UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST NANOPARTICLES FOR REMOVAL OF NITROBENZENE

LIMAN MUHAMMAD GIDADO

FS 2015 58

DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST NANOPARTICLES FOR REMOVAL OF NITROBENZENE

By

LIMAN MUHAMMAD GIDADO

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

December 2015

COPYRIGHT

DEDICATION

This thesis is dedicated to my late father (Liman Muhammad Bello) and the entire Muslim Ummah**.**

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

DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST NANOPARTICLES FOR REMOVAL OF NITROBENZENE

By

LIMAN MUHAMMAD GIDADO

December 2015

Chairman : Associate Professor Abdul Halim Abdullah, PhD
Faculty : Science

The increasing rise of world population and rapid industrial development across the globe is not without problem, especially in terms of availability of potable drinking water. The photocatalytic oxidation of zinc oxide, ZnO, under UV irradiation on organic pollutants in water is well establish and nitrobenzene, NB, has been classified under persistent organic pollutants and reported as being carcinogenic. In this study, ZnO catalyst was synthesized via sol-gel and, for the first time, via combination of sol-gel and hydrothermal method, in the presence of ethylene and polyethylene glycol surfactants. The resulting powder was calcined at different temperatures (400, 500, 600^{o}C) and for a different calcination periods (2, 4, 6 hours). The prepared samples were characterized using X-ray Diffraction (XRD, Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), Surface Area Measurement (BET method), Diffuse Reflectance Spectroscopy (DRS), X-ray Florescence (XRF) and Electron Diffraction Spectroscopy (EDS). All ZnO samples were spherical with hexagonal structure and particle size ranges from 16 to 96 nm. The variation in surfactants, calcination temperature and calcination time have no significant effect on the properties of ZnO. The photocatalytic activity of the prepared ZnO was evaluated by degradation of NB, under 2h of UV light irradiation. ZnO prepared by a combined sol-gel and hydrothermal method, exhibits the highest photocatalytic activity (75% of NB removal). This is attributed to high surface area and small particle size. In order to enhance its photoactivity, the ZnO catalyst was doped with various percentage of cobalt, Co. The addition of Co onto ZnO did not change the morphology of the catalyst. There was no remarkable change in the band gap (3.20 eV for the 0.5% Co-doped ZnO and 3.22 eV for the undoped ZnO) but an increased in the surface area (12.6 m^2/g for undoped ZnO to 17.6 m^2/g for the 0.5% Co-doped ZnO) was observed. The photocatalytic activity of Co-doped ZnO catalysts in degradation of NB under UV light irradiation is 86% which is higher than that of ZnO (SGHP).

The effects of catalyst mass, NB concentration as well as the solution pH were examined using the Co-doped ZnO catalyst, SP2. The best conditions for degrading NB were 0.75 g catalyst loading, 20 ppm NB and at a solution pH of 7. Under these conditions and for a 2 hours irradiation time, SP2 removed 86% and 83% of NB under UV light and visible light irradiation, respectively. The ability of the SP2 catalyst to

effect 83% NB removal under visible light irradiation is a landmark achievement because greater part of solar radiation consists of visible light. The degradation of NB follows first-order reaction with a rate constant k_1 equals to 2.16×10^{-2} mgL^{-1} min^{-1} and a half-life period of 32 min. Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) analyses, after a 2 hour photodegradation period, showed a 79% and 66% removal of NB, respectively, indicating a substantial degradation of the pollutant. The SP2 catalyst showed no significant loss in photoactivity after 5 cycles of photodegradation reaction suggesting that many more cycles are possible before reaching 50% drop in the photoactivity; a pointer to its reusability.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktar Falsafah

PEMBANGUNAN FOTOMANGKIN KOBALT-DIDOPKAN ZINK OKSIDA NANOPARTIKEL BAGI PENYINGKIRAN NITROBENZENA

Oleh

MUHAMMAD GIDADO LIMAN

Disember 2015

Pengerusi : Profesor Madya Abdul Halim Abdullah, PhD
Fakulti : Sains

Peningkatan kepadatan penduduk dunia dan pembangunan industri yang pesat di seluruh dunia bukan tanpa masalah, terutamanya dari segi ketersediaan air minuman yang boleh diminum. Proses pengoksidaan pencemar organik dalam air berfotopemangkinkan zink oksida, ZnO, di bawah sinaran UV telah pun mantap dan nitrobenzena, NB, telah diklasifikasikan di bawah pencemar organik kekal dan dilaporkan sebagai karsinogenik. Dalam kajian ini, mangkin ZnO telah disintesis melalui kaedah sol gel dan untuk pertama kalinya melalui gabungan kaedah sol gel dan hidroterma dengan kehadiran surfaktan etilena dan polietilena glikol. Serbuk yang terhasil dikalsin pada suhu yang berbeza (400, 500, 600^{o}C) dan bagi tempoh pengkalsinan yang berbeza (2, 4, 6 jam). Sampel yang tersedia dicirikan menggunakan Pembelauan sinar-X (XRD), Mikroskopi Transmisi Elektron (TEM), Mikroskopi Medan Pancaran Pengimbas Elektron (FESEM), pengukuran luas permukaan (kaedah BET), Spekstroskopi Pantulan Resap (DRS), Pendaflor sinar-X (XRF) dan Spektroskopi Pembelauan Elektron (EDS). Semua sampel ZnO berbentuk sfera dengan struktur heksagon dan dengan saiz zarah antara 16-96 nm. Perubahan jenis surfaktan, suhu pengkalsinan dan masa pengkalsinan tidak memberi kesan yang besar ke atas sifat ZnO. Aktiviti fotopemangkinan ZnO yang disediakan telah dinilai dengan mendegradasi NB di bawah sinaran cahaya UV selama 2 jam. ZnO yang disediakan dengan kaedah gabungan sol-gel dan hidroterma mempamerkan aktiviti fotopemangkinan tertinggi (75% penyingkiran NB). Ini adalah disebabkan oleh luas permukaan yang tinggi dan saiz zarah yang kecil. Dalam usaha untuk meningkatkan fotoaktivitinya, pemangkin ZnO telah didop dengan pelbagai peratusan kobalt (Co). Penambahan Co ke ZnO tidak mengubah morfologi pemangkin. Tiada perubahan yang ketara dalam jurang jalur tenaga (3.20 eV bagi 0.5% Co didop ke ZnO dan 3.22 eV bagi ZnO) tetapi peningkatan luas permukaan (12.6 m^2/g bagi ZnO ke 17.6 m^2/g bagi 0.5% Co didop ke ZnO) telah diperhatikan. Aktiviti fotopemangkinan Co didop ke ZnO dalam mendegradasikan NB di bawah sinaran cahaya UV adalah 86% iaitu lebih tinggi dengan yang dicatatkan oleh ZnO (SGHP).

Kesan jisim mangkin, kepekatan NB serta pH larutan telah dikaji menggunakan mangkin Co didop ke ZnO, SP2. Keadaan yang terbaik untuk mendegradasikan NB adalah 0.75 g mangkin, 20 ppm NB dan pada pH larutan 7. Di bawah keadaan ini, dan

untuk 2 jam masa penyinaran, SP2 menyingkirkan 86% dan 82% NB , masing-masing, di bawah sinaran cahaya UV dan cahaya nampak. Keupayaan pemangkin SP2 dalam penyingkiran 83% NB di bawah sinaran cahaya nampak adalah satu pencapaian mercu tanda kerana sebahagian besar sinaran suria terdiri daripada cahaya nampak. Degradasi NB mengikut tertib pertama tindak balas dengan pemalar kadar, k_1,bersamaan dengan 2.16×10^{-2} mgL^{-1} min^{-1} dan dengan tempoh separuh hayat selama 32 min. Analisa keperluan oksigen kimia (COD) dan jumlah karbon organik (TOC), selepas 2 jam fotodegradasi, menunjukkan penyingkiran NB, masing-masing 79% dan 66%, menunjukkan degradasi bahan pencemar yang besar. Pemangkin SP2 tidak menunjukkan sebarang kehilangan fotoaktiviti yang ketara selepas 5 kitaran tindak balas fotodegradasi menunjukkan kemungkinan lebih banyak kitaran sebelum penurunan fotoaktiviti mencapai 50%; petunjuk bagi kebolehgunaan pemangkin tersebut.

ACKNOWLEDGEMENTS

First and foremost I wish to express my deep sense of appreciation to my supervisory team chaired by Associate Professor Dr. Abdul Halim bin Abdullah ably supported by Professor Dr. Mohammed Zobir Hussein and Professor Dr. Zulkarnain bin Zainal. The guidance and support I received from the team is enormous and largely rewarding. The humility and open-mindedness of Associate Professor Dr. Abdul Halim throughout my studentship requires special mention, indeed it has been one of the driving force towards my success in this academic journey. I am therefore very grateful to the supervisory committee.

Universiti Putra Malaysia and its staff deserve to be mentioned and appreciated for the enabling environment and cordial relationship. In particular, I am indebted to all the staff of Universiti Putra Malaysia in the Department of Chemistry, Institute of Biosciences, Institute of Advanced Technology, Faculty of Environment, School of Graduate Studies, International Office, Students Affairs Division and Sultan Abdussamad Library. I would also like to express my gratitude to my laboratory mates with whom I traveled with, in this long journey. My friends and acquaintances at Universiti Putra Malaysia are numerous but I would like to specifically mention and appreciates the contributions of Dr. Faruq Ahmad Ali, Dr. Umar Ibrahim Gaya, Dr. Abubakar S. Junaidu, Dr. Sanusi Ahmad, Dr. Salisu Buhari, Dr. Bello Umar Tambuwal, Dr. Muhammad Sani Jabo, Dr. Lauwali A. Alkali, Dr. Kabiru Mohammed, Dr. Aisha Larba Yusuf, Malam Abubakar Roko, Malam Ja'afar Ahmad, Dr. Ibrahim Mu'azu, Dr. Abubakar Alhaji Amali, Dr. Garba Ibrahim Tanko, Dr. Nura Allumi Abubakar, Dr. Muhammad Kamal Uddeen, Dr. Eshraq A. Ahmad, Alhaji Faruk Sani Baiti, Malam Sani Muhammad, Engr. Dr. A. S. Abdullahi, Dr. Shafi'u Abdullahi Kamba (of blessed memory), Malam Shamsuddeen A. Rufa'i, Malam Danlami Umar Zuru, Mrs. Hannatu Abubakar Sani, Malam Aliyu Muhammad, Malam Aliyu Umar Gusau, Malam Faruk Umar Ambursa and Brothers Lamin Sanyang and Al'amin (Junior). To all of them and the countless others that I could not mention I am grateful and pray for your successes in this world and the next one.

This acknowledgement would be deficient without appreciating the tremendous support I received from my extended family members, childhood friends and colleagues in Nigeria. Almost everyone from my extended family has supported me in one way or the other towards the success of my studies and spaces of this thesis may not be sufficient to contain the list. The moral upbringing by my father of blessed memory (Alhaji Muhammadu Bello Liman) and my aged mother Alhajiya Aminatu Liman Bello served as the wheels of my beautiful without which I wouldn't have reached this far. May they be rewarded with the Garden of Paradise of the highest rant, aameen. For other family members too numerous to mention, I would only specifically mention the supports from Alhaji Ahmadu Bello Liman (Tafidan Tambuwal), Alhaji Faruk Liman, Alhaji Usman Liman, Professor Riskuwa Arabu Shehu, Alhaji Arabu Liman, Alhaji Aminu Liman, Alhaji Bello Liman, Hajiya Hadizatu Liman, Basharu Liman, Hodio Bello Liman, Sambo Liman, Alhaji Abba Shehu, Kabiru Liman, Alhaji Ibrahim Liman, Alhaji Sanusi Liman, Alhaji Gazali Liman, Alhaji Ibrahim Shehu, Mujtaba Liman Arabu, Mu'azu Shehu, Alhaji Zayyanu Shehu and Buhari Bello Bayero. I am greatly indebted to all of you and those I couldn't mention due to limited space. Amongst my

colleagues and childhood friends who has made great impact on this rough journey are: Dr. Aminu Muhammad Bayawa, Dr. Ahmad Uba, Dr. Abdullahi Bako Rabah, Dr. Abdullahi Muhammad Sokoto, Malam Hassan Shehu Bodinga, Malam Kabiru Sidi, Malam Abubakar Aliyu, Malam Mode Muhammad Shagari, Malam Abubakar Bala, Malam Abdullahi Zubairu, Malam Sani Muhammad Dogon Daji, Malam Ibrahim Hassan Mustapha, Malam Dahiru Danliti Gambo, Alhaji Usman Abubakar Masanawa, Alhaji Yahaya Abdullahi Shinkafi, Alhaji Lamido Mamman, Buhari Muhammad Sallama, Alhaji Abubakar Bello, Abubakar Alhaji Tambuwal, Alhaji Umaru Shehu Aula. I also wish to single out my teacher, mentor and now a senior colleague, Professor Lawal G. Hassan for immeasurable support I received from him throughout my study period. May all of you be rewarded handsomely, aameen.

It is inconvenient upon me to register my profound appreciation to the management of Usmanu Danfodiyo University, Sokoto for completely sponsoring my study and being there for me at all times of need. Their magnanimous support is unquantifiable and the bedrock of my success. In particular, I wish to acknowledge the former Vice chancellor, Professor Riskuwa Arabu Shehu, the current Vice chancellor (who doubles as my teacher), Professor Abdullahi Abdu Zuru and the current Registrar, Alhaji Muhammad Kakale Jabo for their supports especially towards the end of my program. The support from the Sokoto State Government through the Sokoto State Scholarship Board is also appreciated. May the organizations and the individuals who contributed towards my success be rewarded in the best way, aameen.

No matter how beautiful a car appears, you cannot reach your destination with it if the engine is not in good working condition. My immediate family served not only an engine of my beautiful car but a sound one. All the supports and encouragements I received from all the groups above wouldn't have made my journey an easy and successful one if I had lost the love, patience and enthusiasm of my family on this rough road of my journey. My lovely and humble wives (Hajiya Rabi'atu Shehu and Malama Asma'u Saa'idu Aliyu) were very supportive to me throughout this journey and have trained and imbibed in my children the good morals that have equipped them in persevering the injuries inflicted on them by the absence of their dear father. Nasiru, Fatima (Ummi), Usama, Harisu, Sanusi, Abubakar (Sadiq), Muhammadu Bello (Baffa), Umar Al-Faruq and Usman (Zunnurain) I love you all and appreciate your patience and understanding. May we all live long to enjoy the fruits of these efforts and sacrifices we collectively made, aameen.

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

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

Mohd Zobir Hussein, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work
- quotations, illustrations and citations have been duly referenced
- the thesis has not been submitted previously or comcurrently for any other degree at any institutions
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be owned from supervisor and deputy vice –chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature: _____ Date: _____

Name and Matric No: Liman Muhammad Gidado, GS27253

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature: _____
Name of Chairman of Supervisory Committee: Abdul Halim bin Abdullah, PhD

Signature: _____
Name of Member of Supervisory Committee: Mohd Zobir Hussein, PhD

Signature: _____
Name of Member of Supervisory Committee: Zulkarnain Zainal, PhD

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBRAVIATIONS

BET	Brunauer – Emmet – Teller
BJH	Barret – Joyner – Haalenda
COD	Chemical Oxygen Demand
DRS	Diffuse Reflectance Spectroscopy
EDS	Electron Diffraction Spectroscopy/Energy Dispersive (X-ray) Spectroscopy
EG	Ethylene glycol
FESEM	Field Emission Scanning Electron Microscopy/Microscope
FWHM	Full Width at Half Maximum
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
JCPDS	Joint Committee of Powder Diffraction Standards
NB	Nitrobenzene
PEG	Polyethelene glycol
S400	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 400 ^{o}C for 2 hours.
S500	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 2 hours.
S600	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 600 ^{o}C for 2 hours.
SGE1	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 2 hours.
SGE2	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 4 hours.
SGE3	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 6 hours.
SGP1	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 2 hours.
SGP2	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 4 hours.
SGP3	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 ^{o}C for 6 hours.
SGHP	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method and calcined at 500 ^{o}C for 2 hours.

SP1	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 0.25% Co and calcined at 500 ^{o}C for 2 hours.
SP2	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 0.50% Co and calcined at 500 ^{o}C for 2 hours.
SP3	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 1.0% Co and calcined at 500 ^{o}C for 2 hours.
TEM	Transmission Electron Microscopy/Microscope
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
UHPLC	Ultra High Performance Liquid Chromatography
UV	Ultraviolet
Vis	Visible
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
ZC	Commercial zinc oxide (Sigma-Aldrich)

CHAPTER 1

INTRODUCTION

1.1 Background

There is no disputing the fact that, rapid globalization and industrialization brought about by advancement in science and technology has been a source of blessing to this world. However, the development has not being without many challenges. The major of these challenges is inadequacy of clean and sanitized drinking water. It was estimated that around 4 billion people worldwide are suffering from clean and sanitized water supply and millions people died due to severe water borne diseases annually (Malato et al., 2009). Richardson (2008) and Wintgens et al., (2008) reported that, the discharge of wastewater and chemical spillage from industries into water channels has exacerbated the water quality crisis. For instance, Yang and Cheng (2007) and Lu et al., (2009) have reported that, by-products of disinfection process generated from chlorination are carcinogenic to human health, thus leading the world researches to develop more efficient water treatment technologies to remove the persistent organic contaminants from wastewater. Many efforts have been devoted to develop technologies that are capable to eradicate the hazardous materials from wastewater (Orloff, 2003 and Pera-Titus et al., 2004). Among many options, the development of processes to transform the toxic and hazardous pollutants into harmless compounds is one of the most effective solutions. However, initially, traditional methods were employed in the purification of water which later turns out to be nondestructive (Abramovic et al., 2004), because of their inability to degrade the organic pollutants. Allegre et al., (2004), Padmanabhan et al., (2006), and Gaya and Abdullah (2008) indicated that further treatment is required to destroy the pollutants into final harmless products such as CO_2 and H_2O, which indirectly increases operational cost (Gaya & Abdullah, 2008). Other researchers who worked on Advanced Oxidation Processes includes, Kaniou et al., (2005), Erquez and Pichat (2006), Parida et al., (2006), Uddin et al., (2007), Kaneco et al., (2009) and (Rao et al., (2009). The advanced - oxidation processes -are designed based on the generation of highly reactive species such as $H_2O_2, {}^{\bullet}OH, {}^{\bullet}O_2^{-}$ and O_3 for the complete destruction of refractory organic compounds (Konstantinou and Albanis, 2004 and Pera-Titus et al., 2004). The commonly used semiconductors employed in the photocatalytic processes includes, TiO_2, ZnO, CuO, Nb_2O_5 and ZnS. The photocatalytic process is normally undertaken under ambient condition and atmospheric oxygen (Chatterjee and Dasgupta, 2005). Fujishima, Rao, & Tryk, (2000), Carp et al., (2004), Grasian (2005) and Zainal et al., (2005) have identified TiO_2 as the main semiconductor used owing to its inertness (chemically and biologically), efficiency, cost effectiveness and being readily available. However, Daneshvar, Salari, & Khataee, (2004) and Akyol et al., (2004) both viewed ZnO as a suitable alternative to TiO_2 because of the former's having nearly the same band gap as the latter, follows the same mechanism of photodegradation and sometimes rated high in photocatalytic performance. Gaya and Abdullah (2008) have extensively reviewed the papers related to the use of TiO_2 in heterogeneous photocatalytic degradation of organic contaminants. In their review,

they have identified important achievements and problems recorded in recent work done until 2007 (Gaya & Abdullah, 2008).

Nitroaromatic compounds such as nitrobenzene and nitrophenols are largely synthesized and particularly often occur in water bodies as toxic pollutants. The degradation of these compounds in the environment via direct photolysis and by biological treatment is difficult and usually slow. Experimental results suggested the UV:H_2O_2 process as an effective and efficient technology for complete mineralization of nitrobenzene and nitrophenols. Comprehensive reaction mechanism for nitrobenzene photolysis was proposed with detailed discussions (Bing et al., 2006). The degradation mechanism of p-nitrophenol (p-NP) exposed to 254 nm UV light was studied in the presence and absence of oxygen respectively via both steady-state photolysis and time-resolved laser flash photolysis (LFP) experiments (S. Zhao et al., 2010).

1.2 Research problem and Objectives

1.2.1 Research problem

Although, substantial research reports are available on the semiconductor photocatalytic activity in the removal of many organic pollutants very little has been reported on nitrobenzene removal. There are reports on the removal of chlorinated phenolic compounds using TiO_2. (Sehili et al., (1989, 1991) reported the use of ZnO on the removal of 4-choloro phenol and 2,4-dicholoro phenol in the presence of UV light. Also, there are many reports on the removal of chorophenoxy herbicides by titania (Tanaka and Reddy 2002; Kamble et al., 2006; Bahnemann et al., 2007; Giri et al., 2007; and (Singh et al., 2007; Singh et al., 2007) with few reports on the same herbicides utilizing ZnO (Djebbar and Sehili, 1998). Nitrobenzene is a nitro aromatic hydrocarbon used to produce aniline and it was nominated by the National Institute of Environmental Health Sciences for listing in the Report on carcinogens based on the conclusions of an International Agency for Research on Cancer (IARC) working group that there is sufficient evidence of its carcinogenicity in experimental animals and that it is possibly carcinogenic to humans (Technology Planning and Management Corporation, 2002). Minero et al., (1994) reported that degradation of nitrophenols is slightly faster than that of nitrobenzene. They also reported that TiO_2 showed better efficiency on the degradation of nitrobenzene than ZnO. Nitrobenzene is considered to be highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, and dye production (Li et al., 2006) yet very little work was conducted on its removal. Li et al., (2006) reported the use of excimer UV lamp (λ = 172 nm) in degrading nitrobenzene and confirmed that, the degradation is more efficient with UV/H_2O_2 combination than using UV alone. Many synthesis methods were reported for the preparation of semiconductor photocatalysts including using mixed oxides/couple semiconductor, combined methods, doping etc. But no report has been seen where ZnO was synthesized via the combination of sol-gel and hydrothermal method, especially the one utilizing polyethelene glycol or ethylene glycol surfactants. Hence, the reason why this research focuses its attention on the removal of this persistent organic pollutant using ZnO, particularly ZnO prepared via a combined method of sol-gel and hydrothermal methods.

The use of ZnO synthesized via different methods and the comparison with commercial ZnO in terms of photoactivity in degrading organic pollutants vis-a-vis its characteristic properties are well documented by various researchers. The literatures provide the strength and weakness of most methods and suggest ways of improving them. In another part, some literatures studied and compared the role of ZnO in degrading organic pollutants in comparison with some other semiconductor photocatalysts, more especially, TiO_2. In many instances, it was reported that doping semiconductor with metals/metal oxides is capable of enhancing its photoactivity and ZnO was not an exception. Method of synthesis has also been linked up with the photoactivity of synthesized photocatalysts because of its capability to affect its characteristics by transforming its physical and chemical properties. To objectively contribute to the world of photocatalysis especially in organic pollutants degradation, one needs to critically, select the right semiconductor to use; select the synthesis method that is perceived to be economical, friendly and capable of producing a high catalytic product; assess the need or otherwise for modification and also optimize the operational conditions for the photocatalytic reactions. The ZnO nanoparticle has been not to perform very well in degrading many organic pollutant within the UV region but act poorly when exposed to visible light radiation. The fast depleting non renewable energy sources has tilted the attention of many researchers towards harnessing energy from the renewable source towards meeting the world's high energy demand. One of the readily available and affordable source is the solar radiation (46% of which is in the visible region). Therefore, getting a semiconductor that can perform very well in the visible region will a remarkable achievement.

In line with the above criteria and in cognizance with available information in the literature, this research will focus its synthesis on using a combined sol-gel and hydrothermal methods and the modification of the samples using cobalt nitrate. Each of this two methods has merits and demerits in terms of producing a desired product, however, the combination of the two methods is believed to be promising in producing a product with better activity than a product produced via either of the two methods. A combination of the two methods is capable of producing product with high purity, reduced particle size, high crystallinity, nanoscale product, high light harvesting character and which is ecofriendly (Vijayan et. al., 2006). The aim of modification of a semiconductor by doping is to improve the photocatalytic activity of the semiconductor and most probably avoid surface recombination. However, different metal/metal oxide has varied contribution they make towards improving photoactivity of a semiconductor, it is therefore pertinent to note the right metal/metal oxide to select in effecting doping. Cobalt is one of the many transition metals used in doping semiconductor and it has been reported in some literature (Barakat et al., 2005; (Walsh et al., 2008); Rasouli et al., 2011; Udayakumar et al., 2012; Zhao et al., 2012; (Caglar, 2013); (Fu et al., 2013); (Rajbongshi & Samdarshi, 2014) that, it is capable of reducing the particle size of the semiconductor, capable of producing extra absorption peak, capable of producing semiconductor that favors red shift, capable of reducing the band gap energy of the semiconductor. These qualities of cobalt and the fact that its ionic size is almost the same with that of zinc ion informed our choice of cobalt for the modification process. Based on broad literature review, we did not see any work where synthesis of ZnO nanoparticle via a combination of sol-gel and hydrothermal using PEG2000 surfactant and modified using cobalt, was reported. And very few research work on the removal of nitrobenzene by semiconductor photocatalysts were reported, in particular no report has been made on the removal of nitrobenzene using ZnO synthesized via this method. Therefore, this research study with potentials of producing ZnO nanoparticle via

combined sol-gel and hydrothermal and modified with cobalt; capable of degrading nitrobenzene utilizing both UV and visible light sources will be an immense contribution, especially considering the fact that most of the photocatalytic activities of ZnO utilizes UV light.

1.2.2 Project objectives

The main aim of this study is to synthesize cobalt doped ZnO via a combination of sol-gel and hydrothermal methods for the removal of nitrobenzene. The scope of my research includes and limited to synthesizing ZnO nanoparticles via Solgel and combination of Solgel and Hydrothermal methods utilizing ethylene glycol and polyethelene glycol surfactants as well as the modification of some selected samples with cobalt. The Solgel synthesized samples using both surfactants would be subjected to different time of calcinations (2, 4 and 6 hours) while the samples from the best surfactant would further be subjected to different calcination temperature (400, 500 and 600 ^{o}C). Various samples synthesized would be characterize using different techniques to ascertain its properties. The samples characterized would be applied in the removal of nitrobenzene using known concentration, as well as relating the characteristic properties of the samples with their photoactivity against nitrobenzene.

The specific research objectives include:

1. To synthesize ZnO nanoparticles via sol-gel and Solgel-hydrothermal methods using ethylene glycol and polyethelene glycol surfactants under different synthesis conditions and subsequent modification (via doping) of the sample with cobalt.
2. To characterize the different synthesized samples in terms of its phase, crystallinity, surface area, morphology, and band gap using XRD, TEM, FESEM, DRS, BET, EDX and XRF
3. To study the removal of nitrobenzene using the various samples under different operating conditions and ascertain the extent of mineralization of the nitrobenzene.

REFERENCES

AbdElHady, M. M. (2012). Preparation and Characterization of Chitosan/ZnO NP for Imparting Antibacterial and UV Protection to Cotton Fabric. *International Journal of Carbohydrate Chemistry*, 1–6. http://doi.org/10.1155/2012/840591

Abdollahi, Y., Abdullah, A. H., Zainal, Z., & Yusof, N. A. (2011a). Photodegradation of m-cresol by Zinc Oxide under Visible-light Irradiation. *International Journal of Chemistry*, *3*(3), 31–43. http://doi.org/10.5539/ijc.v3n3p31

Abdollahi, Y., Abdullah, A. H., Zainal, Z., & Yusof, N. A. (2011b). Photodegradation of o-cresol by ZnO under UV irradiation, (8), 135–144.

Abdollahi, Y., Abdullah, A. H., Zainal, Z., & Yusof, N. A. (2012). Photocatalytic Degradation of p-Cresol by Zinc Oxide under UV Irradiation. *International Journal of Molecular Sciences*, *13*(1), 302–15. http://doi.org/10.3390/ijms13010302

Abdollahi, Y., & Halim, A. (2011). Photodegradation of p -cresol by Zinc Oxide under Visible Light, *1*(5), 99–105.

Abramovic, B. F, Anderluh, V. B., Topalov, A. S., F. F. G. (2004). Kinetics of photocatalytic removalof 2-amino-5-chloropyridine from water. *APTEFF*, *35*, 1–280.

Akyol, A., Yatmaz, H. C., M., Bayramoglu. (2004). Photocatalytic decolorization of Remazol Red RR in aquoeus ZnO suspensions. *Applied Catalysis B: Environmental, 54*, 19 - 24.

Akyol, A. & Bayramoglu, M. (2005). Photocatalytic degradation of Remazol Red F3B using ZnO. *Journal of Hazardous Materials, 124*, 241 - 246.

Ali, M. M. (2011). Characterization of ZnO thin films grown by chemical bath deposition. *Journal of Basrah Researches (Sciences), 37,(3A)*, 49 - 56.

Allegre, C., Maisseu, M. Charbit, F. and Moulin, P. (2004). Coagulation-flocculation-decantation of dye house effluents: concentrated effluents. *Journal of Hazardous Materials, 116*, 57 – 64.

Anandan, S., Ohashi, N., Miyauchi, M. (2010). ZnO-based visible-light photocatalyst: Band gap engineering and multi-electron reduction by co-catalyst. *Applied Catalysis B: Environmental, 100*, 502 - 509.

Anpo, M., & Y. Kubokawa. (1984). Photoluminnescence of zinc oxide powder as a probe of electron-hole surface processes. *Journal of Physical Chemistry, 88,* 5556 - 5560.

Arana, J., Neito, J. L. M., Melian, J. A. H., Rodriguez, J. M. D., Diaz, O. G., Perna, J. P., Bergasa, O., Alvarez, C., J., Mendez (2004). Photocatalytic degradation of

formaldehyde containing wastewater from veterinarian laboratories. *Chemosphere, 55,* 893 - 904.

Asl, S. K., Sadrnezhaad, K., Kianpoorrad, M. (2008). Photocatalytic Decolorization of Red Dye in Aqueous ZnO-TiO_2 Suspensions. *Advanced Materials Research, 55 - 57,* 577 - 580.

Atkins, P. & de Paula, J. (2002). Physical Chemistry. New York: Oxford University Press Inc.

Bahadur, H., Srivastava, A. K., Haranath, D., Chander, H., Basu, A., Samanta, S. B. Sood, K. N., Sharma, R. K., Rashmi, R. K., Bhatt, V. Pal, P., Chandra, S. (2007). Nano-structured ZnO films by sol-gel process. *Indian Journal of Pure & Applied Physics, 45,* 395 - 399.

Bahnemann, D. W., Kormann, C., M. R. Hoffmann (1987). Preparation and characterization of quantum size zinc oxide: A detailed spectroscopic study. *Journal of Physical Chemistry, 91,* 3789 - 3798.

Barakat, M. A., Hayes, G., Shah, I. (2005). Effect of Cobalt Doping on the Phase Transformation of TiO_2 Nanoparticles. *Journal of Nanoscience and Nanotechnology, Vol. X,* 1 - 7.

Barick, K. C., Singh, S., Aslam, M., Bahadur, D. (2010). Porosity and photocatalytic studies of transition metal doped ZnO nanoclusters. *Microsporous and Mesoporous Materials, 134,* 195 - 202.

Barnes, R. J., Molina, R., Xu, J., Dobson, P. J., Thompson, I. P. (2013). Comparison of TiO_2 and ZnO nanoparticles for photocatalytic degradation of methylene blue and the correlated inactivation of gram-positive and gram-negative bacteria. *J. Nanopart. Res., 15,* 1432.

Baruah, S., & Dutta, J. (2009). Hydrothermal growth of ZnO nanostructures. *Science and Technology of Advanced Materials*, *10*(1), 013001. http://doi.org/10.1088/1468-6996/10/1/013001

Bauer, C., Boschloo, G. Mukhtar, E., A., Hagfeldt (2004). Ultrafast relaxation dynamics of charge carriers relaxation in ZnO nanocrystalline thin films. *Chem. Phys. Lett., 387,* 176 - 181.

Behnajady, M. A., Modirshahla, N., Hamzavi, R. (2006). Kinetic study on photocatalytic degradation of C. I. Acid and Ywllow 23 by ZnO photocatalyst. *Journal of Hazardous Materials, 133,* 226 - 232.

Bhatkhande, D. S., Kamble, S. P., Sawant, S. B., V. G. Pangarkar (2004). Photocatalytic and photochemical degradation of nitrobenzene using artificial ultraviolet light. *Chem. Eng. J., 102,* 283 - 290.

Bin Liu and Hua Chun Zeng. (2002). Hydrothermal Synthesis of ZnO Nanorods in the Diameter Regime of 50 nm. *Journal of American Chemical Society Communications, 125,* 4430 – 4431.

Brady, J. E., Russell, J. W., Holum, J. R. (2000). Chemistry Matters and its changes. New York: John Wiley and Sons Inc.

Brunauer, S., Emmett, P. H., E. Teller (1938). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc., 60,* 309.

Caglar, Y. (2013). Sol – gel derived nanostructure undoped and cobalt doped ZnO : Structural , optical and electrical studies, *560*, 181–188.

Carp, O., Hiusman, C. L., A. Reller (2004). Photoinduced reactivity of Titanium dioxide. *Prog. Solid State Chem., 32,* 33 - 177.

Cavaleri, J. J., Skinner, D. E., Colombo, Jr., D. P., R. M. Bowman (1995). Fentosecond study of the size-dependent charge carrier dynamics in ZnO nanocluster solutions. *J. Chem Phys. 103,* 5378.

Chatterjee, D. && Dasgupta, S. (2005). Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 6*, 186 - 205.

Chatzitakis, A., Berberidou, C. Paspaltsis, I., Kyriakou, G., Sklaviadis, T., Poulios, I. (2008). Photocatalytic degradation and drug activity reduction of chloramphenicol. *Water research, 42*, 386 - 394.

Chen, B., Yang Chun, G. N. K. (2006). No Title. *Journal of Environmental Science*, *18*(6), 1061–1064.

Chong, M. N., Lei, S., Jin, B., Saint, C., Chow, C. W. K. (2009). Optimization of an annular photoreactor process for degradation of Congo Red using a newly synthesized titania impregnated kaolinite nano-photocatalyst. *Separation and Purification technology, 67*, 355 - 363

Colombo Jr., D. P., Skinner, D. E., Cavaleri, J. J., R. M. Bowman. Fentosecond spectroscopy of quantum and bulk-sized semiconductor particles. Paper presented at the ACS National Meeting, Chicago, United States of America. August 1995.

Comparelli, R., Fanizza, E., Curri, M. L., Cozzoli, P. D., Mascolo, G., Passino, R. A., Agostiano (2005). Photocatalytic degradation of azo dyes by organic-capped anatase TiO_2 nanocrystals immobolized onto substrates. *Applied Catalysis B: Environmental, 55*, 81 - 91.

Curco, D., Gimenez, J., Addardak, A., Cerver a-March, S., S. Esplugas (2002). Effects of radiation absorption and catalyst concentration on the photocatalytic degradation of pollutants. *Catalysis Today, 76,* 177 - 188.

Daneshvar, N., Salari, D., & Khataee, A. R. (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry*, *162*(2-3), 317–322.

Davis, A. & Huang, C. (1989). Removal of phenols from water by a photocatalytic oxidation process. *Water Science and Technology, 21*, 455 - 464.

Djebbar, K. Sehili, T. (1998). Kinetics of heterogeneous photocatalytic decomposition of 2,4-dichlorophenoxyacetic acid over titanium dioxide and zinc oxide in aquoeus solution. *Pesticide Science, 54*, 269 - 276.

-Driscoll, L. S.-M. and J. L. M. (2007). ZnO - nanostructures, defects, and devices. *Materialstoday*, *10*(5), 40 – 48.

Ellapan, P. & Miranda, L. R. (2014). Synthesis and Characterization of Cerium Doped Titanium Catalyst for the Degradation of Nitrobenzene Using Visible Light. *Int. J. of Photoenergy*, Vol. 2014, Article ID 756408, 1 - 9

Erquez, R. & Pichat, P. (2006). Different net effect of TiO2 sintering temperature on the photocatalytic removal rates of 4-chlorophenol, 4-chlorobenzoic acid and dichloroacetic acid in water. *Journal of Environmental Science and Health Part A, 41*, 955 - 966.

Evgenidou, E., Fytianos, K., I. Poulios (2005). Semiconductor-sensitized photodegradation of dichloros in water using TiO_2 and ZnO as catalysts. *Applied Catalysis B: Environmental, 59*, 81 - 89.

Fan, Z., & Lu, J. G. (2005). Zinc Oxide Nanostructures: Synthesis and Properties, Journal of Nanoscience and Nanotechnology, 2005, 1 - 19.

Feng, J., Han, J., X. Zhao (2009). Synthesis of $CuInS_2$ quantum dots on TiO_2 porous films by solvothermal method for absorption layer of solar cells. *Prog. Org. Coat., 64*, 268 - 273.

Fermandez, A., Lassaletta, G., Jimenez, V. M., Justo, A., Gonzalez-Elipe, A. R., Jerrmann, J. M., Tahiri, H., Ait-Ichou, Y. (1995). Preparation and characterization of TiO2 photocatalysts supported on various rigid supports (glass, quartz, and stainless steel): Comparative studies of photocatalytic activity in water purification. *Applied Catalysis B, 7*, 49 - 63.

Friesen, D. A., Morello, L., Headleya, J. V., C. H. Langford (2000). Factors influencing relative efficiency in photo-oxidations of organic molecules by $Cs_3PW_{12}O_{40}$ and TiO_2 colloidal photocatalysts. *J. Photochem. Photobiol. A: Chem., 133*, 213 - 220.

Fu, J., Ren, X., Yan, S., Gong, Y., Tan, Y., Liang, K., Wu, Z. (2013). Synthesis and structural characterization of ZnO doped with Co : Impurity, *558*, 212–221.

Fu, X., Clark, L. A., Zeltner, W. A., M. A., Anderson (1996). Effects of reaction temperature and water vapor content on the heterogeneous photocatalytic oxidation of ethylene. *J. Photochem. Photobiol. A: Chem., 97*, 181 - 186.

Fujishima, A., Rao, T. N., D. A., Tryk (2000). Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C: Photochem.Rev., 1*, 1 - 21.

Gaya, U. I. (2009). *Zinc oxide catalysed photo-oxidative degradation of chlorophenols*. PhD Thesis (unpublished) Universiti Putra Malaysia.

Gaya, U. I., & Abdullah, A. H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *9*(1), 1–12. http://doi.org/10.1016/j.jphotochemrev.2007.12.003.

Gayen, R. N., Bhar, R., Pal, A. K. (2010). Synthesis and characterization of vertically aligned ZnO nanorods with controlled aspect ratio. *Indian Journal of Pure & Applied Physics, 48,* 385 - 393.

Ghanbarnezhad, S., Abolfazli, M., Nemati, A. (2013). Effect of Time and Calcination Temperatures on Synthesis of Zinc Titanate Nano-Crystal Powder via Combustion Technique. *Int. J. Emerg. Sc., 3 (1),* 108 - 118.

Giri, R. R., Ozaki, H., Ishida, T., Takanami, R., Taniguchi, S. (2007). Synergy of ozonation and photocatalysis to mineralize low concentration 2,4-dichlorophenoxyacetic acid in aqueous solution. *Chemosphere, 66,* 1610 - 1617.

Grasian, V. H., *Environmental catalysis*; CRC press, Taylor and Francis Group: New York. 2005.

Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., J-M. Hermann (2003). Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2: Comparison of the efficiency of powder and supported TiO_2. *J. Photochem. Photobiol. A: Chem., 158,* 27 - 36.

Haque, M. M. & M., Muneer (2007). Photodegradation of norfloxacin in aqueous suspensions of titanium dioxide. *Journal of Hazardous Materials, 145,* 51 - 57.

Haque, M. M., M., Muneer, Bahnemann, D. W. (2006). Semiconductor-mediated photocatalyzed degradation of a herbicide derivative, chlorotoluron, in aqueous suspensions. *Environmental Science and Technology, 40,* 4765 -4770.

Hasnat, M. A., Uddin, M. M., Samed, A. J. F., Alam, S. S., Hossain, S. (2007). Adsorption and photocatalytic decolorization of a synthetic dye erythrosine on anatase TiO_2 and ZnO surfaces. *Journal of Hazardous Materials, 147,* 471 - 477.

Hayat, K., Gondal, M. A., Khaled, M. M., Ahmed, S., Shemsi, A. M. (2011). Nano ZnO synthesis by modified sol-gel method and its application in heterogeneous photocatalytic removal of phenol from water. *Applied Catalysis A: General, 393,* 122 - 129.

Hermann, J-M. (1999). Heterogeneous photocatalysis: fundamentals and application to the removal of various types of aqueous pollutants. *Catalysis Today, 53,* 115 - 129.

Hong, R. Y., Zhang, S. Z., Di, G. Q., Li, H. Z., Zheng, Y., Ding, J., Wei, D. J. (2008). Preparation, characterization and application of Fe_3O_4/ZnO core/shell magnetic nanoparticles. *Materials Research Bulletin, 43,* 2457 - 2468.

Hong, R., Pan, T., Qian, J., Li, H. (2006). Synthesis and surface modification of ZnO nanoparticles. *Chemical Engineering Journal, 119,* 71 - 81.

Hsieh, C-H. (2007). Spherical ZnO NP from Zinc Acetate in the Precipitation method. *J. of the Chinese Chem. Soc. 34,* 31 – 34.

Jayaweera, P. V. V., Perera, A. G. U., K. Tennakone (2008). Why Gratzel's cell works so well. *Inorganic Chim. Acta., 361,* 707 - 711.

Jianguo, Lv., Wanbing, G., Kai, H., Jianho, Z., Fanming, M., Xueping, S., Zhaoqi, S. (2011). Effect of annealing temperature on photocatalytic activity of ZnO thin films prepared by sol-gel method. *Superlattices and Microstructures, 50,* 98 - 106.

Jing, L., Xu, Z., Sun, X., Shang, J., W., Chai (2001). The surface properties and photocatalytic activities of ZnO ultrafine particles. *Applied Surface Science, 180,* 308 - 314.

Kamalasanan, M. N., Subhas, C. (1996). Sol-gel synthesis of ZnO thin films, *Thin Solid Films, 288,* 112 – 115

Kamat, P. V. & B., Patrick (1992). Photophysics and photochemistry of quantized ZnO colloids. *J. Phys. Chem., 96,* 6829 - 6834.

Kamble, S. P., Sawant, S. B., Pangarkar, V. G. (2006). Photocatalytic mineralization of phenoxyacetic acid using concentrated solar radiation and titanium dioxide in slurry photoreactor. *Chemical Engineering Research and Design, 84,* 355 - 362.

Kaneco, S., Itoh, K., Katsumata, H., Suzuki, T., Ohta, K. (2009). Titanium dioxide mediated solar photocatalytic degradation of thiram in aquoeus solution: kinetics and mineralization. *Chemical Engineering Journal, 148,* 50 - 56.

Kaniou, S., Pitarakis, K., Barlagianni, I., Poulios, I. (2005). Photocatalytic oxidation of sulfamethazine. *Chemosphere, 60,* 372 - 380.

Karanukaran, C. & R. Dhanalakshmi (2008). Semiconductor-catalyzed degradation of phenols with sunlight. *Sol. Energy Mater. Sol. Cells, 92,* 1315 - 1321.

Kaur, M., Randhawa, B. S., Tarsikka, P. S. (2013). Synthesis of $Mg_{0.3}Zn_{0.7}Fe_2O_4$ nanoparticles from thermolysis of magesium zinc tris(maleato)ferrate (III) heptahydrate. *Indian Journal of Engineering & Materials Sciences, 20,* 325 - 328.

Keshavarzi[a], A., Halim, A., & Zainal, Z. (2009). Low-Temperature Synthesis of ZnO by Wet, *4*(2), 163–168.

Khatae, A. R. & Zarei, M. (2011). Photocatalysis of a dye solution using immobolized ZnO nanoparticles combined with photo electrochemical process. *Desalination, 273,* 453 - 460.

Kogo, K., Yoneyama, H., H. Tamura (1980). Photocatalytic oxidation of cyanide on platinized TiO_2. *J. Phys. Chem., 84,* 1705 - 1710.

Konstantinou, I. K. & Albanis, T. A. (2004). TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigation: A review. *Applied Catalysis B: Environmental, 49*, 1 - 14.

Kositizi, M., Poulios, I., Samara, K., Tsatsaroni, E., Darakas, E. (2007). Photocatalytic oxidation of Cibacron Yellow LS-R. *Journal of Hazardous Materials, 146,* 680 - 685.

Kosmulski, M. (2006). pH-dependent surface charging and points of zero charge III. Update. *J. Colloid Interf. Sci., 298,* 730 -741. turated carboxylic acids

Kraeutler, B. & A. J. Bard (1978). Heterogeneous photocatalytic decomposition of saturated carboxylic acids on TiO_2 powder, decarboxylative route to alkanes. *J. Am. Chem. Soc., 100*, 5958.

Lathasree, S., Rao, A. N., SivaSankar, B. Sadasivam, V., K. Rengaraj (2004). Heterogeneous photocatalytic mineralization of phenols in aqueous solutions. *J. Mol. Catal. A: 223,* 101 - 105.

Li, QR., Gu, CZ., Di, Y., Yin, H., Zhang, JY. (2006). Photodegradation of nitrobenzene using 172 nm excimer UV lamp. *Journal of Hazardous Materials B, 133, 68 – 74.*

Lin, C. -F., Wu, C. -H., Onn, Z. -N. (2008). Degradation of 4-chlorophenol in TiO_2, WO_3, SnO_2, TiO_2/WO_3, and TiO_2/SnO_2 systems. *Journal of Hazardous Materials, 154*, 1033 - 1039.

Liu, B., & Zeng, H. C. (2003). Hydrothermal synthesis of ZnO nanorods in the diameter regime of 50 nm. *Journal of the American Chemical Society*, *125*(15), 4430–1. http://doi.org/10.1021/ja0299452

Liu, Z., Deng, J., Li, F. (2008). Fabrication and photocatalysis of CuO/ZnO nanocomposites via a new method. *Materials Science and Engineering B, 150*, 99 - 104.

Lu, C., Wu, Y., Mai, F., Chung, W., Wu, C., Lin, W., Chen, C. (2009). Degradation efficiencies and mechnisms of the ZnO-mediated photocatalytic degradation of Basic Blue 11 under visible light irradiation. *Journal of Molecular Catalysis A: Chemical, 310,* 159 - 165.

Lu, J., Zhang, T., Ma, J. and Chen, Z. (2009). Evaluation of disinfection by-products formation during chlorination and chloroamination of dissolved natural organic matter fractions isolated from a filtered river water. *Journal of Hazardous Materials, 162*, 140 –145.

Mahlakshmi, M., Arabindoo, B., Palanichmy, M., Murugesan, V. (2007). Photocatalytoc degradation of carbonfuran using semiconductor oxides. *Journal of Hazardous Materials, 143*, 240 - 245.

Maksimov, O. (2010). Recent Advances and Novel Approaches of P-Type Doping of Zinc Oxide. *Rev. Adv. Mater. Sci., 24,* 26 - 34.

Malato, S., Fernandez-Ibanez, P., Maldonado, M. I., Blanco, J. and Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today, 147,* 1 – 59.

McBride, R. A., Kelly, J. M., McCormack, D. E. (2003). Growth of well-defined ZnO microparticles by hydroxide ion hydrolysis of zinc salts. *Journal of Materials Chemistry, 13,* 1-7.

Meulenkamp, E. A. (1998). Synthesis and Growth of ZnO Nanoparticles. *Journal of Physical Chemistry B, 102,* 5566 - 5572.

Mills, A. & Hunte, S. L. (1997). An overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry, 108,* 1 - 35.

Minero, C., E. Pelizzetti, P. Piccinini and M. Vincenti (1994), Photocatalyzed Transformation of Nitrobenzene on TiO_2 and ZnO, *Chemosphere, 28 (6),* 1229 – 1244.

Minero, C. & D. Vione (2006). A quantitative evalaution of the photocatalytic performance of TiO_2 slurries. *Applied Catalysis B: Environmental, 67,* 257 - 269.

Mrowetz, M. & E. Selli (2006). Photocatalytic degradation of formic and benzoic acids and hydrogen peroxide evolution in TiO2 and ZnO water suspensions. *J. Photochem. Photobiol. A: Chem., 180,* 15 - 22.

Muradov, N. Z., Raissi, A. T., Muzzey, D., Painter, C. R., M. R. Kemme (1996). Selective photocatalytic destruction of VOCs. *Sol. Energy, 56,* 445 - 453.

Neppolian, B., Choi, H. C., Sakthivel, S., Arabindoo, B., Murugesan, V. (2002). Solar/UV-induced photocatalytic degradation of thre commercial textile dyes. *Journal of Hazardous Materials B, 89,* 303 - 317.

O'Brien, T. S. and P. (1995). Deposition and characterisation of ZnO thin films grown by chemical bath deposition. *Thin Solid Films, 271,* 35 – 38.

Ohyama, M., Kozuka, H., Yoko, T. (1997). Sol-gel preparation of ZnO films with extremely preferred orientation along [002] plane from zinc acetate solution. *Thin Solid Films, 306,* 78 – 85

Orloff, K., H. F. (2003). An international perspective on hazardous waste practices. *International Journal of Hygiene and Environmental Health, 206,* 291 – 302.

Padmanabhan, P. V. A., Sreekumar, K. P., Triyagarajan, T. K., Satputee, R. U., Bhanumurthy, K., Sengupta, P., Dey, G. K. and Warrier, K. G. K. (2006). Nanocrystalline titanium dioxide formed by reactive plasma synthesis. *Vacuum, 80,* 1252 – 1255.

Pal, U. & Santiago, P. (2005). Controlling the Morphology of ZnO Nanostructures in a

Low-Temperature Hydrothermal process, *Journal of Physical Chemistry B, 109,* 15317 – 15321.

Pan, H., Wang, X., Xiao, S., Yu, L., Zhang, Z. (2013). Preparation and characterization of TiO_2 nanoparticles surface-modified by octadecyltrimethoxysaline. *Indian Journal of Engineering & Materials Sciences, 20,* 561 - 567.

Parida, K. M., Dash, S. S., Das, D. P. (2006). Physico-chemical characterization and photocatalytic activity of zinc oxide prepared by various methods. *Journal of Colloid and Interface Science, 298,* 787 - 793.

Peng, L. L., Xie, T. F., Lu, Y. C., Fan, H. M., Wang, D. J. (2010). Synthesis, photoelectric propertiesand photocatalytic activity of the Fe_2O_3/TiO_2 heteregeneous photocatalysts. Physical Chemistry Chemical Physics, 12, 8033 - 8041

Pera-Titus, M., Garcia-Molina, V., Banos, M. A. Gimenez, J, and Esplugas, S. (2004). Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B: Environmental, 47,* 219 – 256.

Peternel, I. T., Koprivanac, N., Bozic,, A. M. L., Kusic, H. M. (2007). Comparative study of UV/TiO_2, UV/ZnO and photo-fenton processes for the organic reactive dye degradationnin aqueoue solution. *Journal of Hazardous Materials, 148,* 477 - 484

Piscopo, A., Robert, D., Weber, J. V. (2001). Comparison between the reactivity of commercial and synthetic photocatalysts. *Journal of Photochemistry and Photobiology A: Chemistry, 139,* 253 - 256

Pourata, R., Khatae, A. R., Aber, S., Daneshver, N. (2009). Removal of the herbicide Benzaton from contaminated water in the presence of synthesized nanocrystalline TiO_2 powders under irradiation of UV-C light. *Desalination, 249,* 301 - 307.

Preetam Singh, Ashvani Kumar, Ajay Kaushal, Davinder Kaur, A. P. and R. N. G. (2008). In situ high temperature XRD studies of ZnO nanopowder prepared via cost effective ultrasonic mist chemical vapour deposition. *Bulletin of Material Science*, *31*(3), 573 –577.

Qian-Rong Li, Cheng-Zhi Gu, Yan Di, Hao Yin, J.-Y. Z. (2006). Photodegradation of nitrobenzene using 172 nm excimer UV lamp. *Journal of Hazardous Materials*, 68–74.

Rabindranathan, S., Devipriya, S., Yesodharan, S. (2003). Photocatalytic degradation of phosphamidon on semiconductor oxides. *Journal of Hazardous Materials, 102,* 217 - 229.

Rajbongshi, B. M., & Samdarshi, S. K. (2014). Applied Catalysis B : Environmental Cobalt-doped zincblende – wurtzite mixed-phase ZnO photocatalyst nanoparticles with high activity in visible spectrum, *144*, 435–441.

Rao, A. N., Sivasankar, B., Sadasivam, V. (2009). Kinetic study on the photocatalytic degradation of salicylic acid using ZnO catalyst. *Journal of Hazardous Material, 166*, 1357 - 161.

Rasouli, S., Valefi, M., Moeen, S. J., Arabi, A. M. (2011). Microwave-assisted gel combustion synthesis of ZnO-Co nano-pigments. *Journal of Ceramic Processing Research, 12*, (4), 450 - 455.

Reli, M., Koci, K., Matejeka, V., Kovar, P., Obalova, L. (2012). Effect of Calcination Temperature and Calcination Time on the Kaolinite/TiO_2 Composite for Photocatalytic Reduction of CO_2. *GeoScience Engineering, 58*, (4), 10 - 22.

Richardson, S. D. (2008). Environmental mass spectrometry:Emerging contaminants and current issues. *Analytical Chemistry, 80*, 4373 – 4402.

Saien, J. & Khezrianjoo, S. (2008). Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO_2 process: Optimization, kinetics and toxicity studies. *Journal of Hazardous Materials, 157*, 269 - 276

Sakthivel, S., Neppolian, B., Shankar, M. V., Arabindoo, B., Palanichamy, M. V., Marugesan (2003). Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. *Sol. Energy Mater. Sol. Cells, 77*, 65 - 82.

Schmidt-Mende, L. & MacManus-Driscoll, J. L. (2007). ZnO – nanostructures, defects, and devices. *Materials Today, **10** (5)*, 40 – 48

Sehili, T., Boule, P., J., Lemaire (1989). Photocatalysed transformation of chloroaromatic derivatives on zinc oxide III: Chlorophenols. *Journal of Photochemistry and Photobioogy A: Chem., 50*, 117 - 127.

Sehili, T., Boule, P., J., Lemaire (1991). Photocatalysed transformation of chloroaromatic derivatives on zinc oxide IV: 2,4-dichlorophenol. *Chemosphere, 22*, 1053 - 1062.

Serpone, N., Lawless, D., Khairutdinov, R., E. Pelizzetti (1995). Subnanosecond relaxation dynamics in TiO_2 colloidal sols (Particle sizes R, = 1.0 - 13.4 nm) relevance to heterogeneous photocatalysis. *Journal of Physical Chemistry, 99*, 16655 - 16661.

Serpone, N. & Pelizzetti, E. (1989). Photocatalysis: Fundamentals and Application. New York: John Wiley and Sons Inc.

Shang, M., Wang, W. Z., Zhang, L., Sun, S. M., Wang, L., Zhou, L. (2009). 3D Bi_2WO_6/TiO_2 hierarchical heterostructure: Controllable synthesis and enhanced visible photocatalytic degradation performances. *Journal of Physical Chemistry C, 113*, 14727 - 14731.

Shifu, C. & C. Gengyu (2006). The effect of different preparation conditions on the photocatalytic activity of TiO_2.SiO_2/beads. *Surface Coating Technology, 200*, 3637 - 3643.

Shriver, D. F & Atkins, P. W. (1999), 3rd Edition, Inorganic Chemistry. New York: Oxford University Press.

Sifontes, A. B., Rosales, M., Mendez, F. J., Oviedo, O., Zoltan, T. (2013). Effect of Calcination Temperature on Structural Properties and Photocatalytic Activity of Ceria Nanoparticles Synthesized Employing Chitosan as Template. *Journal of Nanomaterials, 2013*, Article ID 265797, 1 - 9

Singh, A. K., Multani, S. S., Patil, S. B. (2011). ZnO nanorods and nanopolypods synthesized using microwave assisted wet chemical and thermal evaporation method. *Indian Journal of Pure & Applied physics, 49*, 270 - 276.

Singh, H. K., Saquib, M., Haque, M. M., Muneer, M. (2007). Heterogeneous photocatalyzed degradation of 4-chlorophenoxyacetic acid in aqueous suspensions. *Journal of Hazardous Materials, 142*, 374 - 380.

Singh, H. K., Saquib, M., Haque, M. M., Muneer, M., Bahnemann, D. W. (2007). Titanium dioxide mediated photocatalyzed degradation of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic in aqueous suspensions. *Journal of Molecular Catalysis A: Chemical, 264*, 66 - 72.

Sirtori, C., Altvater, P. K., Freitas, A. M. D., Peralta-Zamora, P. G. (2006). Degradation of aqueous solutions of camphor by heterogeneous photocatalysis. *Journal of Hazardous Materials, 129*, 110 - 115.

Skoog, D. A., Holler, F. J., Nieman, T. A. (1998). Principles of Instrumental Analysis. 5th edition. London: Harcout Brace and Company.

Soares, E. T., Lansarin, M. A., C. C., Moro (2001). A study of process variables for the photocatalytic degradation of Rhodamine B. *J. Braz. Chem. Soc., 24*, 29 - 36.

Sohrabi, M. R., Davallo, M., Miri, M. (2009). Influence of operational parameters on eliminating azo dyes from wastewater by advanced oxidation technology. *International Journal of ChemTech. Res.,* **1** (3), 446 – 451.

Sopyan, I., Singh, R., Hamdi, M. (2008). Synthesis of nano sized hydroxyapatite powder usingsol-gel technique and its conversion to dense and porous bodies. *Indian Journal of Chemistry, 47A*, 1626 - 1631.

Sue, K., Kimura, K., Yamamoto, M., Arai, K. (2004a). Rapid hydrothermal synthesis of ZnO nanorods without organics. *Materials Letters, 58*, 3350 - 3352

Sue, K., Kimura, K., Yamamoto, M., Arai, K. (2004b). Hydrotehrmal synthesis of ZnO nanocrystals using microreactor. *Materials Letters 58*, 3229 - 3231.

Sun, J., Dong, S., Feng, J., Yin, X., Zhao, X. (2011). Enhanced sunlight photocatalytic performance of Sn-doped ZnO for Methylene Blue degradation. *Journal of Molecular Catalysis A: Chemical, 335*, 145 - 150.

Sun, J., Wang, X., Sun, R., Sun, S., L. Qiao (2006). Photocatalytic degradation and kinetics study of Orange G using nano-sized Sn(IV)/TiO_2/AC photocatalyst. *Journal Molecular Catalysis A: Chemical., 260,* 241 - 246.

Sun, S., Ding, J., Bao, J., Gao, C., Qi, Z., Li, C. (2010). Photocatalytic Oxidation of Gaseous Formaldehyde on TiO_2: An In Situ DRIFTS Study. *Catalysis Letters, 137*, 239-246.

Suwanboon, S. (2008). Structural and Optical properties of Nanocrystalline ZnO Powder from Sol-Gel Method. *ScienceAsia, 34*, 031 – 034.

Tanaka, K. & Reddy, K. S. N. (2002). Photodegradation of phenoxyacetic acid and carbamate pesticides on TiO_2. *Applied Catalysis B: Environmental, 39*, 305 - 310.

Tariq, M. A., Faisal, M., Muneer, M., D. Bahnemann (2007). Photochemical r actions of a few selected pesticide derivatives and other priority organic pollutants in aqueous suspensions of titanium oxide. *Journal of Molecular Cataysis A: Chemical., 265*, 231 - 236.

Tunesi, S. & M. A. Anderson (1987). Photocatalysis of 3,4-DCB in TiO_2 aqueous suspension; Effects of temperature and light intensity; CIR-FTIR interfacial analysis. *Chemosphere, 16*, 1447 - 1456.

Turchi, C. S. & D. F., Ollis (1990). Photocatalytic degradation of water organic contaminants. *J. Catal., 122*, 178 - 192.

Udayakumar, S., Renuka, V., Kavitha, K. (2012). Structural, optical and thermal studies of cobalt doped hexagonal ZnO by simple chemical precipitation method. *J. of Chemical and Pharm. Research, 4 (2),* 1271 - 1280

Uddin, M. M., Hasnat, M. A., Samed, A. J. F., Majumdar, R. K. (2007). Influence of TiO_2 and ZnO photocatalysts on adsorption and degradation behaviour of erythrosine. *Dyes and Pigments, 75*, 207 - 212.

Ujhidy, A., Szabo-Bardos, E., Horvath, O., Schmidt, K. (2011). Degradation of Organic pollutants in photocatalytic reactors. *Hungarian J. of Industrial Chemistry, 39 (3)* 381 - 386.

Umar Ibrahim Gaya, Abdul halim Abdullah, Z. Z. and M. Z. H. (2010). Photocatalytic Degradation of 2,4-dichlorophenol in Irradiated Aqueous ZnO Suspension. *International Journal of Chemistry*, *2*(1), 180 – 193.

Vafaee, M. & Ghamsari, M. S. (2006). Preparation and characterization of ZnO nanoparticles by a novel sol-gel route. *Materials Letters, 61,* 3265 - 3268.

Verma, A. & Srivastava, A. K. (2011). Sol-gel derived nanostructured zinc oxide for bright luminescence in ultraviolet and visible spectral regions. *Indian Journal of Chemistry, Vol. 50A*, 1697 - 1702.

Vijayan, P., Gurulakshmi, M., Deepa, G., Shanthi, K. (2009). In proceeding of National

level seminar, National Chem. Lab., Pune, India.

Walsh, A., Da Silva, J., & Wei, S.-H. (2008). Theoretical Description of Carrier Mediated Magnetism in Cobalt Doped ZnO. *Physical Review Letters*, *100*(25), 256401. http://doi.org/10.1103/PhysRevLett.100.256401

Wang, C., Shao, C., Wang, L., Zhang, L., Li, X., Liu, Y. (2009). Electrospinning preparation, characterization and photocatalytic propeties of Bi_2O_3 nanofibers. *Journal of Colloid and Interface Science, 333*, 242 - 248.

Wang, C-M., Heller, A., H. Gerischer (1992). Palladium catalysis of O2 reduction by electrons accumulated on TiO_2 particles during photo-assisted oxidation of organic compounds. ournal of *American Chemical Society, 114*, 5230 - 5234.

Wintgens, T., Salehi, F., Hochstrat, R. and M. T. (2008). Emerging contaminants and treatment options in water recycling for indirect potable use. *Water Science and Technology*, *57*, 99 – 107.

Wittmar, A., Gautam, D., Schilling, C., Dorfler, U., Mayer-Zaika, W., Winterer, M., Ulbricht, M. (2014). Stable zinc oxide nanoparticle dispersions in ionic liquids. *Journal of Nanoparticle Resources, 16*, 2341

Wu, L., Wu, Y., W., Lu (2005). Preparation of ZnO nanorods and optical characterizations. *Physica E., 28*, 76 - 82.

Wu, W., Gao, S., Tu, W., Chen, J., Zhang, P. (2010). Intensified photoctalytic degradation of nitrobenzene by pickering emulsion of ZnO nanoparticles. *Particuology, 8*, 453 - 457.

Xia, K., Ferguson, D., Djaoued, Y., Robichaud, J., Tchoukanova, N., Bruning, R., McCalla, E. (2010). Template-free synthesis and photocatalytic activity of hierarchical porous titania with controlled texture and crystalline structure. *Applied Catalysis A: General, 387*, 231 - 241.

Yang, M., Guo, Z., Qiu, K., Long, J., Yin, G., & Guan, D. (2010). Applied Surface Science Synthesis and characterization of Mn-doped ZnO column arrays. *Applied Surface Science*, *256*(13), 4201–4205. http://doi.org/10.1016/j.apsusc.2010.01.125

Yang, H. and Cheng, H. (2007). Controlling nitrite level in drinking water by chlorination and chloramination. *Separation and Purification Technology*, *56*, 392 – 396.

Yu, C., Yang, K., Shu, Q., Yu, J. C., Cao, F. F., Li, X. (2011). Preparation of WO_3/ZnO composite photocatalyst and its photocatalytic performance. *Chinese Journal of Catalysis, 32*, 555 - 565.

Zainal, Z., Hui, L. K., Hussein, M. Z., Taufiq-Yap, Y. H., Abdullah, A. H., I. Ramli (2005). Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps. *Journal of Hazardous Material B, 125*, 113 - 120.

Zhang, X., & Liu, Q. (2008). Visible-light-induced degradation of formaldehyde over titania photocatalyst co-doped with nitrogen and nickel, *254*, 4780–4785. http://doi.org/10.1016/j.apsusc.2008.01.094

Zhao, J., Wang, L., Yan, X., Yang, Y., Lei, Y., Zhao, J., Huang, Y., Gu, Y., Zhang, Y. (2011). Structure and photocatalytic activity of Ni-doped ZnO nanorods. *Materials Research Bulletin*, *46*, 1207 – 1210.

Zhao, S., Ma, H., Wang, M., Cao, C., Xiong, J., Xu, Y., & Yao, S. (2010). Study on the mechanism of photo-degradation of p-nitrophenol exposed to 254 nm UV light. *Journal of Hazardous Materials*, *180*(1-3), 86–90. http://doi.org/10.1016/j.jhazmat.2010.03.076

Zhao, Y., Yan, X., Kang, Z., Fang, X., Zheng, X., Zhao, L., Du, H., Zhang, Y. (2014). Zinc oxide nanowires-based electrochemical biosensor for L-lactic acid amperometric detection. *Journal of Nanoparticle Resources*, *16*, 2398.

LIST OF PUBLICATIONS

M. G. Liman, A. H. Abdullah, M. Z. Hussein and Z. Zainal, Photodegradation of Nitrobenzene Using Cobalt Modified Zinc Oxide Particles, Asian Journal of Chemistry, 2014. **26**: S287 – S290. **Impact 2013 0.335**

M. G. Liman, A. H. Abdullah, M. Z. Hussein and Z. Zainal, Characteristics of ZnO synthesized by combined sol-gel and hydrothermal methods for the removal of Nitrobenzene, Journal of Applicable Chemistry, 2016. (Accepted)

UNIVERSITI PUTRA MALAYSIA

STATUS CONFIRMATION FOR THESIS / PROJECT REPORT AND COPYRIGHT

ACADEMIC SESSION : _____

TITLE OF THESIS / PROJECT REPORT :

DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST NANOPARTICLES FOR REMOVAL OF NITROBENZENE

NAME OF STUDENT : LIMAN MUHAMMAD GIDADO

I acknowledge that the copyright and other intellectual property in the thesis/project report belonged to Universiti Putra Malaysia and I agree to allow this thesis/project report to be placed at the library under the following terms:

1. This thesis/project report is the property of Universiti Putra Malaysia.
2. The library of Universiti Putra Malaysia has the right to make copies for educational purposes only.
3. The library of Universiti Putra Malaysia is allowed to make copies of this thesis for academic exchange.

I declare that this thesis is classified as :

*Please tick (√)

☐	**CONFIDENTIAL**	(Contain confidential information under Official Secret Act 1972).
☐	**RESTRICTED**	(Contains restricted information as specified by the organization/institution where research was done).
☐	**OPEN ACCESS**	I agree that my thesis/project report to be published as hard copy or online open access.

This thesis is submitted for :

☐ **PATENT** Embargo from _____ (date) until _____ (date)

Approved by:

_____ (Signature of Student)
New IC No/ Passport No.:

Date :

_____ (Signature of Chairman of Supervisory Committee)
Name:

Date :

[Note : If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization/institution with period and reasons for confidentially or restricted.]