CONTROLLED RELEASE FORMULATION OF ACTIVE AGENT-ZINC LAYERED HYDROXIDE INTERCALATED NANOCOMPOSITE FOR PEST CONTROL

ZUHAILIMUNA BINTI MUDA

UNIVERSITI PENDIDIKAN SULTAN IDRIS

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ZUHAILIMUNA BINTI MUDA

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ABSTRACT

This research aimed to synthesis active agent-zinc layered hydroxide intercalated agrochemical nanocomposites namely zinc layered hydroxide-sodium dodecyl sulphate-isoprocarb (ZLH-SDS-ISO), zinc layered hydroxide-sodium dodecyl sulphate-propoxur (ZLH-SDS-PRO) and zinc layered hydroxide-sodium dodecyl sulphate-thiacloprid (ZLH-SDS-THI) using ion exchange method for pest control. Surface modification of nanocomposites was performed using chitosan and cellulose acetate. The nanocomposites were characterized using powder x-ray diffraction (PXRD), Fourier transform infrared (FTIR), elemental analysis, thermogravimetric and differential thermogravimetric analysis (TGA/DTG), field emission scanning electron microscope (FESEM), and surface area analysis. The results of PXRD patterns showed the basal spacing in the range of 30.1 Å to 33.1 Å support the successful intercalation process. FTIR spectra for all nanocomposites showed the presence of anion in the interlayer of the nanocomposite. Release study showed that phosphate solution yielded highest percentage release of anion in the range of 90.0 %-97.5 % compared to chitosan and cellulose acetate coated nanocomposite with the range of 77.6 %-87.9 % and 49.1 %-90.0 %, respectively. The results for kinetics study showed that ZLH-SDS-ISO and ZLH-SDS-THI were governed by first order in phosphate solution, meanwhile the release in sulphate and chloride solutions followed the pseudo second order. Whereby, ZLH-SDS-PRO best fitted with pseudo second order in all solutions. All cellulose acetate coated nanocomposites were governed by pseudo second order in all solutions. Chitosan coated ZLH-SDS-ISO (sulphate and chloride) and ZLH-SDS-THI (all solutions) nanocomposites showed best fitted with parabolic, whereas for ZLH-SDS-PRO nanocomposite was best fitted with pseudo second order in all solutions. In conclusion, the nanocomposites were successfully synthesized and the release time for coated nanocomposite was prolonged compared to uncoated nanocomposite. The implication of this research is to improve the cultivation activity by lowering the contamination risk of pesticides in environment.

FORMULASI PELEPASAN TERKAWAL BAGI NANOKOMPOSIT INTERKALASI AGEN AKTIF- ZINK HIDROKSIDA BERLAPIS UNTUK KAWALAN PEROSAK

ABSTRAK

Kajian ini bertujuan untuk mensintesis nanokomposit agrokimia interkalasi agen aktif-zink hidroksida berlapis iaitu zink hidroksida berlapis-natrium dodesil sulfat-isoprokarb (ZHB-NDS-ISO), zink hidroksida berlapis-natrium dodesil sulfat-propoxur (ZHB-NDS-PRO) dan zink hidroksida berlapis-natrium dodesil sulfat-thiakloprid (ZHB-NDS-THI) menggunakan kaedah pertukaran ion untuk kawalan perosak. Pengubahsuaian permukaan nanokomposit telah dilakukan menggunakan kitosan dan selulosa asetat. Nanokomposit telah dicirikan menggunakan pembelauan sinar-x serbuk (PXRD), inframerah transformasi Fourier (FTIR), analisis elemen, analisis termogravimetri dan terbitan termogravimetri (TGA/DTG), mikroskop imbasan elektron pancaran medan (FESEM), dan analisis kawasan permukaan. Dapatan pola PXRD nanokomposit menunjukkan jarak dasar dalam julat 30.1 Å hingga 33.1 Å yang menyokong kejayaan proses interkalasi. Spektra FTIR untuk semua nanokomposit menunjukkan kehadiran anion dalam antara lapisan nanokomposit. Kajian pelepasan menunjukkan bahawa larutan fosfat mengeluarkan peratusan pelepasan anion yang tertinggi dalam julat 90.0 %-97.5 % berbanding nanokomposit bersalut kitosan dan selulosa asetat, masing-masing dengan julat 77.6 %-87.9 % dan 49.1 %-90.0 %. Dapatan untuk kajian kinetik menunjukkan bahawa ZHB-NDS-ISO dan ZHB-NDS-THI dalam larutan fosfat dikawal oleh tertib pertama, manakala pelepasan dalam larutan sulfat dan klorida mengikut tertib pseudo kedua. Sementara itu, ZHB-NDS-PRO padanan terbaik dengan tertib pseudo kedua dalam semua larutan. Semua nanokomposit bersalut selulosa asetat dikawal oleh tertib pseudo kedua dalam semua larutan. Nanokomposit bersalut kitosan ZHB-NDS-ISO (sulfat dan klorida) dan ZHB-NDS-THI (semua larutan) menunjukkan padanan terbaik dengan parabola, manakala untuk ZHB-NDS-PRO adalah padanan terbaik dengan tertib pseudo kedua dalam semua larutan. Kesimpulannya, nanokomposit telah berjaya disintesis dan masa pelepasan untuk nanokomposit bersalut telah dipanjangkan berbanding dengan nanokomposit tak bersalut. Implikasi bagi kajian ini adalah untuk menambah baik aktiviti penanaman dengan mengurangkan risiko pencemaran racun perosak dalam alam sekitar.

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LIST OF ABBREVIATIONS

µm	micrometer
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
CA	cellulose acetate
CHIT	chitosan
CHNO-S	carbon, hydrogen, nitrogen, oxygen and sulphur
EDX	energy dispersive x-ray analysis
Fe^{3+}	ferric
Fe^{2+}	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 arsenide
$NaClO_3$	sodium chlorate

nm	nanometer
PHA	polyhydroxyalkanoate
PLAP	pesticides leaching assessment programme
PXRD	powder x-ray diffractometer
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 sulfate
ZLH-SDS-ISO	zinc layered hydroxide-sodium dodecyl sulfate-isoprocarb
ZLH-SDS-ISO-CA	zinc layered hydroxide-sodium dodecyl sulfate-isoprocarb-cellulose acetate
ZLH-SDS-ISO-CHIT	zinc layered hydroxide-sodium dodecyl sulfate-isoprocarb-chitosan
ZLH-SDS-PRO	zinc layered hydroxide-sodium dodecyl sulfate-propoxur
ZLH-SDS-PRO-CA	zinc layered hydroxide-sodium dodecyl sulfate-propoxur-cellulose acetate
ZLH-SDS-PRO-CHIT	zinc layered hydroxide-sodium dodecyl sulfate-propoxur-chitosan
ZLH-SDS-THI	zinc layered hydroxide-sodium dodecyl sulfate-thiacloprid
ZLH-SDS-THI-CHIT	zinc layered hydroxide-sodium dodecyl sulfate-thiacloprid-chitosan
ZLH-SDS-THI-CA	zinc layered hydroxide-sodium dodecyl sulfate-thiacloprid-cellulose acetate

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CHAPTER 1

INTRODUCTION

1.1 Pest and Disease

Throughout the last few years, a few serious fungal diseases have attained major interest and put a severe menace to the food supply (Bowers, Bailey, Hebbar, Sanogo, & Lumsden, 2001). Come of the famous epiphytotic disease like black pod, witches' broom, and frosty pod rot that may turn on disastrous losses to the plant cultivation area.

In Brazil, the cocoa beans production has decreased at almost 70 % in just 10 years, predominantly being infected by the fungus, *Moniliophthora perniciosa* which is a fungus responsible for witches' broom disease (Bowers et al., 2001). This fungus has reach long way off Brazil into Peru, Ecuador, Venezuela, and Colombia in South America, and Panama in Central America as well as Caribbean islands of Trinidad and Tobago (Pereira, 2000; Purdy & Schmidt, 1996). The fungus attacks only tissue (shoots, flowers and pods) that grows actively, causing cacao trees to produce branches without fruit and damaged leaves.

Another disease which called frosty pod rot, is infected by the basidiomycete *Moniliophthora roreri* (Bowers et al., 2001). It is found in South America in all North-western countries. The very first reports of the infection date back to the end of the 19th century, when its intimidating effects devastated Colombian and Ecuadorian plantations. The fungus has at last spread far and wide throughout the region of Latin America, leading to massive production losses and even to the abandonment of their farms (Evans, Stalpers, Samson, & Benny, 1978). The fungus only infects tissues, especially young pods that grow actively. The time between infectious disease and symptoms is approximately 1- 3 months. The most important symptom is the white fungal mat on the surface of the pod (Bowers et al., 2001; Fulton, 1989).

Besides being attacked by fungus and diseases, strawberry, wheat, cocoa, and cotton plantation also having a bad dream toward pests and insects such as mirid. Since 1908, cacao mirids have been identified as a critical pest because of their devastating effect in Ghana (Mahob et al., 2011). The most common species in Ghana and West African countries are *Distantiella theobroma* and *Sahlbergella singularis*. In South-East Asia the *Helopeltis spp.* is responsible for the damage related to mirids while *Monalonion* species are present in South and Central America. Mirid damage on its own, yet it can reduce yields by up to 75 percent if left unattended for three years (Asogwa, Ndubuaku, Ugwu, & Awe, 2010). Cocoa mirids usually permeate the surface of plant stems, branches and pods, kill the host cells and cause unseen necrotic lesions. Mirids that feed on shoots often kill terminal branches and leaves and cause dieback (Mahob et al., 2011).

Cocoa Pod Borer (CPB), also referred to as cocoa moth, is caused by the *Conopomorpha cramerella* insect. The larvae also feed on *Cynometra cauliflora*, *Dimocarpus longan* (longan), *Litchi chinensis* (lychee), and *Nephelium lappaceum* (rambutan). CPB becomes a real threat in 1841, causing considerable losses in the cocoa industry (Bradley, 1986). CPB is now affects nearly all Indonesian cocoa-producing provinces (Zhang et al., 2014). The rapid spread of CPB and the decrease in cocoa prices also led to decreases in Malaysia's production (Beevor, Mumford, Shah, Day, & Hall, 1993; Day, 1989; Zhang et al., 2014). CPB targets both young and mature cocoa pods lead to irregularity and premature ripening. The infection of young pods causes serious losses, as the quantity and quality of the bean is severely affected (Beevor et al., 1993).

The fruit and chocolate industry is well aware of the need for a consistent quality supply of this product. It is therefore extremely important that the industry and all its associated institutions continue to support scientific research in core areas such as production, integrated pest and disease management, conservation and improvement of germplasm and biotechnology.

1.2 Controlled Release Formulation

Controlled delivery can be defined as a technique or method in which active chemicals are made available at a specified rate and duration to achieve the intended effect (Devi & Maji, 2011). The controlled release system is expected to provide the active ingredient with a constant supply, usually at zero order, by continuously releasing it for a certain period of time (Ummadi, Shravani, Rao, Reddy, & Sanjeev, 2013).

In the past six decades, controlled release technology has progressed. It started in 1952 with the introduction of the first sustained release of the drug delivery system (Park, 2014). The first generation of drug delivery around 1950-1980 focused on the development of sustainable oral and transdermal release systems and the establishment of controlled mechanisms for drug release. Smith Kline & French has introduced the first controlled release formulation (CRF) in 1952 for 12-hour delivery of dextroamphetamine (Dexedrine) (Park, 2014; Wen & Park, 2011). The development of zero-order release systems, self - regulated drug delivery systems, long - term depot formulations and nanotechnology based delivery systems focused on the second generation around 1980-2010. The latter part of the second generation was mainly used to study nanoparticles (Hua, Yang, Wang, & Wang, 2010; Park, 2014). Since then, a basic understanding of controlled drug delivery, such as different mechanisms for the release of drugs, including dissolution, diffusion, osmosis and ion exchange, has been established (Park, 2014). Drug delivery systems have recently received particular interest because they have realized the effective and targeted delivery of drugs and have minimized the side effects of the traditional drug dosage form in the pharmaceutical sector (Hua et al., 2010).

CRF is well known in pharmaceutical field especially in drug delivery system compared to other field. In agrochemical applications, CRF was originally conceived in the 1970s (Park, 2014; Tu, Hurd, Randall, & Tnc, 2001). Over time, the interest in controlled release has increased and expanded as the economic and social benefits of controlled release technology are realized. The excess amount of pesticide runoff into the surface and groundwater in the agricultural sector has caused water pollution. The CRF can therefore be used to reduce the risks of pollution by reducing the amount of pesticides used for the same activity, thereby reducing the non-target effects (Devi & Maji, 2011; Sopena et al., 2009). CRF is also superior to its counterpart and produces higher yields and improved crop quality (Ahmad, Hussein, Kadir, Sarijo, & Yun Hin, 2015). The use of an efficient controlled release system is one approach to minimizing the use of herbicides. In the CRF, the bulk of the herbicide is trapped in an inert formulation matrix, whereas only a portion of the active ingredient is in an immediately available form. The components trapped in the controlled release matrix are less likely to suffer from environmental losses (Zhenlan, Heng, Bin, & Wanguo, 2009). A number of systems were used to control the release of herbicides. These include alginate encapsulation (Garrido-Herrera, González-Pradas, & Fernández-Pérez, 2006; He et al., 2015) and microencapsulation (He et al., 2015; Li, Dunn, Grandmaison, & Goosen, 1992). More recently, intensive research interests focus on pesticide-layered nanocomposite materials to be used as a controlled pesticide release (Zhenlan et al., 2009). This formulation is also used in active agents such as herbicides, pesticides and regulators for plant growth, in which the active agents are successfully intercalated into layered materials to produce controlled release formulations (Hussein, Rahman, Sarijo, & Zainal, 2012a).

1.3 Zinc Layered Hydroxide

Layered metal hydroxide compounds have attracted a huge interest due to their good intercalation properties. These layered metal hydroxide compounds have a brucite-like structure and their structures and chemical compositions are classified into two types. One is layered double hydroxides (LDHs) and another type is layered basic metal salts or layered hydroxide salt (LHS) (Bae & Jung, 2012; Liu, Zhang, & Zhang, 2015; Miao, Xue, & Feng, 2006). Over the various different two-dimensional lamellar, LHSs have attracted great interest because of their simple synthesis process and their unique anion exchange properties (Miao et al., 2006). The structure of LHS is based on the structure of the mineral brucite ($Mg(OH)_2$) and consists of hydroxide layers with charge-compensating anions in the interlayer spaces. Positive charges on layers are developed from under-coordination or mixed coordination geometries of interlayer cations. Counter-anions are therefore necessary to stabilize the electrostatic charge on the layers (Bae & Jung, 2012).

Zinc layered hydroxide is the one of categorized under LHS. ZLH consists of only one type of divalent metal cation which is differ from LDH that comprised of two metal cations; either one monovalent or one divalent and one trivalent cations (Ahmad et al., 2016). Recently, ZLH catch huge attention due to versatile properties and their wide technological application. ZLH has high zeta potential, which is 20-30 mV likes to that of LDH, which is a strong driving force to the surface of the cell that prevents the accumulation of inorganic nanoparticle (Hussein, Ghotbi, Yahaya, & Rahman, 2009b; Saifullah, Hussein, Hussein-Al-Ali, Arulselvan, & Fakurazi, 2013). The biocompatibility, controlled released and easier degradation without accumulation gives a significant characteristic of ZLH as well as LDH, which makes them a strong candidate as a drug-delivery system (Saifullah et al., 2013). The appealing aspect of ZLH is their simple synthesis and high anion-exchange capacity comparable to LDH. On that point, $Zn(OH)_2$ lamellae represent attractive nanobuilding blocks for production of zinc oxide nanosheets (Demel et al., 2010).

Previous study also prove that ZLH has improves thermal stability of the nanohybrid materials in the thermal decomposition profiles (Bashi, Hussein, Zainal, & Tichit, 2013; Saifullah et al., 2013). This is probably due to barrier effect that preventing the heat to transmit quickly and limiting the continuous decomposition of the nanocomposite (Wei'an, Yu, Luo, & Yue'e, 2003). Thus the transfer rate can be retarded, and the combustion time can be prolonged (Zhang, Kang, & Hu, 2013). LHS thermal decomposition profiles generally consist of two isolated thermal events: (i) loss of hydration water and (ii) release of dehydroxylated water, as well as release of gas from the counter-ions, for example NO_2 (Hashim et al., 2018), Cl_2 (Arizaga, 2012), CO_2 (Bitenc, Marinsek, & Crnjak Orel, 2008), SO_3 (Machovsky, Kuritka, Sedlak, & Pastorek, 2013) or CH_3COOH (Rajamathi, Britto, & Rajamathi, 2005). In the second stage, the largest percentage of mass losses occurs, while the remaining compounds being metal oxides. This last step is the slowest due to the effects of absorption / adsorption on the remaining layered structures and/or the oxides (Arizaga, Satyanarayana, & Wypych, 2007). Due to the fact that ZLH is a single metal hydroxide, it is a suitable precursor for upcoming product in which the size of these particles may play a role in determining the properties of the resultant product (Ghotbi, Bagheri, & Sadrnezhaad, 2011; Hussein et al., 2009).

The effect of the anion size and its simultaneous controlled release property using zinc-layered hydroxide as the host material can be used as a promising new host delivery system similar to LDHs for controlled release purposes (Hussein, Rahman, et al., 2012b). The previous release study of 2, 4-dichlorophenoxyacetic acid (2, 4-D) from the interlayer 2, 4-dichlorophenoxy acetate-zinc layered hydroxide nanocomposite into an aqueous solution of sodium carbonate reported that the amount release of 2, 4-D from ZLH nanocomposite was higher than Zn/Al-LDH nanocomposite (Bashi et al., 2013, Hussein et al., 2009). This was due to the weaker electrostatic interaction of the anionic 2, 4-D species with ZLH layers than LDH layers (Bashi et al., 2013). LDH nanocomposite may have stronger attraction between LDH and 2, 4-D anions due to higher positive charge involving Zn^{2+} and Al^{3+} ions. Whereas, ZLH layer only involving Zn^{2+} ions that provide a weak attraction towards the 2, 4-D anions, make it easy to be released into the aqueous solution. Both ZLH and LDH have good potential as host lattice for herbicide guest anion in controlled release formulation.

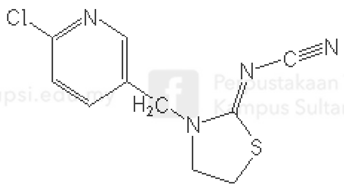
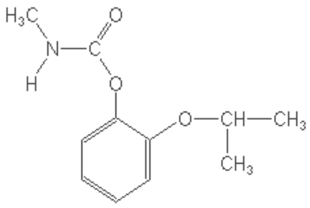
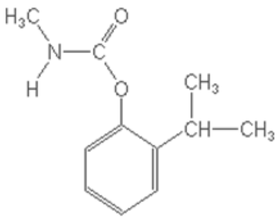
1.4 Problem Statements

In the present day, most of the agricultural activities utilize pesticide in order to boost their production in order to achieve good quality and market requirements to protect their plant from disease and pest attack. The use of pesticide has shown a remarkable effect in increasing the production for the farmer. For example, the control of diseases and pests in the cocoa belt of Western Nigeria, have increased the cocoa production about 40-50 % by employing the pesticide in cocoa plantation (Idris et al., 2013). In year 2014, Department of Statistics Malaysia press has reported that the production of cocoa in Malaysia has decrease by 3.6 % compared to year 2013 (“Department of Statistics Malaysia press release,” 2014). Idris et al., (2013) reported that, one of the major problems facing cocoa production is pests and diseases outbreak. The effect of pests and diseases reduced crop yield, losses in the value of foreign exchange, reduction in farmer’s income and also reduction in government revenue.

The decline in plant production was affected by many factors such as pest attacks (cocoa mirids, whiteflies, aphids, codling moths, ants and leafhoppers) and diseases (black pod disease, capsids and swollen shoot disease), high cost of inputs (fertilizers, pesticides, and seeds), and shortage of labor (Asogwa et al., 2010; Beevor et al., 1993; Bradley, 1986; Fulton, 1989; Mahob et al., 2011; Rudgard & Butler, 1987; Soberanis et al., 1999). Yield losses attributed to mirids have been reported to be 30-40 % (Asogwa et al., 2010). In 1989, the cocoa moths or cocoa pod borer has contributed to the severe decline of the cocoa industry over a 3-year period in Sabah ranging from £336 to £1128 ha^{-1} (assuming a cocoa price of £800 t^{-1}) (Beevor et al., 1993). As a solution, various active agent such as thiacloprid, propoxur and isoprocarb has been use to control pest and overcome diseases. Pesticides are rarely used in the way they are synthesized. In addition to the active ingredient, chemicals such as additives are added in order to meet administrative standards without lowering the effectiveness of the active ingredient (Sopena et al., 2009). In view of the negative role that pest and diseases play in cocoa production, their control has been of utmost importance among agriculturists (Idris et al., 2013). Thiacloprid was applied to control whiteflies, aphids, and codling moths. Whereas, propoxur and isoprocarb used to control ants, gypsy moths, leafhoppers and mollusk (Bakhti & Hamida, 2014; Englert, Bundschuh, & Schulz, 2012; Pandey & Guo, 2014). Table 1.1 shows the structure, chemical family and mode of action of respective pesticides.

Table 1.1

List of Pesticide Correspondent to their Chemical Family and Mode of Action

Herbicide	Structure	Chemical family	Mode of action
Thiacloprid		Neonicotinoids	Nicotinic Acetylcholine Receptor agonists/ antagonists
Propoxur		Carbamate	Acetylcholine esterase inhibitors
Isoprocarb		Carbamate	Acetylcholine esterase inhibitors

Although, nowadays there are many pesticides and plant growth regulator in the market, the efficiency of these chemical is quite questionable. The use of these chemical in extensive doses will cause a great impact to the environment. The presence of residual pesticide in soil has many possible causes. Sometimes it is due to aerial treatments applied directly to the plant foliage in order to control pests and diseases, following which approximately 50% of the used product finally deposits in soil. Another case, it occurs by pesticide drift from the host by rain or wind. The pesticide residue may come from excess amount of pesticide applied to the soil and derive from plant residues remaining in the soil after harvest (Sopena et al., 2009). Kamble (2007) has reported that the total percentage abnormalities in pollen mother cells increase with increased in concentration of pesticide on meiosis of *Cannabinus Lin*. The pesticide use also should be environmental friendly and safer for worker (Sopena et al., 2009). The uses of pesticides can also risk human via drinking water. Pesticides are 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. Idris et al. (2013) has reported 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 lead to pollution.

The previous study done by Zafiropoulos et al. (2014) focuses on the long-term effects of repeated low-level exposure to diazinon, propoxur, and chlorpyrifos pesticides on cardiac function in rabbits. It was found that all pesticides tested increased the oxidative stress and oxidative modifications in the genomic DNA content of the cardiac tissues, resulting in cardiac tissue damage and potentially cell death (Zafiropoulos et al., 2014). Lethal cardiac complications leading to death and various arrhythmias have been reported after organophosphate and/or carbamate poisonings. A recent market study predicts that the global agrochemical market is estimated to reach $261.9 billion by 2019. But while opportunities abound, concerns about safety and risks remain. From accidental water contamination to colony collapse disorder, people worry about environmental impact. A few issues have caused feedback; most strikingly, the ecological harm produced, including erosion, salinization and flooding of heavily watered soils, aquifer consumption, deforestation and natural defilement because of the unreasonable utilization of pesticides (Sopena et al., 2009).

As a response to these problems, this study will involve the hybridization of the isoprocarb, propoxur, and thiacloprid pesticides with zinc layered hydroxide (ZLH). This nanocomposite is deeming to be advantageous and is believed to be released in a controlled manner. The isoprocarb, propoxur, and thiacloprid pesticide is poorly-soluble pesticides which are difficult to be intercalating into the interlayer of ZLH. The majority of literatures are only focusing to the anionic pesticides. For poorly water-soluble pesticides, their intercalation is usually dependent on anionic surfactant that forms a hydrophobic region in the gallery (Dekany, Berger, Imrik, & Lagaly, 1997; Pavan, Crepaldi, De A. Gomes, & Valim, 1999). The hydrophobic nature and accessibility of the interlayer region of ZLH is helpful for adsorption of target pesticide molecules. In the previous study, Liu et al., (2015) have developed a novel method to make chlorpyrifos (CPF) adsolubilize into the interlayer of zinc hydroxide nitrate (ZHN) intercalated with dodecylbenzenesulfonate (DBS). The cationic and anionic surfactants interact to form neutral micelles, leaving the ZLH free to capture the desired anion. Since the interlayer spacing in the starting materials for this procedure is already quite large, this method offers particular promise for the incorporation of bulky anions (Auerbach, Carrado, & Dutta, 2004).

Therefore, this research aims to intercalate pesticides (isoprocarb, propoxur, and thiacloprid) into the interlayer of ZLH modified with sodium dodecyl sulfate (SDS) and study the controlled release of those active agents. Those layered material nanocomposite also will be coated with chitosan/cellulose acetate in order to control the rate of pesticide release, sustain the duration of the pesticide release and targeting the release of the pesticide to a specific part of the tree. Chitosan, the deacetylated derivative of chitin is one of the most abundant naturally occurring polysaccharide and possess immense potential as a packaging material owing to its biodegradability, biocompatibility and antimicrobial activity (Mathew & Abraham, 2008). Whereas, cellulose acetate (CA) is the classic membrane material used by the pioneers of modern membrane technology to create asymmetric membranes. It has been widely applied in the biomedical, pharmaceutical, and agricultural fields. In many of these applications CA is extremely attractive due to its low price, good biodegradability, and nontoxicity (Wu & Liu, 2008). Therefore, the intercalation of isoprocarb, propoxur, and thiacloprid pesticides into the interlayer of zinc layered hydroxide-sodium dodecyl sulfate (ZLH-SDS) coated chitosan/cellulose acetate would be an ideal slow-release formulation and believed to be crucial for the continued good agricultural practice in plant cultivation.

1.5 Significance of the Study

The study of pesticide formulation will be a significant endeavor to obtain a high biological effectiveness, throughout the time required to control harmful weeds. This study will also be beneficial in promoting good work environment by ensuring safer use of pesticide by workers and users. For the plantation industry and business practitioners, the use of pesticide formulation will save the cost by reducing the amount of chemical use for agrochemical activities. Sustainable cocoa will not only help the cocoa and chocolate manufacturers maintain a constant and reliable supply of raw material, but it also will move small holder farmers into a more favorable economy. Moreover, this study will lower the environmental risk factors by avoiding excess use of herbicide to the crops. Consequently, this research might offer some information for future researchers of physical and chemical properties of the active agent used. Their compatibility will conduct future research to formulate new formulation with better performance.

1.6 Objectives of Study

The objective of this study is as below:

a) to synthesis zinc layered hydroxide-sodium dodecyl sulfate-isoprocarb (ZLH-SDS-ISO), zinc layered hydroxide-sodium dodecyl sulfate-propoxur (ZLH-SDS-PRO), and zinc layered hydroxide-sodium dodecyl sulfate-thiacloprid (ZLH-SDS-THI) nanocomposites via ion exchange method.

b) to synthesis layered material-pesticide nanocomposites coated with chitosan/cellulose acetate.

c) to study the physicochemical properties of layered material-pesticide nanocomposites using PXRD, FTIR, CHNO-S, ICP-OES, TGA/DTG, FESEM, and BET analysis.

d) to study the controlled release behavior of pesticide from the interlayer of layered material-pesticide nanocomposites and coated nanocomposites.

e) to compare the release behavior of pesticide from the interlayer of layered material-pesticide nanocomposite and coated nanocomposite into sodium phosphate, sodium, sulfate, and sodium chloride solutions.

f) to study the effect of single, binary and ternary anion of sodium phosphate, sodium, sulfate, and sodium chloride for the controlled release of layered material-pesticide nanocomposite.