ELECTRODEPOSITION OF TITANIUM, TUNGSTEN AND ZINC LAYERED OXIDES AS PHOTOCATALYSTS FOR THE DEGRADATION OF BENZENE-TOLUENE-XYLENE IN AQUEOUS PHASE

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Specially for my beloved family

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ABSTRACT

Water pollution has become a critical global problem as it is a potential risk for the public health. Photocatalysis have been used as a potential system in the degradation of hazardous organic compounds from the petrochemical industries such as benzene, toluene and xylene (BTX) in wastewater. In this research, the electrodeposited photocatalysts namely ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn films were prepared under different electrodeposition conditions. The potential catalysts were characterized using FESEM-EDX, XRD and Image Analyser. The XRD revealed that the ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn photocatalysts are in crystalline phase. Result from FESEM analysis showed that most of the potential photocatalysts displayed well-dispersed nanoparticles. The thickness measurement using image analyser revealed that the metal oxide thickness of ZnO/Zn (prepared under 12 V within 20 min in 0.8 M NaOH) was only 6.47 μm while the bimetallic oxide and trimetallic oxide films such as TiO_2/ZnO/Zn (prepared under 10 V within 20 min), WO_3/ZnO/Zn (prepared under 10 V within 20 min in pH 6 electrolyte) and WO_3/TiO_2/ZnO/Zn have thicker metal oxides layer which were 10.50, 8.91 and 9.71 μm, respectively. Photocatalytic activity of the electrodeposited photocatalysts were determined on the simulated BTX in aqueous phase (1000 ppm) and under UV-light (6 W, λ = 354 nm) irradiation. The percentage degradation of BTX in aqueous phase was measured by using UV-Vis spectrophotometer. The results revealed that ZnO/Zn (prepared under 12 V within 20 min in 0.8 M NaOH), TiO_2/ZnO/Zn (prepared under 10 V within 20 min), WO_3/ZnO/Zn (prepared under 10 V within 20 min in pH 6 electrolyte), TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn films gave 32.37%, 64.59%, 62.05%, 38.20% and 63.66% of BTX degradation, respectively. Experimental parameters such as pH value of sample solution, addition of H_2O_2 and pre-sonication on the degradation efficiency were studied on BTX solution together with the existence of TiO_2/ZnO/Zn films prepared under the optimum conditions. The optimum pH for the photodegradation of BTX solution using TiO_2/ZnO/Zn was 6, which is the original initial pH of BTX. Addition of 20 ppm H_2O_2 enhanced the BTX degradation to 67.24%. The effect of 30 min sonication time improved the BTX degradation up to 70.66%. Total organic carbon analysis showed that TiO_2/ZnO/Zn film prepared under 10 V within 20 min gave the optimum of 54.85% mineralization in BTX aqueous solution.

ABSTRAK

Pencemaran air telah menjadi masalah global yang kritikal kerana berisiko tinggi kepada kesihatan awam. Fotopemangkinan telah digunakan sebagai sistem yang berpotensi dalam degradasi sebatian berbahaya organik daripada industri petrokimia seperti benzena, toluena dan xilena (BTX) dalam air kumbahan. Dalam kajian ini, fotomangkin elektroenapan seperti filem ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn dan WO_3/TiO_2/ZnO/Zn disediakan di bawah parameter elektroenapan yang berbeza. Pencirian mangkin yang berpotensi dijalankan dengan menggunakan FESEM-EDX, XRD dan alat Penganalisis Imej. Analisis XRD menunjukkan filem ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn dan WO_3/TiO_2/ZnO/Zn adalah dalam fasa hablur. Keputusan FESEM menunjukkan fotomangkin yang berpotensi memperlihatkan partikel bersaiz nano terserak rapi. Pengukuran dengan menggunakan alat Penganalisis Imej menunjukkan ketebalan oksida logam pada ZnO/Zn (disediakan di bawah 12 V dalam 20 min dan dalam 0.8 M NaOH) hanya 6.47 μm manakala filem dwilogam oksida dan trilogam oksida iaitu TiO_2/ZnO/Zn (disediakan di bawah 10 V dalam 20 min), WO_3/ZnO/Zn (disediakan di bawah 10 V dalam 20 min dan elektrolit pH 6) dan WO_3/TiO_2/ZnO/Zn (disediakan di bawah 10 V dalam 20 min) mempunyai lapisan logam oksida yang lebih tebal iaitu 10.50, 8.91 dan 9.71 μm. Aktiviti fotopemangkinan bagi mangkin elektroenapan terhadap BTX dalam fasa akueus (1000 ppm) telah dilakukan dengan menggunakan radiasi di bawah sinaran cahaya lampu UV (6 W, λ = 354 nm). Peratusan degradasi BTX dalam fasa akueus telah diukur menggunakan spektrofotometer UV-Vis. Keputusan menunjukkan bahawa ZnO/Zn (disediakan di bawah 12 V dalam 20 min dan elektrolit 0.8 M NaOH) TiO_2/ZnO/Zn (disediakan di bawah 10 V dalam 20 min), WO_3/ZnO/Zn (disediakan di bawah 10 V dalam 20 min dan elektrolit pH 6), TiO_2/WO_3/ZnO/Zn dan WO_3/TiO_2/ZnO/Zn memberikan 32.37%, 64.59%, 62.05%, 38.20% dan 63.66% degradasi BTX. Parameter ujikaji seperti nilai pH larutan sampel, penambahan H_2O_2 dan pra-sonikasi pada degradasi juga dikaji ke atas larutan BTX bersama dengan kehadiran filem TiO_2/ZnO/Zn yang disediakan di bawah keadaan optimum. pH optimum untuk degradasi BTX menggunakan TiO_2/ZnO/Zn ialah pH 6 (pH asal BTX). Penambahan 20 ppm H_2O_2 meningkatkan degradasi BTX kepada 67.24%. Kesan penambahan masa pra-sonikasi kepada 30 min telah meningkatkan degradasi BTX sehingga 70.66%. Analisis jumlah karbon organik menunjukkan filem TiO_2/ZnO/Zn disediakan di bawah 10 V dalam masa 20 min memberikan 54.85% mineralisasi terhadap BTX dalam larutan akueus yang telah dirawat.

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LIST OF ABBREVIATIONS

AOPs	-	Advanced Oxidation Process(s)
BTX	-	Benzene-Toluene-Xylene
CB	-	Conduction band
DC	-	Direct current
EDX	-	Energy Dispersive X-ray analyzer
EPA	-	Environmental protection agency
FESEM	-	Field Emission Scanning Electron Microscopy
min	-	Minutes
MW	-	Molecular weight
VB	-	Valence band
VOCs	-	Volatile Organic Compound(s)
U.S.A	-	United States of America
UV	-	Ultra Violet
WHO	-	World Health Organization
XRD	-	X-Ray Power Difraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water pollution is always a serious global problem. Water pollution is a widespread problem all over the world and a potential risk for the public health (Gavagnin *et al.***,** 2002). The polluted water does not only affects the plants and organisms living in these bodies of water; but the effect is detrimental in almost all cases as does not only to individual species and populations, also to the natural biological communities.

Organic pollution is the most common form of water pollution. It is caused by the natural occurring compounds like proteins, fats, carbohydrates etc, as well as synthetic compounds like fatty ester, fatty alcohol, glycerine, glycerol, dyes, pesticides, etc. The synthetic organic derivatives cause more harm to the environment than the naturally occurring ones. Before these compounds are acted upon by microorganisms these manifest their toxic effects on the aquatic living community. Thus, such compounds elicit a wide range of environmental hazards. It is important to treat the polluted water by the employment of some technique to convert the pollutants into harmless species as it is a leading worldwide cause of deaths and diseases when the untreated water is consumed in some amount. In these cases, many conventional methods had been proposed on the treatment of contaminated water. A series of purification operations are required to restore the natural characteristics and life sustaining qualities of water.

Many conventional methods had been proposed on the treatment of contaminated water. Various physical and chemical processes such as flocculation, reverse osmosis, coagulation, electrocoagulation, separation of pollutants and chemical precipitation, and elimination by adsorption on activated carbon are the most frequently used for the removal of organic pollutants in the surface water system (Daneshvar *et al.*, 2004). The disadvantages and difficulty of these techniques is that they are non-destructive but only transfer the contamination from one phase to another. Hence, further treatment process is necessary to convert the pollutants to harmless substances. An alternative promising technique photocatalysis or also known as Advanced Oxidation Processes (AOPs) which had been studied during the last 20 years that can degrade all toxic compounds into harmless compounds(Salah *et al.*,2004)

AOP based on the generation of powerful oxidizing agent, hydroxyl radical (•OH) which can oxidizes and completely destroy a broad range of organic contaminations in water quickly and nonselectively (Daneshvar *et al.*, 2004, Salah *et al.*, 2004, Sobanaand Swaminathan, 2007). Most of the AOPs are energy intensive which use various combinations of ozone, hydrogen peroxide and UV-light to generate •OH. In recent years, concern has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from gas or aqueous phase. This method has been proposed for environmental protection due to its ability to oxidise the organic and inorganic contanimants (Fox and Dulay, 1993).The advantage of semiconductor photocatalysis over other AOPs was its ability to utilize the solar energy to generate the reactive species •OH (Salah *et al.*,2004). Moreover, this process utilizes cheaply available non-toxic semiconductors such as zinc oxide and titanium dioxide, and leads to total decomposition of organic pollutants to harmless substances, such as carbon dioxide gas, water and other mineral acids (Sobana and Swaminathan, 2007).

Heterogeneous photocatalysts has been used as a promising material for photodecomposition reactions and it was widely used for the purpose of water treatment processes (Yamaguchi *et al.*, 1998, Ishikawa and Matsumoto, 2001). Recently, various preparation and fixation methods for TiO_2 had been reported

(Ishikawa and Matsumoto, 2001) due to some practical problems arising from the usage of powdered photocatalysts as stated below.

- The suspended photocatalysts tend to aggregate especially at the high concentration,
- The difficulty in separation of the insoluble catalyst from the suspensions and,
- Suspensions are difficult to apply to continuous flow systems (Andronic and Duta, 2007).

Therefore, thin films as an alternative form of photocatalysts have been reported degraded organic compounds successfully (Andronic and Duta, 2007). There are a number of preparation methods to obtain thin films photocatalysts, including chemical vapour deposition, spin coating, electrodeposition, spray coating and sol-gel method. Electrodeposition is a low-cost electrochemical method where the photocatalyst is directly deposited onto the metal oxide substrate (Ishikawa and Matsumoto, 2001). Although electrodeposited photocatalysts entails mass transfer and active area limitations, it can prevent the troublesome filtration step of suspended particles. Thus it can offer better performance to replace the powdered photocatalysts to be commercialized for treating industrial wastewater (Georgieva *et al.*, 2011).

1.2 Benzene-Toluene-Xylene (BTX) in Petrochemical Industrial Wastewater

Pollutants in petrochemical wastewater are dangerous even at a very low quantity especially aromatic compounds that are very well known for its toxicity. BTX collectively stands for benzene, toluene and xylene (BTX) and are also considered as organic compounds in aromatic form. Benzene, toluene and xylene compounds are considered as among the most hazardous pollutants according to World Health Organization (WHO). They are also known as volatile organic compounds (VOCs) where it vaporized easily under normal conditions or room temperature. Benzene is a six-carbon cyclic compound that has very unusual stability.

Its exceptional chemical stability and thermodynamic of the system was contributed to resonance stabilization of a conjugated cyclic triene. The delocalisation of electrons in benzene ring is known, gives it a great stability. So, these compounds will remain in the natural environment for a very longer period than several other water pollutants (Pardeshi and Patil, 2008).

BTX compounds are the major constituent in petroleum fuel. They are discharged to the environment through effluents disposal by industries such as petroleum refining, pharmaceuticals, coal tar, pesticides, synthetic resins, dyestuff, paper and pulp mills, tanning and paint stripping operations and as agricultural chemicals byproduct (Parida and Parija, 2006; Pardeshi and Patil, 2008). The pollutants can also enter natural environment including soil, air and groundwater through leakage from underground pipelines and storage tanks or occasional accidents and worsen by the absence of proper treatment technologies (Shim and Yang, 1999; Yoon and Park, 2002). Other than that, Yadav and Reddy (1993) reported that leakage from underground pipelines and storage tanks, improper waste disposal practices, accidental spills and leaching landfill are also the causes of wastewater contaminated with BTX compounds.

BTX is among the most toxic and harmful organic compounds and it has achieved a worldwide attention because of its adverse health to human, animal and ecosystem (Jean *et al.*, 2008). BTX compounds can be classified as carcinogenic and neurotoxic compunds. US Environmental Protection Agency had classified BTX compounds as the priority pollutants they are common organic contaminants in groundwater and oxygen-limited soils (Jean *et al*., 2008). As been reported by Yoon and Park (2002), VOCs such as benzene, chloroform, trichloroethylene and isoprene are very well known to cause cancers even at very low exposure levels, while in high dosages, they may lead to cardiac dysfunctions, convulsions, and cessation of breathing, coma and even death (Alegretti *et al.*, 2004).

The toxic effects of BTX are similar to those caused by ethanol by leading to euphoria, loss of hallucinations and inhibition at first, followed by slurred speech, lethargy and other depressor effects of the central nervous system (Alegretti *et*

al.,2004). Toluene level in blood which reaches concentrations of 500–5000 mg/L can induce severe abnormalities and encephalopathy, including cortical atrophy, brain degeneration and damage in mental and intellectual performances (Alegretti *et al.*, 2004).

BTX can enter our body through many ways such as by inhalation, direct contacts to skin, mouth or eyes. They can also indirectly endanger us if we use water that has been polluted by BTX compounds for drinking, bathing or cleaning in our daily life. Due to its volatile properties, when BTX is inhaled accidentally or by purpose, these organic compounds can be absorbed directly by the lungs, which is very dangerous. Alegretti *et al.* (2004) reported that inhalant abuse is a significant worldwide problem. Due to their toxicity and carcinogenic characteristic, it is crucial to remove all VOCs especially the BTX compounds to preserve human health and the environment (Pardeshi and Patil, 2008).

1.3 Photocatalysis

In traditional wastewater treatments such as neutralization, coagulation, fluocculation, flotation, sedimentation, filtration, clarification, biodegradation, etc. generate huge amounts of sewage sludge. Sometimes, after the biological treatment still it contains non-biodegradable organic pollutants. These pollutants are removed using chemical-physical processes that produce large quantity of sludge. In order to reduce the production of sludge by these wastewaters tertiary treatments, new systems must thus be explored.

Since wastewater treatments become more significant nowadays, photocatalysis as an alternative wastewater treatment technique shows a promising potential. According to Braslavsky and Houk (1988), photocatalysis was defined as a catalytic process involving absorption of photons or light by a semiconductor photocatalyst or a substrate. Basically, photocatalysis is a reaction which uses light

or photons to activate a substance which modifies the rate of a chemical reaction without being involved itself (Serpone and Emeline, 2002).

Photocatalysis involving degrading organic pollutants utilizing a metal oxide semiconductor to generate a clean environment has been a dream of humankind for several decades (Hou *et al.*, 2007). Semiconductors are usually selected as photocatalysts due to its narrow band gap energy between the valence and conduction bands. In order for photocatalysis to occur, the semiconductors need to absorb energy equal to or more than its band gap energy. Then, e^-/h^+ or negatively charged electron/positively charged hole pairs will be formed due to these movement of electrons. The hole can oxidize donor molecules and the electron in the conduction band can reduce an acceptor species as shown in Figure 1.1.

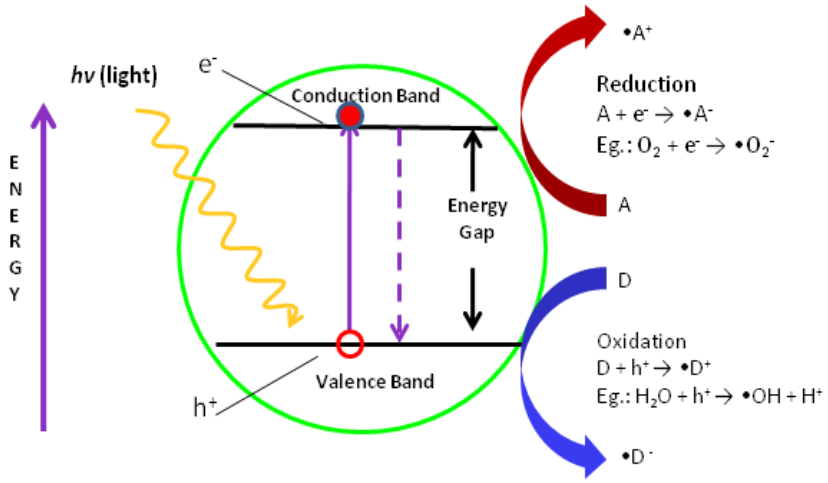

Figure 1.1 Schematic diagram of photocatalytic activation

Heterogeneous photocatalysis using semiconductor oxides has been established to be truely effective to treat pollutants in aqueous phase (Augugliaro *et al.*, 2006). This promising technique utilizes nano-sized semiconductors like ZnO, TiO_2, WO_3, $SrTiO_3$ and $FeTiO_3$ to carry out photo induced oxidation process to dismantle VOCs into CO_2 and H_2O, and extensively mineralize NO_x and SO_x. This process is a efficient process for photodegradation and complete mineralization of organic compounds (Parida and Parija, 2006). Complete mineralization is crucial due to the fact that there are probabilities of formation of intermediates which may be more toxic than the parent pollutant (Sakhtivel *et al.*, 2003). The concept of

heterogeneous photocatalysis process which possesses high efficiency and able to generate harmless by products has therefore caught the attention of many researchers and environmentalist globally.

Normally, photocatalysis in powdered form was used in previous study of photocatalytic degradation of organic pollutants. However, the photodegradation process using powdered form was time consuming due to filtration process that is not suitable for the real environment. In the study conducted by Yassitepe *et al.* (2008) on the photocatalytic efficiency of azo dye using ZnO powder and ZnO plate, although the results obtained showed that the total mineralization for azo dye using ZnO plate needs a longer reaction time compared to powdered form. The use of semiconductor films avoided the time consuming and costly removal and recycling process of the semiconductors suspensions after the treatment. Thus, the use of photocatalyst in thin film is an alternative for photocatalytic degradation of organic compounds.

1.4 Electrodeposition

An electrodeposition is also called electrochemical deposition. Electrodeposition is also defined as the deposition of ions rather than colloidal particles (Lee and Tu, 2008). Electrodeposition is the process of coating a thin layer of a material on top of a different metal to modify its surface properties in order to attain the desired electrical and corrosion resistance, for decoration and improve heat tolerance, reduce abrasion and wear. Electrodeposition is a surface coating technique that forms an adherent layer of a material on another.

As in Figure 1.2, this technique works when two electrodes are immersed in an electrolyte of an ionic salt which ionized in aqueous solution into its constituent ions; negative ions are deposited at the anode (positive electrode) and vice versa (Lee and Tu, 2008).The morphology and composition of electrodeposits vary significantly, as it depends on current density, the nature of the cations or anions in the electrolyte

solution, electrolyte bath composition, electrolyte temperature, electrolyte solution concentration, power supply current waveform, the presence of impurities and physical and chemical nature of substrate surface.

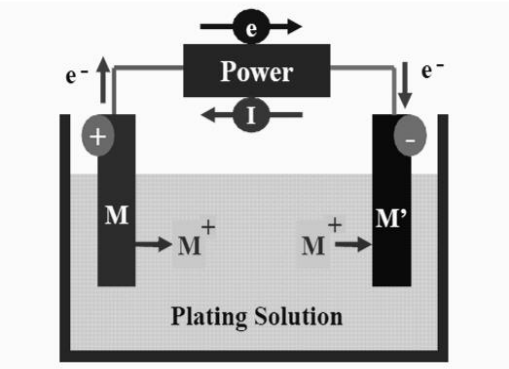

Figure 1.2 Electroplating model

The growth phenomena of oxide films can be described in terms of electrochemistry as the negative charged ions are attracted to the positive surface of the metal. The reactions that occur at the anode and cathode can be represented by the following equations:

Anode: $$M + nH_2O \rightarrow MO_n + 2nH^+ + 2ne \quad (1.1)$$

Cathode: $$2ne + 2nH_2O \rightarrow nH_2 \uparrow + 2nOH^- \quad (1.2)$$

From the equations shown above, the metal oxide will grow on the metal anode surface and hydrogen gas will evolve at the cathode. The pH value of an electrolyte is an important part in order to obtain a coherent oxide film. If the pH of the electrolyte is too low or too high, the film will dissolve as it grows and porous oxide structure will result in certain case. Coherent film can be grown by anodizing on a variety of metals by a given suitable pH value of the electrolyte. The final thickness obtained will depend on several parameters such as type of metal, the temperature of the bath, the voltage applied on the anode and the time of the anodization process (Bunshah, 1982).

1.5 Statement of Problem

In this modern industrialization world, the industrial process often discharges that are harmful and toxic to the environment. The untreated wastewater that contained organic compounds if discharged untreated would definitely cause a lot of adverse impact upon the environmental system. The effect of water pollution is not only being harmful to the animals and the aquatic life but also to human beings. It declines the aesthetic quality of rivers and lakes. The contaminated water destroys the aquatic organism and diminishes its reproductivity. Furthermore, it can be hazardous to human's health. Hence, it is authentically important to treat the toxic chemicals in the petrochemical wastewater into harmless species such as CO_2, H_2O and other inorganic ionic salts. Conventional methods such as precipitation, adsorption and fluocculation have been tested but it was less efficient due to time consuming treatment and the pollutants are transforming into the other phase but not completely destructed into harmless compounds. Therefore, the photocatalytic process that has been explored recently is the most promising technique to be applied as it shows high efficiency in treating organic pollutants in industrial wastewater.

1.6 Objective of Study

The research objectives are:

1. To prepare the metal oxide photocatalysts ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn using electrodeposition technique.
2. To study the optimum experimental parameters for electrodeposition of monometallic and bimetallic oxides on zinc plate.
3. To characterize the prepared photocatalyst using various analytical techniques.

4. To study the photocatalytic activity of the prepared catalysts on photodegradation of the BTX in aqueous solution.
5. To study the effects of pH, addition of H_2O_2 and pre-sonication on the photocatalytic degradation process.

1.7 Scope of Study

This research is focusing on the development of a photocatalysts with high photocatalytic activities that were tested on the photodegradation of BTX in aqueous solution. It covered the preparation of metal oxide photocatalysts such as ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn films by electrodeposition method. The performances of the ZnO/Zn, TiO_2/ZnO/Zn, WO_3/ZnO/Zn, TiO_2/WO_3/ZnO/Zn and WO_3/TiO_2/ZnO/Zn films are investigated on the photodegradation under the UV-light and was monitored by UV-Vis spectrophotometer. All photocatalytic degradation processes were conducted under room temperature and pressure. The effect of various concentration of electrolyte and various applied voltages will also be studied. The potential catalysts are characterized using Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Analyser (EDX), X-Ray Power Difraction (XRD) and Image Analyser.

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