SYNTHESIS AND CHARACTERIZATION OF LAYERED METAL HYDROXIDE-3-(4-HYDROXYPHENYL)PROPIONATE NANOCOMPOSITES FOR CONTROLLED RELEASE FORMULATION

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ABSTRACT

The aim of this research is to synthesize and characterize the nanocomposites and also to determine the controlled release behaviour of 3-(4-hydroxyphenyl)propionic acid (HPP) anion. Zinc layered hydroxide-3-(4-hydroxyphenyl)propionate (ZLH-HPP) nanocomposite was synthesized by direct reaction method. Meanwhile, layered double hydroxide-3-(4-hydroxyphenyl)propionate (LDH-HPP) nanocomposite was synthesized by ion-exchange method. The ZLH-HPP and LDH-HPP nanocomposites physicochemical properties was characterized using powder x-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), carbon, hydrogen, nitrogen, oxygen and sulphur analysis, inductive coupled plasma-optical emission spectrometer, thermogravimetric analysis and derivative thermogravimetry, and field emission scanning electron microscope. Research findings confirmed that two nanocomposites ZLH-HPP and LDH-HPP were successfully synthesized with PXRD pattern of ZLH-HPP and LDH-HPP nanocomposites show well order layered structure with basal spacing 25.1 Å and 17.7 Å respectively. FTIR and compositional studied revealed the presence of the HPP anions between the interlayer of nanocomposites. Result of controlled release study showed that release of HPP anions from both nanocomposites into sodium dihydrogen phosphate solution yielded the highest percentage accumulated release of HPP anions compared to sodium sulphate and sodium chloride solutions. The kinetic study of HPP anions from ZLH interlayer galleries into sodium dihydrogen phosphate, sodium sulphate and sodium chloride solutions was found to be governed by pseudo-second order, parabolic diffusion and first order model respectively. Meanwhile, the kinetic study of HPP anion from LDH interlayer in all solutions was controlled by pseudo-second order. As a conclusion, ZLH-HPP and LDH-HPP nanocomposites were successfully synthesized and intercalation of HPP anions between the interlayer was confirmed by characterization data. Controlled release study of herbicides was governed to one of the kinetic model that has been proposed. The implications of this study explained that the new nanocomposite formulations are highly effective, involve a low production cost and safer for environment.

SINTESIS DAN PENCIRIAN NANOKOMPOSIT LAPISAN LOGAM HIDROKSIDA-3-(4-HIDROKSIFENIL)PROPIONAT BAGI FORMULASI LEPASAN TERKAWAL

ABSTRAK

Kajian ini bertujuan mensintesis dan mencirikan nanokomposit serta menentukan tingkah laku lepasan terkawal bagi anion asid 3-(4-hidroksifenil)propionik (HFP). Nanokomposit lapisan zink hidroksida-3-(4-hidroksifenil)propionat (LZH-HFP) telah disintesis dengan kaedah tindak balas langsung. Manakala, nanokomposit lapisan berganda hidroksida-3-(4-hidroksifenil)propionat (LBH-HFP) disintesis dengan kaedah pertukaran ion. Sifat fisikokimia nanokomposit LZH-HFP dan LBH-HFP telah dicirikan menggunakan pembelauan serbuk sinar-x (PSSX), spektroskopi inframerah transformasi Fourier (IMTF), analisis karbon, hidrogen, nitrogen, oksigen dan sulfur, spektrometer pancaran optik plasma gandingan aruhan, analisis termogravimetri dan terbitan termogravimetri, dan mikroskop imbasan elektron pancaran medan. Dapatan kajian membuktikan dua nanokomposit LZH-HFP dan LBH-HFP telah berjaya disintesis dengan corak PSSX menunjukkan struktur susunan lapisan yang baik dengan jarak dasar masing-masing 25.1 Å dan 17.7 Å. IMTF dan kajian komposisi telah mengesahkan kewujudan anion HFP di antara lapisan nanokomposit. Hasil kajian lepasan terkawal menunjukkan lepasan anion HFP daripada kedua-dua nanokomposit ke dalam larutan natrium dihidrogen fosfat memperolehi peratusan pelepasan terkumpul tertinggi berbanding larutan natrium sulfat dan natrium klorida. Kajian kinetik anion HFP daripada galeri ruang antara lapisan LZH ke dalam larutan natrium dihidrogen fosfat, natrium sulfat dan natrium klorida adalah masing-masing mengikut tertib pseudo-kedua, penyebaran parabola dan model tertib pertama. Manakala, kajian kinetik anion HFP daripada ruang antara lapisan LBH ke dalam semua larutan menunjukkan kelakuan pelepasan mengikut tertib pseudo-kedua. Kesimpulannya, nanokomposit LZH-HFP dan LBH-HFP telah berjaya disintesis dan interkalasi anion HFP di antara lapisan disahkan oleh data pencirian. Kajian lepasan terkawal racun rumpai mengikut salah satu model kinetik yang telah diusulkan. Implikasi kajian ini menjelaskan bahawa formulasi nanokomposit baharu ini adalah sangat efektif, melibatkan kos pengeluaran yang rendah dan lebih selamat untuk alam sekitar.

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LIST OF ABBREVIATIONS

Å	Angstrom
CHNOS	Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
HDS	Hydroxyl Double Salt
HPP	3-(4-hydroxyphenyl)propionic acid
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
LDH	Layered Double Hydroxide
LDH-HPP	Layered-double hydroxide-3-(4-hydroxyphenyl)propionate
LHS	Layered Hydroxide Salt
LMH	Layered Metal Hydroxide
PXRD	Powder X-ray Diffraction
R	Ratio
TGA/DTG	Thermogravimetric Analysis and Derivative Thermogravimetry
UV-vis	Ultraviolet-visible Spectrophotometer
ZLH	Zinc layered hydroxide
ZLH-HPP	zinc-layered hydroxide-3-(4-hydroxyphenyl)propionate
ZnO	Zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology

Nanotechnology gives great impact in the development of science and technology and attracts great interest in new research opportunities in chemistry, physics, materials science, engineering and many other fields (Ramsden, 2011). According to Diwan and Bharadwaj (2006), nano is derived from Greek word nanos and latin nanus meaning dwarf. Based on Rao, Muller and Cheetham (2004), nanotechnology is science, engineering and technology conducted at the nanoscale, which is about 1 to 100 nanometers. Meanwhile, Ramsden (2011) explained that nanotechnology is the application of science knowledge to measure, create, pattern, manipulate, utilize or incorporate materials and component in the nanoscale. Capek (2006) reported that nanotechnology is a field that focuses on the development of synthetic methods and surface analytical tools for building structures and materials, typically on the sub-100 nanometer scale, identification of the chemical and physical consequences of miniaturization and the use of such properties in the development of novel and functional materials and devices. On the previous definition reported by Kuzma (2011), the nanotechnology was defined as technological revolution which it involves the engineering of matter at the nanoscale, approximately the size of a few molecules. Basically nanotechnology is the manipulation of matter on an atomic and molecular size.

The uncanny ability of nanotechnology to design, synthesize and manipulate structures at the nanoscale has attracted great interest amongst researchers because they are expected to be used in various applications as well as in the development of science and technology (Rao *et al.*, 2004). It was supported by Kuzma (2011) that nanotechnology can be used across the science field such as chemistry, biology, physics, material science and engineering which brings to the next technological revolution in manufacturing, consumer products, electronics, medicine, health care and energy. Wick, Foley and Guston (2012) reported that nanoscience can bring the solutions to the urgent challenges of environmental degradation, resource depletion, growth in population and cities and in energy usage. Other than that, devices in the nanoscale need less material to make them, use less energy and other consumables (Ramsden, 2011).

Today's scientist and engineers are developing materials at the nanoscale because of their enhanced properties such as higher strength, lighter weight, thermal properties and greater chemical reactivity than larger-scale counterparts (Diwan &

Bharadwaj, 2006). The reasons of these unique features are when the characteristic structural feature is intermediate in extent between isolated atoms and bulk materials, the object may display physical attribute substantially different from display by either atom or bulky materials (Kelsall, Hamley & Geoghegan, 2005). The parallel development of the nanomaterials, a variety of new tools to characterization and manipulation of atom and molecules such as scanning tunnelling microscopes (STM), atomic force microscope (AFM) and scanning probe microscopy (SPM) were emerged (Capek, 2006).

1.1.2 Nanocomposite

The development of nanotechnology has attracted scientists, engineers, and industries to invent new multi-functional material called nanocomposite materials with various unique combinations of properties (Manocha, Valand, Patel, Warrier & Manocha, 2006). Nanocomposite is defined as a multiphases solid material where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nanoscale repeated distances between the different phases that make up the material (Spowart, 2009). Nanocomposite is a composite material, in which one of the components has at least one dimension that is nanoscopic in size, which is around 10^{-9} m (Manocha *et al.*, 2006).

The properties of nanocomposites not only depend on individual component used, but it is also depend on the morphology and the interfacial characteristics as well (Capek, 2006). Meanwhile Jeon and Baek (2010) define nanocomposite as multiphase materials, where one of the phases has nanoscale additives. Nanocomposite imparts improved properties led to brand new materials with increasing functionality offer a new scope for developing new hybrid materials at nanoscale dimensions (Hussein, Nazarudin, Sarijo & Yarmo, 2012).

1.2 Agrochemical Herbicides

Agriculture plays an important role in the world's primary food resources. Increasing in human population leads to the development of new technologies to maximize the cultivated yield to fulfil the human need. Basically, weeds are objectionable to farmers primarily because they reduce the quality and quantities of cultivated production and produce allergens or contact dermatitis that affect public health. Conventionally, farmers used cultivation, hoeing and hand pulling to control the weed. With recent development in agricultural technologies, herbicides are used to control the weed and provide more effective and economical means. Herbicides have largely replaced mechanical method of weed control in countries where intensive and highly mechanized agriculture is practiced. Herbicide comes from the Latin herba, meaning plant, and caedere meaning to kill. Therefore, herbicides are any chemical substance that is partially or totally used to kill the specific plant (Zimdahl, 2007). Most herbicides kill plants by disrupting or altering one or more metabolic process (Turgeon, McCarty & Christian, 2009

Dissipation of herbicides can occur above the soil surface as soon after the application of herbicides by drift, volatilization, photolysis and runoff. Meanwhile adsorption into soil surfaces, leaching and dilution through the soil profile, adsorption by plant, chemical reaction, and microbial degradation are processes that occur below the soil surface (Cespedes, Sanchez, Garcia & Perez, 2007). Drift can lead to the contamination of adjacent land and surface water resources by movement of airborne herbicides particles from the target site to a nontarget site (Turgeon *et al.,* 2009).

Volatilization is the changes of molecules, physical state of herbicides from liquid to gas and lost to the atmosphere (Tu, Hurd & Randall, 2001). In the gases state volatile herbicides can travel for a long-distance and affect environmental quality. Photodegradation is the breakdown of herbicides by radiation on the internal chemical bond when herbicide molecules absorb electromagnetic radiation at wavelength 290 until 450 nanometers, which cause excitation of electrons resulting in the formation or breakage of chemical bonds within the molecule (Zimdahl, 2007).

Adsorption is a process of accumulation at an interface and is contrasted with absorption or passage through an interface. Leaching and runoff should give environmental concern because they can lead to ground water contamination. Runoff is the surface movement of herbicides across the ground surfaced and usually occurs as a result of surface water movement during irrigation or natural rainfall. Meanwhile, leaching is the process by which an herbicide is carried downward in the soil profile with water and may transported them down the water table, where it can, consequently, move in drain tile to ponds, streams, storm sewers or other receptacle (Turgeon *et al.,* 2009).

1.2.1 3-(4-hydroxyphenyl)propionic Acid (HPP)

3-(4-hydroxyphenyl)propionic Acid (HPP) or phloretic acid or also known as 3(*p*-hydroxyphenyl)propionic acid have chemical formula $HOC_6H_4CH_2CH_2CO_2H$ with molecular weight 166.17 is an herbicides. The molecular structure of 3-(4-hydroxyphenyl)propionic acid (HPP) shown in Figure 1.1. One of the ways to classify the herbicides is based on the site of action where the specific site of action in plant cell takes place with respective mechanism (Zimdahl, 2007). Generally, herbicides come with several mechanisms of action, but most of the herbicides have the primary site of action. The mechanism of action is the series of the biochemical or biophysical lesions that creates the herbicide's initial phytotoxic effect (Turgeon *et al.,* 2009). Classification scheme developed by Devine (Zimdahl, 2007) divide herbicides into seven sites or mechanism of action group; plant growth regulator, amino acid biosynthesis inhibitors, respiration inhibitors, cell growth inhibitors, cell membrane disruptors and inhibitors, pigment production inhibitor and fatty acid biosynthesis inhibitors. The seven groups undergo further subdivided using the site of action described by Mallory-Smith and Retzinger into 25 subdivisions (Zimdahl, 2007). HPP is an auxinic growth regulator under class of plant growth regulator.

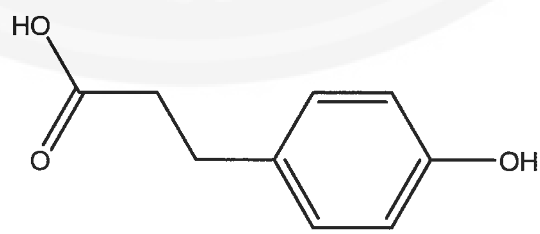

Figure 1.1. Molecular structure of 3-(4-hydroxyphenyl)propionic acid (HPP)

The plant growth influenced by hormone, which is chemicals produced in one location and act in very low concentration at another location. Auxins are one of the hormones that regulate cell growth and development, particularly the growth of excised coleoptiles tissue and their activity within the plant are under direct metabolic control. Meanwhile auxinic growth regulators herbicides are not under metabolic control and they cause abnormal growth in susceptible plant (Turgeon *et al.*, 2009). The plant growth regulators include auxinic and non-auxinic subgroups. Auxinic growth regulators are believed to have multiple sites of action at which they disrupt the balance of hormone and alter the synthesis of protein and nucleic acid by disrupting at one or two specific auxin-binding protein in the plasma membrane which leads to various plant growth abnormalities, especially on new tissues (Tu *et al.*, 2001). HPP is an auxinic growth regulator who can interfere with RNA production and change the properties and development in the plasma membrane. The present of HPP affects the rate of protein synthesis and increases the concentration of RNA, which also disrupts the auxin level.

1.3 Problem Statement

Agriculture plays an important role in production of basic food crops. The growing demand for food placed agriculture to increase their production. Herbicide is one of the tools used to ensure an abundant food supply. However, studied by Caspedas *et al.*, (2007) reported that effectiveness of the herbicides is losses about 30% when they are applied. To get a better result, normally farmers are applied the herbicides repeatedly and relatively in high doses (Sopena, Maqueda & Morilla, 2009). However, these herbicides can be easily washed into the stream or infiltrate the soil by herbicide drift, volatilization, and leach through soil to groundwater or carried in surfaces or substances runoff.

Herbicides are rarely applied in the form in which they are synthesized but along with the active ingredient, substances are added to fulfil the regulatory standard without diminishing the effectiveness of the herbicides (Sopena *et al.*, 2009). Degradation occurs when an herbicide is decomposed to smaller component compound. When the herbicide degraded, it usually yields several compounds, each of which has its own chemical properties including toxicity. Meanwhile, the behaviour of herbicides in water depends on its solubility in water. Salts and acid tend to remain dissolved in water until degraded through photolysis or hydrolysis while ester will absorb to the suspended matter in water and precipitate to the sediments. Highly acidic or alkaline water can chemically alter an herbicide and change its behaviour in water (Tu *et al.*, 2001).

As the result of their dissipation of time of the agrochemical applications by using greater amounts of agrochemicals over a long period than what is actually needed, lead to crop damage and environmental contamination (Aouada, Maura, Orts & Mattoso, 2009). In addition, the widespread used of herbicides does not only affect targeted weed, but also non-target plant and animals. For example, loss of invasive riparian plant can cause changes in water temperature and clarity that can potentially impact the entire aquatic community and the physical structure of the system through bank erosion. Other than that, herbicides have been varying effect on soil microbial population depending on herbicides concentration and microbic present (Tu *et al.*, 2001).

In order to overcome this problem, controlled release formulation of herbicides is one of the well-known methods that had been used to get higher yield and better crop quality (Bashi, Hussien, Zainal & Tichit, 2013). In this method layered double hydroxide and layered metal hydroxide have been used as the host for herbicides due to high-capacity materials toward herbicide and very easy to synthesize (Bruna *et al.*, 2009; Hussein *et al.*, 2012a). In this study 3-(4-hydoxyphenyl)propionic acid (HPP) (Figure 1.1), herbicides have been used to be intercalated between ZLH and LDH layered using direct co-precipitation and ion-exchange method respectively.

1.4 Objectives

The objectives of this study are:

1. to synthesize zinc-layered hydroxide-3-(4-hydroxyphenyl)propionate (ZLH-HPP) nanocomposite via direct reaction method.
2. to synthesize Zn/Al-layered-double hydroxide-3-(4-hydroxyphenyl)propionate (LDH-HPP) nanocomposite via ion-exchange method.
3. to characterize the ZLH-HPP nanocomposite and LDH-HPP nanocomposite using powder X-ray Diffraction (PXRD), Fourier transform infrared (FTIR), carbon, hydrogen, nitrogen, oxygen and sulphur analysis (CHNO-S), inductively coupled plasma-optical emission (ICP-OES), thermal analysis TGA/DTG and field emission scanning electron microscope (FESEM).

4. to study the controlled release formulation of HPP anion from interlayer of ZLH-HPP and LDH-HPP nanocomposites into various concentration solutions.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanomaterials

Nanomaterials have received much recent attention in recent years due to their unique properties by manipulating structures at the nanoscale (Rao *et al.,* 2004). Nanomaterials is a material having one or more external dimensions in the nanoscale or having internal or surface at the nanoscale (Ramsden, 2011). Nanomaterials have a large surface area to volume ratio or high interfacial reactivity that contribute to unique physical and chemical properties that are not found in their bulk counterpart and lead to new classes of nanomaterials (Fryxell & Cao, 2007). The properties of the nanomaterials are affected by the size, hence the thermodynamic, electronic, optical and other characteristic can be modified by reducing the dimension-confinement and the dimension (Capek, 2006).

To develop complex-based structures and devices, the crucial aspect are the assembling the nanostructure into ordered array and functionality of the nanobuilding blocks (Rao *et al.,* 2004). There are various well-known method to synthesize nanomaterials such as sol-gel synthesis (Kurajica *et al.,* 2008), rehydration using structural memory effect (He *et al.,* 2006) and laser induced sputtering (Koper, Rajagopalan, Winecki & Klabunde, 2007). Explosive growth of methods of synthesizing nanomaterials leads to new nanomaterials such as nanoparticles, nanowires, nanotubes, nanosensors, nanoporous solid, nanocrystals and a variety of inorganic nanomaterials have been discovered as shown in Table 2.1 (Rao *et al.,* 2004). Khanan (2012) classifies nanomaterials into three main classes; nanoparticles or zero dimensions nanomaterials like atom clusters with particle diameter below 100 nm. Meanwhile, nanowires, nanotubes and nanocables having a width less than 100 nm is belong to one dimensional nanomaterials classes and the third class is two-dimensional nanomaterials such as nanofilm and superlatices with layer thickness in the nano-range.

Tables 2.1

Examples of nanomaterials (Rao *et al.,* 2004)

	Size (approximate) diameter(nm)	Materials
Nanocrystals and clusters (quantum dots)	1-10	Metals, semiconductors, magnetic materials
Other nanoparticles	1-100	Ceramic oxides
Nanowires	1-100	Metals, semiconductors, oxides, sulphides, nitrides
Nanotubes	1-100	Metal, layered metal chalcogenides
Nanoporous solids	Pore diam. 0.5-10	Zeolites, phosphate, etc.
Surface and thin films	Thickness1-1000	A variety of materials