UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF ZINC OXIDE AND TITANIUM OXIDE POLYETHERSULFONE HYBRID FILM PHOTOCATALYSTS FOR DEGRADATION OF METHYL ORANGE

ZUL ADLAN BIN MOHD HIR

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By

ZUL ADLAN BIN MOHD HIR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

July 2018

DEDICATION

To my beloved family:

With special gratitude to my dearest mother (Khalijah Abu Bakar) and father (Mohd Hir Johari),
the best parents I can imagine for their greatest love and blessing.

And to Along, Alang, Atih, Kak Long Mieza and families,
each of whom has a special place in my heart.

To my treasured friends, teachers and lecturers:

Thank you so much for your continuous support and encouragement.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Associate Professor Abdul Halim bin Abdullah, PhD
Faculty: Institute of Advanced Technology

Environmental issues and scarcity of water reserves have led to the development of photocatalyst technology to recycle the polluted water. The photocatalyst is usually applied in powder form but suffers several drawbacks; (i) agglomeration which led to a decrease in photoactivity and (ii) difficult and costly recovery process. These problems could be overcome by immobilizing the catalyst on a support. With the aim to provide alternative solution to the solid–liquid separation problem, polyethersulfone (PES) was chosen as the support due to its stability against radicals produced during photocatalytic reaction. This work investigated the physicochemical characteristics of TiO_2/PES, ZnO/PES and reduced TiO_2 ($rTiO_2$)/PES hybrid film photocatalyst prepared via phase inversion technique and reported, for the first time, its synergistic contribution in the field of photocatalysis. The films were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and UV-vis Diffuse Reflectance Spectroscopy (UV-vis DRS) analyses. XRD, SEM and EDX analyses revealed that the TiO_2, ZnO and reduced TiO_2 ($rTiO_2$) were homogeneously dispersed and embedded onto the PES film. XPS and UV-vis DRS results confirmed the existence of interstitial site of TiO_2 (458.2 and 463.9 eV), ZnO (1021.0 and 1043.8 eV) and $rTiO_2$ (456.1 and 461.8 eV) with their respective band gap energy of 3.00, 3.15 and 2.85 eV. The films exhibited higher surface roughness and enhance hydrophilicity compared to PES film alone. The photoactivity of the films was evaluated with respect to methyl orange (MO) degradation under both UV and visible light irradiation. Emphasis was placed on the effect of catalyst loading, pH, concentration, number of films and recyclability study. The best film photocatalysts displayed pseudo first-order kinetics with almost 80% and 30% for PES–TiO_2 (13 wt%), 100% and 56% for PES–ZnO (17 wt%), 76% and 55% for PES–$rTiO_2$ (13 wt%) of MO removal under original condition against UV and visible light irradiation, respectively. A complete removal of MO was achieved at pH 2.0 for both PES–TiO_2 (13 wt%) and PES–$rTiO_2$ (13 wt%) and pH 5.8 for PES–ZnO (17 wt%). The degradation percentage decreased with increasing initial concentration of MO (5–20 mg/L) but increased with increasing number of films. The major active species were found to be $\bullet O_2^-$ for both PES–TiO_2 (13 wt%) and PES–$rTiO_2$ (13 wt%) and h^+ for PES–ZnO (17 wt%). The best films can be recycled for up to

five times while retaining its stability and degradation efficiency without being subjected to any regeneration process. The degradation of palm oil mill effluent (POME) was monitored through chemical oxygen demand (COD) analysis with degradation percentage of 20%, 27%, 12% and 12%, 18%, 15% under UV and visible light irradiation, respectively with some reduction in American Dye Manufacturers' Institute (ADMI) colour values.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PENYEDIAAN DAN PENCIRIAN FOTOMANGKIN FILEM HIBRID POLIETERSULFON ZINK OKSIDA DAN TITANIUM OKSIDA BAGI DEGRADASI METIL OREN

Oleh

ZUL ADLAN BIN MOHD HIR

Julai 2018

Pengerusi: Profesor Madya Abdul Halim bin Abdullah, PhD
Fakulti: Institut Teknologi Maju

Isu-isu alam sekitar dan ketandusan sumber air telah membawa kepada pembangunan teknologi fotomangkin untuk mengitar semula air tercemar. Fotomangkin tersebut kebiasaannya digunakan dalam bentuk serbuk tetapi mengalami beberapa kelemahan; (i) penggumpalan yang membawa kepada penurunan fotokeaktifan dan (ii) proses pemulihan yang mahal dan sukar. Permasalahan ini boleh diatasi dengan memegunkan mangkin tersebut keatas satu sokongan. Dengan tujuan untuk memberikan penyelesaian alternatif kepada masalah pemisahan pepejal–cecair, polietersulfon (PES) telah dipilih sebagai sokongan kerana kestabilannya terhadap radikal yang terhasil semasa tindak balas fotopemangkinan. Kerja ini menyiasat pencirian fizikokimia fotomangkin filem hibrid TiO_2/PES, ZnO/PES dan TiO_2 terturun ($rTiO_2$)/PES yang disediakan melalui teknik fasa penyongsangan dan dilaporkan, buat kali pertama, sumbangan sinergisnya dalam bidang fotopemangkinan. Filem-filem tersebut dicirikan menggunakan analisa mikroskopi pengimbasan elektron (SEM), serakan tenaga sinar-X (EDX), pembelauan sinar-X (XRD), spektroskopi fotoelektron sinar-X (XPS), mikroskopi daya atom (AFM) dan spektroskopi kepantulan resap UV-vis (UV-vis DRS). Analisa XRD, SEM dan EDX mendedahkan bahawa TiO_2, ZnO dan TiO_2 terturun ($rTiO_2$) diserakkan secara homogen dan tertanam keseluruh filem PES. Keputusan XPS dan UV-vis DRS mengesahkan pembentukan ruang–antara TiO_2 (458.2 and 463.9 eV), ZnO (1021.0 and 1043.8 eV) dan $rTiO_2$ (456.1 and 461.8 eV) dengan tenaga jurang jalur masing-masing adalah 3.00, 3.15 dan 2.85 eV. Filem-filem tersebut memperlihatkan kekasaran permukaan yang lebih tinggi dan meningkatkan hidrofilik berbanding filem PES sahaja. Fotokeaktifan filem–filem yang telah disediakan dinilai dengan degradasi larutan metil oren (MO) di bawah kedua-dua penyinaran cahaya UV dan nampak. Penekanan diberikan pada kesan muatan pemangkin, pH, kepekatan, bilangan filem dan kajian kitar semula. Filem pemangkin terbaik memaparkan kinetik tertib pertama pseudo dengan hampir 80% dan 30% untuk PES–TiO_2 (13 wt%), 100% dan 56% untuk PES–ZnO (17 wt%), 76% dan 55% untuk PES–$rTiO_2$ (13 wt%) penyingkiran MO dalam keadaan asal masing-masing terhadap penyinaran cahaya UV dan nampak. Penyingkiran lengkap MO dicapai pada pH 2.0 untuk kedua-dua PES–TiO_2 (13 wt%) and PES–$rTiO_2$ (13 wt%) dan pH 5.8 untuk PES–ZnO (17 wt%). Peratusan degradasi berkurangan dengan peningkatan kepekatan awal MO (5–20 mg/L) tetapi meningkat dengan peningkatan bilangan filem. Spesis aktif

utama yang ditemui adalah $\bullet O_2^-$ untuk kedua-dua PES–TiO_2 (13 wt%) and PES–rTiO_2 (13 wt%) dan h^+ untuk PES-ZnO (17 wt%). Filem–filemterbaik boleh dikitar semula sehingga lima kali sementara mengekalkan kestabilan dan kecekapan degradasi tanpa dikenakan sebarang proses pemulihan semula. Degradasi efluen kilang minyak kelapa sawit (POME) dipantau melalui analisa keperluan oksigen kimia (COD) dengan peratusan degradasi sebanyak 20%, 27%, 12% dan 12%, 18%, 15% masing-masing di bawah penyinaran cahaya UV dan nampak, dengan beberapa pengurangan dalam nilai-nilai warna Institut Pengilang Pewarna Amerika (ADMI).

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I certify that a Thesis Examination Committee has met on 17 July 2018 to conduct the final examination of Zul Adlan bin Mohd Hir on his thesis entitled "Preparation and Characterization of Zinc Oxide and Titanium Oxide Polyethersulfone Hybrid Film Photocatalysts for Degradation of Methyl Orange" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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Name of Member of Supervisory Committee: Janet Lim Hong Ngee

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LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers' Institute
AFM	Atomic force microscopy
AOPs	Advanced oxidation processes
cb	Conduction band
COD	Chemical oxygen demand
e^-	Electron
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
g	gram
h^+	Positive hole
hv	Energy (photon)
L	Liter
mg	Milligram
mL	Milliliter
MO	Methyl orange
nm	Nanometer
PES	Polyethersulfone
POME	Palm oil mill effluent
ppm	Part per million
p-BQ	1,4-benzoquinone
$rTiO_2$	Reduced titanium dioxide
SEM	Field emission scanning electron microscopy
*t*BuOH	*Tert*-butanol
TOC	Total organic carbon
UV	Ultraviolet
UV-vis	Ultraviolet-visible
UV-vis DRS	Ultraviolet-visible diffuse reflectance spectroscopy
µm	Micrometer
vb	Valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Presently, modern societies around the world are facing serious environmental problems (water and air pollution) due to rapid industrial development. According to The United Nation World Water Development Report in 2017 (UNESCO, 2017), small and medium-sized enterprises (SMEs) and informal industries typically discharge their wastewater to municipal systems or directly to the environment. Following the appropriate standard operating procedures (SOPs), the related industries shall comply with the regulations to avoid penalties, which means that, the wastewater must be adequately treated before being released to the water bodies. Unfortunately, some industries may find it to be easier to pay the fines rather than to invest in wastewater treatment plant as to comply with regulations. There are also some cases where the occurrence of pollutants in the aquatic environments are sourced by hospital effluents, landfill leachates, livestock and chemical runoff from industries into water channels which further exacerbate the quality of water (Luo *et al*., 2014; UN-Water, 2015).

Besides, the use of pharmaceutical and personal care products such as fragrances, sunscreens, artificial sweeteners, antibiotics and pesticides in our daily activities could possibly worsen the existing environmental problems. These wastes are continuously release from these sources and drift into water bodies (Rodriguez-Narvaez *et al*., 2017). Since 1980 and 1990's, water pollution remediation has become a high priority due to the health risk attributed by the polluted water in which millions of people rely on freshwater from the rivers for cleaning and household purposes. The water systems in both developed and developing countries is also struggling to confront with the growing pressure from the discharge of hazardous chemicals and toxic industrial wastes which considered as the core pollutants responsible for the pollution of water. Without adequate water treatment process, this poses a greater risk to public health, food security and economy growth while cultivating the unhealthy lifestyle affecting the poor, women and children (UNEP, 2016).

Up to this point, several conventional methods have been employed to recycle and use the industrial wastewater. However, most of these methods are concentrating on the management and removal of pollutants by using physical, chemical, electrochemical, biological, filtration, electrical and chemical oxidation. Filtration and sedimentation are physical methods used to treat municipal wastewater, industrial wastewater and drinking water. In sedimentation method, settling of suspended particles is achieve gravitationally. Filtration technology involves removals via microfiltration, ultrafiltration, nanofiltration and reverse osmosis. However, it is not feasible for treating wastewater because of its high working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life. Reverse osmosis is effective for discolouring and desalting of the most diverse range of wastes, and hence it is employ for recycling the wastewater. Biological treatment (aerobic, anaerobic and combined aerobic–anaerobic)

is the most common and widespread technique used in wastewater treatment. It offers great advantages by being relatively inexpensive, having low running costs and the end products are not being toxic. However, this process depends on the presence of specific microorganism or potential bacteria to mitigate targeted chemicals and it needs longer time for the bacteria to grow before degradation process takes place. Considering several drawbacks from these methods, there is a need to develop more effective water treatment technologies to remove the persistent organic compounds from wastewater. Alternatively, the development of this new method could possibly reduce the problem of water shortages and the deterioration of water sources globally.

In recent times, treatment of wastewater by means of semiconductor photocatalysis has brought great attentions to the scientist worldwide. This technique, one of the Advanced Oxidation Processes (AOPs), is believed to be a beautiful approach in water treatment process with best prospect and advance development. It converts the pollutants into harmless by products such as water, carbon dioxide and other inorganic ions via photocatalytic oxidation process. When properly developed, the technique could mitigate the pollutants completely and effectively. This method normally works at or near ambient temperature and pressure to degrade organic pollutants present in various kind of industrial wastewater (Ribeiro *et al*., 2015). Photocatalysis utilizes cheaply available non-toxic semiconductors such as titanium dioxide and zinc oxide. Most AOPs are energy intensive which use various combinations of hydrogen peroxide, ozone, and UV light to generate •OH radicals that are responsible for the complete oxidation of a broad range of organic pollutants in the wastewater quickly and non-selectively (Oturan and Aaron, 2014; Deng and Zhao, 2015). However, the current trend is shifted to the more convenient ways of producing *in-situ* oxidative radical species via heterogeneous photocatalysis. In this context, the process is characterized by the formation of •OH and $\bullet O_2^-$ radicals on the surface of the semiconductor photocatalyst at the time of treatment (Asghar *et al*., 2015). The advantage of rapid formation of the radical species would induce direct interaction between the catalyst surface and the pollutants, which eventually lead to the mineralization of the pollutants into harmless species such as CO_2 and H_2O molecules, through a series of redox reaction.

1.2 Problem Statement

Pollution of water bodies by industrial effluence containing some lethal organic compounds even at a low concentration brought a rush of threats to human health and become a matter of worldwide distress (UN-Water, 2015). The removal of the pollutants is challenging due to its unique chemical and physical characteristics. However, photocatalysis has been proposed as an effective method to combat the toxic and harmful pollutants in the wastewater using semiconductor oxide as photocatalyst. This system has been a promising technique since it is safe and environmental friendly, low cost, requires the use of efficient light-harvesting and non-toxic semiconductor materials such as ZnO and TiO_2 as the photocatalyst to degrade the organic pollutants (Ribeiro *et al*., 2015).

The photocatalyst is typically being applied in suspension mode during water remediation process. Nonetheless, this technique suffered from some technical aspects

that impeded its industrial application, i.e., the ineffective utilization of ultraviolet or visible light due to agglomeration, lower adsorption performance for hydrophobic pollutants, inhomogeneous dispersion in aqueous suspensions and post-treatment recovery of the nanoparticles after the degradation process in regard to economic, health and safety concern. Post-treatment recovery is both costly and time consuming. This is because catalyst requires longer settling time and effective solid–liquid phase separation techniques (Singh *et al*., 2013; Dong *et al*., 2015). While in most cases, recycling the powder photocatalyst have significantly reduced its performance due to loss of photocatalyst particles during separation process and thus creating secondary pollution (Zheng *et al*., 2017).

Previous study shows that the separation of the powder photocatalyst from the organic substrate can be accomplished by means of immobilization on a support or magnetic approach. Some researchers immobilized the photocatalyst onto various support such as glass, stainless steel, beads, etc. Although these studies provide a solution to the solid–liquid separation issue, the photoactivity of the supported photocatalyst is usually reduced due to the reduction of surface active sites and the hindrance in light absorption caused by the inactive support. Moreover, the supported photocatalyst could possible experience some leaching during the photoreaction. Another attempt was carried out by preparing composite photocatalyst comprises of a magnetic core and semiconductor oxide, making the powder photocatalyst recoverable due to its magnetic properties. This type of composite photocatalyst is normally dependent on the magnetic core size which affect the magnetic properties of the materials. Besides, the degradation performance also lowers as compared to unrestricted powder photocatalyst in which the direct deposition of photocatalyst materials onto the surface of the magnetic particles would stimulate high levels of photo-dissolution of the magnetic core when its surface is irradiated. The composite magnetic photocatalyst is also still in powder form which make them difficult to be retrieved for a large scale practice. Thus, both of these immobilization methods still suffer several drawbacks which impractical for industrial scale water remediation process (Dong *et al*., 2015).

Driven by the growing need of emerging hybrid photocatalyst and effective separation properties for continuous water remediation process, the immobilization of photocatalyst onto polymeric materials is now becoming a topic of priority. The recent development of microporous and mesoporous polymeric materials have attracted considerable attention as a catalyst support due to their outstanding chemical and thermal resistance, high mechanical stability for long term period, good affinity for anchoring the nanoparticles, as well as high durability against the oxidative condition of the photocatalyst–substrate upon light irradiation (Singh *et al*., 2013; Zheng *et al*., 2017). All these features are the characteristics for a good polymer support that are easily applicable for industrial water treatment at reduced cost technologies. Several polymers including polyimide (PI), polysulfone (PSf), polyvinylidene fluoride (PVDF), polypropylene (PP), polyacrylonitrile (PAN), and cellulose acetate (CA) have been introduced as the support for semiconductor photocatalyst (Bet-moushoul *et al*., 2015; AL-Hobaib *et al*., 2016; Nor *et al*., 2016). However, earlier studies have demonstrated the suitability of polymer resin such as polyethersulfone (PES) as a support material in photocatalyst as it is stable under UV exposure and is not degraded by hydroxyl radicals formed along the photocatalysis process (Fischer *et al*., 2015; Mozia *et al*., 2015). The incorporation of nanoparticles inside the PES matrix simultaneously improved its

physicochemical properties such as surface roughness, hydrophilicty, porosity, thermal and mechanical strength.

Although a large amount of literature on PES–semiconductor oxide mixed matrix membranes is available, they only focused on the application related to filtration and antifouling studies (Yin and Deng, 2014). Hence, it is important to investigate the physicochemical characteristics of hybrid film photocatalyst incorporating high amount of stable TiO_2, ZnO and reduced TiO_2 ($rTiO_2$) into PES via phase inversion technique and its synergistic contribution especially in the field of photocatalytic reaction has not previously been reported. Therefore, this research has continued focuses on the photoreaction of the film influence by some operational variables which include photocatalyst loading, initial pH, initial concentration, different types of light (UV and visible), reusability and radical trapping investigation over methyl orange degradation. The advantages of this approach cover several aspects such as cost and energy effective in terms of its cut–down size for photoreactor installation and practicability for the removal of pollutant in real wastewater. Hypothetically, the synergistic effect between the polymer and photocatalyst materials would simultaneously increase the degradation efficiency and provides an alternative solution to the solid–liquid phase separation problem.

1.3 Research Objectives

The main aim of this study is to prepare and characterize PES–nanoparticles hybrid film photocatalysts for easier solid–liquid phase separation. This study also concerned with the physicochemical properties of the prepared photocatalysts and its feasibility to degrade methyl orange (MO) dye and palm oil mill effluent (POME) under UV and visible light irradiation. To achieve the main aim, there are three research objectives have been addressed as follows:

1. To investigate the physicochemical characteristics of PES–TiO_2, PES–ZnO and PES–$rTiO_2$ film photocatalysts prepared via phase inversion method.
2. To evaluate the catalytic activity, degradation rate and kinetic study of the prepared film photocatalyst in degrading methyl orange (MO) solution under UV and visible light irradiation under the experimental conditions of the study.
3. To test the photocatalytic performance of the best film photocatalyst in the degradation of POME.

1.4 Scope of Research

The scope of this research covers the preparation of hybrid film photocatalyst of PES–TiO_2, PES–ZnO and PES–$rTiO_2$ via phase inversion technique. Subsequently, the surface morphology and physicochemical property of PES–nanoparticle hybrid film photocatalysts were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analyzer (EDX), X-ray Diffraction Analysis (XRD), X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and UV-vis DRS Spectroscopy analyses. The percentage of porosity (ε) of the prepared film photocatalyst

was determined by a gravimetric method. The performance of the prepared photocatalysts was evaluated by degradation of MO solution under both UV and visible light irradiation at room temperature and pressure. The effect of some variables such as the photocatalyst loading, initial pH, initial concentration, number of films, type of lights and recyclability study during the photocatalytic degradation process were also carried out. The total organic compound (TOC) analysis was employed to monitor the degradation of MO by determining the residual total carbon in the dye sample. In the final stage, the best film photocatalysts were tested in the degradation of palm oil mill effluent (POME). The progressive degradation and decolourization of the POME was monitored by measuring the chemical oxygen demand (COD) and the American Dye Manufacturers' Institute (ADMI) colour values.

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