



UNIVERSITI PUTRA MALAYSIA

**ZINC OXIDE-CATALYSED PHOTO-OXIDATIVE DEGRADATION OF
CHLOROPHENOLS**

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**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



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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September 2009

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-zeroth 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-} , $\text{S}_2\text{O}_8^{2-}$ 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 KLOOROFENOL SECARA FOTO-OKSIDAAN

Oleh

UMAR IBRAHIM GAYA

September 2009

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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 keberkesannya 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 ampai 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 berkadar 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-} , $\text{S}_2\text{O}_8^{2-}$ 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.

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

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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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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 |
| $[]_0$ | Initial concentration of |
| C | Concentration |
| C_0 | 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 |