SYNTHESIS AND CONTROLLED RELEASE PROPERTIES OF PHENOXYHERBICIDES-LAYERED HYDROXIDE NANOHYBRIDS

NORHAYATI HASHIM

ITMA 2012 4
SYNTHESIS AND CONTROLLED RELEASE PROPERTIES OF PHENOXYHERBICIDES-LAYERED HYDROXIDE NANOHYBRIDS

NORHAYATI HASHIM

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

May 2012
SYNTHESIS AND CONTROLLED RELEASE PROPERTIES OF
PHENOXYHERBICIDES-LAYERED HYDROXIDE NANOHYBRIDS

By

NORHAYATI HASHIM

May 2012

Chairman: Professor Mohd Zobir Bin Hussein, PhD
Institute: Institute of Advanced Technology

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 phenoxyherbicides 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 NANOHIRBID FENOKSIHERBISIDA-HIDROKSIDA BERLAPIS**

Oleh

**NORHAYATI HASHIM**

Mei 2012

Pengerusi: Profesor Mohd Zobir Bin Hussein, PhD

Institut: Institut Teknologi Maju

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 ciri-ciri pencapaian 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-

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 fenosiherbisida dari matrik menunjukkan bahawa hidroksida zink aluminium lapisan berganda dan hidroksida zink berlapis berpotensi untuk digunakan sebagai perumah untuk formulasi pelepasan terkawal.
ACKNOWLEDGEMENTS

Alhamdulillah, praise be to Allah for giving me the strength to complete this dissertation despite several difficulties encountered throughout this study. Firstly, I would like to express my sincere appreciation to my supervisors, Prof. Dr. Mohd Zobir Hussein, Assoc. Prof. Dr. Asmah Hj.Yahaya, and Prof. Dr. Zulkarnain Zainal for the guidance, concern, support and encouragement which have kept me going up until to this stage. I would like to thank the entire laboratory officers of the Institute of Advanced Technology (ITMA), UPM and also thanks to UPSI for study leave and scholarship. Thank you to all my friends in the Advanced Material Laboratory for the support and understanding throughout my study. Special thanks for Adila, Ikin, Faiza, Rafaei, Zahiri and Jaffri who always had time for me, long hours of discussing ideas and helping me out with this dissertation. Thank you for your companionship. Finally my family, who have been great over the years. To Ayah, Mak, Kak Ini & Abg family, Simah & Lan family and Shah. Last but not least, my beloved husband, Mohd Husni Lebai Isa, my daughter, Nur Aina and my son, Ahmad Shahir, thank you so much, I truly can’t completely express my appreciation for the unlimited patience, love, guidance, encouragement it took to get me through this study and thank you for having faith in me to complete this study.
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.

Members of the Thesis Examination Committee are as follows:

**Kamaliah Sirat, PhD**
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

**Md Jelas Haron, PhD**
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

**Halim Abdullah, PhD**
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

**Ambar Yarmo, PhD**
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Independent Examiner)

_______________________
SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:
This thesis was submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mohd. Zobir Hussein, PhD  
Professor  
Advance Material Laboratory  
Institute of Advanced Material  
Universiti Putra Malaysia  
(Chairman)

Asmah Hj. Yahaya, PhD  
Associate Professor  
Centre of Foundation Studies for Agricultural Science  
Universiti Putra Malaysia  
(Member)

Zulkarnain Zainal, PhD  
Professor  
Department of Chemistry  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

BUJANG BIN KIM HUAT, PhD  
Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia  

Date:
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.

________________________
NORHAYATI BT. HASHIM
DATE: 15 May 2012
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>viii</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>ix</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xxviii</td>
</tr>
<tr>
<td><strong>CHAPTER 1</strong></td>
<td></td>
</tr>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td></td>
</tr>
<tr>
<td>1.1 Nanotech for Agrochemicals</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 Herbicides in Agriculture</td>
<td>1</td>
</tr>
<tr>
<td>1.1.2 Herbicides and Environmental Problems</td>
<td>2</td>
</tr>
<tr>
<td>1.1.3 Herbicides and Nanotechnology</td>
<td>4</td>
</tr>
<tr>
<td>1.2 Problem Statement</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Objectives of the Study</td>
<td>8</td>
</tr>
<tr>
<td><strong>CHAPTER 2</strong></td>
<td></td>
</tr>
<tr>
<td><strong>LITERATURE REVIEW</strong></td>
<td></td>
</tr>
<tr>
<td>2.1 Nanocomposite</td>
<td>10</td>
</tr>
<tr>
<td>2.2 Layered Double Hydroxide</td>
<td>13</td>
</tr>
<tr>
<td>2.2.1 Historical Background</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Structural and Chemical Composition</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3 Characteristic of Cations and Anions of Layered Double Hydroxide</td>
<td>19</td>
</tr>
<tr>
<td>2.2.4 Orientation of the Anions</td>
<td>26</td>
</tr>
<tr>
<td>2.3 Syntheses of Layered Double Hydroxide</td>
<td>28</td>
</tr>
<tr>
<td>2.3.1 Co-precipitation Method</td>
<td>29</td>
</tr>
<tr>
<td>2.3.2 Ion Exchange Method</td>
<td>32</td>
</tr>
<tr>
<td>2.3.3 Rehyration/Reconstruction Method</td>
<td>33</td>
</tr>
<tr>
<td>2.3.4 Other Method</td>
<td>35</td>
</tr>
<tr>
<td>2.4 Application of Layered Double Hydroxide</td>
<td>35</td>
</tr>
<tr>
<td>2.4.1 Application of LDH in Polymer</td>
<td>36</td>
</tr>
<tr>
<td>2.4.2 Application of LDH in Environmental Remediation</td>
<td>37</td>
</tr>
<tr>
<td>2.4.3 Application of LDH in Medicine</td>
<td>39</td>
</tr>
<tr>
<td>2.4.4 Application of LDH in Precursors to Magnetic Materials</td>
<td>40</td>
</tr>
<tr>
<td>2.4.5 Application of LDH in Controlled Release Formulation</td>
<td>41</td>
</tr>
<tr>
<td>2.5 Layered Metal Hydroxide</td>
<td>43</td>
</tr>
<tr>
<td>2.6 Herbicides and Mode of Action</td>
<td>45</td>
</tr>
<tr>
<td>2.7 The Used of Phenoxyherbicides in Agriculture</td>
<td>46</td>
</tr>
</tbody>
</table>
2.8 Phenoxyherbicides, 4-(2,4-dichlorophenoxy)butyric Acid, 2-(2,4-dichlorophenoxy)propionic Acid and 2(3-chlorophenoxy)propionic Acid as Guest Anion

3 MATERIALS AND METHODS

3.1 Materials

3.2 Instrumentation and Apparatus

3.3 Synthesis of Layered Double Hydroxide

3.3.1 Layered Double Hydroxide of Zn/Al-nitrate (LDH)

3.4 Synthesis of Nanohybrids

3.4.1 Nanohybrid of Zn/Al-4-(2,4-dichlorophenoxy)butyrate

3.4.2 Nanohybrid of Zn/Al-2-(2,4-dichlorophenoxy)propionate

3.4.3 Nanohybrid of Zn/Al-2(3-chlorophenoxy)propionate

3.4.4 Nanohybrid of ZLH-4-(2,4-dichlorophenoxy)butyrate

3.4.5 Nanohybrid of ZLH-2(3-chlorophenoxy)propionate

3.5 Release of anion from the Nanohybrid

3.6 Characterisation of LDHs and Nanohybrids

3.6.1 Powder X-Ray Diffraction

3.6.2 Fourier Transform Infrared Spectroscopy

3.6.3 Inductively Coupled Plasma-Atomic Emission Spectrometry

3.6.4 Carbon, Hydrogen, Nitrogen and Sulphur Analysis

3.6.5 Thermogravimetric and Differential Thermogravimetric Analysis

3.6.6 Analysis of Surface Area and Porosity

3.6.7 Scanning Electron Microscopy

3.6.8 Ultraviolet-visible Spectrometry

4 RESULTS AND DISCUSSION

SYNTHESIS AND CONTROLLED RELEASE PROPERTY OF LAYERED DOUBLE HYDROXIDE-PHENOXYHERBICIDES NANOHYBRIDS

4.1 Physico-Chemical Properties of Zn/Al-Layered Double Hydroxide

4.1.1 Powder X-Ray Diffraction

4.1.2 Fourier Transform Infrared Spectroscopy

4.1.3 Elemental Analysis

4.1.4 Thermal Stability

4.1.5 Surface Morphology

4.1.6 Surface Area Analysis

4.2 Formation of Zn/Al-DPBA Nanohybrid by Direct Co-precipitation and Ion Exchange Methods.

4.2.1 Powder X-Ray Diffraction

4.2.2 Molecular Arrangement of DPBA

4.2.3 Fourier Transform Infrared Spectroscopy
4.2.4 Elemental Analysis
4.2.5 Thermal Stability
4.2.6 Surface Morphology
4.2.7 Surface Area Analysis
4.3 Formation of Zn/Al-DPPA Nanohybrid by Direct Co-precipitation and Ion Exchange Methods.
4.3.1 Powder X-Ray Diffraction
4.3.2 Molecular Arrangement of DPPA
4.3.3 Fourier Transform Infrared Spectroscopy
4.3.4 Elemental Analysis
4.3.5 Thermal Stability
4.3.6 Surface Morphology
4.3.7 Surface Area Analysis
4.4 Formation of Zn/Al-CPPA Nanohybrid by Direct Co-precipitation and Ion Exchange Methods.
4.4.1 Powder X-Ray Diffraction
4.4.2 Molecular Arrangement of CPPA
4.4.3 Fourier Transform Infrared Spectroscopy
4.4.4 Elemental Analysis
4.4.5 Thermal Stability
4.4.6 Surface Morphology
4.4.7 Surface Area Analysis
4.5 Release Study of Zn/Al-DPBA, Zn/Al-DPPA and Zn/Al-CPPA Nanohybrids
4.5.1 Release Study of DPBA from Zn/Al-DPBA into Various Aqueous Solution
4.5.2 Release Study of DPPA from Zn/Al-DPPA into Various Aqueous Solutions
4.5.3 Release Study of CPPA from Zn/Al-CPPA into Various Aqueous Solutions
4.6 Kinetic Study of Zn/Al-DPBA, Zn/Al-DPPA and Zn/Al-CPPA Nanohybrids
4.6.1 Kinetic Study of the Release of DPBA from Zn/Al-DPBA into Various Aqueous Solutions
4.6.2 Kinetic Study of the Release of DPPA from Zn/Al-DPPA into Various Aqueous Solutions
4.6.3 Kinetic Study of the release of CPPA from Zn/Al-CPPA into Various Aqueous Solutions
4.7 Effect of Single, Binary and Ternary Anion of Sodium Chloride, Sodium Carbonate and Sodium Phosphate for the Controlled Release of Phenoxyherbicides Nanohybrid
4.7.1 Release Study of DPBA from Zn/Al-DPBA into Mixture Aqueous Solution
4.7.2 Release Study of DPPA from Zn/Al-DPPA into Mixture Aqueous Solutions
4.7.3 Release Study of CPPA from Zn/Al-CPPA into Mixture Aqueous Solutions

5 RESULTS AND DISCUSSION
SYNTHESIS AND CONTROLLED RELEASE PROPERTY OF ZINC LAYERED HYDROXIDE-PHENOXYHERBICIDES NANOHYBRIDS
5.1 Synthesis and Characterization of ZLH-DPBA and ZLH-CPPA Nanohybrids
5.1.1 Powder X-Ray Diffraction
5.1.2 Molecular Arrangement of DPBA and CPPA Anions
5.1.3 Fourier Transform Infrared Spectroscopy
5.1.4 Elemental Analysis
5.1.5 Thermal Stability
5.1.6 Surface Morphology
5.1.7 Surface Area Analysis
5.2 Release Study of ZLH-DPBA and ZLH-CPPA Nanohybrid
5.2.1 Release Study of DPBA from ZLH-DPBA into Various Aqueous Solutions
5.2.2 Release Study of CPPA from ZLH-CPPA into Various Aqueous Solutions
5.3 Kinetic Study of ZLH-DPBA and ZLH-CPPA into Various Aqueous Solutions
5.3.1 Kinetic Study of the Release of DPBA from ZLH-DPBA into Various Aqueous Solutions
5.3.2 Kinetic Study of the Release of CPPA from ZLH-CPPA into Various Aqueous Solutions
5.4 The Effect of Single, Binary and Ternary Anions of Chloride, Carbonate and Phosphate on the Release of DPBA and CPPA Intercalated into the Zinc Layered Hydroxide

6 CONCLUSION
REFERENCES
BIODATA OF STUDENT
LIST OF PUBLICATIONS
LIST OF PAPER PRESENTED IN SEMINAR/CONFERENCES