DEPOSITION OF ZINC OXIDE ON ZINC PLATES FOR PHOTOCATALYTIC REMOVAL OF DYES IN AQUEOUS SYSTEM

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A Special Dedication to my Beloved Family…

Saadon Pyeman

Rohana Harun

Syaiful Fadzly Saadon

Puteri Fatin Amira Saadon

Muhammad Danial Ariff Saadon

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In the name of Allah, the Most Gracious, the Most Merciful,

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ABSTRACT

This research involves modification of Zn pure and Zn alloy plates to be utilized for dye removal. The modification is aimed to produce ZnO layer on the surface of Zn pure and Zn alloy plates. Sand blasting technique is used to remove a naturally formed oxide layer on Zn pure and Zn alloy plates. The sand blasting technique is also intended to produce a curved groove site to strengthen the ZnO layer formed on the surface of modified Zn pure and Zn alloy plates. The modification of Zn pure and Zn alloy plates consist of three different methods, electrolysis, immersing in H_2O_2 and heating. Based on the analysis of DR UV-Vis, SEM and XRD, all three modification methods successfully produced ZnO layer on Zn pure and Zn alloy plates. The formation of ZnO layer is different in thickness and electrolysis is chosen as the best technique for the ZnO layer production. Methylene blue dye (20 ppm, pH 6.56) is utilized as a sample solution to study the removal activity of modified Zn pure and Zn alloy plates. Results obtained from UV-Vis spectra shows that the percentage of methylene blue removal by modified Zn pure plate and was 81.9% and 70.0% respectively Zn alloy plate. Results also showed that adsorption and photocatalysis are involved in the removal of methylene blue dye. Adsorption becomes a major contributor for the removal of methylene blue dye where it contributes 50% of methylene blue removal and photocatalysis only contributes 30% of methylene blue removal. It was also observed that desorption of the methylene blue will occur if the plates are placed in beaker containing distilled water. Modified Zn pure and Zn alloy plates have a “weak adsorption” and “strong desorption” characteristics. The “weak adsorption” and “strong desorption” behaviours of the modified Zn pure and Zn alloy was utilized to create an integrated chemical for application in wastewater treatment in textile industry. This system combines adsorption and photocatalysis techniques for the removal of dye molecules in textile wastewater. The main benefit of this system is that it can separate the dye molecules from wastewater by weak adsorption and transferred dye molecule into a special tank by “strong desorption”. The transferred dye molecules could be recycled and used again by the factories.

ABSTRAK

Kajian ini melibatkan modifikasi plat Zn tulen dan aloi Zn untuk digunakan bagi menghilangkan pewarna. Modifikasi ini bertujuan untuk memendapkan lapisan ZnO pada permukaan plat Zn tulen dan aloi Zn. Teknik tembakan pasir digunakan untuk menghilangkan lapisan oksida yang terbentuk secara semulajadi pada permukaan plat Zn tulen dan aloi Zn. Teknik tembakan pasir juga bertujuan untuk mewujudkan satu lapisan yang kasar dan berlekuk-lekuk pada permukaan plat Zn tulen dan aloi Zn, seterusnya mengukuhkan lapisan ZnO yang dihasilkan. Terdapat tiga teknik memodifikasi plat Zn tulen dan aloi Zn iaitu; teknik elektrolisis, teknik rendaman di dalam larutan H_2O_2 dan teknik pemanasan. Analisis daripada DR UV-Vis, SEM dan XRD membuktikan bahawa ketiga-tiga teknik tersebut berjaya menghasilkan lapisan ZnO pada permukaan plat Zn tulen dan aloi Zn. Teknik modifikasi menghasilkan lapisan ZnO yang berbeza-beza ketebalan dan teknik elektrolisis telah menghasilkan lapisan ZnO yang paling tebal pada permukaan plat Zn tulen dan aloi Zn. Pewarna metilena biru (20 ppm, pH 6.56) digunakan sebagai sampel untuk mengkaji aktiviti plat Zn yang telah dimodifikasi. Spektrometer UV-Vis menunjukkan bahawa peratus maksimum bagi pewarna metilena biru yang berjaya dihilangkan oleh plat Zn adalah sebanyak 81.9% (tulen) dan 70.0% (aloi). Data-data yang perolehi menunjukkan bahawa pewarna metilena biru dihilangkan oleh plat Zn dengan melalui dua cara iaitu; secara penjerapan dan secara fotopemangkin. Proses penjerapan menjadi penyumbang utama kepada penghilangan pewarna metilena biru (50%) sementara proses fotopemangkin menjadi penyumbang minor (30%). Kajian ini mendapati pewarna metilena biru yang melekat pada permukaan plat Zn tulen dan aloi Zn boleh ditanggalkan melalui proses penyahjerapan di dalam air suling. Kesimpulan dibuat bahawa plat Zn tulen dan aloi Zn yang telah dimodifikasi mempunyai ciri-ciri “penjerapan yang lemah” dan “penyahjerapan yang kuat”. Ciri-ciri istimewa yang dipunyai oleh plat Zn tulen dan aloi Zn mendorong untuk menghasilkan satu sistem iaitu; sistem kimia bersepadu, di mana sistem ini akan diaplikasikan untuk merawat air kumbahan dari industri tekstil. Sistem ini menggabungkan teknik penjerapan dan teknik fotopemangkin bagi menghilangkan molekul pewarna dalam air kumbahan industri tekstil. Manfaat utama bagi sistem ini adalah ia dapat memisahkan pewarna daripada air kumbahan melalu “penjerapan yang lemah” dan pewarna yang diserap akan dipindahkan ke dalam satu tangki khas melalui “penyahjerapan yang kuat”. Seterusnya pewarna yang dipindahkan itu akan dikitar dan digunakan semula dalam industri tekstil.

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LIST OF ABBREVIATIONS

M.B	Methylene Blue
C.R	Congo Red
T.B	Trypan Blue
Zn	Zinc
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
UV	Ultra violet
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide solution
ppm	Part per million
E	Band gap energy
h	Planks constant
c	Speed of light
λ	Adsorption edge
nm	Nanometer
DR	Diffuse reflectance
AOP	Advance oxidation process
MWCO	Molecular weight cut off

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Textile industry is currently one of the rapidly growing industries as it becomes the main source in the production of color-based product such as garments, upholstery and furnishings. Textile industry can be divided into branches of paper production, food technology, agriculture research, light-harvesting arrays, photoelectron chemical cell and hair coloring. The collection of incomes generated from the textile industry worldwide has been recorded reach to almost 11 billion dollars a year and almost 1.45 million people have been given job opportunities in this textile industry [1].

Dye was used by textile industry as a coloring reagent for their products and besides that it also produced 700,000 tons of dye consisting of 10,000 different classes each year [2]. The chemical classes of synthetic dyes that are often used are azo, anthra quinine, sulfur, inahigoine, tripehonyl methyl and phthalocyanine derivatives, however azo dye is the mostly used among others. It was also recorded that almost 15% of the dye produced was escaped into the environment during manufacturing and processing operation [3]. Textile industries use a large volume of water and synthetic dyes for their wet processing and this increases the probability of dye residues to be released into textile wastewater which poses a threat to the environment. Wastewater from textile industry has hazardous characteristics such high concentration of salts, oil, grease, detergents, soaps, sulphate, sodas and as highly colored water by the presence of dye molecules.

The coloured effluent from textile industry is known to be toxic and if the effluent enters into the water bodies (lakes and rivers), it will interfere with the growth of aquatic life as the dyes contained in coloured textile effluent will pervert the sunlight from penetrating the water surface. Thus, the aquatic life photo-initiated by the chemical reaction will be disturbed and during the biological reaction path way, the dye compounds will release toxic compounds and depletes the dissolved oxygen in water bodies and this will threaten the aquatic life. Dyes are known as toxic compound since it is made from carcinogen such as benzidine and other aromatic compounds and its exposure to human can result in skin irritation, allergic dermatitis, cancer and mutations [4]. Although, dyes usage is important in industry but in the other hand it can also lead to the water pollution problems. Therefore, an efficient method for the textile wastewater treatment must be found to avoid the dye pollution in our ecosystem.

To protect the aquatic environment, many methods such as adsorption, electrocoagulation, ultrasonic decomposition, advanced chemical oxidation, nanofiltration, and chemical coagulation followed by sedimentation were used to remove dyes from wastewater [5]. The traditional techniques used for colour removal are activated carbon (charcoal), filtration and coagulation. Each method has few advantages and disadvantages. For example, the use of charcoal is technically easy but has high waste disposal cost. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants from one phase to another phase rather than destroying them [6]. Biological treatment is a proven method and cost effective. However, it has been reported that majority of dyes are only adsorbed on the sludge and not degraded, due to the biorecalcitrant nature of these dyes molecules [7].

Thus, there is a need to develop treatment methods that are more effective in eliminating dyes from the wastewater. Advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. AOP generates a powerful oxidizing agent hydroxyl radical, which completely destroys the pollutants in wastewater quickly and nonselective [8]. AOPs such as Fenton and photo-Fenton catalytic reactions, H_2O_2/UV processes and semiconductor

photocatalysis have been studied under a broad range of experimental conditions in order to reduce the colour and organic load of dye containing wastewaters [9].

Among AOPs, semiconductor photocatalysis has emerged as an important destructive technology leading to the total mineralization of most of the organic pollutants. This process utilizes very cheap available nontoxic semiconductors (TiO_2, ZnO) and leads to total mineralization of organic compounds to CO_2, water and mineral acids [10]. Usually, the semiconductor utilized for the wastewater treatment is in powder form and this created problem to filter catalyst powder from treated wastewater before it can be permissible to enter into waster bodies.

The advantage and the weakness of several techniques for textile wastewater treatment lead us to create an integrated system in order to maximize the efficiency of textile wastewater treatment. Our integrated system is a combination of two techniques, adsorption and photocatalysis, where these techniques have become the main focus in industry for wastewater treatment. Adsorption techniques is considered as a suitable technique for dye removal due to the character of dye molecules that easily adsorbs on the solid surface but the usage of activated carbon as an absorbent is not effective since it is highly cost to produce. This problem can be solved by substituting the usage of activated carbon with Zn plates modified with ZnO as it is much cheaper and readily available.

ZnO layer is created on Zn plate's surface by utilizing modification of three different methods, electrolysis, immersing in H_2O_2 and heating. Thus, the combination of techniques, adsorption and photocatalysis into an integrated system is a proper way since the adsorbed dye molecules will be mineralized by photocatalysis technique.

1.2 Heterogeneous Photocatalytic Oxidation

Heterogeneous photocatalytic oxidation is a part of Advance Oxidation Technologies (AOP). These methods offer the advantage of destroying the pollutants, in contrast to conventional techniques such as activated carbon or air stripping that only transfers the contaminants from one phase to another. In this way, organic or inorganic compounds and even microorganism, are degraded or transformed into less harmful substances. The common characteristic of all AOP is the generation of very reactive free radicals, principally hydroxyl radical (•OH) [11].

Photocatalytic oxidation (PCO) is an attractive technology for the remediation of organic pollutants. It is economical, simple and can be easily implemented. This process harnesses radiant energy from natural or artificial light sources with heterogeneous catalyst to degrade the organic pollutants into their mineral components [12]. PCO has a promising application for the degradation of molecules into smaller molecules at ambient conditions using molecular oxygen as the primary oxidant. However complex pollutants are often more difficult to degrade with undesirable intermediates and by products formed. In addition, the rate of decomposition is usually slow [13].

1.3 Photocatalysis

Photo catalysis is defined as the acceleration of a photoreaction by the presence of a catalyst [14, 28]. Moreover, the catalyst may accelerate the photoreaction by interacting with the substrate in its ground or excited state and with a primary photoproduct in which depends upon the mechanism of the photoreaction. In the heterogeneous photocatalysis, the metal-catalyzed photoreaction of organic substrates can be represented generically by Equation (1.1):

$$O + M \xrightarrow{h\nu} P + M \qquad (1.1)$$

Where O and P denote the organic compound and product respectively, and M is the metal-containing catalyst or catalyst precursor. The transition metals such as titanium, tungsten, tungsten and zinc were usually used as a semiconductor catalyst in heterogeneous photocatalysis.

In early 1980s, Salomon [15] proposed that description of photocatalysis can be sub diverted into two operationally distinct classes; that is photogenerated catalysis and catalyzed photolysis. Photogenerated catalysis is catalytic in photons which involves the light-induced generation of a ground-state catalyst, C from M (Equation 1.2). Meanwhile, the catalyzed photolysis is non-catalytic in photons. In one or more subsequent reactions, C catalyzes the conversion of organic substrate, O to product P (Equation 1.3) [14].

$$M \xrightarrow{h\nu} C \quad (1.2)$$

$$C + O \longrightarrow C + P \quad (1.3)$$

A semiconductor is characterized by an electronic band structure in which the highest occupied energy band, called valence band (vb), and the lowest empty band, called conduction band (cb), are separated by a band gap, which is a region of forbidden energies in a perfect crystal. When a photon of energy or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the vb is promoted to the cb with simultaneous generation of a hole (h^+) in the vb [16]. The example for the heterogeneous photocatalytic process is shown in **Figure 1.1**.

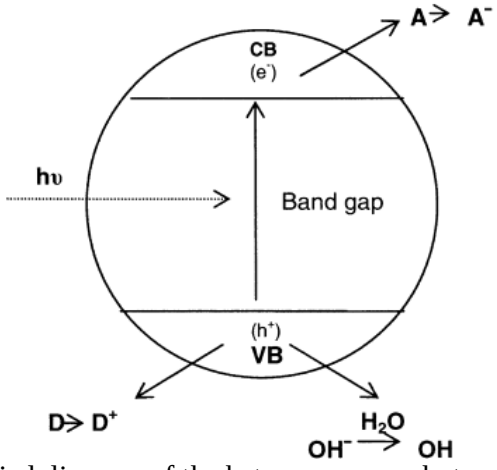

Figure 1.1: Simplified diagram of the heterogeneous photocatalytic process.

Furthermore, photocatalysis is also based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb both reactants and to adsorb efficient photons. Besides various types of photocatalytic reaction (selective mild oxidation of organics, dehydrogenation of alcohol, D_2-alkane isotopic exchange), UV-irradiated titanic becomes a total oxidation catalyst once in water because of the photogeneration of •OH radicals by neutralization of OH^- surface groups by positive photo-holes. A large variety of organics could be totally degraded and mineralized into CO_2 and harmless inorganic anions [17].

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 [18].

1.4 Titanium Dioxide, TiO_2 as Photocatalyst

TiO_2 is a promising material as a photocatalyst for photodedegradation reactions such as the degradation of wastewater [19]. It has been proven to be one of the most suitable photocatalyst for widespread environmental applications [18]. Yamaguchi *et al*. reported some applications of photocatalytic reactions by using TiO_2 for the purpose of water purification, deodorization and antibacterial effect. TiO_2 is an n-type semiconductor that has a wide band gap of 3.2 eV and the hole and electron pairs are generated by UV light at considerably high potential [20].

It was suggested that the high potential of generated holes on TiO_2 makes it possible to decompose organics, bacteria and other toxic compounds [21]. The photochemical assisted formations of some reactive species are presented in the following reaction sequence:

$$TiO_2 + hv \longrightarrow TiO_2 (e_{CB}^- + h_{VB}^+) \quad (1.4)$$

$$h^+ + OH^- \longrightarrow OH \quad (1.5)$$

$$O_2 + e^- \longrightarrow O_2^- \quad (1.6)$$

$$O_2^- + H^+ \longrightarrow HO_2 \quad (1.7)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (1.8)$$

$$H_2O_2 + hv \longrightarrow 2OH \quad (1.9)$$

$$H_2O_2 + e^- \longrightarrow OH^- + OH \quad (2.0)$$

Recently, it has been found that TiO_2 coated with metal oxide was able to generate hole and electron pairs under visible light instead of under UV light [22]. TiO_2 has several advantages compared to other photocatalyst such as high photosensitivity, high stability and large band gap [23]. The biological and chemical inertness, abundant availability, cost-effectiveness and chemical stability are some of TiO_2 properties that make it practical for a large scale application [18].

1.5 Zinc Oxide, ZnO as Photocatalyst

Current researches show that ZnO can also be used as a very efficient semiconductor photocatalyst when compared with TiO_2 [24]. As it has almost the same bandgap energy as titanium dioxide (TiO_2). Hence its photocatalytic activity is anticipated to be similar to that of TiO_2. Their band gap energies are around 3.2 eV and their oxygenation capacity is anticipated to be also almost similar [24]. When ZnO is irradiated with UV light of appropriate energy greater than its bandgap, highly mobile electron–hole pairs can be generated. These carriers then migrate to the surface and in turn are trapped by reactants adsorbed on the surface, giving rise to powerful redox chemistry.

ZnO efficiences as photocatalyst have been reported to be particularly noticeable in the advanced oxidation process of many pollutants such as dye solution [24], herbicides [25] and pesticides [26].

There are many advantages for using ZnO as photocatalyst. ZnO is a technologically important compound semiconducting material because of its

interesting properties, such as transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability, direct band gap, abundance in nature, and absence of toxicity [27, 29].

ZnO had adsorption capacity with larger fraction of solar spectrum than TiO_2. Due to the ability of ZnO to treat wastewater containing pollutants, ZnO is continuously become one of the world most demanded photocatalyst.

1.6 Statement of the Problem

Textile industries release high amount of dyes in their wastewater and liquid effluents which are normally discharged into water bodies and ecological systems. Dyes presence in textile wastewater might constitute a group of toxic organic residues such as benzene and phenol derivatives, aniline derivatives and organic acid derivatives. The toxicity of dyes causes a serious threat and direct destruction of aquatic living organisms due to the large degree of aromatic present in dyes molecule. Thus, to protect the aquatic life, dyes in wastewater have to be removed before it is released into the water bodies systems.

Advance oxidation process (AOP) is one of the effective ways to remove dyes in textile wastewater. Among this AOP, heterogenous photocatalysis has emerged as the most efficient technology for textile wastewater treatment due to their completely mineralization. ZnO are the most commonly utilized photocatalysts for dyes removal. However, the use of ZnO in powder form is not effective because it needs to be filtered from the treated textile wastewater. Moreover, after wastewater treatment, there is still having dye molecules stickled on the surface of ZnO particles. This consequently restricts the reusability of ZnO photocatalysts. This study attempts to introduce photocatalyst in a plate form and unlimited reusability.

1.7 Research Objective

The research objectives are as follows:

1. To produce ZnO on Zn pure and Zn alloy plates.
2. To characterize the modified zinc pure and zinc alloy plates.
3. To evaluate the ability of modified zinc pure and zinc alloy plates over the removal of methylene blue dye.

1.8 Scope of Study

ZnO was produced on Zn plates (pure and alloy) plates via modification of three different techniques; electrolysis, immersing in H_2O_2 solution and heating techniques. The modification was aimed to produce ZnO on the surface of Zn plates. The modified metal plates were characterized by using SEM, XRD and UV-Vis DR spectrometer. The photocatalytic efficiency of ZnO produce on Zn plate surface was studied via the degradation of methylene blue dye. The removals of methylene blue dye over the modified Zn plates were carried out under UV light irradiation for 5 hours. The percentage of methylene blue dye removal was monitored by using UV-Vis spectrometer.

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