SYNTHESIS OF MAGNESIUM LAYERED HYDROXIDE-3-(4-METHOXYPHENYL)PROPIONATE NANOCOMPOSITE FOR CONTROLLED RELEASE FORMULATION PROPERTIES

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THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE (CHEMISTRY) (MASTER BY RESEARCH)

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ABSTRACT

This study aims to synthesise magnesium layered hydroxide-3-(4-methoxyphenyl)propionate (MLH-MPP) and coated nanocomposites for controlled release formulation of herbicide. Direct reaction method has been used to intercalate MPP into the space between layers of MLH. Further, carboxymethyl cellulose (CMC) and chitosan, was coated on the external surface of the MLH-MPP nanocomposite to form new materials, named MLH-MPP/CMC and MLH-MPP/chitosan nanocomposites, respectively. The physicochemical properties of all nanocomposites were characterised using powder x-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), carbon, hydrogen, nitrogen and sulphur (CHNS) analyser, inductive coupled plasma optical emission spectrometry (ICP-OES), thermogravimetric analysis and derivative thermogravimetry (TGA/DTG), field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). Results of this study showed that the XRD pattern revealed an intense and sharp peak with basal spacing of 18.9 Å, which is proved that MPP anions were successfully intercalated into the space between layers of MLH in a monolayer arrangement. The XRD pattern for both coated nanocomposites indicates the adsorption of the polymer on the surface of MLH-MPP nanocomposite. TGA/DTG spectra have shown an increase in the thermal stability of the MPP anion in all nanocomposites. Both coated nanocomposites showed a slower controlled release compared to the MLH-MPP nanocomposite and the release behaviours of MPP anion from all nanocomposites were controlled by the pseudo-second order kinetics. In conclusion, the MLH-MPP and coated nanocomposites have been successfully synthesised and can be used as a host for the controlled release formulations of herbicide. The implications from these results highlight the potential of the nanocomposite as encapsulation materials for controlled release formulations of herbicide in the agriculture sector.

Sintesis Nanokomposit Lapisan Hidroksida Magnesium-3-(4-Metoksifenil) Propionat Dan Bersalut Untuk Formulasi Pelepasan Terkawal Herbisida

ABSTRAK

Kajian ini bertujuan mensintesis nanokomposit lapisan hidroksida magnesium-3-(4-metoksifenil)propionat (LHM-MFP) dan bersalut untuk formulasi pelepasan terkawal herbisida. Kaedah tindak balas langsung telah digunakan untuk menginterkelasi MFP ke dalam ruang antara lapisan LHM. Selanjutnya, karboksimetil selulosa (KSS) dan kitosan, masing-masing telah disalut ke atas permukaan luar nanokomposit LHM-MFP untuk membentuk bahan baru, yang dinamakan nanokomposit LHM-MFP/KSS dan LHM-MFP/kitosan. Sifat fisikokimia untuk semua nanokomposit telah dicirikan menggunakan pembelauan serbuk sinar-x (PSSX), spektroskopi inframerah transformasi Fourier (IMTF), penganalisis karbon, hidrogen, nitrogen dan sulfur (KHNS), spektrometri pancaran optik plasma gandingan aruhan (SPO-PGA), analisis termogravimetri dan termogravimetri terbitan (ATG/TGT), mikroskop imbasan pancaran medan elektron (MIPME) dan mikroskop transmisi elektron (MTE). Keputusan kajian ini menunjukkan bahawa pola PSSX mendedahkan puncak yang jelas dan tajam dengan jarak dasar 18.9 Å, yang membuktikan bahawa anion MFP telah berjaya diinterkelasikan ke dalam ruang antara lapisan LHM dalam susunan monolapisan. Pola PSSX untuk kedua-dua nanokomposit bersalut menunjukkan terdapatnya penjerapan polimer pada permukaan nanokomposit LHM-MFP. Spektra ATG/TTG telah menunjukkan peningkatan dalam kestabilan terma bagi anion MFP dalam semua nanokomposit. Kedua-dua nanokomposit bersalut menunjukkan pelepasan terkawal yang lebih perlahan berbanding nanokomposit LHM-MFP dan tingkah laku pengeluaran anion MFP daripada semua nanokomposit dikawal oleh kinetik tertib pseudo-kedua. Kesimpulannya, nanokomposit MLH-MFP dan bersalut telah berjaya disintesiskan dan boleh digunakan sebagai perumah bagi formulasi pelepasan terkawal herbisida. Implikasi dapatan ini telah menyerlahkan lagi potensi nanokomposit sebagai bahan pengkapsulan untuk formulasi pelepasan terkawal bagi herbisida dalam sektor pertanian.

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LIST OF ABBREVIATIONS

Al^{3+}	Aluminium ion
Co	Cobalt
Cr	Chromium
CRF	Controlled release formulation
CFX	Ciprofloxacin
CHNS	Carbon, hydrogen, nitrogen, sulphur
CMC	Carboxymethyl cellulose
CM-chit	Carboxymethyl-chitosan
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
CPPA	2-(3-chlorophenoxy)propionate
DEX	Dextran
DPBA	4-(2,4-dichlorophenoxybutyrate)
DRS	Diffuse reflectance spectra
FTIR	Fourier transform infrared
FESEM	Field emission scanning electron microscope
H-bent	Bentonite
HDS	Hydroxide double salt
ICP-OES	Inductively coupled plasma/optical emission spectrometer
LDH	Layered double hydroxide
LHS	Layered hydroxide salts
LMH	Layered metal hydroxide
$MgCO_3$	Magnesium carbonate

MLH	Magnesium layered hydroxide
MoS_2	Molybdenite
MPP	3-(4-methoxyphenyl)propionic acid
$NaNO_3$	Sodium nitrate
NH_3-N	Ammonia-nitrogen
N_2O	Nitrous oxide
NPK	Nitrogen, phosphorus and potassium
n-TiO_2	Nano-size titanium oxide
NZA	Zinc hydroxyl acetate
PASA	Para-amino salicylic acid
pCA	P-coumaric acid
PEG	Poly(ethylene)glycol
PVA	Polyvinyl alcohol
PXRD	Powder X-ray diffraction
SWCNT	Single-walled carbon nanotube
TB	Tuberculosis
UV	Ultraviolet
UV/Vis	Ultraviolet visible
ZBS	Zinc basic salt
ZCA	Zinc copper hydroxyl acetate
ZHN	Zinc hydroxide nitrate
ZLH-CPPA	Zinc layered hydroxide-2-(3-chlorophhenoxy)propionate
ZLH-MPP	Zinc layered hydroxide-3-(4-methoxyphenyl)propionate

CHAPTER 1

INTRODUCTION

1.1 Exploration of Nanotechnology

Nanotechnology has grown tremendously in the past few years and the application of nanotechnology has developed flourishly. A stained glass window is one of the example applications of nanotechnology. Stained glass windows that are found in medieval churches contain different sizes of gold nanoparticles. The specific size of the particles created orange, purple, red or greenish colour to the glass. Stained glass windows can also be found in Sultan Abdul Samad Mosque or KLIA mosque. In the biomedical field, application of nanotechnology can be seen in tissue engineering scaffolds, drug delivery and cosmetics (Schulte, 2005). Tissue engineering scaffolds is a synthetic biodegradable tissue that provides temporary templates for cell seeding, invasion, proliferation and differentiation, resulting in regeneration of biologically functional tissue. From the application that was developed, it is proven that nanotechnology is not just one science, but it touches on a variety of sciences, such as physics, chemistry, mechanical engineering, materials science and biology. Therefore, nanotechnology is an interdisciplinary field that is interesting to be explored.

There are a number of definitions used to explain nanotechnology. Roco, Mirkin and Hersam (2011), stated that nanotechnology is the control and restructuring of matter at the nanoscale, at the atomic and molecular levels in the size range of about 1-100 nm. Ramsden (2011), also defined nanotechnology as the application of scientific knowledge to measure, create, pattern, manipulate, utilize or incorporate materials and components in the nanoscale. As mentioned before, definitions of nanotechnology vary, but it generally refers to understand and manipulate of matter on the nanoscale, from 1 nm to 100 nm (Zhu, Bartos & Porro, 2004). The ability to control the size of matter is important in order to create materials, devices and systems with new properties and wide functions.

Nanotechnology has entered one of the most promising scientific fields of research for decades. This is due to the nanotechnology deals with the production, processing and application of materials with sizes less than 100 nm, the reduction in size of matter to nanoscale range will increase to surface-to-volume ratio. Thus, improved the properties of materials (Neethirajan & Jayas, 2010). For example, discovery on silicon chips by nanotechnology for two decades has led to the rise of advances in electronics, computing and communications. Silicon chip is electronics equipment consisting of a small crystal of a silicon semiconductor fabricated to carry out a number of electronic functions in an integrated circuit. The advancement created a better application like speed, accuracy for nowadays computers and transforms it from room-sized devices to the portable sized.

The European Technology Platform (ETP) group has defined nanomedicine as the application of nanotechnology to achieve breakthroughs in healthcare. Nanotechnology and nanomedicine are rapidly growing fields that encompass the creation of materials and devices at atomic, molecular and supramolecular level, for potential clinical use. Advances in nanotechnology have brought us closer to the development of dual and multi-functional nanoparticles that challenge the traditional distinction between diagnostic and treatment agents. Nanomedicine consists of several sub domains including diagnostics and imaging, drug delivery, and regenerative medicine (Adlakha-Hutcheon et al., 2009). In January 2005, nanotechnology-based drug called Abraxane was approved, and it is used in the battle against breast cancer (Criswell, 2007). Nanomedicine is dominated by nanoparticle drug delivery systems due to their ability to cross biological barriers, accumulate at tumour sites and increase the solubility of drugs.

Malaysia's goal known as *Wawasan 2020* is to become an industrialised and developed nation by the year 2020. There are nine key points of *Wawasan 2020* and one of them is, to establish a progressive and inventive in science and society. Thus, Malaysians are encouraged to be contributors to the scientific and technological civilisation and not only consumers of technology. Therefore, the exploration in nanotechnology will pave the way of Malaysia to achieve this *Wawasan 2020*.

1.2 Nanomaterial

The term use of nanotechnology and nanomaterials are often misleading (Bawa, Audette & Rubinstein, 2016). Nanotechnology referred to the technology used, while nanomaterials referred to chemical substances or materials that are used at the nanoscale. Nanomaterials are materials that have structural components smaller than 100 nm in at least one dimension (Khot, Sankaran, Maja, Ehsani & Schuster, 2012).

Nanomaterials are implicated in several domains such as chemistry, electronics, high-density magnetic recording media, sensors, biotechnology and many more. The applications of nanomaterials are very wide due to their excellent and unique optical, electrical, magnetic, catalytic, biological or mechanical properties. Those properties are originated from finely tuned nanoarchitectures and nanostructures of these materials (Capek, 2006). The syntheses of nanomaterials are achieved mainly through two approaches identified as top-down and bottom-up approach. The top-down approach involves breaking down the bulk size of the materials to the nanometer scale, while the bottom-up approach refers to the approach that builds a material up from the bottom. Attrition or milling is a typical top-down method in making nanoparticles whereas the colloidal dispersion is a good example of bottom-up method (Cao & Wang, 2011).

Several researches were carried out on the risk faced by the environmental, health harms and industrial. Thus, nanomaterials give solution for the arising risk. Earlier in 1900, carbon black was discovered as a nanomaterial that is used in car tyre to increase the life of the tyre and provide the black colour. Nanomaterials can also be used in the treatment of wastewater. Water is the most essential substance for all living life. As mention before, nanomaterials often possess novel size-dependent properties different from their large counterparts. In the treatment of wastewater utilise the smoothly scalable size-dependent surface area, such as fast dissolution, high reactivity, strong sorption and superparamagnetism (Qu, Alvarez & Li, 2013). Nano-absorbents can be integrated into existing treatment processes in slurry reactors or adsorbers. These nano-adsorbents can be highly efficient since all surfaces of the adsorbents are utilised and the mixing greatly facilitates the mass transfer. The example of nano-adsorbents is carbon based nano-adsorbents, like carbon nanotubes (CNTs) which is used in organic and heavy metal removal (Pan & Xing, 2008). It is clear that nowadays, nanotechnology and nanomaterials have received a great deal of interest in the various research areas. Thus, nanomaterials soon will be recognised in commercial market.

1.2.1 Nanomaterials for Agrochemicals

The development of nanotechnology collaborates with biotechnology has significantly expanded the application of nanomaterials in various fields. The application of nanotechnology in agriculture normally focused on the significance of the nanomaterials in order to improve the efficiency and productivity. There are some studies that have been done on the function of nanomaterials towards plant germination and growth. The effect of nano-size titanium oxide (n-TiO_2) on the germination of tomato, onion and radish seeds had been carried out and the germination of tomato seed showed the most positive outcomes. The positive results are involved with two main reasons which are, the nano size of TiO_2 and a great contact area between this nanomaterials with the root and testa. The acceleration of seed germination that caused by n-TiO_2 depends on the species, surface structure of testa, timing and method of application of n-TiO_2 (Haghighi & Silva, 2014b). Carbon nanotubes (CNTs) can be applied to change the morphology and physiology characteristics of plant cells. Haghighi and Silva (2014a) carried out a research on the effect of CNT on the seed germination and seeding growth of tomato, onion, radish and cabbage. From the previous research, it showed that CNTs had a greater positive impact on germination percentage and seedling length of anion compared to other crops.

Nanomaterials also help in plant protection and production. Pesticides are used to protect plant from pests. Nanopesticides can be used to increase the pesticidal properties, thus give a huge impact to the production plants. There are lots of researches on nanopesticides carried out nowadays, for examples the nanopesticide with photocatalysis (Jianhui, Kelong, Yuelong & Suqin, 2005), nanoencapsulation of imidacloprid with chitosan and alginate (Guan, Chi, Yu & Li, 2010) and the controlled delivery system of water-soluble pesticide validamycin (Liu et al., 2006). This is due to the useful properties of nanopesticides itself. Nanopesticides has a higher stiffness, permeability, crystallinity, thermal stability, solubility and biodegradability (Bouwmeester et al., 2009). In addition, nanomaterial can also be applied in agricultural as a pesticide residue detectors and plant pathogen detectors (Khot et al., 2012).