PREPARATION AND CONTROLLED RELEASE OF AGROCHEMICAL HERBICIDE ZINC LAYERED HYDROXIDE-3-(4-METHOXYPHENYL)PROPIONATE AND LAYERED DOUBLE HYDROXIDE-3-(4-METHOXYPHENYL)PROPIONATE NANOCOMPOSITES

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ABSTRACT

This research aimed to prepare and study the controlled release of agrochemical herbicide based on new nanocomposites, namely zinc layered hydroxide-3-(4-methoxyphenyl)propionate (ZLH-MPP) and layered double hydroxide-3-(4-methoxyphenyl)propionate (LDH-MPP). This research is divided into three parts which are synthesis of nanocomposites, characterization and controlled release. ZLH-MPP nanocomposite was synthesized using direct reaction of an aqueous suspension of zinc oxide with MPP solution. Whereas, LDH-MPP nanocomposite was synthesized using an ion exchange method between nitrate ion and MPP anion. The physiochemical properties of ZLH-MPP and LDH-MPP nanocomposites were characterized using powder x-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), carbon, hydrogen, nitrogen, oxygen and sulphur analysis (CHNO-S), inductive coupled plasma optical emission spectrometry (ICP-OES), thermogravimetric analysis and derivative thermogravimetry (TGA/DTG), and field emission scanning electron microscope (FESEM). Based on the results, PXRD patterns of ZLH-MPP and LDH-MPP nanocomposites showed the expansion of interlayer of layered material with the values of 27.3 Å and in the range of 18.7 Å to 20.5 Å respectively. FTIR spectra for both nanocomposites revealed the presence of MPP in the interlayer of ZLH-MPP and LDH-MPP nanocomposites. The controlled release of MPP from ZLH-MPP and LDH-MPP nanocomposite was found that phosphate solution yielded the highest percentage release compared to sulphate and chloride solutions. The kinetics data for MPP herbicide release from ZLH interlayer were best fitted to the pseudo-second order for phosphate solution and first order for both sulphate and chloride solutions. While, LDH-MPP nanocomposite governed by pseudo second order for all three solutions. The conclusions of this study are, ZLH-MPP and LDH-MPP nanocomposites were successfully synthesized and the intercalation was confirmed by characterization data. Besides that, the release behavior of herbicide was also according to one of the models that have been proposed. Implication of this research is to boost the agrochemical activity leading to safer herbicide for environment.

PENYEDIAAN DAN PELEPASAN TERKAWAL RACUN RUMPAI AGROKIMIA NANOKOMPOSIT LAPISAN ZINK HIDROKSIDA-3-(4-METOKSIFENIL)PROPIONAT DAN LAPISAN BERGANDA HIDROKSIDA-3-(4-METOKSIFENIL)PROPIONAT

ABSTRAK

Kajian ini bertujuan mengkaji pelepasan terkawal racun rumpai agrokimia berdasarkan nanokomposit baru, yang dinamakan lapisan zink hidroksida-3-(4-metoksifenil)propionat (LZH-MFP) dan lapisan berganda hidroksida-3-(4-metoksifenil)propionat (LBH-MFP). Kajian ini dibahagikan kepada tiga bahagian iaitu sintesis nanokomposit, pencirian dan pelepasan terkawal. Nanokomposit LZH-MFP telah disintesis menggunakan tindak balas langsung ampaian akueus zink oksida dengan larutan MFP. Manakala, nanokomposit LBH-MFP telah disintesis menggunakan kaedah pertukaran ion antara ion nitrat dan anion MFP. Sifat fisikokimia nanokomposit LZH-MFP dan LBH-MFP telah dicirikan menggunakan pembelauan serbuk sinar-x (PSSX), spektroskopi inframerah transformasi Fourier (IMTF), analisis karbon, hidrogen, nitrogen, oksigen dan sulfur (KHNO-S), spektrometri pancaran optik plasma gandingan aruhan (SPO-PGA), analisis termogravimetri dan terbitan termogravimetri (ATG/TTG), dan mikroskop imbasan elektron pancaran medan (MIEPM). Berdasarkan dapatan kajian, pola PSSX nanokomposit LZH-MFP dan LBH-MFP menunjukkan pengembangan antara lapisan bagi lapisan bahan dengan nilai masing-masing 27.3 Å dan dalam julat 18.7 Å hingga 20.5 Å. Spektra IMTF untuk kedua-dua nanokomposit menunjukkan kehadiran MFP dalam antara lapisan nanokomposit LZH-MFP dan LBH-MFP. Pelepasan terkawal MFP daripada nanokomposit LZH-MFP dan LBH-MFP didapati bahawa larutan fosfat menghasilkan peratusan pelepasan yang tertinggi berbanding dengan larutan sulfat dan klorida. Data kinetik untuk pelepasan racun rumpai MFP daripada antara lapisan LZH memberikan padanan terbaik kepada tertib pseudo-kedua untuk larutan fosfat dan tertib pertama untuk kedua-dua larutan sulfat dan klorida. Sementara itu, nanokomposit LBH-MFP dikawal oleh tertib pseudo-kedua untuk ketiga-tiga larutan. Kesimpulan bagi kajian ini adalah nanokomposit LZH-MFP dan LBH-MFP telah berjaya disintesis dan interkalasi telah dibuktikan oleh data pencirian. Selain itu, tingkah laku pelepasan racun rumpai telah mengikut salah satu model yang telah dicadangkan. Implikasi bagi kajian ini adalah untuk meningkatkan aktiviti agrokimia yang membawa kepada penggunaan racun rumpai yang lebih selamat untuk alam sekitar.

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LIST OF ABBREVIATIONS

µm	micrometre
2,4-D	2,4-(dichlorophenoxy)acetic acid
2D	2 dimension
4-ASA-ZLH	zinc layered hydroxide-4-aminosalicylate nanocomposite
A549	adenocarcinomic human alveolar basal epithelial cells
CHNO-S	carbon, hydrogen, nitrogen, oxygen and sulphur
EDX	energy dispersive x-ray analysis
$Fe_2[SO_4]$	ferric
$FeSO_4$	ferrous
FTIR	fourier transform infrared spectrophotometer
ICP-OES	inductive coupled plasma optical emission spectrometry
KBr	potassium bromide
LDH	layered double hydroxide
LDH-MPP	layered double hydroxide-3-(4methoxyphenyl)propionate nanocomposite
LHS	layered hydroxide salt
LMS	layered metal hydroxide
MPP	3-(4-methoxyphenyl)propionic acid
$NaAsO_2$	sodium arsenite
$NaClO_3$	sodium chlorate
nm	nanometre
PHA	polyhydroxyalkanoate
PLAP	pesticides leaching assessment programme
PXRD	powder x-ray diffractometer

R_f	final molar ratio of Zn^{2+} to Al^{3+}
R_i	initial molar ratio of Zn^{2+} to Al^{3+}
SEM	scanning electron microscope
Temp	Temperature
TGA/DTG	thermogravimetric analysis and derivative thermogravimetry
Z-CFX	zinc layered hydroxide-ciprofloxacin
ZLH-CPPA	zinc layered hydroxide-2-(3-chlorophenoxy)propionate nanocomposite
ZLH-MPP	zinc layered hydroxide-3-(4methoxyphenyl)propionate nanocomposite
ZLHN	zinc layered hydroxide nitrate
ZLHS	zinc layered hydroxide sulphate

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology

The simplest meaning of nanotechnology is "technology at nanoscale" (Ramsden, 2011). It is a technology that deals with small structures or small-sized materials. The term nano itself refers to 0.000 000 001 or 10^{-9} based on metric prefix measurements. The United States Foresight Institute states that, nanotechnology is a group of rising knowledge in which the structure of matter is controlled at the nanometer scale to generate new materials and devices that have practical and distinctive properties (Ramsden, 2011). Recently, the development of nanotechnology is increased rapidly in various fields. The research and development team competing among themselves in producing a new implementation in nanotechnology leading to a better future.

Nanotechnology offers the chemical industries at least six particular opportunities, which are tool for research, new materials, new process for fabrication, nanoelectronics, nanoparticle technology, and the revolutionary unknown (Whitesides, 2005). As describe adequately by Ramsden (2011), nanotechnology is associated with at least three distinct advantages. It offers the possibility of creating materials with novel combination of properties. Besides that, devices in the nanoscale require fewer materials to make them, utilize less power and other consumables, their function may be enhanced by reducing the characteristic dimensions, and they may have an unlimited series of approachability. Lastly, it also offers a universal fabrication technology, the apotheosis of which is the personal nanofactory.

Application approaches from nanotechnology could be in both direct and indirect ways. For example, an information processor in the computer is built based on extensive integrated chips with individual circuit machinery in the nanoscale, but the whole dimension of the device and the components is sizable than the nanoscale which means, the direct application of the nanotechnology is to the realization of the integrated circuit and the numerous function of the circuitry which is considered as indirect application of nanotechnology (Ramsden, 2011).

The evolutions of nanotechnology are developed in research and technology field, which includes production of materials, information storage and biomedical opportunities and medical application (Schmid et al., 2006). Materials with size-dependent properties and engineered functions play an important role in practical applications. These applications are included in properties of metals, semiconductors, insulators, hybrids and so on. Meanwhile, information storage is a physical fact that presents systems of information storage exclusively based on silicon advance technologies and other application like electric and electronics, magnetic, optical, mechanics and thermal (Ramsden, 2011, Schmid et al., 2006). Whereas, in biomedical field, nanotechnology contributes a lot in nanomaterial and their biomedical application, nanoanalytical tools as well as bioinspired engineering, biomineralisation and tissue engineering. Additional to the biomedical application of nanotechnological tools, the nanosized building blocks can be used for the construction of tailor made materials using biological principles (Schmid et al., 2006, Cormode et al., 2009).

1.2 Nanomaterials

Nanomaterials are usually illustrated as possess within limit one dimension smaller than 100 nm. In a generous definition, it refers to the indicated materials that are managed at an atomic, molecular, or macromolecular scale in order to perform functionality that is altered from that found in molecular form (Linkov & Steevens, 2009). Meanwhile, Ramsden (2011) defines nanomaterial as having one or more apparent dimension in the nanoscale or possessing internal or surface structure in the nanoscale. Nanomaterial can be classified into two, which are nano-object and nanostrustured materials. Nano-objects are categorized into their external dimension as shown in Figure 1.1. Nanostructured material is explicitly clarified as processing internal surface structure in the nanoscale (Ramsden 2011).

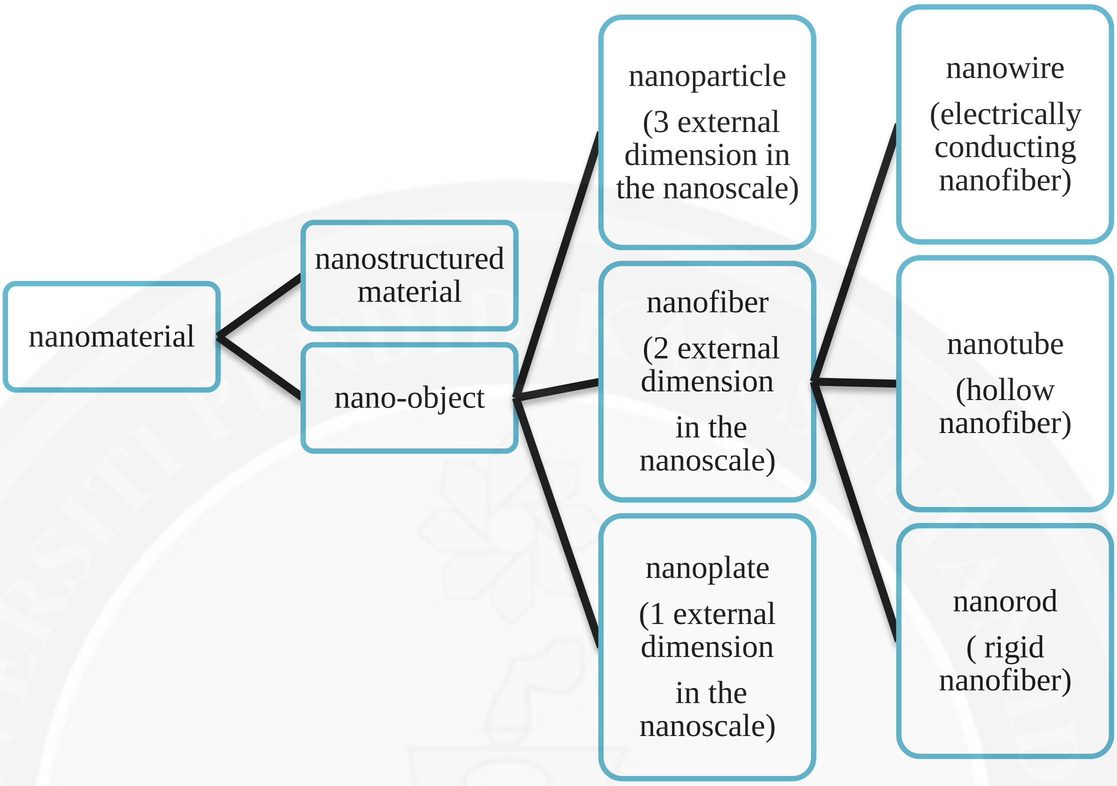

Figure 1.1. Concept systems for nanotechnology (Ramsden, 2011)

Nanomaterials depend on size of dependent properties. Based on Viswanathan (2009), generally, they can be recognized as chemical properties (reactivity and catalyst), thermal property (melting temperature), mechanical property (adhesion and capillary forces), optical property (absorption and scattering light), electrical properties (tunneling of current), and magnetic properties (super paramagnetic effect). This list can play an important role for biochemical properties and sensor application. There are two approaches to the synthesis of nanomaterials which are top down and bottom-up. Attrition or milling is a typical top down method in manufacturing nanoparticles, whereas the colloidal dispersion is a bottom-up approach in synthesis of nanoparticle (Cao & Wang, 2011). Furthermore, Ramsden (2011) state that nanostructured materials should be produced using bottom to bottom technology, which is also known as molecular manufacturing or mechanosynthesis or "pick and place" chemistry that literally construct things atom-by-atom.

Currently, nanomaterials are often synthesized using carbon-based, for example, buckyballs or fullerenes, nanotube and also metal based, for example, Zn, Al, Mg, Cd, and Ti oxides molecule, but other materials have been extensively used as well, and are more consistently expected in the future (Linkov et al., 2007).

Nanomaterials can be used in many applications such as enhancing sensing or detection of the environmental contaminants, for example, the uses of zinc (II) oxide (ZnO) as a gas sensor. The early nanostructure of ZnO used as a gas sensor is nanoparticles. The higher activity and fast response of the nanoparticle based sensors are due to the enhancement of surface area at nanodimensions coupled with the possible low assembly cost, ease of miniaturization, and the compatibility with microelectronic circuitry provides a renew interest in the gas sensing properties of metal oxide semiconductors (Fryxell & Cao, 2007).

1.3 Environmental Application of Nanomaterial

Nanotechnology is used widely in environmental perseverance. In the present day, nanotechnology plays a highly important role towards agricultural. The discoveries in this field lead the cultivated field to tremendous changes and in better cultivation. It is used in removal of nitrogen and sulphur oxides, water purification, nuclear waste treatment and many more. Nanotechnology consists of nanopaticles and nanocomposite that are used in many applications of nanotechnology.

Nanoparticle is like a bridge between bulk material and atomic or molecular structure. It possesses optical properties as, they were small enough to confine their electrons and produce quantum effect. In general, the massive reduction in the particle size results in an increase in surface to bulk atom ratio and increases in surface area (Viswanathan, 2009). Nanoparticulate materials impart improved properties for the devices, systems or formulation in which they are key components (Higgins, 1999). Despite being the largest current mercenary segment of nanotechnology, nanoparticle has yet relatively few direct large-scale commercial uses. However, most of the application like photographic emulsions and carbon black are in composite; a mixture of components are added (Ramsden, 2011).

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material (Spowart, 2010). A nanocomposite differs from a conventional composite only as the additive is nanosized and better dispersed in the matrix (Ramsden, 2011). The same interpretation gives by Viswanathan (2009), nanocomposite is defined as materials derived by the combination of two or more building blocks in one material, containing at least one of the components in the nanometer length scale.

In the broadest sense, nanocomposite is a combination of 2 or purer substances with different properties in order to create new material with desirable and better properties. For example, the use of existing polypropylene based composite with polyhydroxyalkanoate (PHA)-nanoclay composite for automobile parts (Viswanathan, 2009). PHA is biodegradable as well as easily recyclable, and it is lighter than polypropylene that leads to reduction of vehicle weight as well as fuel consumption. Another application is metal coated TiO_2 nanoparticle for sunlight based applications. TiO_2 particles coated with silver and gold nanoparticles show photocatalytic activity in a visible region (Viswanathan, 2009). The positive impact of this material is not only on the environmental front which is photodecomposition of pollutants, but also on the development of new solar based technologies, photovoltaic cells, photochemical splitting of water, and artificial photosynthesis.

1.4 The Use of Herbicides

Herbicides are chemical substance that is used to specifically kill plants and a key component of successful agriculture (Ornostay et al., 2013). It belongs to a group of chemicals known as pesticides, which destroy, prevent, repel, or mitigate any pest. Herbicides substantially minimize or eliminate labor and machine requirements and modify crop production techniques to increase farm efficiency, reduce horse power, and perhaps lessen energy requirements (Zimdahl, 2007). The preliminary of the organic herbicides which is dinitrophenols, were discovered in the 1930s in France; however, their utility in turf was limited by their relatively poor selectivity and efficacy. Whereas the first turf grass herbicides dated back to the early 1900s when many inorganic compounds, including ferrous ($FeSO_4$) and ferric ($Fe_2(SO_4)$), sulphate, sodium chlorate ($NaClO_3$), and sodium arsenite ($NaAsO_2$) were used for selectively controlling some annual grasses and broadleaf weeds (Turgeon *et al.*, 2009).

Mode of action of herbicides is the bio chemical or physical mechanism, including absorption into plant and translocation to the site action and also disrupting or altering one or more metabolic process resulting in plant death (Tu et al., 2001). There are two types of mobility of herbicides, which are non mobile and mobile. Non mobile herbicides are contact herbicides that cause the injury symptoms, confine to the side of uptake when the herbicides contact with the plant. Whereas, mobile herbicides are systemic herbicides that cause the injury symptoms that will be where the herbicides translocate and concentrate in the plant.

Even supposing that herbicides are applied to plant and soil which control plant parasites and weeds, they may as well affect soil properties, microorganisms, and hosts. These herbicides are also deposited into aquatic environments via agricultural runoff and leaching (Ornostay et al., 2013). Herbicide's contamination of soils, water, and either matrix may also be caused by accident spills during manufacturing, formulation, and shipment or at local agrochemical dealerships (Joo & Cheng, 2006). Based on the Pesticides Leaching Assessment Program (PLAP), leaching is determined on sandy and loamy soils as the weighted average concentration in soil water and drainage water where the pesticides is applied nearby (Brüsch *et al.*, 2013). Hence, this situation might be the major jeopardize for human health and give bad effect for environment. Some herbicides such as 2,4-(dichlorophenoxy) acetic acid (2,4-D) are comparatively low biodegradability, while others are considerably long-term persistence in soil and more resistant, including most chlorinated insecticides such as endosulfan, heptachlor, and diedrin (Joo & Cheng, 2006, Ornostay et al., 2013).

1.5 Problem Statements

In the present day, most of the agricultural activities utilize herbicides as weed killers in order to boost their production, which will ensure in extensive doses of organic and inorganic wastes being discharged to the environmental. When this agrochemical reaches non-target area such as the lower soil layer, ground water, rivers, and the atmosphere, they will endow inimical effect to the ambience.

Kamble (2007), studies the effect of herbicides on meiosis of Hibiscus *Cannabinus Linn*, discovers that the total percentage abnormalities in pollen mother cells increase with increased in concentration of herbicide. Several studies have shown the same result; management practices could give acute impact to plant pathogens. Herbicide application has often been cited as an example of a management practice that affects plant pathogens and disease development in various cropping systems. The activity of herbicides can extend beyond their target organisms and inhibit spore germination or mycelial growth, alter the level of phytoalexins, or interfere with other physiological processes in plants (Debajan & Anil, 2008).

The uses of herbicides can also risk human health. Herbicides are firmly conceived to present a bigger menace because they are highly concentrated in the water supply due to runoff from the agricultural use. The prevalent exposure of the world population to this substance has caused concern over their potential health consequences. Joo and Cheng (2006) also state that residue of pesticides has a significant environmental impact on aquatic ecosystems and mammals. These uncontrolled released pesticides may flow into the drainage and irrigation canal that may led to pollution.

The controlled release formulation is a condition where pesticide is incorporated in a matrix or carrier before application, whereby limiting the amount available for unwanted process (Hashim et al., 2012). Pesticides play a critical role in worldwide agriculture, but uncontrolled releases are major environmental concerns (Joo & Cheng, 2006). Therefore, the control release formulation can be used to lower the hazards of environmental pollution by slashing the unrequired amount of herbicides released to the surroundings.

Previous studies have been done for controlled release formulation of zinc layered hydroxide-2-(3-chlorophenoxy)propionate nanocomposite (ZLH-CPPA) into chloride and carbonate solution, but there is no report on zinc layered hydroxide-3-(4-methoxyphenyl)propionate nanocomposite (ZLH-MPP) and layered double hydroxide-3-(4-methoxyphenyl)propionate nanocomposite (LDH-MPP). 3-(4-methoxyphenyl)propionic acid (MPP) is one of the herbicides that is employed in agricultural activities. It can also be called as 4-methoxyhydrocinnamic acid or p-methoxyhydrocinnamic acid with the formula $C_{10}H_{12}O_3$, and the molecular weight is

180.2 g/mol. The structure of 3-(4-methoxyphenyl)propionic acid is shown in Figure 1.2. This study is conducted to synthesize ZLH and LDH nanocomposites by intercalate MPP anions into ZLH and LDH interlayer and then followed by their controlled release study.

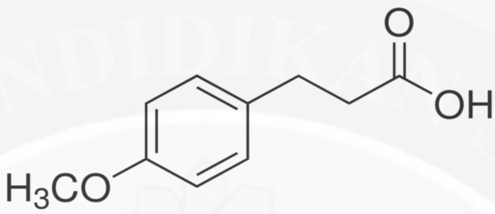

Figure 1.2. Molecular structures of 3-(4-methoxyphenyl)propionic acid

1.6 Objectives of Study

a) To prepare zinc layered hydroxides-3-(4-methoxyphenyl)propionate (ZLH-MPP) nanocomposite and layered double hydroxide-3-(4-methoxyphenyl)propionate (LDH-MPP) nanocomposite.

b) To characterize the physiochemical properties of ZLH-MPP and LDH-MPP nanocomposite using PXRD, FTIR, CHNO-S, ICP-OES, TGA/DTG, and FESEM.

c) To study the controlled release of 3-(4-methoxyphenyl)propionic acid (MPP) from interlayer zinc layered hydroxide (ZLH) and layered double hydroxide (LDH) in various concentrations of salt solutions.