



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CONTROLLED RELEASE CHARACTERIZATION OF ZINC-
ALUMINIUM-LAYERED DOUBLE HYDROXIDE-CHLOROPHENOXYACETATES
NANOHYBRIDS**

SITI HALIMAH BINTI SARIJO

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ZINC-ALUMINIUM-LAYERED DOUBLE HYDROXIDE-
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By

SITI HALIMAH BINTI SARIJO

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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SEPTEMBER 2008

Chairman: Professor Mohd. Zobir bin Hussein, PhD

Faculty: Institute of Advanced Technology

The massive use of agrochemicals, such as herbicides has led to the contamination of these chemicals in the environment especially surface and ground-water reservoir. One approach to solve this problem is to develop controlled release agrochemical, in which the chemical is embedded into a matrix/support system, and can be released in a controlled manner. This study aimed at the synthesis of new controlled release of herbicides, namely 2-chlorophenoxyacetate, 4-chlorophenoxyacetate and 2,4,5-trichlorophenoxyacetate via intercalation of the chlorophenoxyherbicides into zinc-aluminium-layered double hydroxide by self-assembly and anion-exchange methods. Upon the successful intercalation of the herbicides, release profiles and the factors govern its release from their matrices into various aqueous media were determined. In this study, relatively phase-pure with well ordered layered nanohybrid materials were successfully synthesized by both methods at optimum condition. Expansion of basal spacing was observed from 8.9 Å in the



zinc-aluminium-layered double hydroxide to 18.5, 20.1 and 26.2 Å, in zinc-aluminium-2-chlorophenoxyacetate, zinc-aluminium-4-chlorophenoxyacetate and zinc-aluminium-2,4,5-trichlorophenoxyacetate nano-hybrids respectively, obtained from self-assembly method, compared to 19.6, 19.5 and 25.8 Å, respectively, in the nano-hybrids synthesized by anion-exchange method. Controlled release study of the herbicides into the aqueous solutions of sodium carbonate, sodium sulfate and sodium chloride as well as in distilled water at pH = 3, 6.25 and 12 is in the order of: 2-chlorophenoxyacetate > 4-chlorophenoxyacetate > 2,4,5-trichloro-phenoxy acetate. Release of herbicides into the aqueous media is in the order of: sodium carbonate > sodium sulfate > sodium chloride and pH 12 > pH 3 > pH 6.25. The release profiles are best described by pseudo-second order kinetic model as shown by the regression values of about 1.0. The 4-chlorophenoxyacetates anion was selectively intercalated into zinc-aluminium-layered double hydroxide than 2,4,5-trichlorophenoxyacetate, with percentage anion of 35.5 and 21.0 %, for 4-chlorophenoxyacetates and 2,4,5-trichlorophenoxyacetate, respectively while 2,4,5-tri-chloro-phenoxyacetate was preferably intercalated compared to 2-chloro-phenoxyacetates with the percentage loading of 57.8 and 31.4 %, respectively, for the latter and the former. This study shows that the zinc-aluminium-layered double hydroxide can be used as a matrix for controlled release formulation of chlorophenoxyacetic acid herbicides. The release of chlorophenoxyherbicides from the matrix was found to be controlled by the concentration and the anion in the release aqueous solution as well as the pH of the release media.

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

SINTESIS DAN SIFAT PERLEPASAN TERKAWAL HIBRID NANO ZINK-ALUMINIUM- HIDROKSIDA BERLAPIS GANDA-KLOROFENOKSIASETAT

Oleh

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Penggunaan bahan agrokimia seperti herbisid secara meluas telah menyebabkan pencemaran alam sekitar terutama air dan punca air bawah tanah. Satu pendekatan untuk menyelesaikan masalah ini ialah dengan memajukan bahan agrokimia berperlepasan terkawal di mana bahan kimia ini diselitkan di dalam matrik/sistem penyokong dan boleh dilepaskan secara terkawal. Kajian ini bertujuan untuk mensintesis herbisid lepasan terkawal yang baru, iaitu 2-klorofenoksiasetat, 4-klorofenoksiasetat dan 2,4,5-triklorofenoksiasetat dengan penyisipan ke dalam lapisan berganda zink-aluminium hidroksida secara pemendakan bersama dan penukargantian anion. Setelah penyisipan herbisid berjaya dilakukan, kajian mengenai perlepasan terkawal dan faktor-faktor yang mengawal perlepasannya ke dalam berbagai media berakuaes telah dilakukan. Dalam kajian ini, bahan hibrid nanokomposit yang berfasa tulen dengan struktur yang teratur telah berjaya disintesis dengan kedua-dua kaedah pada keadaan optima. Pengembangan jarak lapisan



daripada 8.9 Å dalam lapisan hidroksida berlapis ganda zink-aluminium kepada masing-masing 18.5, 20.1 dan 26.2 Å, dalam nanohibrid zink-aluminium-2-klorofenoksiasetat, zink-aluminium-4-klorofenoksiasetat dan zink-aluminium-2,4,5-triklorofenoksiasetat telah dihasilkan daripada kaedah pemendakan bersama berbanding dengan masing-masing 19.6, 19.5 dan 25.8 Å, dengan kaedah penukargantian ion. Kajian perlepasan terkawal klorofenoksiasetat dalam larutan akuas natrium karbonat, natrium sulfat dan natrium klorida serta air suling pada pH = 3, 6.25 dan 12 adalah dalam turutan: 2-klorofenoksiasetat > 4-klorofenoksiasetat > 2,4,5-triklorofenoksiasetat. Peratus perlepasan terkawal dalam media berakueus adalah dalam turutan: natrium karbonat > natrium sulfat > natrium klorida dan pH 12 > pH 3 > pH 6.25. Profil perlepasan terkawal didapati mematuhi kinetik tertib pseudo-kedua dengan nilai regresi bagi kesemua profil hampir 1.0. 4-klorofenoksiasetat lebih mudah disisipkan berbanding dengan 2,4,5-triklorofenoksiasetat dengan 35.5 dan 21.0 % tersisip, masing-masing, bagi 4-klorofenoksi-asetat dan 2,4,5-triklorofenoksiasetat sementara 2,4,5-triklorofenoksiasetat lebih cenderung untuk disisipkan ke dalam lapisan berganda hidroksida berbanding 2-klorofenoksiasetat dengan masing-masing 57.8 dan 31.4 % anion tersisip. Kajian ini menunjukkan hidroksida berlapis ganda zink-aluminium boleh digunakan sebagai matrik bagi formulasi perlepasan terkawal herbisid asid klorofenoksiasetik. Perlepasan klorofenoksi-asetat daripada matriksnya didapati dikawal oleh kepekatan dan jenis anion di dalam larutan akuas dan juga pH media.

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I certify that an Examination Committee met on the 23 September 2008 to conduct the final examination of Siti Halimah binti Sarijo on her Doctor of Philosophy thesis entitled “Synthesis and Controlled Release Characterization of Zinc-Aluminium-Layered Double Hydroxide-Chlorophenoxyacetates Nanohybrids” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

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

SITI HALIMAH BINTI SARIJO

Date: 4.11.2008

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