UNIVERSITI PUTRA MALAYSIA

ZINC OXIDE-CATALYSED PHOTO-OXIDATIVE DEGRADATION OF CHLOROPHENOLS

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FS 2009 22

ZINC OXIDE-CATALYSED PHOTO-OXIDATIVE DEGRADATION OF CHLOROPHENOLS

By

UMAR IBRAHIM GAYA

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

September 2009

UPM

DEDICATION

I dedicate this work to my beloved father Alhaji Ibrahim Abdulkadir Gaya, the memory of my late mother Hajiya Fatima Ibrahim and as service to humanity.

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

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Chairman: Associate Prof. Abdul Halim Abdullah, PhD

Faculty: Science

Chlorophenols are priority pollutants that must be eradicated from the environment owing to the severity of their toxicity and resistance to traditional treatment. Photocatalytic oxidation is an advanced oxidation method which has proven reliability to eliminate persistent pollutants from air and water. The activity of zinc oxide for pollutant removal by photocatalytic oxidation has been well established. In this work the photocatalytic transformation of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in irradiated ZnO suspensions at 299 K was studied. The effect of operating parameters such as catalyst and concentration doses on the decomposition rate of these para-chlorinated compounds has been investigated and optimised. It was discovered that the optimum feed concentration for the phenolic compounds is 50 mg L^{-1}. The optimum amount of ZnO was determined for the degradation of 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol which decreased as with increasing of chlorine substituent. For 4-chlorophenol degradation,

the first clearer description of the effect of doses using response surface was reported.

Kinetic profiles on the decomposition of chlorophenols over ZnO were consistent with pseudo-zeroeth order rate scheme. For 2,4-dichlorophenol and 2,4,6-trichlorophenol the decomposition was slow at the short irradiation time. It was found that the degradability of chlorophenols increased as the number of ring-chlorine increased. The effect of pH on the destruction rate was found to be influenced by chlorophenol adsorption and dissociation equilibrium.

The effect of different anions on the rate of chlorophenol degradation was evaluated by utilising sodium salts as additives. Except for 4-chlorophenol it was found that, inorganic anion additives such as SO_4^{2-}, $S_2O_8^{2-}$ and Cl^- demonstrated inhibition to the decomposition rate of chlorophenol. HPO_4^{2-} was found to show strongest inhibition and could even hamper the degradation of 4-chlorophenol.

The progression of intermediates during the mineralisation of chlorophenols was chromatographed on high performance liquid chromatograph (HPLC). The structure elucidation of pathway products en route to mineralisation of chlorophenols was performed by the combined gas chromatography-mass spectrometry (GC-MS) and HPLC methods. The study disclosed some hitherto unreported intermediates of photocatalytic decomposition of 4-chlorophenol and 2,4-dichlorophenol. Catechol was detected as new intermediate of 4-chlorophenol degradation. Similarly, 4-hydroxybenzaldehyde, benzoquinone and 4-chlorophenol are for the first time reported for 2,4-dichlorophenol degradation. The work also revealed the intermediates of 2,4,6-trichlorophenol which have not been in literature. It is highlighted herein the mechanism of formation of all pathway intermediates.

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

ZINK OKSIDA MEMANGKIN PENGURAIAN KLOROFENOL SECARA FOTO-OKSIDAAN

Oleh

UMAR IBRAHIM GAYA

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Sebatian klorofenol merupakan bahan pencemar utama yang perlu disingkirkan daripada alam sekitar disebabkan oleh kadar toksik yang tinggi dan keampuhan terhadap rawatan secara konvensional. Pengoksidaan secara pemangkinan foto merupakan kaedah pengoksidaan termaju yang telah terbukti keberkesanannya bagi menyingkirkan bahan-bahan pencemar yang terkandung di dalam udara dan air. Peranan zink oksida dalam penyingkiran bahan pencemar melalui proses pengoksidaan secara pemangkinan foto adalah diiktiraf umum. Di dalam kajian ini, transformasi 4-klorofenol, 2,4-diklorofenol dan 2,4,6-triklorofenol secara pemangkinan foto di dalam ampaian ZnO pada suhu 299 K telah pun dikaji. Kesan daripada parameter seperti dos pemangkin dan kepekatan terhadap kadar penguraian sebatian paraklorin telah dikaji dan dioptimumkan. Telah terbukti bahawa kepekatan optimum untuk sebatian fenolik adalah 50 mg L^{-1}. Jumlah optimum ZnO bagi degradasi 4-klorofenol, 2,4-diklorofenol dan 2,4,6-triklorofenol telah ditentukan

yang mana ianya berkurangan dengan peningkatan kandungan klorin. Bagi degradasi 4-klorofenol, penjelasan yang lebih terperinci mengenai pengaruh kepekatan dengan menggunakan respons permukaan adalah yang pertama dilaporkan.

Profil kinetik penguraian sebatian klorofenol dengan menggunakan ZnO adalah konsisten dengan skema tertib pseudo-kosong. Bagi 2,4-diklorofenol dan 2,4,6-triklorofenol, kadar penguraian adalah perlahan pada masa radiasi yang singkat. Kebolehan degradasi sebatian klorofenol didapati adalah berkadaran dengan peningkatan klorin. Kesan pH terhadap kadar penguraian didapati dipengaruhi oleh penyerapan klorofenol dan keseimbangan penceraian.

Kesan anion yang berlainan terhadap kadar degradasi klorofenol telah diukur dengan menggunakan garam natrium sebagai bahan tambah. Selain daripada 4-klorofenol bahan tambah anion tak organik seperti SO_4^{2-}, $S_2O_8^{2-}$ dan Cl^- telah didapati menunjukkan kesekatlakuan terhadap kadar degradasi klorofenol. Di samping itu, HPO_4^{2-} didapati menunjukkan kesekatlakuan tertinggi dan hampir menyebabkan proses degradasi 4-klorofenol tidak berlaku.

Perkembangan bahan perantara semasa pemineralan klorofenol telah dianalisa dengan menggunakan kromatografi cecair berprestasi tinggi (HPLC). Penentuan struktur bahan perantara sewaktu proses pemineralan klorofenol telah dilaksanakan dengan menggunakan teknik gabungan kromatografi gas-spektroskopi jisim (GC-MS) dan HPLC. Kajian ini telah mendedahkan beberapa bahan perantara hasil daripada proses penguraian secara pemangkinan foto sebatian 4-klorofenol dan 2,4-diklorofenol yang masih belum dilaporkan sehingga kini. Katekol telah dikesan sebagai bahan perantara terbaru dari penguraian 4-klorofenol. Manakala 4-hidroksibenzaldehida, benzokuinon dan 4-klorofenol adalah bahan perantara bagi 2,4-diklorofenol yang pertama dilaporkan. Kajian ini juga mendedahkan bahan

perantara 2,4,6-triklorofenol yang belum pernah dilaporkan sebelum ini. Mekanisma pembentukan kesemua bahan perantara dilaporkan secara terperinci di dalam tesis ini.

ACKNOWLEDGEMENT

If it is really true that 'Charity begins at home' my gratitude would first go to my best friend the last 10 years, the rack of the family Ummi Nasiru Dori for her unyielding support during the period of my PhD study.

I am indebted to my supervisor Associate Professor Dr. Abdul Halim Abdullah, and to my co-supervisors Professor Zulkarnain Zainal and Professor Mohd Zobir Hussein for their immeasurable contribution and patience towards the success of this PhD project. I cherish the knowledge and understanding of this learned supervisory team. The emerging name and credit for sure goes to them.

I gratefully acknowledge the sponsorship offered to me by Kano State Government of Nigeria through the Kano State Scholarship Board (KSSB). I am grateful to my organisation Bayero University Kano for allowing me to study and for securing additional support for me from Mc Arthur foundation. I express immense gratitude to Universiti Putra Malaysia for the position of graduate fellow (GRF) during the second semester of 2007/2008 session. I thank Universiti Putra Malaysia International Students Association (UPMISA) for giving me the opportunity to serve as Nigeria representative, treasurer and now as financial secretary. I extend this message to UPM international office and UPMISA officials from different countries who I worked together with to address the interest of international students. May I accordingly seize this opportunity to thank all postgraduate students whom I have worked with for two years as International Students' Representative, Chemistry Postgraduate Club, Universiti Putra Malaysia.

I thankfully acknowledge all my relatives and friends for keeping in touch while I stay for 3 years thousands of kilometres away from them.

I am grateful to the technicians in the Department of Chemistry, Universiti Putra Malaysia, for their inspiring attitudes. Many thanks to Encik Zainudin Samadi for allowing me to use HPLC, Zainal Abidin Kassim for GC-MS and Choo Chai Syam for ICP-OES. I would like to express gratitude to Ing Yu Seng and Wong Chen Wai of Research Instruments for permission to use Waters Ultra High Performance Liquid Chromatograph (UHPLC). I am thankful to Nor Fairus Aida for running adsorption-desorption measurements. I thank Perkin Elmer Sdn Bhd for the measurement of band gap. I would seize this opportunity to thank my laboratory mates for the brotherly togetherness we had despite differences in complexion and tongue – Haniff Mohd Bin Wahid, Lee Kian Mun, Hudah Abdullah, Khairul Basyar Baharuddin, Appri Beyan, Nurul Haidah Daud, Saliza Asman, Nor Dyana Zakaria, Sook Keng Chang, Lee Ek Giat, Mageswary Manickam, Yadollah Abd. I enjoin the Malaysians among them to keep on the widely known 'Malaysian Hospitality'.

All the grants that served this research are hereby acknowledged. I also seize this opportunity to thank the Faculty of Science, Universiti Putra Malaysia for inviting me to make an academic presentation to new graduates of the 2008/2009 session on publishing. I am thankful to all fellow Nigerians studying in Malaysia. And, moving all the way down to Singapore, I thankfully acknowledge the invitation of the Singapore catalysis society to attend the Suzuki C-C coupling short course in Oct, 2008. Similarly, I owe the organisers of the 17th conference of commonwealth education ministers (17CCEM) a debt of gratitude for their invitation. Finally, to those whom by oversight I have not mentioned their names I am equally very much grateful.

I certify that a Thesis Examination Committee has met on September 11, 2009 to conduct the final examination of Umar Ibrahim Gaya on his thesis entitled "Zinc oxide-catalysed photo-oxidative degradation of chlorophenols" in accordance with the Universities and University Colleges Act 1971 and the constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the degree of Doctor of Philosophy.

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Date: 10th December 2009

DECLARATION

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

_____

UMAR IBRAHIM GAYA

Date:

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

4CP	4-chlorophenol
ANOVA	Analysis of variance
CB	Conduction band
Contd.	Continued
DI-MS	Direct infusion mass spectrometry
DI-MS	Direct insertion mass spectra
DRS	Diffuse reflectance spectrometry
EPRC	Emergency Planning and Community Right-To-Know
Eq.	Equation
Et	Ethyl
GC-MS	Gas chromatography-mass spectrometry/spectrometer
HPLC	High performance liquid chromatography/chromatograph
HPR	Hydroxyphenyl radical
ICP-OES	Inductively-coupled plasma
LC	Liquid chromatography/chromatograph
m	Meta
m/z	mass-to-charge ratio
N.A.	Not applicable
ND	Not determined
NDMA	N-nitrosodimethylamine
NIR	Near infra red
NNLS	Non Negative Least Square

OES	Optical emission spectrometry/spectrometer
OLEA	Oleic acid
OSHA	Occupational safety and health administration
PCCS	Photon cross correlation spectroscopy
Ph	Phenyl
RSD	Relative standard deviation
SC	Semiconductor
SEM	Scanning electron microscope/microscopy
SD	Standard deviation
TOPO	tri-n-octylphosphine oxide
UHPLC	Ultra high performance liquid chromatography/chromatograph
US EPA	United States environmental protection agency
UV	Ultraviolet
VB	Valence band
Vis	Visible
VOC	Volatile organic compound
2,4,6-TCP	2,4,6-trichlorophenol
1,2-diHPR	1,2-dihydroxyphenyl radical
2,4-DCP	2,4-dichlorophenol

Symbols

ε	Molar extinction coefficient
α	Star point coordinate
$[\ ]_o$	Initial concentration of
C	Concentration
C_o	Initial concentration
C_t	Concentration at time t
D	Diffusion coefficient
e^-	Electron
e^-_{cb}	Conduction band electron
E_g	Band gap energy
e^-_{tr}	Deeply trapped electron
e^-_{tr*}	Shallowly trapped electron
F-value	A measure of distance between individual distributions
h	Planks constant
h^+	Positively charged hole
h^+_{tr}	Deeply trapped hole
h^+_{tr*}	Shallowly trapped hole
h^+_{vb}	Valence band hole
K	Adsorption coefficient
k	Rate constant
K_{app}	Apparent rate constant
n_{ads}	Number of moles adsorbed
p/p^0	Relative pressure
p^0	Partial pressure

pK_a	Negative logarithm of acid dissociation constant
p-value	Probability value for hypothesis testing
r	Initial rate
r	Radius (e.g. of semiconductor particle)
R^2	Square of correlation coefficient
T	Temperature
t	Time
t_{equi}	Equilibrium time
v	Speed of light
V_{ads}	Volume of gas adsorbed
Y_{exp}	Experimental response factor
ζ_r	Relative photonic efficiency
θ	Surface coverage
λ	Wavelength
τ	Half-life or transit time
Φ	Quantum yield