 M NaOH) prepared in three different applied voltages after 20 minutes

Characterization of ZnO/Zn Photocatalyst

XRD Analysis

X-ray Diffraction (XRD) diffractogram pattern of ZnO/Zn plate is presented in Figure 4. It is evident from Figure 4 that the plate prepared by electrodeposition exhibit high crystallinity for Zn metal with hexagonal structure. However, electrodeposited ZnO of hexagonal structure possesses profound degree of amorphous phase which occurred at $2\theta = 36.54^\circ$ (I_{100}), 32.04° (I_{57}), 34.62° (I_{44}) and 56.92° (I_{32}) or d spacing values = 2.45 Å, 2.79 Å, 2.59 Å and 1.62 Å (d_{ref} ZnO (JCPDS) = 2.48 Å, 2.81 Å, 2.60 Å and 1.62 Å). The amorphous structure of ZnO species increases the porosity of the catalyst, so it increases the surface area and these properties are likely contributing to higher performance of catalytic activity.

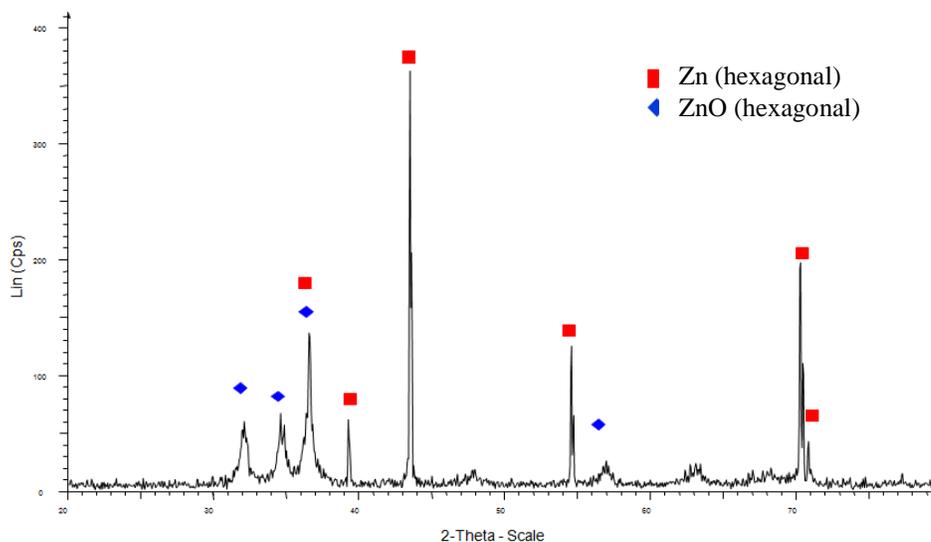


Figure 4. XRD diffractogram pattern of ZnO/Zn plate prepared by electrodeposition method

Conclusion

The electrodeposited photocatalysts has been recognized as an alternative to replace powdered form photocatalyst that can be used to study the destruction of many VOCs (benzene, toluene, xylene). ZnO/Zn photocatalyst was successfully synthesized using anodic electrodeposition method. The optimum condition used to prepare ZnO/Zn photocatalyst was by using 0.8 M NaOH under DC bias of 12V. In this study, the ZnO/Zn photocatalysts prepared by 0.8 M NaOH under 12V gave the highest photocatalytic degradation of BTX wastewater at 32.37%. The XRD pattern revealed that ZnO/Zn photocatalyst is highly crystalline.

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