



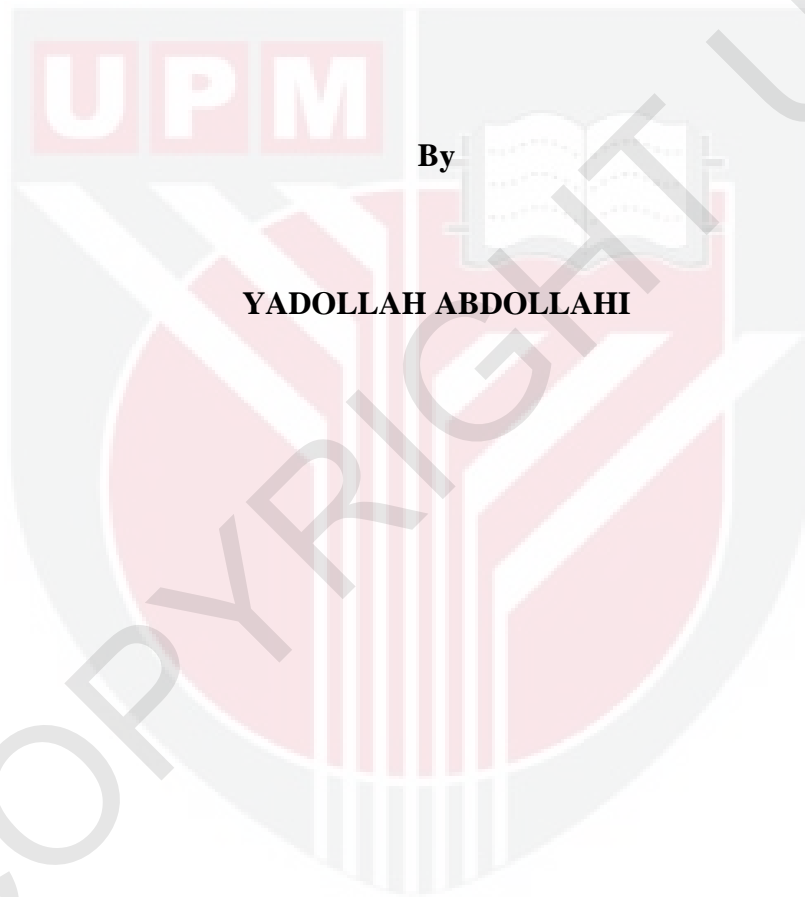
UNIVERSITI PUTRA MALAYSIA

**PHOTODEGRADATION OF CRESOLS BY ZnO
AND Mn-DOPED ZnO NANOPARTICLES**

YADOLLAH ABDOLLAHI

ITMA 2011 17

**PHOTODEGRADATION OF CRESOLS BY ZnO AND Mn-DOPED
ZnO NANOPARTICLES**



By

YADOLLAH ABDOLLAHI

**This thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

May 2011

DEDICATION

To:

My lovely wife



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

**PHOTODEGRADATION OF CRESOLS BY ZnO AND Mn-DOPED
ZnO NANOPARTICLES**

By

YADOLLAH ABDOLLAHI

May 2011

Chairman: Associate Prof. Abdul Halim Abdullah, PhD

Faculty: Institute Of Advanced Technology

Environmental pollution and particularly water pollution on a global scale has drawn the attention of scientists to the vital need for an environmentally clean and friendly chemical process. Photocatalytic oxidation, an advanced oxidation method, has proven reliability to eliminate persistent organic pollutants from water. Recently, interest in ZnO as a photocatalyst has increased but it has been mainly used under ultra violet (UV) irradiation. Since 46% of solar energy consists of visible light, and is more economical than UV light when used on a large scale, there has been much interest in

modifying ZnO in order to apply it under visible irradiation. However, no study has been conducted on aquatic cresols photodegradation using commercial ZnO, synthesized ZnO (undoped), and Mn-doped ZnO under UV and visible irradiation. In this study, photodegradation of cresols was investigated using commercial ZnO suspension under UV irradiation and visible light irradiation. The background of the study shows that cresols are stable under UV irradiation and visible light irradiation and about 7% of cresols are adsorbed over ZnO in the dark. The different variables studied include cresols concentration, photocatalyst dosage, and pH on the efficiency of photocatalytic degradation. In the optimum condition, photodegradation of cresols under UV irradiation is 100-ppm cresols at 2.5g/L ZnO, while under visible irradiation it is 25 ppm at 1.5g/L ZnO. Cresols photodegradation is favorable in pH range 6 to 9. In photodegradation of cresols, kinetics of photodegradation ($R^2 \approx 0.99$) is consistent with pseudo-zero order rate scheme. UPLC detected intermediates for *o*-cresol are 2-methylresorcinol, 2,5-hydroxybenzaldehyde and salicylaldehyde under UV irradiation and 2-methylresorcinol, 2,5-hydroxybenzaldehyde under visible light irradiation. For *m*-cresol, detected intermediates are 2,5-hydroxy-benzaldehyde, 3,5-hydroxytoluene and 3-hydroxy-benzaldehyde under UV irradiation, while 3,5-hydroxytoluene is detected as intermediate under visible light irradiation. The *p*-cresol detected intermediates are 4-hydroxy-benzaldehyde and methyl-4-hydroxybenzoate under UV irradiation, while only 4-hydroxy-benzaldehyde is detected in visible light irradiation. TOC studies indicate that 77% (*o*-cresol), 72% (*m*-cresol) and 85% (*p*-cresol) under

UV irradiation, and 75% (*o*-cresol), 75% (*m*-cresol) and 85% (*p*-cresol) under visible light irradiation, of total organic carbon are exited from the solution during irradiation time. It was observed that photodegradation of cresols under UV is more effective than under visible light irradiation. To enhance photodegradation of cresol under visible light, ZnO and Mn-doped ZnO (0-2.0% Mn) were synthesized by the co-precipitation method. The results of photocatalysts characterization show that 1%wt Mn-doped ZnO in comparison with undoped, 0.5%, 1.5% and 2% Mn-doped ZnO has higher surface area, lower particle size and lower agglomerate. Moreover, the calculated band gap of 1% Mn-doped ZnO is lower than others. The photocatalyst studies show that photodegradation efficiency and rate of reaction of undoped ZnO are comparable to or slightly better than commercial ZnO. The photocatalyst studies show that 1%wt Mn-doped ZnO has maximum adsorption, %efficiency and rate of reaction. In conclusion, 1%wt Mn-doped ZnO was selected as the best photocatalyst for removing cresols. The optimization of reaction condition illustrates that the maximum photodegraded cresols concentration is 35 ppm. The proper amount of photocatalyst is 1.5g/L and the maximum cresols photodegradation observed in pH 6-9. The detected intermediates are 2-methylresorcinol, 2.5-hydroxybenzaldehyde and salicylaldehyde for *o*-cresol, 3.5-hydroxytoluene and 2.5-hydroxy-benzaldehyde for *m*-cresol, and 4-hydroxy-benzaldehyde for *p*-cresol. TOC studies show that 70% (*o*-cresol), 68% (*m*-cresol) and 73% (*p*-cresol) of total organic carbon are exited from the solution during irradiation time. Reusability studies show that 1% wt Mn-doped ZnO can be used more than three

times. The final conclusion is that 1% wt Mn-doped ZnO may enhance the photocatalyst activity of ZnO under visible light.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**FOTODEGRADASI KRESOL OLEH ZnO DAN Mn TERDOP
NANOPARTIKEL ZnO**

Oleh

YADOLLAH ABDOLLAHI

Mei 2011

Pengerusi: Prof. Madya Abdul Halim Abdullah, PhD

Fakulti: Institut Teknologi Maju

Pencemaran alam sekitar dan terutamanya pencemaran air secara global, telah menarik perhatian saintis ke arah untuk mewujudkan proses kimia yang bersih dan mesra alam. Pengoksidaan fotokatalitik, suatu kaedah pengoksidaan yang lebih maju, telah membuktikan kebolehpercayaannya dalam penghapusan bahan-bahan pencemaran organik yang gigih dari air. Baru-baru ini, penggunaan ZnO sebagai fotokatalis telah bertambah tetapi teknologi ini lebih digunakan di bawah sinaran ultra ungu (UV). Memandangkan 46% tenaga solar terdiri daripada cahaya nampak dan ia adalah lebih ekonomi berbanding dengan sinaran UV apabila digunakan dalam skala besar, ramai

berminat dalam pengubahsuaian ZnO agar ia dapat digunakan di bawah sinaran nampak. Walaubagaimanapun, tiada kajian khusus pernah dijalankan ke atas fotodegradasi kresol-kresol akuatik dengan menggunakan ZnO komersial, ZnO sintesis (tidak terdop) dan Mn-terdop ZnO di bawah sinaran UV dan sinaran nampak. Dalam kajian ini, fotodegradasi kresol-kresol telah dikaji dengan menggunakan ampaian ZnO komersial di bawah sinaran UV dan sinaran cahaya nampak. Latar belakang kajian menunjukkan bahawa kresol-kresol adalah stabil di bawah sinaran UV dan sinaran cahaya nampak, dan lebih kurang 7% kresol-kresol telah dijerap oleh ZnO dalam keadaan gelap. Pembolehubah-pembolehubah berlainan yang dikaji termasuklah kepekatan kresol-kresol, dos fotokatalis dan pH terhadap keberkesanan degradasi fotokatalitik. Dalam keadaan optima, fotodegradasi kresol-kresol ialah 100-ppm kresol dengan 2.5g/L ZnO di bawah sinaran UV dan 25 ppm dengan 1.5g/L ZnO di bawah sinaran nampak. Fotodegradasi kresol adalah baik dalam larutan-larutan asid lemah, neutral dan bes. Dalam fotodegradasi kresol-kresol, kinetic fotodegradasi ($R^2 \approx 0.99$) adalah tekal dengan skema kadar tertib pseudo-sifar. Perantaraan-perantaraan o-cresol yang dikesan oleh UPLC ialah 2-metilresorsinol, 2.5-hidroksibenzaldehyd dan salisilaldehyd di bawah sinaran UV serta 2-metilresorsinol, 2.5-hidroksibenzaldehyd di bawah sinaran cahaya nampak. Bagi m-kresol, perantaraan-perantaraan yang dikesan ialah 2.5-hidroksi-benzaldehyd, 3.5-hidroksitoluena dan 3-hidroksi-benzaldehyd di bawah sinaran UV, manakala 3.5-hidroksitoluena dikesan sebagai perantaraan di bawah sinaran cahaya nampak. Bagi p-kresol, perantaraan-perantaraan yang dikesan

ialah 4-hidroksi-benzaldehid dan metil-4-hidroksibenzoat di bawah sinaran UV, manakala hanya 4-hidroksi-benzaldehid dapat dikesan di bawah sinaran cahaya nampak. Kajian TOC mendapati bahawa 77% (o-kresol), 72% (m-kresol) dan 85% (p-kresol) di bawah sinaran UV serta 75% (o-kresol), 75% (m-kresol) dan 85% (p-kresol) di bawah sinaran cahaya nampak, dari jumlah keseluruhan karbon organik telah diasingkan daripada larutan sepanjang masa penyinaran. Ia didapati bahawa fotodegradasi kresol-kresol di bawah sinaran UV adalah lebih efektif berbanding dengan sinaran cahaya nampak. Untuk meningkatkan fotodegradasi kresol di bawah sinaran cahaya nampak, ZnO dan Mn-terdop ZnO (0-2.0% Mn) disintesis melalui kaedah ko-pemendakan. Keputusan pencirian fotokatalis menunjukkan bahawa 1% wt Mn-terdop ZnO mempunyai luas permukaan yang lebih tinggi, saiz partikel yang lebih rendah dan juga aglomerat yang lebih rendah berbanding dengan tidak terdop, 0.5%, 1.5% dan 2% Mn-terdop ZnO. Selain itu, luang jalur 1% Mn-terdop ZnO yang dikira juga didapati lebih rendah daripada yang lain. Kajian fotokatalis mempamerkan bahawa kecekapan fotodegradasi dan kadar tindak balas bagi ZnO tidak terdop adalah setanding atau lebih baik sedikit jika dibandingkan dengan ZnO komersial. Kajian fotokatalis menunjukkan bahawa 1% wt Mn-terdop ZnO mempunyai penjerapan, peratus kecekapan dan kadar tindak balas yang maximum. Kesimpulannya, 1% wt Mn-terdop ZnO dipilih sebagai fotokatalis terbaik bagi penghapusan kresol-kresol. Pengoptimuman keadaan tindak balas mempamerkan bahawa kepekatan maximum kresol-kresol yang telah difotodegradasi ialah 35 ppm. Jumlah fotokatalis yang sesuai

ialah 1.5g/L dan fotodegradasi kresol-kresol yang maximum dapat diperhatikan pada pH 6-9. Perantaraan- perantaraan yang dikesan ialah 2-metillresorsinol, 2.5-hidroksibenaldehid dan salisilaldehid bagi o-kresol, 3.5- hidroksitoluena dan 2.5-hidroksi-benzaldehid bagi m-kresol serta 4-hidroksi-benzaldehid bagi p-kresol. Kajian TOC menunjukkan 70% (o-kresol), 68% (m-kresol) dan 73% (p-kresol) dari jumlah keseluruhan karbon organik telah diasingkan daripada larutan sepanjang masa penyinaran. Kajian kebolegunaan semula mempamerkan 1% wt Mn-terdop ZnO boleh digunakan lebih dari tiga kali. Sebagai kesimpulan terakhir, 1% wt Mn-terdop ZnO dapat mempercepatkan aktiviti fotokatalis ZnO di bawah sinaran cahaya nampak.

ACKNOWLEDGEMENT

I would like to take this opportunity to express my utmost gratitude to the chairman of my supervisory committee, Assoc. Prof. Dr. Abdul Halim Abdullah, for his invaluable guidance throughout the duration of this study. Without his helpful advice and support, it would not have been possible for me to complete my research. His guidance and advice throughout the project have been crucial in so many ways and to him I owe a debt of gratitude.

I certify that a Thesis Examination Committee has met on (23/5/2011) to conduct the final examination of Yadollah Abdollahi on his thesis entitled “Photodegradation of Cresols by Zinc Oxide and Manganese doped Zinc Oxide Nanoparticles” in accordance with the Universities and University Colleges Act 1971 and the Constitution of Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Azmi b Zakaria, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Anuar b Kassim, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Irmawati bt. Ramli, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Adesoji Adediran Adesina, PhD

Professor
School of Chemical Engineering
University of New South Wales Australia
(External Examiner)

NORITAH OMAR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 27 June 2011

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 Abdullah, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zulkarnain Zainal, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Nor Azah Yusof, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

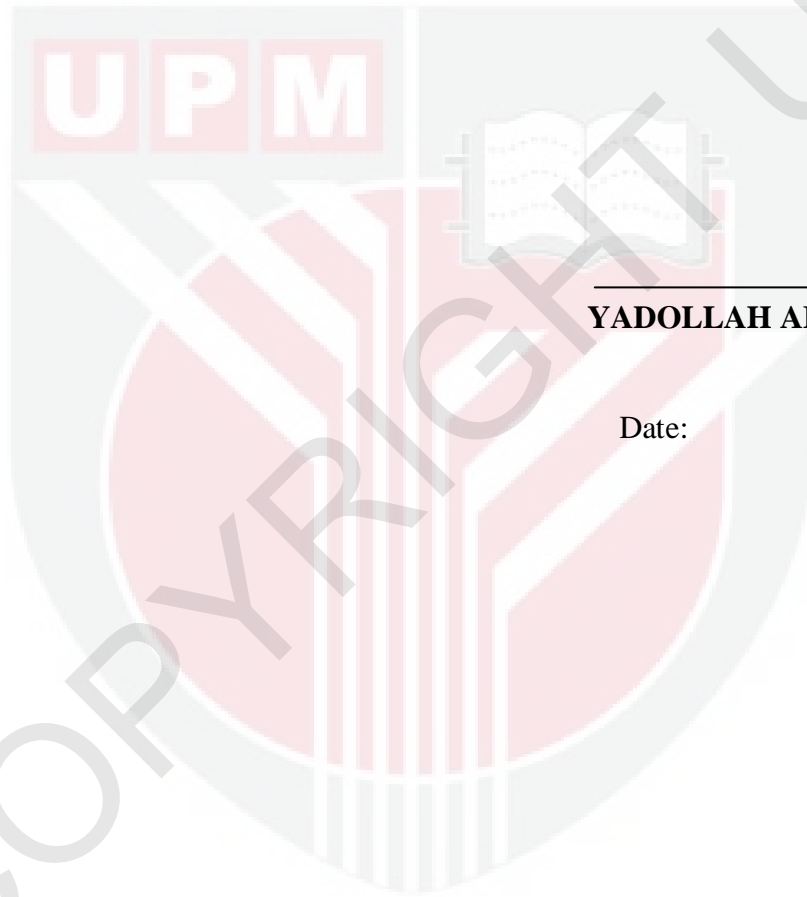
HASANAH MOHD GHAZALI, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 23 May 2011

DECLARATION

I declare that the thesis is my original work except for 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 institutions



YADOLLAH ABDOLLAHI

Date:

TABLE OF CONTENTS

	Page
ABSTRACT	iii
ABSTRAKT	vi
ACKNOWLEDGEMENT	x
DECLARATION	xiii
LIST OF TABLES	xviii
LIST OF FIGURES	xix
LIST OF ABBREVIATIONS	xxv
SYMBOLS	xxvi
CHAPTER	
1 INTRODUCTION	1
1.1 Background of Study	1
1.2 Research problem and research objective	3
1.2.1 Research problem	3
1.2.2 Hypothesis and research scope	6
1.2.3 Research objective	7
2 LITRATURE REVIEW	8
2.1 Historical Cornerstones	8
2.2 Fundamentals of Photocatalyst	10
2.2.1 Light Properties	10
2.2.2 Principles of semiconductor activity	12
2.2.3 Reactive Species	15
2.3 Photophysical processes in photocatalysis	17
2.3.1 Photogeneration of active species	17
2.3.2 Charge carrier and recombination	18
2.3.3 Dynamics of charge carrier	20
2.3.4 Effect of quantum size	21
2.3.5 Interfacial transfer reaction	23
2.4 ZnO	26
2.4.1 Defect	30
2.4.2 Doping	31
2.4.3 Synthesis ZnO and Mn doped ZnO nanoparticles	34
2.4.4 Photodegradation by ZnO and metal doped ZnO	36
2.5 Cresols	46

3	MATERIALS AND METHODS	49
3.1	Apparatus and Chemicals	49
	3.1.1 Photoreactors	49
	3.1.2 Visible Photoreactor	49
3.2	Chemicals	51
3.3	Preparation of photocatalyst	52
3.4	Characterization	55
	3.4.1 Phase determination	55
	3.4.2 Surface morphology	56
	3.4.3 Energy Dispersive X-ray	57
	3.4.4 Inductively Coupled Plasma (ICP)	57
	3.4.5 Surface Area Measurements	58
	3.4.6 Particles size analysis	60
	3.4.7 Band gap determination	61
3.5	Photodegradation of cresols	62
	3.5.1 General Photocatalytic procedure	62
	3.5.2 Background of studies	63
	3.5.3 Effect of photocatalyst loading	64
	3.5.4 Effect of substrate concentration	64
3.6	Kinetics	65
3.7	Effect of pH	66
3.8	Reusability	66
3.9	Analysis	67
	3.9.1 UV – Vis spectrophotometry	67
	3.9.2 Ultra performance liquid chromatography	69
	3.9.3 TOC & TIC analyzer	70
4	PHOTODEGRADATION OF CRESOLS BY COMMERCIAL ZnO UNDER UV AND VISIBLE LIGHT IRRADIATION	73
4.1	Introduction	73
4.2	Background studies	73
	4.2.1 Photolysis of cresols	73
	4.2.2 Adsorption cresols on ZnO	76
	4.2.3 Photocatalysis	79
4.3	Effect of operating parameters on the photodegradation of cresols	80
	4.3.1 Cresols concentration	80
	4.3.2 Concentration of photocatalyst	91
	4.3.3 Effect of pH	93
	4.3.4 Mineralisation and Photoproducts	99
	4.3.5 Reusability	106
4.4	Summary	107

5	PHOTODEGRADATION OF CRESOLS BY UNDOPED ZINC OXIDE AND MANGANESE DOPED ZINC OXIDE NANOPARTICLES UNDER VISIBLE-LIGHT IRRADIATION	109
5.1	Introduction	109
5.2	Characterization	110
	5.2.1 Phase determination	110
	5.2.2 Elemental analysis	113
	5.2.3 Surface morphology	114
	5.2.4 Particles size analysis	116
	5.2.5 Surface Area Measurements	119
	5.2.6 Band gap measurement	120
5.3	Photodegradation studies	125
	5.3.1 Adsorption	125
	5.3.2 Photodegradation of cresols by commercial and undoped ZnO	126
	5.3.3 Photodegradation of cresols by Mn-doped ZnO	128
5.4	Optimization of reaction condition	133
	5.4.1 Cresols concentration	133
	5.4.2 Photocatalyst loading	136
	5.4.3 Effect of pH	139
	5.4.4 Mineralisation and photoproducts	141
	5.4.5 Reusability	143
5.5	Summary	144
6	CONCLUSION AND RECOMMENDATION FOR FUTURE RESEARCH	146
	REFERENCES	149
	APPENDICES	170
	BIODATA OF STUDENT	184