UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF ZINC OXIDE AND ZINC OXIDE / IRON OXIDE CATALYSTS AND THEIR PHOTOCATALYTIC ACTIVITY IN DEGRADING HERBICIDES

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By

LEE KIAN MUN

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

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May 2013

Chair : Associate Professor Abdul Halim bin Abdullah, PhD

Faculty : Science

In this study, ZnO and ZnO/Fe_2O_3 catalysts were synthesized via precipitation method. The effect of Fe addition, calcination temperature and duration on the characteristics of the resulting catalyst were investigated by performing Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), surface area measurement (BET method), Diffuse Reflectance Spectroscopy (DRS) and Inductively-coupled plasma atomic emission spectroscopy (ICP-AES). XRD analysis showed that the addition of Fe resulted in the formation of hexagonal structure of ZnO and cubic structure of γ-Fe_2O_3 by calcining the sample at 450 °C for one hour. The catalysts produced were spherical in shape. The increase in the calcination temperature and duration does not change the morphology and band gap energy of the resulting catalysts. However, the surface area of the catalyst decreased and hence leads to an increment in its particle size as the calcination temperature and duration increased. ICP-AES results revealed that the iron content in ZnO/γ-Fe_2O_3 is in good agreement with the calculated values.

The efficiency of the synthesized ZnO/γ-Fe_2O_3 as photocatalysts was evaluated by photodegrading herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), phenoxyacetic acid (PAA) and 4-chlorophenoxyacetic acid (4-CPA) under the irradiation of ultraviolet (UV, λ_{max} = 365 nm) light. Various parameters affecting the degradation performance such as catalyst dosage, initial concentration of herbicides and initial pH were examined. The removal percentage of chlorophenoxyacetic acids increased with increasing mass of ZnO/γ-Fe_2O_3 up to an optimum loading (0.4 g L^{-1} for 2,4-D and 2,4,5-T with 66.07 and 68.16 %, respectively and 0.5 g L^{-1} for PAA and 4-CPA with 60.90 and 74.38 %, respectively) but decreased with increasing initial concentration (from 10 - 50 mg L^{-1}) of the herbicides. The removal of chlorophenoxyacetic acids is highest at pH 7. The photodegradation of chlorophenoxyacetic acids followed first-order kinetic scheme. The intermediates detected by UPLC for 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), phenoxyacetic acid (PAA) and 4-chlorophenoxyacetic acid (4-CPA) are 2,4-dichlorophenol, 2,4,5-trichlorophenol, phenol and 4-chlorophenol, respectively.

Experimental design methodology was applied using response surface methodology (RSM) to optimise the degradation percentage of chlorophenoxyacetic acids. The multivariate experimental design was employed to develop a quadratic model as a functional relationship between the degradation percentage of chlorophenoxyacetic acids and catalyst dosage, initial concentration of herbicides and initial pH. The degradation percentage of 2,4-D approached 99.26 % under optimised conditions of 0.50 g ZnO/γ-Fe_2O_3, 10.00 mg L^{-1} 2,4-D and at a pH of 7.49 whereas 2,4,5-T achieved 83.58 % under optimised conditions of 0.41 g ZnO/γ-Fe_2O_3, 10.60 mg L^{-1}

2,4,5-T and at pH 7.11. The maximum removal percentage of PAA approached 76.43 % under optimised conditions of 0.51 g ZnO/γ-Fe_2O_3, 10.20 mg L^{-1} PAA and at pH 6.63. Further, 4-CPA showed maximum removal of 91.87 % under optimised conditions of 0.49 g ZnO/γ-Fe_2O_3, 10.10 mg L^{-1} 4-CPA and at pH 7.25. In addition, the experimental data showed good agreement with the predicted results obtained from statistical analysis which indicates response surface methodology is applicable in optimising the degradation percentage of chlorophenoxyacetic acids.

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

ZINK OKSIDA DAN ZINK OKSIDA / FERUM OKSIDA SINTESIS DAN AKTIVITI FOTOPEMANGKINAN KE ATAS HERBISID

Oleh

LEE KIAN MUN

Mei 2013

Pengerusi : Profesor Madya Abdul Halim bin Abdullah, PhD

Fakulti : Sains

Dalam kajian ini, ZnO dan ZnO/Fe_2O_3 disintesis melalui kaedah pemendakan. Kesan penambahan ferum, suhu dan tempoh pengkalsinan ke atas ciri-ciri mangkin yang dihasilkan dikaji dengan Analisis Termogravimetrik (TGA), Pembelauan Sinar-X (XRD), Mikroskopi Pengimbasan Elektron (TEM), Pengukuran Luas Permukaan (kaedah BET), Spektroskopi Penyerapan Pantulan (DRS) dan Induktif ditambah plasma-spektroskopi pemancaran atom (ICP-AES). Daripada analisis XRD, penambahan ferum menghasilkan ZnO dengan struktur heksagon dan struktur kiub γ-Fe_2O_3 melalui pengkalsinan pada suhu 450 °C selama 1 jam. Pemangkin yang terhasil berbentuk sfera. Peningkatan dalam suhu dan tempoh pengkalsinan tidak mengubah bentuk dan tenaga jurang jalur mangkin yang terhasil. Tetapi, luas permukaan mangkin menurun dan menyebabkan penambahan dalam saiz zarah apabila suhu dan tempoh pengkalsinan meningkat. ICP-AES menunjukkan kandungan ferum dalam $ZnO/\gamma\text{-}Fe_2O_3$ sepadan dengan nilai pengiraan.

Kecekapan ZnO/γ-Fe_2O_3 yang disintesis sebagai fotomangkin telah diuji dengan fotodegradasi herbisid asid 2,4-diklorofenoksiasetik (2,4-D), asid 2,4,5-triklorofenoksiasetik (2,4,5-T), asid fenoksiasetik (PAA) dan asid 4-klorofenoksiasetik (4-CPA) di bawah penyinaran cahaya ultralembayung (UV, λ_{maks} = 365 nm). Pelbagai parameter yang mempengaruhi prestasi fotopemangkinan seperti dos mangkin, kepekatan herbisid dan pH larutan telah dikaji. Peratusan penyingkiran asid klorofenoksiasetik meningkat dengan peningkatan jisim ZnO/γ-Fe_2O_3 ke tahap optimum (0.4 g L^{-1} bagi 2,4-D dan 2,4,5-T dengan 66.07 dan 68.16 % masing-masing dan 0.5 g L^{-1} bagi PAA dan 4-CPA dengan 60.90 dan 74.38 % masing-masing) tetapi menurun dengan peningkatan kepekatan herbisid (dari 10 - 50 mg L^{-1}). Penyingkiran asid klorofenoksiasetik tertinggi dicapai pada pH 7. Fotopemangkinan asid klorofenoksiasetik mengikut skema kadar tertib pertama. Perantaraan-perantaraan yang dikesan oleh UPLC bagi asid 2,4-diklorofenoksiasetik (2,4-D), asid 2,4,5-triklorofenoksiasetik (2,4,5-T), asid fenoksiasetik (PAA) dan asid 4-klorofenoksiasetik (4-CPA) masing-masing adalah 2,4-diklorofenol, 2,4,5-triklorofenol, fenol dan 4-klorofenol.

Kaedah rekabentuk ujikaji telah digunakan dengan kaedah respons permukaan (RSM) untuk mengoptimumkan peratusan degradasi asid klorofenoksiasetik. Kepelbagaian variasi rekabentuk ujikaji juga digunakan untuk membangunkan model kuadratik sebagai fungsi hubungan di antara dos mangkin, kepekatan herbisid dan pH larutan terhadap peratusan degradasi asid klorofenoksiasetik. Peratusan degradasi 2,4-D mencapai 99.26 % di bawah keadaan optimum 0.50 g ZnO/γ-Fe_2O_3, 10.00 mg L^{-1} 2,4-D dan pH larutan 7.49 manakala 2,4,5-T mencapai 83.58 % di bawah keadaan optimum 0.41 g ZnO/γ-Fe_2O_3, 10.60 mg L^{-1} 2,4,5-T dan pH larutan 7.11.

Peratusan degradasi maksimum PAA mendekati 76.43 % di bawah keadaan optimum 0.51 g ZnO/γ-Fe_2O_3, 10.20 mg L^{-1} PAA dan pH larutan 6.63. Di samping itu, 4-CPA menunjukkan maksimum penyingkiran 91.87 % di bawah keadaan 0.49 g ZnO/γ-Fe_2O_3, 10.10 mg L^{-1} 4-CPA dan pH larutan 7.25. Keputusan eksperimen menepati keputusan ramalan daripada analisis statistik dan ini menunjukkan bahawa kaedah respons permukaan boleh digunakan untuk mengoptimumkan peratusan degradasi asid klorofenoksiasetik.

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I certify that a Thesis Examination Committee has met on 23 May 2013 to conduct the final examination of Lee Kian Mun on his Doctor of Philosophy thesis entitled "**Synthesis of Zinc Oxide and Zinc Oxide / Iron Oxide Catalysts and their Photocatalytic Activity in Degrading Herbicides**" 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 Doctor of Philosophy.

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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:

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DECLARATION

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

LEE KIAN MUN

Date: 23 May 2013

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