CONTROLLED RELEASE FORMULATION OF PADDY PESTICIDES INTERCALATED LAYERED METAL HYDROXIDE VIA POLYSACCHARIDE ENCAPSULATION

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ABSTRACT

This research aimed to synthesis intercalated nanocomposites of paddy pesticides for controlled release formulation (CRF), namely zinc/aluminium–layered double hydroxide–quinclorac (Zn/Al–LDH–QC), zinc hydroxide nitrate–sodium dodecylsulphate–bispyribac (ZHN–SDS–BP) and zinc hydroxide nitrate–sodium dodecylsulphate–imidacloprid (ZHN–SDS–IC) using coprecipitation method. Surface modification of the nanocomposites, were then performed using carboxymethyl cellulose (CMC) and chitosan coatings. The physicochemical properties, CRF and kinetic behaviour were monitored using powder X–ray diffraction (PXRD), thermogravimetric analysis, Fourier transform infrared spectroscopy (FTIR), elemental analysis, field emission scanning electron microscopy (FESEM), gas sorption analysis and ultraviolet–visible spectrometer. The appearance of intercalation peaks at lower 2θ angle in the PXRD pattern, 15.8–16.7 Å (Zn/Al–LDH–QC), 28.2–28.6 Å (ZHN–SDS–BP) and 32.0–32.2 Å (ZHN–SDS–IC) confirmed the intercalation of pesticides in the nanocomposite, which also supported by FTIR and elemental analysis. All coated nanocomposites showed better performance in releasing pesticides, with prolong release time ranging from 2465–6083 min, compared to 1478–4117 min for the uncoated nanocomposites. Releasing of quinclorac and imidacloprid were governed by pseudo second order kinetic model, whereby the bispyribac was governed by pseudo second order and parabolic diffusion kinetic models. In conclusion, the nanocomposites of paddy pesticides for CRF were successfully synthesised. The CMC and chitosan coatings obviously enhance the release behaviour of the pesticides from the nanocomposites. These synthesised nanocomposites are hopefully beneficial in overcoming the excessive usage of pesticide in paddy cultivation.

FORMULASI PELEPASAN TERKAWAL RACUN PEROSAK PADI TERINTERKALASI LAPISAN LOGAM HIDROKSIDA MELALUI PENKAPSULAN POLISAKARIDA

ABSTRAK

Kajian ini bertujuan untuk mensintesis nanokomposit terinterkalasi dengan racun perosak padi untuk formulasi pelepasan terkawal (FPT), iaitu zink/aluminium lapisan berganda hidroksida–kuinklorak (Zn/Al–LBH–KK), zink hidroksida nitrat–natrium dodesilsulfat–bispiribak (ZHN–NDS–BP) dan zink hidroksida nitrat–natrium dodesilsulfat–imidakloprid (ZHN–NDS–IK) menggunakan kaedah sepemendakan. Pengubahsuaian permukaan nanokomposit, kemudiannnya dilakukan menggunakan salutan karboksimetil selulosa (KMS) dan kitosan. Sifat fizikokimia, kelakuan FPT dan kinetik dipantau menggunakan belauan sinar–X serbuk (PXRD), analisis termogravimetri, spektroskopi inframerah transformasi Fourier (FTIR), analisis unsur, mikroskop elektron pengimbasan pemancaran medan (FESEM), analisis erapan gas dan spektrometer ultralembayung–nampak. Kemunculan puncak interkalasi pada sudut 2θ yang lebih rendah dalam pola PXRD, 15.8–16.7 Å (Zn/Al–LBH–KK), 28.2–28.6 Å (ZHN–NDS–BP) dan 32.0–32.2 Å (ZHN–NDS–IK) mengesahkan interkalasi racun perosak di dalam nanokomposit tersebut, yang juga disokong oleh analisis FTIR dan unsur. Semua nanokomposit yang bersalut menunjukkan prestasi yang lebih baik dalam melepaskan racun perosak, dengan pelanjutan masa pelepasan berjulat antara 2465–6083 minit, berbanding 1478–4117 minit untuk nanokomposit yang tidak bersalut. Pelepasan kuinklorak dan imidakloprid dikawal oleh model kinetik tertib pseudo kedua, manakala bispiribak dikawal oleh model kinetik tertib pseudo kedua dan peresapan parabolik. Kesimpulannya, nanokomposit terinterkalasi dengan racun perosak padi untuk FPT telah berjaya disintesis. Salutan KMS dan kitosan jelas meningkatkan kelakuan pelepasan racun perosak daripada nanokomposit. Nanokomposit yang disintesis diharapkan bermanfaat dalam mengatasi penggunaan berlebihan racun perosak yang dalam penanaman padi.

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LIST OF ABBREVIATIONS

BET	Brunauer–Emmett–Teller
BP	bispyribac
CHNS	carbon, hydrogen, nitrogen and sulphur
CMC	carboxylmethyl cellulose
CPF	chlorpyrifos
CRF	controlled released formulation
DB	dodecyl betaine
DBS	dodecylbenzenesulfonate
FESEM	field emission scanning electron microscope
FTIR	Fourier transform infrared
IC	imidacloprid
ICP/OES	inductively coupled plasma optical emission spectrometry
LDH	layered double hydroxide
LHS	layered hydroxide salt
MWCNT	multi–walled carbon nanotube
NAFP	The National Agro–Food Policy
PXRD	powder X–ray diffraction
QC	quinclorac
TGA/DTG	thermogravimetric analysis and differential thermogravimetric analysis
TX–10	polyoxyethylene(10)nonyl phenyl ether
Uv–vis	Ultraviolet visible spectroscopy

ZHN	zinc hydroxide nitrate
ZLH	zinc layered hydroxide
ZLH–CPPA	zinc layered hydroxide intercalated with 2(3–chlorophenoxy)propionate
ZHN−SDS−BP	zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac
ZHN−SDS−BP−Chi	zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac–chitosan
ZHN−SDS−BP−CMC	zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac–carboxymethyl cellulose
ZHN−SDS−IC	zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid
ZHN−SDS−IC−Chi	zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid−chitosan
ZHN−SDS−IC−CMC	zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid−carboxymethyl cellulose
Zn/Al–LDH	zinc/aluminium–layered double hydroxide
Zn/Al–LDH–QC	zinc/aluminium–layered double hydroxide–quinclorac
Zn/Al–LDH–QC−Chi	zinc/aluminium–layered double hydroxide–quinclorac−chitosan
Zn/Al–LDH–QC−CMC	zinc/aluminium–layered double hydroxide–quinclorac−carboxymethyl cellulose

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CHAPTER 1

INTRODUCTION

1.1 Rice Production in Malaysia

Rice (*Oriza sativa* L.) is among the world's most vital crop, the principle food in numerous countries around the world. Rice was served on a daily basis by more than half of the world's population that contributes about 20% of the total man calorie intake, and was taken as a source of carbohydrates, lipids, vitamins and minerals (Walter, Marchezan, & Avila, 2008). Approximately, 90% of the worldwide rice production was yielded and consumed in Asia, including Malaysia (Jamal, Kamarulzaman, Abdullah, Ismail, & Hashim, 2014).

Around 715 000 ha of arable area in Malaysia are subjected to paddy cultivation, which cultivate both lowland and upland paddy. Huge financial resources has been allocate annually to support the paddy production in Malaysia through various research and development approach. Even though the yield of paddy production in year 2016 was increased by 27.52% compare to year 2015 (from approximately 2 738 000 to 3 492 000 t), the average yields of paddy in Malaysia is still lower compare to other ASEAN countries (ASEAN Food Security Information System, 2016).

The low paddy productivity in Malaysia was contributed by several factors, which include the outbreak of invasive pests and weeds competitions in paddy cultivation area. Based on the statistics, 1705 ha of the paddy cultivation area in Malaysia were destroyed due to the weed competition and pest invasion, while another 1070 ha, 259 ha and 45 ha were related to the obliteration caused by the diseases, drought and flood, respectively (ASEAN Food Security Information System, 2016). Water, nutrients, sunlight and carbon dioxide gas are the main reasons for the occurrence of the competition between the cultivated paddy and the undesirable weeds (Babar & Velayutham, 2012). The damage caused by weeds and pests such as brown planthopper must be controlled as the resulting damage may decrease the rice yield thus affecting the profits gained by the farmers (Qing et al., 2014).

1.2 Pest control in Paddy cultivation

The invasion of insects, weeds, diseases, nematodes and other pests have considerably affected the rice productivity, which therefore, resulting to the economic loss in the paddy cultivation sector. Hence, numerous approach were reported to be applied by the farmer around the world, with the attention of controlling these invasive pests. In general, the approach can be classified into cultural, mechanical, biological and chemical control.

Pest control by cultural approach implicate practicing good land management that will benefit both crop production and overcoming pest problem (Heinrichs, 1994). In the cultural practices, some of the way executed by the paddy farmers in dealing with weed competition in paddy cultivation area is by planting more competitive rice cultivars in their paddy cultivation area, crop rotation, minimising the use of nitrogen fertilisers and carry out well–timed paddy planting (Chauhan, 2013; Haden, Duxbury, DiTommaso, & Losey, 2007; Hong–xing et al., 2017; Singh, Vasisht, Kumar, & Das, 2008; Suzuki et al., 2002). Another good cultural practices that were executed by the farmers in the paddy cultivation area include deep summer ploughing which helps in buries the weeds, insect larvae and the pupae (Singh et al., 2008). Even though the cultural method is effective, this approach, however, are reported to be labour intensive, demand repeated effort, and no longer relevant to the growth of agricultural modernisation (Ip et al., 2014; Wong, Kwong, & Qiu, 2009; Zhang, 2003).

Using more competitive rice cultivars in paddy cultivation is also one of the cultural methods that was applied by farmers. Significant difference amongst rice cultivars, in terms of their competitiveness against weeds were reported in several studies (Fischer, Chatel, Ramirez, Lozano, & Guimaraes, 1995; Fischer, Ramirez, & Lozano, 1997; Garrity, Movillon, & Moody, 1992; Tachibana & Watanabe, 1998; Tachibana, Watanabe, Uchino, & Kohara, 1999). These previous studies were generally discovered that paddy plant with tall and leafy traits were found to be more competitive, as these traits helps in minimising the light absorption for the weeds. Insufficient light absorption by the weeds, is therefore resulting the distortion of their growth. The competitiveness against weeds were also found to be affected by the root and shoot system of the paddy plant, owing to the fact that the soil nutrients and the light were obtained through these systems, respectively (Suzuki et al., 2002).

Adjusting the rice sowing time, for instance, was proven to affect the occurrence of the diseases caused by rice virus. This finding was based on a study conducted in northern Zhejiang Province, China, which revealed that postponing the rice sowing time until the end of May or early June does reduce the occurrence of rice stripe virus disease and black streaked dwarf virus disease, that were transmitted by the small brown planthopper (Sun, Wang, Cao, Zhu, & Zhong, 2008; Zhu et al., 2009). The nitrogenous fertilisers applied to the paddy cultivation area not only provide the required nutrients for the planted paddy plants, but could improve the nutritional condition of the invasive insects as well (Lu, Yu, Heong, & Hu, 2006). Overly supplied nitrogen into the paddy cultivation area will, therefore, enhance the survival, reproduction and development quality of the invasive insects, and causing more damage on the paddy cultivation (Lu et al., 2006). This fact was proven in the previous study conducted in the Zhejiang

Province of China, which shows that lowering the average nitrogen usage (from 250 to 200 kg/hm^2) will increase the percentage yield by 5%, and decreasing the damage rates causes by the pests (Zheng et al., 2015).

The mechanical and physical control practices use the principle of physic, such as mass, motion, energy and force in overcoming the pest problem (Heinrichs, 1994). Motion and force were applied in the mechanical method, such as by mechanically removing the weeds and capturing, trapping or crushing the invasive insect directly using hand, tool or machines (Latif, Ali, Islam, Badshah, & Hasan, 2009). Mechanically removing the weeds can be considered as an effective and direct pest control, however, this approach is becoming challenging as a result of labour shortage, cost increases and the reliance on the weather conditions. Delayed weeding may also lead to crop loss and reduced the rice production (Antralina, Istina, Yuwariah, & Simarmata, 2015). Using light energy in the light trap to attract and kill those nocturnal insects and using heat energy by exposing the straw under hot sunlight to kill the rice stem borer larvae are some of the examples of physical control methods used by the paddy farmer in dealing with the pest problem (Heinrichs, 1994). The usage of modern light trap was found to be capable of attracting a higher number of insects. The operative cost, however, are quite expensive. Using light trap in paddy cultivation was also found to trigger several disadvantages, such as the risk of being stolen, erratic attraction, short–life, non–availability of bulbs and the fact that not all insect species were attracted to the light and trapped (Heinrichs, 1994; Singh et al., 2008).

Hand picking is the most direct manual method to remove the weeds and insects that invade the paddy cultivation area (Liang et al., 2013; Salleh, Arbain, Daud, Pilus, & Nawi, 2012; Sin, 2003; Wong et al., 2009). Even though it is hard to capture the fast moving insects, it is possible to pick those slow moving and aggregated insects and their larvae and eggs directly from the foliage. Adult grasshopper were happened to be more inactive at night, which make it easier to be captured from the foliage (Pedigo & Buntin, 1993). As for the flying insect like a moth, it is inconvenient to be picked by hand therefore capturing using net would be a wiser option. Handpicking immobile eggs, especially for the species that lay abundant of eggs in a time is also preferable by the farmer in the paddy cultivation area (Heinrichs, 1994). The usage of the tools were very beneficial when eliminating the insects by hand. The farmers in Japan were found to use a large comb to run through the foliage in the paddy cultivation area to collect the invaded caterpillars (Hirai, Oya, & Miyahara, 1986). Applying sticky materials, such as latex and grease on the nets or basket when sweeping the paddy plant is also helpful in removing the rice bugs (Heinrichs, 1994).

Other mechanical method practices used by the farmer in overcoming the pest problem is roguing. Roguing is defined as the elimination of the pest infested plant or certain part of that plant, either by hands or tools (Heinrichs, 1994). Even though in this case, the plant or the part of the plant is already damaged from the pest attack, this method could help in preventing the infestation or diseases from spreading to the other plants in that area. The pest problem can also be reduced by conventional mechanical approach such as crushing, beating and dragging (Singh et al., 2008). Recurrently pounding the harvest using stick can help to drive away the rice bugs, and beating the locust breeding ground using malls can help in crushing their eggs, thus avoiding the growth of the pest population (Heinrichs, 1994).

In the pest control using biological approach, the targeted pest population is controlled using their natural enemies (Vincent, Goettel, & Lazarovits, 2007). A number of living organisms, such as frog, fish, duck and variety of arthropods have been used as a predator to kill, capture or feed on the pests that invade the paddy cultivation area (Khatiwada et al., 2016; Liang et al., 2013; Lou, Zhang, Zhang, Hu, & Zhang, 2014; Wong, Kwong, & Qiu, 2009). This approach is used to reduce the dependency on the chemical pesticide in dealing with the problem brought by those invasive pests. Biological control was reported to be an innovative, economical and environmental friendly approach (Gomathinayagam, Rekha, Murugan, & Jagessar, 2010). Despite the interesting benefits offered by the biological control practice, there also has been long standing argument and debate concerning the risk of this approach owing to the complexity of species interactions. Some of the critics highlighted are the challenge in predicting the holistic outcome, the downside effect on the non–target organisms and the balance of the ecosystem in the paddy cultivation area (Howarth, 1991).

Owing to the effectiveness and easy application of chemical control like herbicides, insecticides and bactericides, this approach seems to be very preferable in dealing the pests in paddy cultivation area (Bhagirath & Mahajan, 2014). The usage of pesticide was also found to lessen the need of cultivation in paddy cultivation (Zhang, 2003). Propanil, saflufenacil, thiobencarb, molinate, and imazethapyr are some of the example of active ingredients in pesticide that are commonly used in paddy cultivation (Camargo, Senseman, McCauley, & Guice, 2012; Zhang, 2003). Overly used of either natural or synthetic pesticide, however, will lead to serious problems such as the development of resistance in weeds towards the pesticide, tendency of killing the beneficial non–target pests and may jeopardise the health of humans and animals (Dal Bello, Padin, López Lastra, & Fabrizio, 2001; Wong et al., 2009). Due to the benefits offered by the pesticide, the application of pesticide in dealing with the weed problem appears to be indispensable. The practicality, selectivity and cost–effectiveness of pesticide allowing the pesticide to be used during the early stage of the paddy cultivation, hence providing competitive superiority and better survival chance to the crops (Antralina et al., 2015).

1.3 Excessive Usage of Pesticides and Environmental Issues Arise

Various formulation of pesticides was applied to overcome the outbreaks of these uninvited pests. Pesticide refer to a chemical used to control, repel, attract or exterminate pests that are believed to be a threat to the crops. Pesticides can be divided into three major classes, which are fungicides, herbicides and insecticides. Each type of the pesticides was specifically used to manage different pests (Mahmoud & Loutfy, 2012).

Before World War II, the common pesticides used were mainly composed of inorganic materials, including sulphur, lead, copper, arsenic, boron, and mercury (Dureja & Rathore, 2012). The modern chemical age of pesticide were initiated in 1939, with the discovery of insecticidal potential of dichlorodiphenyltrichloroethane (Foo & Hameed, 2010). The discovery lead to the development of a variety of other synthetic pesticides, which can be classified according to their chemical compounds, such as chlorinated hydrocarbons, organophosphates, carbamate compounds, pyrethroids and inorganic pesticides (Marrs & Ballantyne, 2004; Ujváry, 2001).

Chlorinated hydrocarbons such as dieldrin, chlordane and aldrin are typically a large molecules with a huge number of chlorine atoms bonded to their molecules (Stoytcheva, 2011). This type of pesticides will gradually break down and remain in the environment for a long term. Organophosphate pesticides are mostly contain thionate bond (P=S) whereas the carbamates pesticides contain N–substituted esters of carbamic acid, with general formula R^1NH—CO—OR^2 (R^1 and R^2 are aliphatic or aromatic moieties) (Ujváry, 2001). They are highly toxic to mankind, but only last in the environment in a short period of time, for instance parathion, malathion and thimet. Carbamate compounds are pesticides that are very toxic to humans such as carbaryl and aldicarb pesticides. Pesticides containing metallic elements or organometallic compound, such as arsenic trioxide, sodium arsenite, mercury sublimate, copper ammonium carbonate and mercury acetate were classified as inorganic pesticide (Marrs & Ballantyne, 2004; Ujváry, 2001). Pyrethroids united the high toxicity to insects with low mammalian toxicity and significantly enhanced the stability of this insecticides. Other minor classes of insecticides may include insect growth regulators, imidates, and phenylpyrazoles (Mahmoud & Loutfy, 2012).

Owing to different chemical composition, each class of pesticide may exhibit different physical and chemical properties. There are certain pesticides which may dissociate to form anionic pesticide, such as dicamba and various phenoxyherbicide, meanwhile some pesticide, such as chlorpyrifos remain as neutral charge pesticide (Campbell, Schnitzer, & Kahn, 1978). The properties and behaviour of inorganic pesticide may also not be similar compared to organic species, especially in terms of kinetics, absorption, distribution, and excretion. Hence, their toxicology effect may particularly differ, except for those organic species that immediately metabolized to the inorganic form in the body (Ujváry, 2001).

Great improvement on the paddy productivity were observed since the usage of various pesticides in paddy cultivation (Matsunaka, 2001). Despite the benefit offered, the continuous use of pesticides has resulting massive pesticide loads in paddy cultivation. The toxicity of most pesticides is not just harmful to the mankind, yet to the environments indeed. The losses of active ingredients to the environment through numerous processes such as biodegradation, chemical degradation, photolysis, evaporation and surface runoff are nevertheless seems to cause other worldwide environmental issues (Céspedes, Sánchez, García, & Pérez, 2007). These include the quality degradation of natural water resources (Proia et al., 2013), ecological imbalance (Shi, Lu, Meng, Guo, & Zheng, 2013) and lethal effect on human health (Sugeng, Beamer, Lutz, & Rosales, 2013).

Recent studies on monitoring of pesticide residue has found high concentration of paddy pesticide in rivers all around the world, such as Greece, Philippines and Japan (Gao et al., 2008; Inao, Watanabe, Karpouzas, & Capri, 2008; Papadopoulou–Mourkidou et al., 2004). In fact, the pesticide residues were also found in inland watercourse and major rivers in Malaysia such as in Penang marine fish, Selangor rivers and Sabah sediments (Abdullah, 1995). The river system in Malaysia, are an integral part of water resources system that provide around 98% of country’s water necessities.

Therefore, any occurrence of river pollution may lead to serious consequence on community health.

Thus, it would be a tough challenge developed countries like Malaysia to yield sufficient food supply for the growing population, protect plant, animal, and human health and at the same time conserve the environment.

1.4 Controlled Release Formulation

The application of pesticides in agriculture is essential so as to upsurge the productivity of the harvested yield (Azejjel, Del Hoyo, Draoui, Rodríguez–Cruz, & Sánchez–Martín, 2009). However, the continuous usage of pesticides may lead to various consequences such as air pollution, water contamination and extinction of endangered species. Hence, controlled released formulation (CRF) was introduced as a new approach to alleviate the environmental issues triggered by the pesticides residues and correspondingly, improve the effectiveness of the pesticides (Grillo et al., 2012). CRF can be defined as the formulations that slowly and continuously lose the toxic element into the environmental interface over a period of time measured in months or years (Cardarelli, 2018). Therefore, the CRF in pesticide implies that the formulations involved are so created as to deliver the proper dosage for effective long or short term pest control.

CRF has attracted great interest in the past years and has been exploited in various fields numerous agrochemicals. CRF was implemented as several agrochemical ingredient including fertilizers, plant growth enhancer and pesticides. CRF has been proven to enhance the weed management by increasing the prolonged hour of the release of active ingredient in pesticides and minimize the ecological contamination caused by pesticides by permitting lower and continued concentration of pesticides to the surroundings (Bakhtiary, Shirvani, & Shariatmadari, 2013). Therefore, the pest problems can be diminished without polluting the environment or risking the health of pesticides applicator.

The application of CRF can bring several benefits to the pesticides innovation. For instance, CRF may extend the activity duration of pesticides by supplying continuously low concentration of pesticides, nevertheless sufficient for long lasting performance. The slow release of the pesticides enable the farmers to reduce the repetition usage of pesticides, thus resulting in time–efficient and more economical cultivation practices. Besides, CRF also assist in preventing environmental pollutions by minimising the distribution of excess pesticides residues to the environment (via evaporation, degradation or leaching by rain into the waterway), commonly occurred due to the simultaneous releases of high pesticides concentration. In facts, CRF implement the usage of solid pesticides formulation instead of conventional liquid pesticides, thus lessening the flammability of the pesticides. CRF also reduce the high mobility of the pesticides in soil, thus lowering the mammalian and phytotoxicity by reducing the pesticides residue in food chain (Dubey, Jhelum, & Patanjali, 2011).

Various materials has been proposed as a carrier of CRF of pesticides in agriculture. Clay mineral is one of the example of commonly used as host materials to demonstrate the controlled release behaviour of active compounds intercalated in them. Due to their relatively low cellular cytotoxicity, high adsorption capacity and particular colloidal properties, this materials were widely explored in agrochemical formulation (Ureña–Amate, Boutarbouch, Socias–Viciana, & González–Pradas, 2011). The negatively charged cationic clays such as smectite and positively charged anionic clays like LDHs have been extensively used as controlled released systems in insecticides, fertilisers, herbicides, fungicides and plant growth regulator (Park et al., 2010; Qiu et al., 2009; Touloupakis, Margelou, & Ghanotakis, 2011; Ureña–Amate et al., 2011; Woo et al., 2011). Other materials that were reported to be used as host material in controlled release formulation are starch, chitosan, liposomes, cyclodextrins, silica, lignin, and polymeric microparticles (Agnihotri & Aminabhavi, 2004; Barik, Sahu, & Swain, 2008; Cao et al., 2005; Guo, Zhang, Liu, Yang, & Sun, 2010; Lobo et al., 2011; Pérez, Sánchez, Céspedes, García, & Fernández, 2010; Sánchez–Verdejo, Undabeytia, Nir, Maqueda, & Morillo, 2008; Silva et al., 2011).

The mechanism of material with controlled release properties is quiet complicated to be conceived, owing to the fact that the mechanism may be affected by various factors, including the nature of coating material, porosity, ratios between core and coating, solubility of coating materials and core materials, type of CRF, agronomic conditions and much more (Azeem, Kushaari, Man, Basit, & Thanh, 2014; Liu, Kost, Fishman, & Hicks, 2008). Although different release mechanisms have been reported, the release process can be mainly categorised into four common mechanisms, which are diffusion, erosion, fragmentation and swelling (Matalanis, Jones, & McClements, 2011). In the diffusion mechanism, the active ingredient was easily diffuse into the release media through the polysaccharide coater without damaging the coater. The diffusion rate will be more affected by the mesh size of the polysaccharide network rather than the size of the active ingredient, besides the electrostatic or hydrophobic attraction that exist between the polysaccharide coater and active ingredient. As for the erosion mechanism, the active ingredient were released into the release media due to the erosion process that occurred at either external layer or entire volume of the polysaccharide matrix. Several possible factor of the matrix erosion include physical, chemical or enzymatic degradation processes, such as dissociation of physical bonds or the hydrolysis of covalent bonds. In the fragmentation mechanism, the release of active ingredient into the release media is caused by the disruption of the host, which is either fragmented or fractured, by applying shear or compression forces. As for the swelling mechanism, the release of active ingredient were triggered by the hydration of the polysaccharide coater, causing the polysaccharide to swell, hence allowing the active ingredient to diffuse out. The illustration of all four common release mechanisms; diffusion, erosion, fragmentation and swelling were shown in Figure 1.1.

In a multi-stage diffusion model release mechanism demonstrated by coated fertilisers, irrigation water enters the coating to condense on the solid fertilizer core followed by partial nutrient dissolution (Liu et al., 2008). Osmotic pressure were then builds within the containment, causing the granule to swell. The dissolved nutrients are either gradually released by diffusion or immediately released if the rupture occurs. The multi-stage diffusion model release mechanism was illustrated in Figure 1.2.

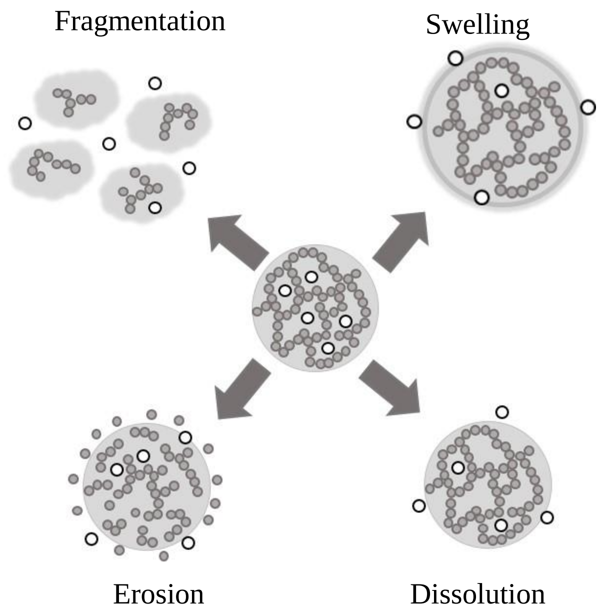

Figure 1.1. Some Common Release Mechanisms of Active Ingredient; Diffusion, Swelling, Erosion and Fragmentation (Matalanis et al., 2011)

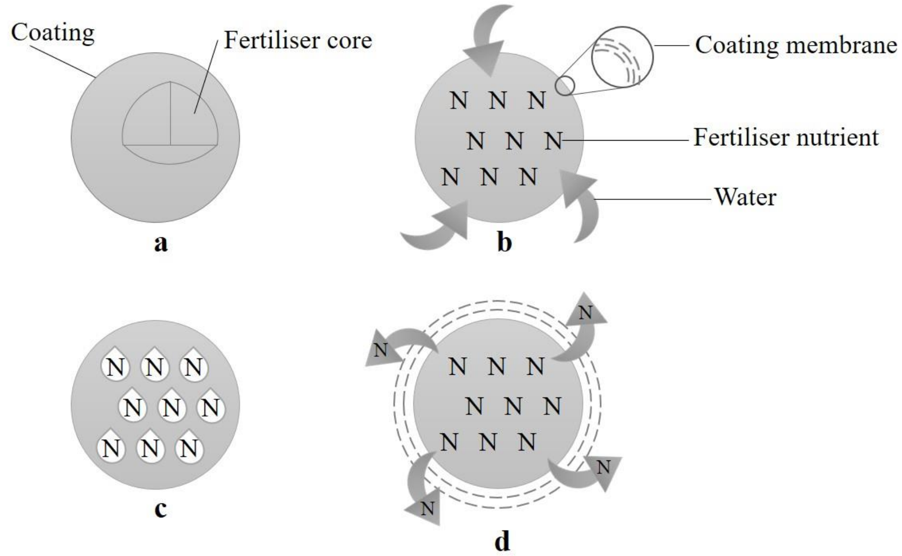

Figure 1.2. Diffusion Mechanism of Controlled Release; (a) Fertilizer Core with Coating, (b) Water Penetrates into the Coating and Core Granule, (c) Fertilizer Dissolution and Osmotic Pressure Development (d) Controlled Release of Nutrient through Swollen Coating Membrane (Azeem et al., 2014)

As for the release mechanism involving swellable and erodible hydrophilic matrices, such as carboxymethylcellulose, chitosan, hydroxypropyl methylcellulose, cellulose triacetate, and alginate–chitosan, the release mechanism may not only involved the swelling and diffusion, but may involved the erosion mechanism as well (Chaibva, Khamanga, & Walker, 2010; Emeje, Kunle, & Ofoefule, 2006; Ghori & Conway, 2015; Kajjari, Manjeshwar, & Aminabhavi, 2014; Lucinda-Silva, Salgado, & Evangelista, 2010). A general drug release mechanism on the basis of solubility of incorporated drugs, involving erosion mechanism was proposed in recent studies and was illustrated in Figure 1.3 (Ghori & Conway, 2015).

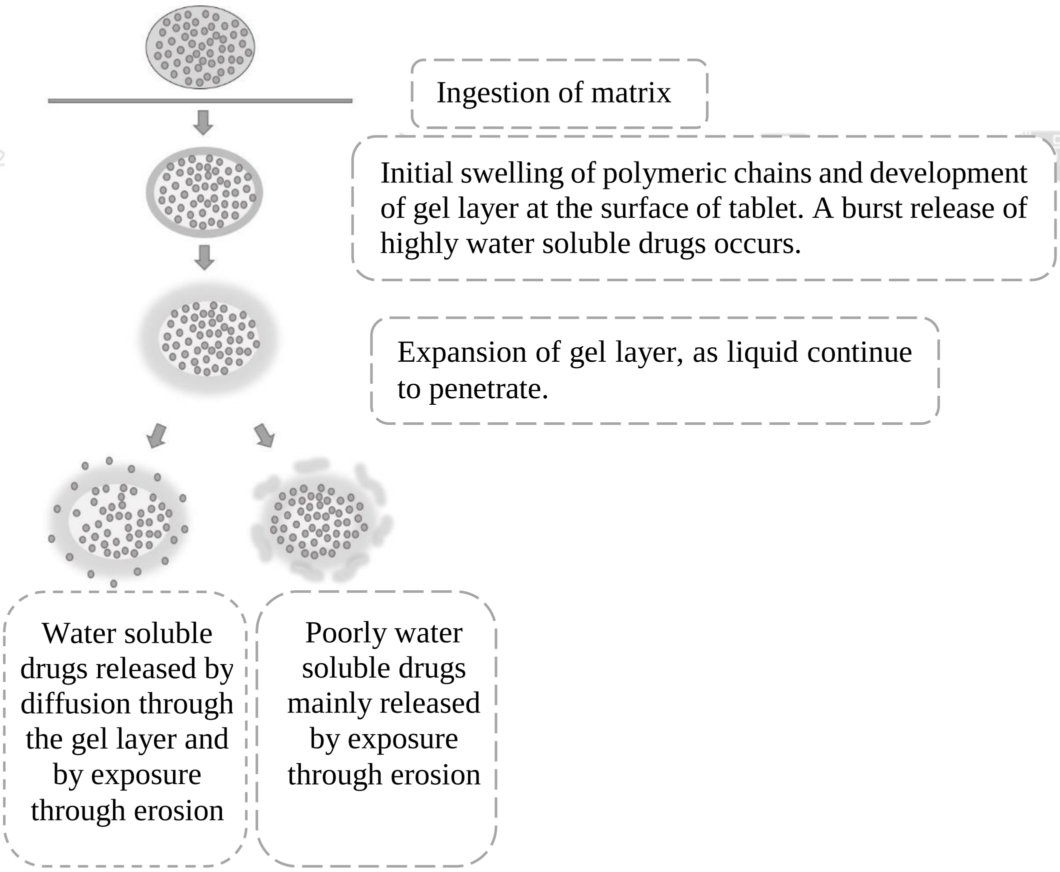

Figure 1.3. Release Mechanism of Water Soluble and Poorly Water Soluble Drugs from Hydrophilic Matrix Tablet (Ghori & Conway, 2015)

1.5 Nanotechnology, Nanomaterials and Nanocomposites

The study on nanotechnology has become an important trend for these recent years, thus attracted great interest from the worldwide researcher (Kuzma, 2010). The term 'nanotechnology' can be defined as the set of technology related to the interaction between atoms, ions or molecules with the formation of nanostructures with distinctive nature (Kodolov & Trineeva, 2014). Based on recent progress, nanotechnology is predicted to transformed both science and community, thus provide numerous advantages (Lane & Kalil, 2005).

Nanomaterials is one of the subject that can be studied in the nanotechnology field. Nanomaterials refer to the materials with particle size less than 100 nm in at least one dimension (Schubert & Hüsing, 2012). Due to the rapid growth in nanotechnology the application of nanomaterials has been progressively developed in various fields including agriculture, medicines and electronics. Hence, this triggers the development of numerous carbon–based, metal and metal oxide–based and biocomposites nanomaterials, including multi–walled carbon nanotubes, magnetised iron (Fe) nanoparticles, aluminium (Al), copper (Cu), gold (Au) and zinc oxide (ZnO) (Khot, Sankaran, Maja, Ehsani, & Schuster, 2012). Nanomaterials exhibit great quality that distinguished them from other macroscopic materials in two major ways. Unlike other large scale materials, nanomaterials follow the law of quantum chemistry instead of the laws of classical physics. Secondly, owing to the high surface area, nanomaterials tend to show better sensitivity to surface processes (Martín–Yerga, González–García, & Costa–García, 2012). Other remarkable properties of nanomaterials include greater penetrability and reactivity, easy derivatisation method, and distinctive thermal, mechanical or electronic properties (Kuzma, 2010).

A composite material was formed when two or more different materials were combined so as to blend the properties of both materials in producing better outcome. Referring to the definition provided by the International Union for Pure and Applied Chemistry (IUPAC), a composite material is defined as a multicomponent material comprising multiple different (non-gaseous) phase domains in which at least one type of phase domain is in a continuous phase (Work, Horie, Hess, & Stepto, 2007). IUPAC also extends its definition to nanocomposite materials as those composites in which at least one of the phases has at least one dimension of nanometre scale (Schubert & Hüsing, 2012; Work et al., 2007). Founded on these definitions, various systems can be categorised among these materials, the dispersions of nanosized objects of different nature such as metal particles or carbon nanotubes or intercalated/exfoliated layered material in continuous/polymeric phases being major examples (Sattler, 2011).

Intercalation is one of the popular way to produce these nanocomposite materials (Ghotbi, Hussein, Yahaya, & Rahman, 2009). Presently, nanocomposite has been widely used in numerous fields including food industry, sensors fabrication, pharmaceuticals industry and agriculture (Lee et al., 2012). Hence, the term of ‘nanohybrid’ or ‘nanocomposite’ has become a familiar concept in the development of nanomaterials in their respective application. Layered nanocomposite has received more attention compare to the other nanocomposite developed. This is particularly because of the unique physical, chemical and mechanical properties own by the layered nanocomposite, which cannot be attained in other corresponding nanocomposite (Ruiz–Hitzky, Aranda, Darder, & Rytwo, 2010).

Generally, these layered nanocomposite was synthesised using soft–chemical lattice engineering method, based on the concept of intercalation. The intercalation reaction refers to the reversible insertion of guest species, either polymer, organic, inorganic molecules or ions into certain inorganic host without altering any structural features of the guest species (Lee et al., 2012). This reaction has become one of the most efficient routes in fabricating new inorganic–inorganic, organic–inorganic, and bio–inorganic nanocomposites at low dimension. Since the past years, countless effort have been executed in synthesising and manipulating the hybrid systems of layered nanomaterials through various modification. Due to an easy manipulative nature of these nanocomposites, numerous hybrid materials were exploited and proposed, including as a controlled release herbicide, modified electrode for iodate determination and controlled release of non–steroidal anti–inflammatory drugs (Hussein, Rahman, Sarijo, & Zainal, 2012; Li et al., 2009; Rives, Del Arco, & Martín, 2013).

1.6 Problem Statement

The National Agro–Food Policy (NAFP) 2011–2020 is a programme launched by Malaysia government in 2011 with the purpose to ensure that our country continues to have sustainable food resources by increasing the paddy productivity (Rezai, Shamsudin, & Mohamed, 2016). Although government has allocated huge financial support in paddy cultivation through various subsidisation, the domestic rice production however, have not yet shown impressive productivity in the past year (Agricultural Department of Peninsular Malaysia, 2012). Recent annual average paddy production in Malaysia was yielded 4.91 t/ha, which is apparently lower than yielded in other developed countries, such as Indonesia and Vietnam (ASEAN Food Security Information System, 2016). The main problem confronted by the farmers during the germination and vegetative stage in paddy cultivation is the depleted of soil and water quality due to the excessive and continuous usage of pesticides (Wu, Wang, Zhou, & Zhou, 2018; Xu et al., 2017). Consequently, greater funds and effort need to be invested, in order to recover the polluted soil and water (Alves, Cardoso, Martines, Sousa, & Pasini, 2013; Bocos, Fernandez-Costas, Pazos, & Sanroman, 2015; Chen et al., 2015; Navarro, Fenoll, Vela, Ruiz, & Navarro, 2011; Ribeiro, Nunes, Pereira, & Silva, 2015; Rulkens, Tichy, & Grotenhuis, 1998).

Even though the negative impact of pesticides to the ecological system has been acknowledged, the paddy cultivation in our country is nevertheless greatly reliant on the usage of pesticides to exterminate various invasive pests and weeds. The invasion of the uninvited pests seem to cause massive economic loss to the farmer in these recent years. In January 2013, around 80 ha paddy cultivation area in Bota, Perak was destroyed due to the outbreaks of brown planthopper (Sulaiman, 2013). The total loss due to the attack was estimated around half millions ringgit. Under these tragic circumstance, the application of pesticides in paddy cultivation seems to be unavoidable.

Therefore, in order to increase the rice productivity in our country, it is necessary to propose an alternative way in controlling the invasive pests without polluting the environments. The encapsulated controlled release formulation applied on pesticides is one of the recent innovation made in agricultural field to reduce the environmental pollution (De Oliveira, Campos, Bakshi, Abhilash, & Fraceto, 2014). This formulation helps to minimize the amount of pesticides used in pest management, hence decreasing the non–target effect. Controlled release formulation is superior to its counterpart and results in higher yield and better crop quality (Garrido, Cagide, Melle–Franco, Borges, & Garrido, 2014).

To overcome the aforementioned environmental issues, this research will deal with the work to synthesise several new nanocomposites, using several pesticides namely quinclorac, bispyribac and imidacloprid as guest ions, whereas zinc hydroxide nitrate (ZHN) and zinc/aluminium–layered double hydroxide (Zn/Al–LDH) was used as the host material. These host materials were selected due to their easy preparation, inexpensive and showed great potential as host carrier for various pesticide (Bashi, Hussein, Zainal, & Tichit, 2013; Bruna et al., 2008; Qiu, Hou, Xu, Liu, & Liu, 2009; Sarijo, Ghazali, Hussein, & Sidek, 2013; Wang, Yang, Chen, & Evans, 2008). The synthesised nanocomposites then undergo coating process using chitosan (natural polysaccharide) and carboxymethyl cellulose (synthetic polysaccharide), and the controlled release behaviour of both uncoated and coated nanocomposites were studied. Previous studies have proven that the coated process will enhance the controlled release properties of the nanocomposite and prevent the unintentionally spread of pesticides residue to the environment (Park, Hwang, Oh, Yang, & Choy, 2013). Therefore, the influence of the material used as the coating material on the controlled release behaviour of the synthesised nanocomposite was investigated.

1.7 Significant Study

Although there were numerous approaches that can be used to control the pest problem in paddy cultivation, up until this day the dependency on pesticide in overcoming the pest issues is undeniable. Therefore, this study is important since it proposes a safer way to use the pesticides, which allow those pesticides to be continuously used in paddy cultivation while prevent their downside effect.

This study will benefit the community by minimising the risk of environmental pollution caused by the conventional pesticides. The CRF properties own by the layered material–pesticide nanocomposites that were synthesised in this study helps to release pesticide residues into the environment in slower manner and reduce the non–targeted effects of pesticides towards the environment. Consequently, this will reduce the risk of health problems of living organisms and environmental pollution, thus provide better life quality to the community.

The method proposed in this study can be applied by the pesticide manufacturers to implement the CRF into the pesticides produced by their factory, so that more pesticide with CRF will be available in the market. Easily access and various choices of pesticides with CRF will make it more convenient for the farmer to obtain this type of pesticides, thus attract them to use it. This is, therefore, will help in minimising the usage of the conventional pesticide.

1.8 Limitation Study

It is important to acknowledge that this study is bounded by several limitations. Although there are numerous type of pesticides that were used for pest control in paddy cultivation, this study only focussing on three different pesticides; quinclorac, bispyribac and imidacloprid. This is owing to the fact that the nature of these three pesticides match all of the criteria needed to be selected as the intercalation ions for this study, which include (i) commonly used in paddy cultivation, (ii) may either dissociate in water to form anion or form micelle in the presence of sodium dodecyl sulphate surfactant (iii) delocalised electrons are present in the structure of the pesticide.

During the intercalation process, the host zinc/aluminium–layered double hydroxide were selected for quinclorac whereas zinc hydroxide nitrate−sodium dodecylsulphate were selected for both bispyribac and imidacloprid. After several attempts were made in synthesising the nanocomposite, it was discovered that the host selection was also greatly depend on the nature of the pesticides. Therefore, it is not possible to standardise the type of layered material used as the host for all three pesticides.

Each synthesised nanocomposites; zinc/aluminium–layered double hydroxide–quinclorac, zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac and zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid nanocomposites were coated with chitosan, using only one composition chitosan mixture which is 0.02% (%w/w). The composition was selected based on good result obtained from the PXRD analysis, therefore the composition was fixed throughout the study. Similar composition was also used when the carboxymethyl cellulose was used as the coater for all synthesised nanocomposites.

It is also important to emphasise that the main purpose of the controlled release study of uncoated, carboxymethyl cellulose–coated and chitosan–coated nanocomposites synthesised performed is to study the potential of the nanocomposites in controlled release formulation, hence the result from the release study and the comparison made will be focussing on the release time needed to achieve the maximum accumulated release. Owing to the fact that the release study was ran in laboratory scale, it is important to put into consideration that all the data provided from the release data were obtained for the release of 0.6 mg nanocomposite. No study on real samples were carried out in this study.

1.9 Objectives

The objectives of this study are:

- to synthesise the new zinc/aluminium–layered double hydroxide–quinclorac, zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac and zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid nanocomposites
- to coat the zinc/aluminium–layered double hydroxide–quinclorac, zinc hydroxide nitrate−sodium dodecylsulphate−bispyribac and zinc hydroxide nitrate−sodium dodecylsulphate−imidacloprid nanocomposites with carboxymethyl cellulose and chitosan using direct reaction method.

- to study the physicochemical properties of uncoated, carboxymethyl cellulose–coated and chitosan–coated nanocomposites synthesised using PXRD, FTIR, ICP/OES, CHNS, TGA/DTG, BET and FESEM instruments.
- to study the controlled release properties and kinetic behaviour of uncoated, carboxymethyl cellulose–coated and chitosan–coated nanocomposites synthesised in various concentration of anion solutions.
- to compare the behaviour of controlled release properties uncoated, carboxymethyl cellulose–coated and chitosan–coated nanocomposites synthesised.
- to compare the kinetic behaviour of uncoated, carboxymethyl cellulose–coated and chitosan–coated nanocomposites synthesised