

Electrodeposition of Metal Oxide Semiconductor Photocatalysts on Support for degradation of BTX

Hazlini Mohamad Ameran, Rusmidah Ali, and Wan Azelee Wan Abu Bakar

Abstract—In this 21st century, the theory of photocatalysis catalyzed by photocatalyst achieves acceptance at the international level. Since water pollution has become a very serious problem to agriculture, ecosystem and human health, photocatalytic degradation technique has become one of the promising methods to overcome this problem. Therefore, an investigation on the catalytic activity of semiconductor materials namely Zn/ZnO/TiO₂ and Al/Al₂O₃/TiO₂ on the photodegradation of BTX (Benzene-Toluene-Xylene) in aqueous system was conducted under UV-light irradiation. Zn/ZnO and Al/Al₂O₃ photocatalysts plate were prepared by electrodeposition process using sodium hydroxide, NaOH and sulphuric acid (H₂SO₄) respectively. Both prepared photocatalysts plate were coated with TiO₂ using cathodic electrodeposition method. In the optimization of Zn/ZnO preparation via anodic oxidation process on zinc plate, it was found that the optimum applied voltage used was 12 V. The study on recycle catalyst shows a drastic decrease on photodegradation efficiency of BTX from 88% of fresh Zn/ZnO/TiO₂ photocatalyst to 61.49% by using the spent catalyst. A comparative study was conducted to investigate the photocatalytic activity of Al/Al₂O₃/TiO₂ photocatalyst towards UV-induced photodegradation of BTX compound. Zn/ZnO/TiO₂ gave higher percentage of BTX degradation (91.54%) after four hours of UV irradiation by comparison to Al/Al₂O₃/TiO₂ photocatalysts. The surface morphology on Al/Al₂O₃ and Al/Al₂O₃/TiO₂ plate shows the existence of large porous surface of the photocatalyst plate that might attributed to the large amount of TiO₂ deposited onto the surface of the photocatalyst. This porous surface might leads to a great performance on UV-Induced degradation of BTX solution using Al/Al₂O₃/TiO₂ plate.

Keywords—Photocatalyst, degradation, electrodeposition, Al₂O₃, ZnO, TiO₂

I. INTRODUCTION

POLLUTANTS in wastewater are dangerous even at a very low quantity especially aromatic compounds that are very well known for its toxicity. Benzene, toluene and xylene all

together as BTX are very dangerous to the human health and ecosystem [1]. Our major concern is that BTX can easily enter our body through many ways such as by inhalation, direct contacts to skin, mouth or eyes.

Effects of BTX start rapidly, and may lead to severe poisoning [2]. The resultant toxic effects are similar to those caused by other organic compounds, causing, at first, euphoria, loss of inhibition, and hallucinations, followed by lethargy, slurred speech, and other depressor effects of the central nervous system (CNS) [2]. It also reported that even low level of BTX in blood can induce encephalopathy and severe abnormalities, including brain degeneration, cortical atrophy and damage in mental and intellectual performance. Due to their toxicity and carcinogenic character, it is crucial to remove BTX compounds in order to preserve human health and the environment [1].

Various chemical and physical processes such as chemical precipitation, separation of pollutants, coagulation, elimination by adsorption on activated carbon, chemical oxidation technique, biochemical treatment and ion exchange method are applied on previous studies for removal of organic pollutants from waste water [11]. However, many wastewater treatment methods have some limitations and disadvantages. As example, the chemical oxidation technique is economically suitable for removal of pollutants of high concentration but it is unable to mineralize all organics [1]. Biochemical treatment is slow and requires control of proper pH and temperature along with the problem of disposal of activated sludge [1]. Activated carbon is a very good adsorbent for adsorption of pollutants in waste water, but the cost of adsorbent is quite high. In addition, activated carbon adsorption involves phase transfer of pollutants without decomposition, which induces another pollution problem [1]

Thus, using a semiconductor as the photocatalyst to degrade various organic and inorganic pollutants in wastewater has become a new kind of water treatment technology with the best prospect of exploitation and utilization [3]. Since pollutants could be completely degraded into harmless matters by photocatalysis method under normal temperature and air pressure, scientists predicted that in the near future photocatalysis will become one of the most effective means in dealing with various kinds of industrial wastewater [4, 5].

Hazlini Mohamad Ameran is with the Universiti Teknologi Mara, UiTM Kampus Puncak Alam, 42300 Selangor, Malaysia (hazlini@salam.uitm.edu.my).

Rusmidah Ali is with the Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, UTM, 81310 Johor Bahru, Johor, Malaysia (rusmidah@kimia.fs.utm.edu.my).

Wan Azelee Wan Abu Bakar is Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, UTM, 81310 Johor Bahru, Johor, Malaysia (wanazelee@kimia.fs.utm.edu.my)

TiO₂ is a promising material as a photocatalyst for photodegradation reactions such as the photolysis of wastewater [6]. TiO₂ is the most suitable photocatalyst for widespread environmental applications [3]. ZnO and Al₂O₃ efficiencies as photocatalyst has also been reported to be particularly noticeable in the advanced oxidation process of many organic pollutants. The ability of the photocatalytic technique to completely degrade organic compounds to produce water and CO₂ materials without generating any harmful byproducts has popularized its role as a wastewater purifier [7].

II. PROCEDURE

A. Anodic Oxidation of ZnO Film on Zinc Plate

Zinc plate was set as anode while graphite plate was set as cathode and both plates were dipped into 0.8 M of the electrolyte solution (NaOH). The direct current voltage was applied for 20 minutes each time using a various voltages (6V, 8V, 10V and 12 V) as power supply of PL Regulated 303 DC. The plate obtained was referred as Zn/ZnO plate and was denoted as ZV1, ZV2, ZV3 and ZV4 respectively. The optimum applied voltages for the preparing the Zn/ZnO plate was determined by comparing the degradation rate of BTX solution.

B. Preparation of Zn/ZnO/TiO₂ Film by Electrodeposition Process

TiO₂ film was electrodeposited on the ZnO substrate using mixture of solution containing ammonium titanyl oxalate monohydrate, (NH₄)₂[TiO(C₂O₄)₂].H₂O (1.0x10⁻² M) and oxalic acid, (COOH)₂ (2.5 x 10⁻³ M) was used as the electrolyte. NH₄OH was added drop wise to the solution mixture so that the pH of the solution was below pH 4. The plate obtained was referred as Zn/ZnO/TiO₂ plate and the prepared plate was denoted as ZT4.

C. The Preparation of Al/Al₂O₃ Plate by Electrodeposition Process

In the anodization process, 2.0 M of sulphuric acid, H₂SO₄ was used as the electrolyte solution and procedure A was repeated but the zinc plate was replaces with aluminium plate for 60 minutes. This anodization process was done in a fume cupboard due to stingy smell from the gas produces in this reaction. The aluminium oxide plate obtained was referred as A1. Then, various concentrations (2.5 M, 3.0 M, and 3.5 M) of H₂SO₄ solution were used for preparing the other three Al/Al₂O₃ plates and were referred as A2, A3 and A4.

D. The Preparation of Titanium Dioxide Film on Alumite Substrate by Electrodeposition Process

The same procedure as mentioned in procedure B was repeated by replacing Zn/ZnO plate by four different types of Al/Al₂O₃ plate prepared in C. After the coating process with TiO₂ layer, the plates obtained were known as Al/Al₂O₃/TiO₂ plates. They are referred as AT1, AT2, AT3 and AT4.

E. Recycled Catalyst Study

After photocatalytic degradation of BTX using ZT4 was conducted, the photocatalyst was then used once again for recycle catalyst study. The similar method for photodegradation process was repeated but the fresh photocatalyst was replaced by recycled photocatalyst. Calculation for the percentages of photodegradation was calculated and the result obtained from the calculation was then compared to the percentages of photodegradation using fresh ZT4 photocatalyst.

F. Photocatalytic Degradation of BTX Using Prepared Photocatalysts

50 mL of BTX solution (500 ppm) was pipetted into square pyrex glass reactor and the reactor was sealed with parafilm. The solution was stirred with magnetic stirrer for 10 minutes and UltraViolet Lamp (6 Watt, 354 nm) was used as light source in this experiment. 3 mL of sample solution was taken out using syringe at starting time and every minutes using UV-Vis spectrophotometer Shimadzu 2510PC at λ range 220-300 nm. The experiment was repeated using photocatalyst plates prepared using various applied voltages. The percentage of photodegradation was calculated using (1) where A₀ is the initial absorption and A_t is the absorption at time, t.

$$\% \text{ of degradation} = (A_0 - A_t) / A_0 \times 100 \% \quad (1)$$

III. RESULTS AND DISCUSSION

A. The optimization of Applied Voltage in Zn/ZnO Preparation

ZT4 photocatalyst was chosen for the study of the optimum applied voltage. Figure 1 shown that the order of increasing percentage of BTX degradation is as follows: 6V < 8V < 10V < 12V. The amount of DC voltage been applied to the electrolysis circuit influenced the photodegradation efficiency of the photocatalyst prepared. It was observed from the experimental results that the photocatalytic degradation efficiency of photocatalyst is proportional to the amount of voltage applied in the electrolysis cell.

Figure 1 shows the results obtained for BTX photodegradation under irradiation of UV light for three hours using Z4 photocatalyst with different applied voltages. After 180 minutes of irradiation time, the lowest percentage of BTX degradation was 44.05% by using ZT4 photocatalyst prepared in a NaOH solution with 6V applied voltage. Meanwhile, for the applied voltage of 8V and 10V, the photocatalytic degradation percentages of BTX were 61.49% and 80.06% respectively. It was observed that the maximum percentage of BTX photodegradation was obtained using 12V applied voltage gave the highest percentage of degradation which is 88.2%.

As the amount of voltage been applied to the electrolysis

cell increased, more energy been given to it so that the conversion of ions in electrolyte solution to oxide layer on the zinc plate surface increased. More oxide was deposited onto the surface per time and this may also leads to the increase of its porosity and the photocatalytic efficiency of the photocatalyst prepared.

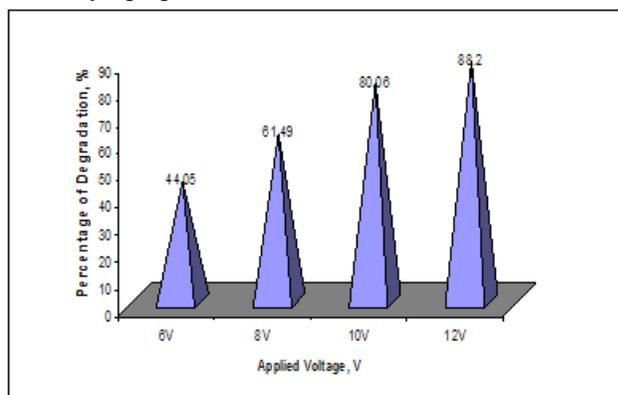


Fig.1 The maximum percentage of BTX degradation after 180 minutes using Zn/ZnO (0.8M)/TiO₂ plates prepared in various applied voltages. [BTX]:500ppm, pH neutral UV irradiation: 3 h.

It was suggested that when high voltage of 12V was applied in the electrolysis cells, the formation of oxide particles on the photocatalyst surface is easier which resulting in the more fine porous area and high photocatalytic activity. These were supported by Mehmood et al [8]. It was reported that the increase of voltage applied in the anodic oxidation process of metal oxide gave a better ordering or the particles as revealed by the parallel arrangement of cells, larger domain size and narrow domain boundaries. As the more voltage been applied to the electrolyte, the higher porosity of Zn/ZnO plate formed. Hence, this will enhanced its photocatalytic performance in degrading organic compounds.

However, according to them, if further high optimum voltage was applied in the system, the oxide particles will exhibits mixed character formation and ordered domains are dispersed in the order-less matrix [8]. Too high applied voltage will decrease the porosity of ZnO film. Since the direct current voltage from the power supply used in this research can only reach to 12 V, it was considered that 12V is the best applied voltage for the preparation of Zn/ZnO plate.

B. The Study on Recycled Catalyst

Degradation of BTX by using fresh prepared Zn/ZnO/TiO₂ plate and recycle Zn/ZnO/TiO₂ plate under UV-light after 180 minutes was illustrated in Figure 2.

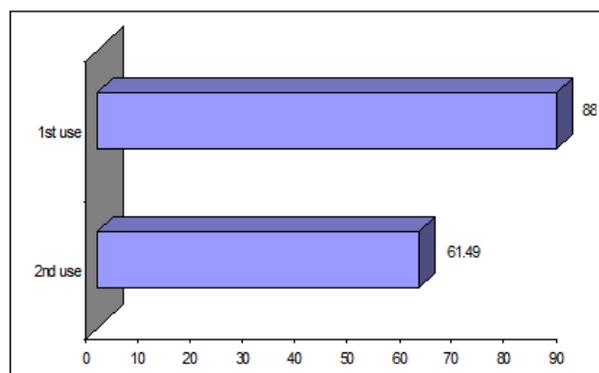


Fig. 2 The optimum percentages of BTX photodegradation using fresh Zn/ZnO/TiO₂ plate and recycled Zn/ZnO/TiO₂ plate. [BTX]:500ppm, UV irradiation: 3 h, UV lamp wavelength: 354 nm.

It can be seen from Figure 2 that the photodegradation efficiency of photocatalyst decreased when the same photocatalyst plate was used twice for photodegradation of BTX. The highest percentage of photodegradation of BTX by using fresh photocatalyst plate was 88.0%. In contrast, the photocatalytic activity of the photocatalyst was lower than using fresh photocatalyst with 61.49% of BTX degradation. The photocatalytic efficiency was decreased for about 26.51% using recycled photocatalyst plate.

Photocatalyst is very well known for its large porosity surface. The large porous area of the photocatalyst surface was useful for the formation of electron hole pair and thus enhanced the formation of strong radicals which contributes to the enhancement in photocatalytic performance of the photocatalyst.

In addition, the porous surface of photocatalyst is useful for the deposition of TiO₂ particles onto it surface. The more TiO₂ particles deposited on the photocatalyst surface increased the probability of the organic compounds to be degraded. This was also supported by Shifu and Yunzhang [3]. They reported that the increase in the number of TiO₂ particles will increase the number of photons absorbed and also the number of organic compounds absorbed which will enhance the photocatalytic activity by the photocatalyst surface in degrading organic pollutants [3].

However, the decreased of the photocatalytic activity using recycle photocatalyst might attributed to some TiO₂ and ZnO particles that peel off from the surface into the sample solution. This might due to the vigorous stirring of the sample solution using magnetic bar for three hours. When the amount of catalyst presence on the surface catalyst was reduced, the porous surface area of the catalyst will reduced which contributes the decreased of the photocatalytic efficiency of the photocatalyst.

This was also supported by Yassitepe et al [9]. According to them, by testing the re-usability of ZnO plate, the results showed that the photocatalytic activity slightly decreases when the recycle ZnO plate was used. After first photodegradation process, the illuminated surface had less

potential of producing electron and hole pairs since the amount of photocatalyst particles were slightly decreased. These contributed to the less radicals produced and thus reduced its photocatalytic efficiency. It was concluded that fresh prepared ZnO/ZnO/TiO₂ plate is the more suitable to perform UV-induced photodegradation process of BTX solution.

C. The study on photodegradation of BTX using Al/Al₂O₃/TiO₂ photocatalyst.

A comparative study was conducted to investigate the photocatalytic activity of Al/Al₂O₃/TiO₂ photocatalyst towards UV-induced photodegradation of BTX compound. Various concentrations of H₂SO₄ (2.0, 2.5, 3.0 and 3.5 M) were used for the preparation of alumite (denoted by Al/Al₂O₃). All the prepared photocatalysts were denoted as AT1, AT2, AT3 and AT4 respectively. Figure 3 shows the percentage degradation of BTX using different types of Al/Al₂O₃/TiO₂ plates under UV light. The data were tabulated in Table 1.

TABLE I
THE PERCENTAGE DEGRADATION OF BTX USING DIFFERENT TYPES OF AL/AL₂O₃/TiO₂ PLATES UNDER UV LIGHT

IRRADIATION TIME, H	PERCENTAGE OF PHOTODEGRADATION (%)			
	AT1	AT2	AT3	AT4
2	1.6	7.66	14.31	33.98
3	3.41	16.92	24.41	33.70
4	8.07	25.7	26.67	42.48
5	11.49	26.53	38.09	44.92
6	26.53	48.4	52.08	57.52

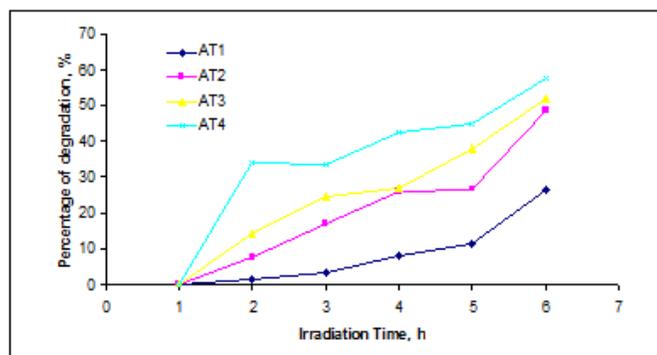


Fig.3 The percentage degradation of BTX using different types of Al/Al₂O₃/TiO₂ plates under irradiation for six hours.

The experimental results showed that the percentage of BTX photodegradation was proportional to the concentration of H₂SO₄ used in alumite preparation. AT4 gave the highest percentage (57.52%) of photodegradation among those four photocatalysts after six hours of irradiation time. This followed by AT3 (52.08%), AT2 (48.4%) and AT1 (26.53%). The sample was taken from the first two hours of irradiation time because according to previous study [10], the photodegradation percentage only gives positive result after 90 minutes of irradiation time.

The higher concentration of H₂SO₄ was not chosen due to the fact that sulphuric acid was considered as strong acid and the aluminium might be corroded in high concentration of

acid solution [10]. The AT4 photocatalyst showed the most effective photocatalytic activity in degrading BTX compounds probably because as the higher concentration of H₂SO₄ used in the preparation of alumite, the more wide porous area of alumite generated.

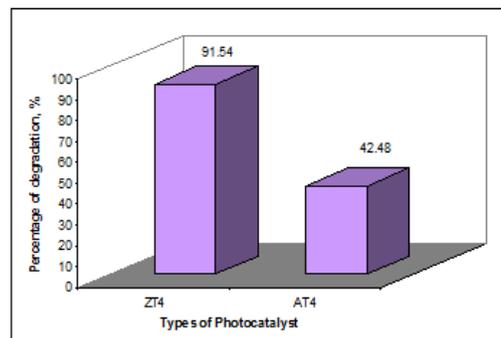


Fig. 4 The maximum percentage degradation of BTX using different types of photocatalyst plates under UV irradiation for four hours.

Figure 4 illustrates the comparison in the percentage of UV-induced photodegradation of BTX by using ZT4 and AT4 photocatalyst after four hours. For the Zn/ZnO/TiO₂ study, the irradiation time for BTX photodegradation was conducted until four hours. In other hand, the photodegradation study using Al/Al₂O₃/TiO₂, was conducted for the maximum time of six hours. For comparative purpose, the time interval of 240 minutes irradiation time was selected.

The highest percentage of BTX degradation for ZT4 was 91.54%. Meanwhile, for AT4 the highest percentage of BTX degradation was 42.48%. The higher photocatalytic efficiency of ZT4 compared to AT4 proved that ZT4 photocatalyst was more effective in degrading of BTX upon UV light.

D. Surface Morphology analysis using Field Emission Spectrometer (FESEM)

A plan view of nanographs of Al/Al₂O₃ film and Al/Al₂O₃/TiO₂ films obtained by FESEM with the magnification of 75 kx are presented in Figure 5 (a) and (b). Al₂O₃ film shows pores on its surface morphology as shown in Figure 5 (a).

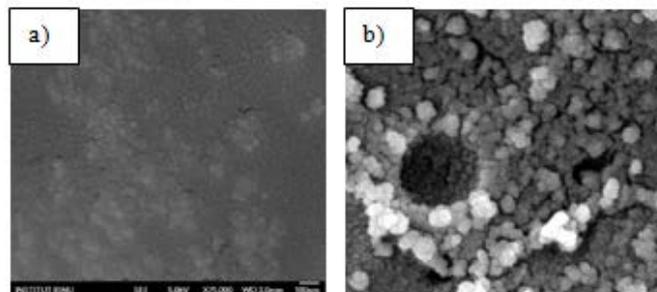


Fig. 5 FESEM images at magnification 75.0 kx. (a) Al/Al₂O₃ (b) Al/Al₂O₃/TiO₂

It was observed that Al₂O₃ has porous area that may contribute to the deposition of TiO₂ onto the surface of Al/Al₂O₃ photocatalyst. However, the pores surface area is quite small and might leads to poorer photodegradation

efficiency of Al/Al₂O₃/TiO₂ in degrading BTX solution compared to Zn/ZnO/TiO₂ plate. A comparative study on surface morphology of photocatalyst plate using Zn/ZnO and Zn/ZnO/TiO₂ plates was done and showed in Figure 6 (a) and 6 (b).

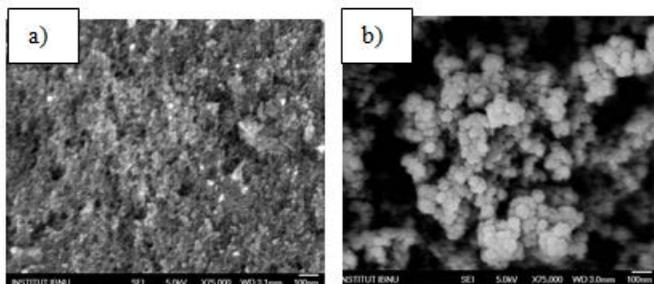


Fig.6 FESEM images at magnification 75.0 kx. (a) Zn/ZnO
(b) Zn/ZnO/TiO₂

In contrast, for the Zn/ZnO film prepared with 0.8 M NaOH, the surface morphology shows a very fine surface with extremely small pores which exhibited a much larger specific area compared to the Zn/ZnO plate prepared with 0.2M NaOH (Figure 5 (b)). It was proven that the surface porosity and particles size of ZnO on the catalyst surface was influenced by the concentration of the electrolyte solution used during anodic oxidation process of Zn.ZnO.

Large surface porosity of the prepared Zn/ZnO plate enhanced the deposition larger amount of TiO₂ particles on the photocatalyst surface. This observation supported the photocatalytic activity of ZT4 photocatalyst which gave better performance and high efficiency on UV-induced degradation of BTX.

IV. CONCLUSION

In this study, it was concluded that the best applied voltage for the anodic oxidation process of Zn/ZnO photocatalyst were 12 V. Zn/ZnO/TiO₂ plate prepared using the prepared Zn/ZnO/TiO₂ was more effective than Al/Al₂O₃/TiO₂ plate in terms of UV-induced degradation of BTX with the highest percentage of photo degradation (91.54%) after 4h. Meanwhile, Al/Al₂O₃/TiO₂ plate prepared using 3.5M H₂SO₄ and 12 V applied voltage gave only 44.92% of BTX degradation after 4 hours of UV irradiation time. The study on spent catalyst shows a decrease at almost half of its photocatalytic efficiency on degrading BTX solution. The FESEM images illustrated the surface morphologies of the different prepared Zn/ZnO plates, Zn/ZnO/TiO₂, Al/Al₂O₃ and Al/Al₂O₃/TiO₂. The observation supported the findings that the high porosity of Zn/ZnO plate prepared using 0.8 M NaOH gave the surface site area for deposition of TiO₂ and gave better performance and effectiveness on degradation of BTX compared with using the lower concentration of NaOH. Al/Al₂O₃/TiO₂ gave lower porous surface and exhibit less effectiveness in degrading BTX.

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