UNIVERSITI PUTRA MALAYSIA

DEGRADATION OF DYES USING ZINC OXIDE AS THE PHOTOCATALYST

LEE KIAN MUN

FS 2008 8

DEGRADATION OF DYES USING ZINC OXIDE AS THE PHOTOCATALYST

LEE KIAN MUN

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2008

DEGRADATION OF DYES USING ZINC OXIDE AS THE PHOTOCATALYST

By

LEE KIAN MUN

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

AUGUST 2008

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

DEGRADATION OF DYES USING ZINC OXIDE AS THE PHOTOCATALYST

By

LEE KIAN MUN

AUGUST 2008

Chair : Associate Professor Abdul Halim bin Abdullah, PhD

Faculty : Science

In this study, ZnO was synthesized via precipitation method. The resulting ZnO catalyst was characterised by X-ray Diffraction (XRD), Fourier Transform Infrared (FT-IR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Particle Size Analysis (PSA) and surface area measurement (BET method). XRD analysis showed that hydrozincite ($Zn_5(CO_3)_2(OH)_6$) was formed during precipitation process and the decomposition of hydrozincite was completed at temperature ~ 400 °C after 2 hours calcination in air. The ZnO produced was spherical in shape (morphology), has a surface area of 25.8 $m^2g^{-1}$and particle size of 255 ± 2 nm with hexagonal crystal structure.

The ZnO produced was tested for photodegradation of Methyl Orange (MO), Methylene Blue (MB), and Reactive Orange 16 (RO 16) under the illumination of ultraviolet (UV, λ_{max} = 365 nm) light. Various parameters affecting the degradation performance such as catalyst loading, initial dye concentrations, initial pH, light intensity, different light sources and addition of oxidants was examined. The removal percentage of dyes increased with increasing mass of ZnO up to an optimum mass

but decreased with increasing initial concentrations of the dye. Enhanced colour removal for MO, MB and RO 16 was observed when the UV lamp used was changed from 6 to 100 watts. In addition, the highest removal was achieved at pH 11 and addition of H_2O_2 and $K_2S_2O_8$ led to an enhancement in the removal of all the three dyes. The photocatalytic degradation of mixed dyes solution (consists of a mixture of MO, MB and RO 16) was conducted and 64.90 % removal was observed. The photodegradation of dyes followed first-order kinetics.

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

DEGRADATION OF DYES USING ZINC OXIDE AS THE PHOTOCATALYST

Oleh

LEE KIAN MUN

OGOS 2008

Pengerusi : Profesor Madya Abdul Halim bin Abdullah, PhD

Fakulti : Sains

Dalam kajian ini, zink oksida (ZnO) disintesis melalui kaedah pemendakan. ZnO yang dihasilkan dikaji dengan Pembelauan Sinar-X (XRD), Inframerah (IR), Analisis Termogravimetrik (TGA), Mikroskopi Pengimbasan Elektron (SEM), Analisis Saiz Zarah (PSA) dan Pengukuran Luas Permukaan (kaedah BET). Daripada analisis XRD, hydrozincite ($Zn_5(CO_3)_2(OH)_6$) telah dihasilkan semasa proses pemendakan dan penguraian hydrozincite berlaku sepenuhnya di suhu sekitar 400 °C selepas 2 jam pengkalsinan dalam udara. ZnO yang dihasilkan berbentuk sfera, mempunyai luas permukaan sebanyak 25.8 m^2g^{-1} dan saiz zarah 255 ± 2 nm dengan struktur kristal heksagon.

Zink oksida yang dihasilkan telah diuji untuk fotopemangkinan Metil Jingga (MO), Metilena Biru (MB) dan Reaktif Jingga 16 (RO 16) di bawah penyinaran cahaya ultralembayung (UV, λ_{maks} = 365 nm). Pelbagai parameter yang mempengaruhi prestasi fotopemangkinan seperti amaun ZnO, kepekatan pewarna, pH larutan, keamatan lampu, sumber cahaya yang berbeza dan penambahan agen pengoksidaan

telah dikaji. Peratusan penyingkiran pewarna meningkat dengan peningkatan amaun ZnO sehingga ke tahap optimum tetapi menurun dengan peningkatan kepekatan perwarna. Peningkatan penyingkiran pewarna juga diperhatikan bagi MO, MB dan RO 16 masing-masing apabila lampu UV yang digunakan ditukar daripada 6 ke 100 watt. Tambahan pula, penyingkiran tertinggi dicapai pada pH 11 dan penambahan H_2O_2 dan $K_2S_2O_8$ membawa kepada peningkatan dalam penyingkiran ketiga-tiga pewarna. Selain itu, fotopemangkinan juga dikaji ke atas campuran pewarna yang terdiri daripada MO, MB dan RO 16 dan sebanyak 64.90 % penyingkiran telah diperhatikan. Fotopemangkinan ketiga-tiga pewarna didapati mengikut model kinetik tertib pertama.

ACKNOWLEDGEMENTS

First and foremost, my deepest appreciation goes to my supervisor, Assoc. Prof. Dr. Abdul Halim bin Abdullah, for his effort and support in guiding me throughout my MSc research. I would also like to express heartfelt thanks to my co-supervisors, Prof. Dr. Zulkarnain bin Zainal and Assoc. Prof. Dr. Azmi bin Zakaria for giving me guidance and opinions to improve my research.

Sincere thanks are also extended to Madam Rusnani Amirudin (FT-IR Perkin-Elmer Model 1725X) and Mr. Kamal Margonal (TGA Mettler Toledo model) from chemistry department of UPM. Beside that, I also would like to express my thank you to Madam Faridah for helping me operates scanning electron microscopy (SEM) analysis at Institute Bioscience. I also would like to express my special thank you to Miss Siti Murni Zawawi who helps me to operate surface area measurement (BET method). My appreciation also goes to all my lab mates Norsalinda, Umar Gaya, Nurulhuda bin Abdullah for their support and encouragement.

Special appreciation also goes to Siew Cheng, Sook Keng, Wenn Jiunn, Kok Leong, Yee Ching and Yuen who gave me a lot of support and assistance whenever I need it.

Last but not least, I would like to thank all those who had contributed to the success of my work in one way or another including my father, mother and brother for their support, encouragement and love that gave me the strength to complete my research and thesis.

I certify an Examination Committee met on **date of viva** to conduct the final examination of Lee Kian Mun on his Master of Science thesis entitled "Photocatalytic Degradation of Dyes using ZnO as Photocatalyst" 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:

Chairman, PhD
Professor
Name of faculty/ institute
Universiti Putra Malaysia
(Chairman)

Examiner 1, PhD
Professor
Name of faculty/ institute
Universiti Putra Malaysia
(Internal Examiner)

Examiner 2, PhD
Professor
Name of faculty/ institute
Universiti Putra Malaysia
(Internal Examiner)

External Examiner, PhD
Professor
Name of faculty/ institute
Universiti Putra Malaysia
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor/ Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkarnain Zainal, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Azmi Zakaria, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

____

AINI IDERIS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 16 October 2008

DECLARATION

I declare that the thesis is my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

____

LEE KIAN MUN

Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BET	Brunauer-Emmet-Teller surface area measurements
E_g	Band gap energy
FT-IR	Fourier Transform-Infra Red
FWHM	Full width at half maximum
JCPDS	Joint Committee of Powder Diffraction Standards
MO	Methyl Orange
MB	Methylene Blue
PSA	Particle Size Analysis
RO 16	Reactive Orange 16
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
UV	Ultraviolet
XRD	X-ray Diffraction
ZnO	Zinc Oxide

CHAPTER 1

INTRODUCTION

There is no possible living world without water. In general, water accounts almost 70 to 90 % of the weight of living organisms. One cannot imagine life without clean water. No doubt, there is no raw material in the world that more than water. Thus, the quality of this valuable resource will directly influence the normal life of human being. In general, water pollution refers to the degradation of water quality. Although natural phenomena may change the water quality and also the ecological status of water, however it cannot be considered as pollution unless it is not suitable to be used in particular application.

The growth of the world's population and industry has increased the demand for water supply. The domestic use and industrial activity especially in developed countries produce large amount of wastewater which then disposed into natural channels that may lead to high pollution risk. In 2007, dos Santos *et al.* commented that colour in water can be resulted either from natural phenomenon like the presence of humic substances or from artificial phenomenon such as the disposal of dyes effluents. Light played a major role for proper development of aquatic life. Thus, the presence of large quantities of coloured wastewater blocked the penetration of light into the water and subsequently causes an imbalance in their ecosystem.

According to Allègre *et al.* (2006), textile industries are one of the industries that consumed large volumes of water in the processing operations including pre-treatment, dyeing, printing and finishing. In dyeing process, water vapour is used as heating agent for the dye baths, while liquid water ensures the transmission of the dyes onto the fibre (Hessel *et al.*, 2007). The release of the treatment baths which are highly toxic and heavily coloured after the dyeing process contributes to water pollution. One cannot estimate the total amount of pollutants being generated each time the dyestuff is discharged into the water stream. Therefore, coloured water required costly treatment operations before being consumed as drinking water. The critical state of the water bodies has raised public concern and awareness as well as stringent legislations being imposed by the government. This has encouraged researchers in developing techniques such as electro-flocculation, reverse osmosis, chlorination, adsorption and ozonation to minimise water pollution and restoring the natural state of the water bodies.

Nowadays, semiconductor photocatalysis attracts increased interest since it has a great potential to contribute to such environmental problems. The usage of ZnO, TiO_2 and SnO_2 has been widely applied in the removal of organic contaminants (Sakthivel *et al.* (2003), Akyol *et al.* (2004) and Irmak *et al.* (2004)). Moreover, some studies have confirmed that ZnO exhibits a better efficiency than TiO_2 in photocatalytic degradation of some dyes, even in aqueous solution (Gouvêa *et al.* (2000) and Dindar and Icli (2001)).

As a well-known photocatalyst, ZnO has received much attention in the degradation and complete mineralisation of environmental pollutants (Richard *et al.* (1997), Driessen *et al.* (1998) and Yeber *et al.* (2000)). Since ZnO has almost the same band-gap energy (3.2 eV) as TiO_2, its photocatalytic capability is anticipated to be similar to that of TiO_2. Moreover, ZnO is relatively cheaper compared to TiO_2 whereby the usage of TiO_2 and platinum catalyst are uneconomic for large scale water treatment operations (Daneshvar *et al.*, 2004b). In addition, ZnO can be a suitable alternative photocatalyst other than TiO_2 since its photodegradation mechanism has been proven to be similar to that of TiO_2 (Dindar and Icli (2001) and Pirkanniemi and Sillanpää (2002)). In some cases, ZnO shows higher photocatalytic tendency towards photodegradation and mineralisation of environmental organic or inorganic pollutants (Richard *et al.* (1997), Gouvêa *et al.* (2000) and Dindar and Icli (2001)).

1.1 Dye

A dye is a coloured substance that has specific affinity to a given substrate. Dyes are applied to various substrates (textiles, leather, paper, hair *etc*.) from liquid in which they are completely, or at least partially soluble (Zollinger, 2003).

Dyes are classified according to their chemical structure or according to the method of application (Christie, 2001). According to Christie, dyes contain two groups which are responsible for their colour. They consist of a group of atoms responsible for the dye colour, called chromophores and the other group is auxochromes, which can be defined as an electron withdrawing or donating substituents that essential for the colour enhancement of the chromophores. The most important chromophores are the azo (–N=N–), carbonyl (–C=O), methine (–CH=) and nitro ($–NO_2$) groups. The most important auxochromes are amine ($–NH_3$), carboxyl (–COOH), sulfonate ($–SO_3H$) and hydroxyl (–OH) groups.

In term of method of application, dye molecules are carefully designed to ensure that they have suitable properties for a particular application. For textile applications, dye molecules are designed so that they are strongly attached to the fibre molecules to which they are applied. Acid dyes and mordant dyes are mostly applied to protein fibres whereas direct dyes, reactive dyes and vat dyes are used for cellulose fibres. Disperse dyes and basic dyes are suitable for acrylic fibres.

1.2 Methods for Treating Dye Effluents

Generally, the release of coloured wastewater from textile industry into water bodies such as lakes, oceans and rivers has created severe environmental problems. Most of the coloured effluents are toxic and potentially carcinogenic hence considered as a threat for human survival. These issues have caused public concern and awareness on water pollution. Although various chemical and physical processes have been employed in the removal of coloured effluents, however, those methods do not lead to complete destruction of the dyes. Moreover, further treatment is needed since the methods employed just transfer the contaminants from one phase to another. This will indirectly enhance the operational cost. Some advantages and drawbacks of current technologies for the removal of pollutants are listed in Table 1.1.

In last decade, advanced oxidation processes (AOPs) have been growing since they are able to deal with the problem of dye destruction in aqueous systems (Konstantinou and Albanis, 2004). The generation of hydroxyl radicals (•OH) that oxidise various pollutants quickly and non-selectively have improved the degradation of organic compounds compared to conventional methods.

Among AOPs, semiconductor photocatalysis appears as the most emerging destructive technology. The main advantages of this process are highlighted below:

i. Inherent destructive nature;
ii. No mass transfer involved;
iii. Can be carried out under ambient conditions and using atmospheric oxygen as the oxidant; and
iv. May lead to complete mineralisation of organic carbon into CO_2.

In addition, semiconductors are chosen due to the following advantages:

i. Inexpensive;
ii. Non-toxic;
iii. Having high surface area;
iv. Having broad absorption spectra with high absorption coefficients;
v. Exhibits tunable properties which can be modified by size reduction, doping, sensitizers, *etc*.;
vi. Can be afforded for multielectron transfer process;
vii. Capable of extended use without substantial loss of photocatalytic activity;
viii. Semiconductor particles recovered by filtration or centrifugation or when immobilised retain much of their native activity after repeated catalytic cycle. (Chatterjee and Dasgupta, 2005)

Table 1.1. Advantages and disadvantages of the current methods of dye removal from industrial effluents.

Physical/chemical methods	Advantages	Disadvantages	References
Chemical methods			
Fentons reagent	1. Suitable treatment for wastewater which resistant to biological treatment or are poisonous to live biomass. 2. Effective decolourisation of both soluble and insoluble dye.	1. Sludge generation.	(Slokar and Le Marechal, 1997) (Pak and Chang, 1999) (Raghavacharya, 1997)
Ozonation	1. Capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons. 2. Colourless effluent and low COD. 3. Can be applied in its gaseous state and doesn't increase the volume of wastewater and sludge.	1. Short ozonation half-life (20 min) and high cost.	(Lin and Lin, 1993) (Xu and Lebrun, 1999)
Sodium hypochloride (NaOCl)	1. Initiates and accelerates azo-bone cleavage.	1. Release of aromatic amines or toxic molecules.	(Banat *et al.*, 1996)
Cucurbituril	1. Good sorption capacity for various types of dyes.	1. High cost.	(Buschmann, 1992)