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SYNTHESIS AND CONTROLLED RELEASE PROPERTIES OF PHENOXYHERBICIDES-LAYERED HYDROXIDE NANOHYBRIDS

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SYNTHESIS AND CONTROLLED RELEASE PROPERTIES OF PHENOXYHERBICIDES-LAYERED HYDROXIDE NANOHYBRIDS

By

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Organic-inorganic nanohybrids of phenoxyherbicides, 4-(2,4-dichlorophenoxy)butyrate, 2(2,4-dichlorophenoxy)propionate and 3(2-chlorophenoxy)propionate into the interlayers of zinc-aluminium-layered double hydroxides have been synthesized using co-precipitation and ion exchange methods. PXRD patterns showed sharp, intense and symmetrical peaks which is due pure phase and good crystallinity of the nanohybrids prepared by both co-precipitation and ion exchange methods. Compositional studies showed the estimated percentage of phenoxyherbicides intercalated in the interlayer zinc-aluminium-layered double hydroxides are 53.9 % and 54.7 % of 4-(2,4-dichlorophenoxy)butyrate, 47.8 % and 58.5 % of 2(2,4-dichlorophenoxy)propionate, 38.3 % and 42.3 % of 3(2-chlorophenoxy)propionate that synthesized using co-precipitation and ion exchange methods, respectively. FTIR and thermal analysis supported that phenoxyherbicides was successfully intercalated into the Zn/Al-layered

double hydroxides. A release study of phenoxyherbicides from interlayer nanohybrid was carried out in various concentrations of sodium chloride, sodium carbonate and sodium phosphate and the mixture of sodium chloride, sodium carbonate and sodium phosphate aqueous solutions. Controlled release study of phenoxyherbicides into the aqueous solutions is in order of: 3(2-chlorophenoxy)propionate > 2(2,4-dichlorophenoxy)propionate > 4-(2,4-dichlorophenoxy)butyrate. The accumulated release percentage of phenoxyherbicides into aqueous solutions is in order of: sodium carbonate > sodium phosphate > sodium chloride. The kinetic study showed that pseudo-second order was the best model to describe almost all the release profiles of the phenoxyherbicides anion from Zn/Al-phenoxyherbicides nanohybrid.

A new layered organic-inorganic nanohybrid material containing an agrochemical, 4-(2,4-dichlorophenoxy)butyrate and 3(2-chlorophenoxy)propionate in the interlayer of zinc-layered hydroxide was also accomplished by direct reaction of aqueous phenoxyherbicides solution with zinc oxide. The nanohybrids showed well ordered crystalline layered structure, a basal spacing of 29.6 Å and 22.7 Å, and percentage loading of 47.9 % and 38.8 % of 4-(2,4-dichlorophenoxy)butyrate and 3(2-chlorophenoxy)propionate, respectively. FTIR study possessed that the absorption bands characteristics of both the phenoxyherbicides and zinc-layered hydroxide which is confirmed the intercalation process. The release study of the phenoxyherbicides into the aqueous solutions of sodium chloride, sodium carbonate and sodium phosphate showed higher accumulated percentage release of 3(2-chlorophenoxy)propionate compared to 4-(2,4-dichlorophenoxy)butyrate. Release of phenoxyherbicides into the aqueous solutions is in order of: sodium carbonate > sodium phosphate > sodium chloride. The release of 4-(2,4-dichlorophenoxy)butyrate and 3(2-chlorophenoxy)propionate from their nanohybrids was also done into a mixture of solution sodium chloride, sodium carbonate and sodium phosphate. The results of the release profile showed high accumulated release of both phenoxyherbicies anion into the solution containing carbonate or mixture of carbonate and phosphate. The kinetic behaviour of both phenoxyherbicides release from its nanohybrid are also agree well with the parabolic diffusion release model.

This study showed that the formation of organic-inorganic nanohybrid materials of, 4-(2,4-dichlorophenoxy)butyrate, 2(2,4-dichlorophenoxy)propionate and 3(2-chlorophenoxy)propionate anions as organic guests and zinc-aluminum-layered double hydroxide and zinc layered hydroxide as hosts were successfully synthesized. 4-(2,4-dichlorophenoxy)butyrate showed the highest percentage intercalation into the interlayer layered metal hydroxide material as shown percentage loading as compared to 2(2,4-dichlorophenoxy)propionate and 3(2-chlorophenoxy)propionate anion. The release of phenoxyherbicides from the matrix revealed that the zinc-aluminium layered double hydroxide and zinc layered hydroxide can be potentially used as a host for controlled release formulation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan untuk Ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN PELEPASAN TERKAWAL NANOHIBRID FENOKSIHERBISIDA-HIDROKSIDA BERLAPIS

Oleh

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Nanohibrid organik tak organik fenoksiherbisida, 4-(2,4-diklorofenoksi)butirat, 2(2,4-diklorofenoksi)propionat dan 3-(2-klorofenoksi)propionat ke dalam antara lapisan hidroksida zink-aluminium lapisan berganda telah disintesis menggunakan kaedah pemendakan bersama dan pertukaran ion. Corak PXRD menunjukkan puncak yang tajam, kuat dan simetri yang disebabkan oleh fasa tulen dan penghabluran baik bagi kedua-dua nanohibrid yang disediakan dengan kaedah pemendakan bersama dan pertukaran ion. Kerencaman kajian menunjukkan peratusan anggaran bagi fenoksiherbisida terinterkalasi di antara lapisan hidroksida zink-aluminium lapisan berganda adalah 53.9 % dan 54.7 % bagi 4-(2,4- diklorofenoksi)butirat, 47.8 % dan 58.5 % bagi 2(2,4-diklorofenoksi)propionat, 38.3 % dan 42.3 % bagi 3-(2-klorofenoksi)propionat yang masing-masing disintesis menggunakan kaedah pemendakan bersama dan pertukaran ion.

Ini bersama dengan FTIR dan analisis terma menunjukkan bahawa fenoksiherbisida telah berjaya diinterkelasikan ke dalam hidroksida Zn/Al lapisan berganda. Kajian pelepasan fenoksiherbisida daripada antara lapisan nanohibrid telah dilakukan dalam pelbagai kepekatan natrium klorida, natrium karbonat dan natrium fosfat dan campuran di antara larutan akueus natrium klorida, natrium karbonat dan natrium fosfat. Kajian perlepasan terkawal fenoksiherbisida ke dalam larutan akueus adalah dalam turutan: 3-(2-klorofenoksi)propionat > 2(2,4-diklorofenoksi)propionat > 4-(2,4-diklorofenoksi)butirat. Peratus perlepasan terkumpul bagi fenoksiherbisida dalam larutan akueus adalah mengikut turutan: natrium karbonat > natrium fosfat > natrium klorida. Kajian kinetik menunjukkan bahawa tertib pseudo kedua merupakan model terbaik untuk menerangkan hampir semua profil pelepasan ion fenoksiherbisida dari nanohibrid Zn/Al- fenoksiherbisida.

Satu bahan baru nanohibrid lapisan organik-tak organik mengandungi agrokimia, 4-(2,4-diklorofenoksi)butirat dan 3-(2-klorofenoksi)propionat dalam antara lapisan hidroksida zink berlapis juga telah didapati dengan tindak balas langsung larutan akueus fenoksiherbisida dengan zink oksida. Nanohibrid susunan struktur lapisan kristal yang sangat baik, jarak lapisan sebanyak 29.6 Å dan 22,7 Å, dan peratus pemuatan adalah 47.9 % dan 38.8 % masing-masing bagi 4-(2,4-diklorofenoksi)butirat dan 3-(2-klorofenoksi)propionat. Kajian FTIR menunjukkan bahawa ciri-ciri puncak penyerapan nanohibrid terdiri daripada kedua-dua fenoksiherbisida dan hidroksida zink berlapis yang mengesahkan proses interkalasi. Kajian pelepasan fenoksiherbisida ke dalam larutan akueus natrium klorida, natrium karbonat dan natrium fosfat menunjukkan peratusan pelepasan terkumpul yang tinggi adalah 3-(2-klorofenoksi)propionat berbanding 4-(2,4-

diklorofenoksi)butirat. Pelepasan fenoksiherbisida ke dalam larutan akueus adalah dalam urutan: natrium karbonat > natrium fosfat > natrium klorida. Pelepasan 4-(2,4-diklorofenoksi)butirat dan 3-(2-klorofenoksi)propionat dari nanohibrid masing-masing juga telah dilakukan ke dalam campuran larutan natrium klorida, natrium karbonat dan natrium fosfat. Keputusan menunjukkan profil pelepasan terkumpul tertinggi bagi kedua-dua anion fenoksiherbisida adalah ke dalam larutan yang mengandungi karbonat atau campuran karbonat dan fosfat. Kelakuan kinetik bagi pelepasan kedua-dua fenoksiherbisida daripada nanohybrid hampir semua mengikuti model pelepasan resapan parabolik.

Kajian ini menunjukkan bahawa pembentukan bahan nanohibrid organik tak organik daripada, 4-(2,4-diklorofenoksi)butirat, 2(2,4-diklorofenoksi)propionat dan 3-(2-klorofenoksi)propionat anion sebagai tetamu organik dan hidroksida zink-aluminium lapisan berganda dan zink hidroksida berlapis sebagai perumah berjaya disintesis. 4-(2,4-diklorofenoksi)butirat menunjukkan peratus interkelasi tertiggi ke dalam antara lapisan bahan hidroksida logam berlapis seperti yang ditunjukkan dalam peratus pemuatan berbanding dengan anion 2(2,4-diklorofenoksi)propionat dan 3-(2-klorofenoksi)propionat. Pelepasan fenoksiherbisida dari matrik menunjukkan bahawa hidroksida zink aluminium lapisan berganda dan hidroksida zink berlapis berpotensi untuk digunakan sebagai perumah untuk formulasi pelepasan terkawal.

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I certify that an Examination Committee met on 15 May 2012 to conduct the final examination of Norhayati Hashim on her Doctor of Philosophy thesis entitled "Synthesis And Controlled Release Properties Of Phenoxyherbicides-Layered Hydroxide Nanohybrids" in accordance with 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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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.

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NORHAYATI BT. HASHIM

DATE: 15 May 2012

TABLE OF CONTENTS