UNIVERSITI PUTRA MALAYSIA

PHOTOELECTROCHEMICAL DEGRADATION OF DYE POLLUTANTS USING TIO2 THIN FILM ELECTRODES

LEE CHONG YONG.

FSAS 2004 26

PHOTOELECTROCHEMICAL DEGRADATION OF DYE POLLUTANTS USING TiO₂ THIN FILM ELECTRODES

LEE CHONG YONG

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2004

PHOTOELECTROCHEMICAL DEGRADATION OF DYE POLLUTANTS USING TiO₂ THIN FILM ELECTRODES

By

LEE CHONG YONG

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

May 2004

DEDICATION

I would like to dedicate my work during Master Science programmed to my departed and beloved father, Lee Boon Hock. Although he was passed away last 12 years ago, his smiles and high spiritual determination always in my mind.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

PHOTOELECTROCHEMICAL DEGRADATION OF DYE POLLUTANTS USING TiO$_2$ THIN FILM ELECTRODES

By

LEE CHONG YONG

May 2004

Chairman: **Associate Professor Zulkarnain Zainal, Ph.D.**

Faculty: **Science and Environmental Studies**

Thin film electrodes were fabricated by immobilizing titanium dioxide (TiO$_2$) onto titanium substrate using sol gel dip-coating method. The electrochemical technique was employed to study the photodegradation process on methyl orange dye. The effects of various parameters and conditions on electrochemical assisted photocatalytic degradation process were investigated by monitoring dyes decolourisation rates using UV-Vis spectrophotometer.

Photosensitivity of the TiO$_2$ thin film electrode was analysed by Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV) techniques combined with illumination. Sample heat-treated at 500°C showed the best photosensitivity. The TiO$_2$ thin films and the dried gel were also analysed using Scanning Electron Microscope (SEM), X-Ray Diffractometry (XRD), UV/Vis Spectroscopy, Fourier Transform-Infra Red (FT-IR), Thermogravimetric Analyser (TGA), Differential Thermal Analyser (DTA) and CHNS analyser. The photoelectrochemical degradation experiment results showed that the rate of dye removal increased with external applied potential between 0.0 V and 1.5 V versus Ag/AgCl reference electrode. Meanwhile, the

photoeletrochemical degradation rate was also affected by initial concentrations, light intensity, light sources, photocatalysts coated area, repeated use, supporting electrolyte, solution pH, agitation and solution temperature.

The photoelectrochemical degradation experiment was also carried out on naphtol blue black, rhodamine 6G, methylene blue, reactive blue 2, direct red 81, mixed dyes (consists of methyl orange, naphtol blue black, rhodamine 6G, methylene blue, reactive blue 2, direct red 81) and actual textile effluents. The removal efficiency was evaluated and compared in terms of UV/Vis decolourisation, Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

DEGRADASI BAHAN PENCEMAR PEWARNA SECARA FOTOELEKTROKIMIA MENGGUNAKAN ELEKTROD LAPISAN NIPIS TiO$_2$

Oleh

LEE CHONG YONG

Mei 2004

Pengerusi: **Profesor Madya Zulkarnain Zainal, Ph.D.**

Fakulti: **Sains dan Pengajian Alam Sekitar**

Elektrod lapisan nipis dihasilkan melalui pemegunan titanium dioksida (TiO$_2$) pada substrat titanium dengan menggunakan kaedah salutan-celup sol-gel. Teknik elektrokimia digunakan untuk mengkaji proses fotodegradasi ke atas pewarna metil oren. Kesan pelbagai parameter dan keadaan pada proses degradasi fotomangkin berbantukan eletrokimia dikaji berpandukan kepada kadar pelunturan warna dengan menggunakan spektrofotometer lembayung cahaya nampak.

Fotosensitiviti bagi elektrod nipis TiO$_2$ dianalisis dengan menggunakan kaedah Voltammetri Pengimbasan Linear (LSV) dan Kitaran Voltammetri (CV) yang disertai dengan penyinaran cahaya. Sampel yang dipanaskan pada suhu 500°C menunjukkan kepekaaan cahaya yang terbaik. Elektrod nipis TiO$_2$ dan gel kering TiO$_2$ dianalisis menggunakan alat Mikroskopi Pengimbasan Elektron (SEM), Pembelauan Sinar-X (XRD), Spektrofotometer lembayung cahaya nampak (UV/Vis), Fourier Transform Infra Merah (FTIR), Analisis Terma Gravimetri (TGA), Analisis Pembezaan Terma (DTA) dan penganalisan CHNS. Keputusan fotoelektrokimia degradasi eksperimen menunjukkan kadar penyingkiran pewarna meningkat dengan mengaplikasikan

v

keupayaan luar antara 0.0 V dan 1.5 V merujuk kepada elektrod Ag/AgCl. Sementara itu, kadar fotoelektrokimia degradasi juga dipengaruhi oleh kesan kepekatan pewarna, keamatan cahaya, sumber cahaya, luas permukaan salutan fotomangkin, ulangan penggunaan, larutan elektrolit pembantu, pH larutan, pengaliran dan suhu larutan.

Eksperimen fotoelektrokimia degradasi juga dijalankan pada naftol biru hitam, rhodamin 6G, metilena biru, reaktif biru 2, direct merah 81, pewarna campuran (terdiri daripada metil oren, naftol biru hitam, rhodamin 6G, metilena biru, reaktif biru 2, direct merah 81) dan efluen sebenar kilang tekstil. Keberkesanan penyingkiran pewarna-pewarna dinilai dan dibandingkan dari segi kadar penurunan warna, Jumlah Karbon Organik (TOC), Permintaan Oksigen Kimia (COD) dan Permintaan Oksigen Biokimia (BOD).

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my earnest appreciation and heartfelt thanks to my project supervisor, Associate Professor Dr. Zulkarnain Zainal for his extraordinary patience, kindness, invaluable guidance, constructive criticisms, advice, continuous supervision and suggestion throughout the duration of the study. My sincere gratitude also goes to the other supervisory committee members, Professor Dr Mohd. Zobir Hussein, Professor Dr Anuar Kassim and Dr Nor Azah Yusof.

I wish to express my sincere thanks to Mr Sujak from Department of Environmental Sciences, UPM for the guidance and technical supports giving while doing BOD and COD analyses. Thanks to Sara, Kong Hui, Woei Long, Nasir, Kok Wei, Soon Minh, Tien Ping, Mas, Dila, Ida and other lab mates as well, I really learned a lot from them. Special thanks I wish to give to last year final year project student, Wong Kee Ann who together with me designed the electrochemical photoreactor. To all who contribute to this study, a lot of thanks.

To my beloved girlfriend, Kar Wai who always been a source of inspiration and strength throughout my study, thanks a lot for your love, concern, understanding and help. To my roommate, Boon Siong, messy room and switch on the light through whole night might give you uncomfortable condition during finishing up this report. Thanks for your understanding and support.

Last but not least, I would like to express my sincerely and heartfelt thanks to my mother, brothers and sisters who give unconditional support and help to me from my

childhood until now. Certainly, it is difficult for me to pay back what you all had contributed to me. But one thing for sure, I'm proud to be your son and brother, if any success I have achieved, this glory certainly belong to you all.

I certify that an Examination Committee met on 11th May 2004 to conduct the final examination of Lee Chong Yong on his Master of Science thesis entitled "Photoeletrochemical Degradation of Dye Pollutants Using TiO$_2$ Thin Film Electrodes" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Mohd. Zaizi Desa, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

Abdul Halim Abdullah, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Tan Wee Tee, Ph.D.
Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

Musa Ahmad, Ph.D.
Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Independent Examiner)

GULAM RUSUL RAHMAT ALI, Ph.D.
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: **19 JUL 2004**

ix

This Thesis Submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows:

ZULKARNAIN ZAINAL, Ph. D
Associate Professor
Faculty Sience and Environmental Studies
Universiti Putra Malaysia
(Chairman)

MOHD. ZOBIR HUSSEIN, Ph. D
Professor
Faculty Sience and Environmental Studies
Universiti Putra Malaysia
(Member)
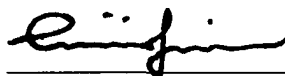
ANUAR KASSIM, Ph. D
Professor
Faculty Sience and Environmental Studies
Universiti Putra Malaysia
(Member)

NOR AZAH YUSOF, Ph. D
Lecturer
Faculty Sience and Environmental Studies
Universiti Putra Malaysia
(Member)
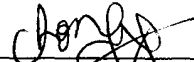
AINI IDERIS, Ph.D,
Professor/Dean
School of Graduate Studies,
Universiti Putra Malaysia

Date: **16 AUG 2004**

DECLARATION FORM

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for other degree at UPM or other institutions.

_____
LEE CHONG YONG

Date: 9/7/04 .

TABLE OF CONTENTS

Page

xiv

LIST OF TABLES

LIST OF FIGURES

xviii

of irradiation time for MB dye

LIST OF ABBREVIATIONS

APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
CB	Conduction Band
COD	Chemical Oxygen Demand
CV	Cyclic Voltammetry
DR 81	Direct Red 81
DTA	Differential Thermal Analyser
E_a	Activation Energy
E_g	Energygap
EDX	Energy Disperse X-ray
EHP	Electron Hole Pair
FAS	Ferum Ammonium Sulphate
FTIR	Fourier Transform-Infra Red
IPCE	Incident Photon Charge Exchange
ITO	Indium Tin Oxide
JCPDS	Joint Committee of Powder Diffraction Standard
LSV	Linear Sweep Voltammetry
MB	Methylene Blue
MIXED	Mixed dye
MO	Methyl Orange
NBB	Naphtol Blue Black
PC	Photocatalytic
PEC	Photoelectrocatalytic
RB 2	Reactive Blue 2