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Develop and evaluate novel nano-porous carrier materials to improve pesticide delivery efficiency

Final report for research project 3.2.001

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- originality

- methodology
- rigour
- compliance with ethical guidelines
- conclusions against results
- conformity with the principles of the Australian Code for the Responsible Conduct of Research (NHMRC 2018), and provided constructive feedback which was considered and addressed by the author(s).

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EXECUTIVE SUMMARY

Pesticide application in agricultural practices is essential for increasing crop production to meet the world's increasing demand for food and raw materials. However, most of the commonly used pesticides are lost during farming or agricultural practices which can have a residual effect on the environment and human health. The cost-effective management or, ideally, the eradication of insects and weeds through efficient applications is critical for sustainable and increased agricultural productivity. Controlled release of pesticides by novel materials is a promising strategy for managing residue issues when pesticides are being applied.

This project focused on the utilisation of low-cost clay minerals for the delivery of one representative pesticide (imidacloprid), which could help reduce loss and residue and achieve targeted and sustainable release. The project comprised three main phases: (1) literature review; (2) synthesis and characterisation; and (3) loading and releasing. The overall aim was to develop a controlled releasing material for imidacloprid. This research project represented an important initiative in the development of controlled release of pesticides and has the potential to be validated in field and pilot studies for agricultural application. It is currently at the technical readiness level 2–3.

In this project, we first conducted a literature review on the utilisation of various materials for pesticide delivery including, but not limited to, organic, inorganic, natural and nanoporous materials. A workshop discussion was also conducted to engage perspectives from farmer groups. This enabled the research team to better understand the requirements for loading and releasing in field applications. Various clay minerals were reviewed for their ability to deliver pesticides. Selection criteria were set for the selection of raw materials for pesticide loading.

Low-cost clay minerals were used for the preparation of carrier materials which were chemically treated on their surfaces. The treated materials were characterised using various techniques in order to understand the surface charge and functional group changes and utilised for the loading of imidacloprid. The treated materials demonstrated higher loading of imidacloprid than did the raw materials.

The clay minerals were further incorporated with polymeric materials to prepare bead products that can be deployed for the slow release of imidacloprid. The clay particles provided an organic and inorganic network that formed a porous structure for the presence of imidacloprid. The materials can release imidacloprid for more than 10 cycles. Morphological analysis of the materials indicated a porous structure and the incorporation of imidacloprid.

The release behaviour in the water and soil samples indicated the influence of the carrier material, soil type, and preparation procedure on the release kinetics. The potential utilisation of these materials in soils requires further investigation in sugarcane farming areas and evaluation of pest control efficacy. The results will firstly be useful for future research, and secondly lead to the use of low-cost materials for slow-release pesticides.

OBJECTIVES

- Potential of nanocarrier materials for encapsulated imidacloprid
- Investigate the loading techniques and mechanism for imidacloprid encapsulation
- Investigate the releasing pattern of pesticide from the carrier materials
- Evaluate the efficacy of encapsulated insecticide on canegrub control

RESULTS

This project focused on the development of controlled-release pesticide for agricultural application, exemplified by the significant support provided by the sugarcane industry. Imidacloprid is heavily used in the sugarcane industry but it has residual effects on the surroundings and soil functions. The project incorporated three research activities: (1) literature review, (2) synthesis and characterisation, (3) loading and releasing. The key findings are listed below.

1. Porous structure carrier materials with low-cost, biocompatible and ecofriendly properties are promising for the development of controlled-release pesticide. Various organic- and inorganic-based materials could be utilised while natural clay minerals are selected for this project given their low-cost, abundant, locally available, environmentally friendly, and manipulatable properties.
2. The chemical treatment of clay minerals enhanced the entrapment and sorption of imidacloprid on the materials. These were achieved through acid erosion and organic functionalisation for the active surface properties. The loading method using sorption proved to be more feasible and easier to be scaled in the pilot study.
3. The incorporation of clay and modified-clay minerals in the polymer product enhanced the product's strength. Larger amounts of imidacloprid were loaded on the product compared to the commercial product. The releasing pattern was similar for both products while the elongated release of imidacloprid in soils was required to verify the releasing behaviour in realistic conditions.

The research results are useful and have important implications for the further development of controlled-release pesticide for commercialisation in the agriculture industry. The research project represents a great opportunity for future research being conducted in this important area.

NEXT STEPS	TIMING
Consideration for future research in the following aspects: • Collaborate with farmers to conduct pest control studies to understand the efficacy and further refine the synthesis of materials • Understand the residue issue of active ingredient in soils.	

1 INTRODUCTION

1.1 PESTICIDE APPLICATION AND ISSUES

Maximising agricultural productivity is crucial for meeting increasing demands for food globally. Agrochemicals play a vital role in improving productivity, particularly by reducing yield loss due to insect pests, plant pathogens and weeds (Pimentel 2009). Although pesticide application is essential for increasing crop productivity, more than 90% of applied pesticides are either lost to the environment or unable to reach the target area required for effective pest control (Ghormade, Deshpande et al. 2011). Up to 20–30% of applied pesticides can be lost through emissions (van den Berg, Kubiak et al. 1999) which may reach up to 50% depending on a number of factors, including the application technique, physicochemical properties of the pesticide, and environmental conditions (e.g. wind speed, humidity and temperature) (van den Berg, Kubiak et al. 1999, Bedos, Cellier et al. 2002). Most often, pesticide formulations fail to deposit properly over the leaf surface. Consequently, pesticides are further lost through leaching, evaporation, deposition, washing away and degradation by photolysis, hydrolysis and microbial activity (Mogul, Akin et al. 1996). Figure 1 shows the pathways of pesticide degradation in the environment. As a result of these losses, the active ingredients in the pesticide are removed prior to performing their action; therefore, the concentration in the target area is well below the minimum effective concentration needed.

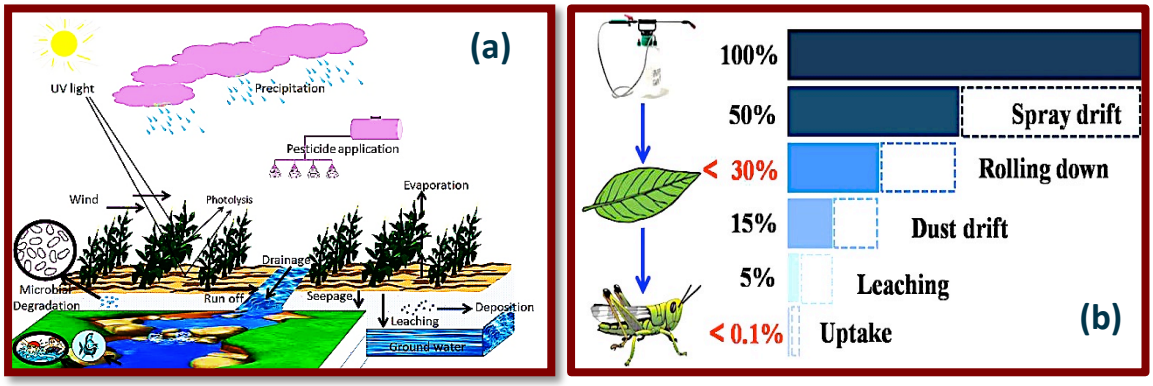


Figure 1. (a) Pesticide losses and degradation pathways. Adapted and modified from (Nuruzzaman, Rahman et al. 2016). (b) Low efficiency of conventional pesticide formulations. Adapted from(Zhao, Cui et al. 2017).

Therefore, nonspecific and periodic application of pesticides is required to achieve the desired biological response in terms of pest control within a given period (Nair, Varghese et al. 2010). In this way, the amount of applied pesticides greatly exceeds the amount actually required to control the target pests (Ghormade, Deshpande et al. 2011). As a result, not only does the cost of treatment increase; such usage results in unfavourable effects either for plants or for the environment, including soil and water pollution which ultimately becomes hazardous to public health (Mogul, Akin et al. 1996, Nair, Varghese et al. 2010). The repeated and indiscriminate use of pesticides increases pest and pathogen resistance, reduces soil biodiversity and nitrogen (N) fixation, increases bioaccumulation

of pesticides, kills predators and pollinators, and destroys the habitats and feeds of birds (Tilman, Cassman et al. 2002). Increasing knowledge of the negative effects of agrochemicals (especially pesticides) on public health and wildlife has resulted in increasingly stringent control of their use.

Despite the negative impacts of pesticides, their utilisation is progressively increasing worldwide. Globally, in 2006 and 2007, ~2.36 million tonnes of pesticide were used (worth US$35.8 billion in 2006 and US$39.4 billion in 2007) (Grube, Donaldson et al. 2011). Where the utilisation of pesticides increased gradually and in 2012, the amount of global pesticide usage reached ~2.9 million tonnes, at an expense of US$56 billion (Atwood and Paisley-Jones 2017). Similarly, the utilisation of pesticides increases Australian crop yield by approximately 40% each year, which increases the value of food production by A$13 billion (Croplife and Australia 2008). It has been reported that the total Australian market for pesticides and other products regulated by the Australian Pesticide and Veterinary Medicine Authority (APVMA) was A$1.6 billion in 2006/07 (Croplife and Australia 2008). This indicated the significance of pesticides for the Australian agroeconomy. It was also reported that more than 6,000 products containing 2,000 technical grade active constituents are currently approved for use in Australia. More than one tonne of chemicals in at least 250 categories are imported and/or manufactured in Australia annually. However, on-farm soil biology has been mostly overlooked, and relatively little attention has been given to this topic due to its complexity and the nascent nature of this field, which is important for sustainable agriculture in Australia. Most often, the functional role of soil organisms was not considered in relation to organic matter turnover, N cycling, phosphorus solubilisation or disease suppression.

On the other hand, several issues affecting pesticide choice have enhanced the dominance of some selective types of pesticides throughout Australia. The issues include:

- pest control efficacy, including the possible development of biological resistance
- pesticide and commodity prices
- the possibility of residues
- toxicity to operators and the community
- off-target impacts
- market implications
- the impact of their use on other pest strategies, such as integrated pest management.

Additionally, the cropping pattern also influences pesticide application. The Australian agricultural chemical industry includes 5 significant segments of the Australian crop protection market, namely, broadacre cropping (wheat, oats, barley, grain sorghum, canola, peanuts, etc.), cotton, sugarcane, horticulture (fruit, vegetables, etc.) and others.

Thus, a single cropping pattern plays a vital role in the continuous exposure to a specific pesticide. Notably, pesticides are formulated in a way that may cause only minor negative effects when applied at the recommended dose, whereas in a real scenario, the effects are quite different. The long-term and repeated application of a specific pesticide greatly exceeds its residual limit in soil. As a result, in some cases soil health and performance are greatly reduced by the damage to soil biological functions caused by pesticides. In contrast, microorganisms play vital roles in degrading pesticides and producing toxic metabolites. An excess amount of pesticidal residue also reduces crop performance by directly inducing phytotoxicity. The accumulation and repeated application of pesticides can also reduce plant-available N by slowing the processes of N cycling. The persistence of pesticides can also increase the incidence of some diseases. An increase in pesticide

residue may threaten the ability of Australian grain to reach its maximum residue limits (MRLs) which can reduce its market value.

To combat the problems of commercially available pesticide formulations, different approaches adapted thus far include integrated pest management (IPM), integrated crop management (ICM), integrated farming, sustainable agriculture, improvement of the spraying instruments (e.g. sprayer nozzle diameter) and increasingly stringent pesticide registration and certification authority.

However, these approaches are not rapid and most often cannot be used to control pests effectively on time. Thus, the utilisation of pesticides is essential, and pesticides are considered one of the major components of IPM. In this regard, in addition to integrated pest management systems, additional in-depth research is needed to develop pesticide formulations that possess low residual effects while increasing pest control efficacy and ensuring new target-oriented delivery systems.

1.2 IMPROVEMENT OF PESTICIDE FORMULATIONS

In agriculture, the development of new plant protection products or formulations is desirable for increasing plant efficacy and overcoming associated problems (Nuruzzaman, Rahman et al. 2016). Safer and more convenient pesticide formulations are always preferred. In the early 1990s, Seaman reviewed the trend of pesticide formulations and noted that wettable powder (WP) and emulsifiable concentrate (EC) were the major conventional pesticide formulations. However, these formulations were less favoured by farmers as well as registration authorities (Seaman 1990). In general, WP is a dry and finely ground powder pesticide formulation composed of pesticide active ingredients (AIs), inert fillers, and other additives. The particles also do not dissolve in water and thus settle quickly in the sprayer during application. In addition, this formulation easily drifted and created runoff into the environment. EC is a liquid pesticide formulation that is formulated by dissolving AIs in solvent, adding an emulsifier, and diluting the mixture in water to form a stable emulsion. However, most toxic solvents, such as xylene and toluene, can directly leach and leak into the environment. Ultimately, this pesticide causes serious pollution in soil and water systems and chemical residues in crops and food products and is a potential threat to human health.

As alternatives to WP and EC, other formulations, such as soluble liquids (SLs), have attracted much attention. Additionally, water-dispersible granules and emulsions in water were found to be promising formulations of capsule suspensions and polymeric surfactants that work more effectively and safely under favourable conditions. These formulations were deemed to lead to the formation of microencapsulated pesticide formulations for the controlled release of AIs. In fact, controlled-release pesticide formulations were first introduced in the middle of the 1960s (Bahadir and Pfister 1990). Because of the need for a large amount of funding for developing new pesticides or bioactive agents, recent studies have focused more on improving delivery systems, especially through the preparation of controlled-release formulations (CRFs).

Controlled-release formulations of pesticides are considered depositories of AIs from which the active constituents are released in a controlled way into their release environment over a defined period of time (Bahadir and Pfister 1990). The main advantage of CRFs is that they reduce the amount of pesticide used much less than conventional pesticides do while retaining a similar period of activity by regulating the supply and release of AIs (Lewis and Cowsar 1977). Figure 2 depicts the ability of CRFs to reduce the amount of pesticide applied compared with that of conventional pesticides. In most cases, the

effectiveness of conventional pesticides is reduced by environmental forces that remove excess pesticide before the plants can perform their functions. The rate of pesticide removal at any time is directly proportional to the amount present in the environment at that time. Thus, periodic application of conventional pesticides is required to maintain an effective concentration. Conversely, an ideal CRF reduces the number of applications as well as the relevant cost and time.

However, the preparation of an ideal CRF has not only been an active area during recent decades but also challenging. Initially, CRFs were prepared by incorporating AIs into a polymeric matrix to obtain a sustained release profile of the active agents. In this system, AIs are released for an extended period of time while maintaining constant exposure. The rate of exposure may decrease due to general loss of AIs or increase due to rupture of the protective barriers. Later, the concept of CRFs was completely changed, although the principles of sustained release or controlled release are the same even when they sometimes overlap with each other. However, the mechanism of release is significantly different. A CRF may exhibit a fast release, a slow release, a constant release or a changing release pattern of the AIs depending on the design of the formulation. Thus, the release rate can be divided into three types: (1) 'zero-order release', where the release rate remains constant until the carrier is exhausted by the active agent; (2) 'first-order release', where the release rate is proportional to the amount of active agent within the reservoir and declines exponentially with time as the reservoir approaches exhaustion; and (3) 'square-root-of-time' release, where the release rate is linear with the reciprocal of the square root of time. The release rate remains finite as the carrier advances toward exhaustion (Baker 1987).

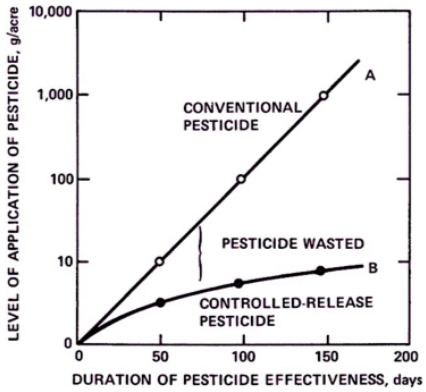


Figure 2. Relationships between the level of application and the duration of action for conventional and controlled release formulations. Adapted from(Lewis and Cowsar 1977).

There are some promising concepts for developing CRFs. First, the preparation of polymeric capsules filled with a solid or liquid pesticide or with a suspension or solution of the agent in a fluid in which the release of pesticide is controlled by Fickian diffusion through the capsule walls or through micropores in the capsule walls. Second, the preparation of a solid biodegradable or nonbiodegradable polymeric matrix with heterogeneous dispersed pesticide particles or droplets from where the release of agent occurs via diffusion through the matrix, erosion of the matrix, or a combination of both diffusion and erosion. Third, the chemical bonding of a pesticide to a natural or synthetic

polymeric material, such as by pendant anhydride or ester linkages or the formation of macromolecules of pesticides via ionic or covalent linkages, which control the release of the agent by hydrolysis, thermodynamic dissociation, microbial degradation or other retrograde chemical reactions of the linkages. The structural properties of CRFs can also significantly affect the release and release of principals (Table 1).

Table 1. Structural principals of physically incorporated polymeric CRFs.

Structure of the CRFs	Release controlling system	Release mechanisms
Capsules (Microcapsule, Macrocapsule)	Release control by membrane	Diffusion
Hollow fibre	Capillary forces	Dissolution, diffusion
Porous polymeric substances	Capillary forces	Dissolution, diffusion
Polymeric gels		Dissolution, diffusion
Semipermeable membrane coating	Release control by membrane pores	Osmotic pump
Layer (film) structured polymers	Laminate system (membrane controlled)	Diffusion
Polymeric matrix (nonporous)	Monolithic system	Matrix erosion, diffusion

Nevertheless, among the various polymeric CRFs, microencapsulates have emerged as promising commercial pesticide formulations. To date, various synthesis techniques have advanced the progress of microencapsulated formulations. For instance, the preparation of emamectin-benzoate (EMB)-embedded slow-release microspheres by the emulsion polymerisation technique is illustrated in Figure 3. Recently, a market survey-based company, MarketsandMarkets™ Research Private Ltd., estimated that the amount of microencapsulated pesticides needed to reach US$312.5 million in 2017 was projected to reach US$539.5 million by 2022, at a cumulative annual growth rate of 11.54% from 2017 to 2022 (Markets and Markets 2017). This is because the encapsulated limited amount of AIs for effective action against the targeted pest was able to protect AIs from volatilisation, reduce the loss from the application site, decrease phytotoxicity to plants and reduce environmental and health risks to the applicators. MarketsandMarkets™ also reported that the market for insecticide formulations was the largest, by type, in 2016, and the interfacial polymerisation technique was most suitable for the preparation of microcapsules. This technique is also less expensive than other methods and is suited to large-scale production. Additionally, Europe is the leading region due to the declining trend in the use of EC formulations because of the harmful effects of these formulations on the environment and the increasing application of IPM. Some of the world's leading pesticide companies, such as BASF (Germany), Bayer AG (Germany), Syngenta (Switzerland), Monsanto (US), ADAMA (Israel), and FMC Corporation (US), have already launched their products on the market. For example, the microencapsulated methyl parathion was commercialised as a Penncap-M by Monsanto Agr. Prod. Co. However, microencapsulated pesticide formulations may retain several major drawbacks, such as poor stability after dilution, and controlled release is affected by wide shell thickness.

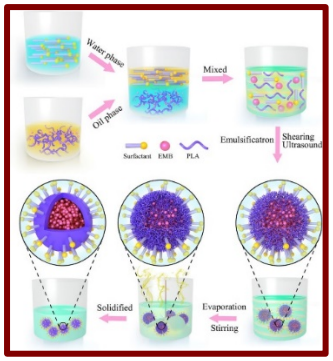


Figure 3. Schematic description of the preparation of emamectin-benzoate (EMB) slow-release microspheres. Adapted from (Wang, Wang et al. 2017).

As such, nanotechnology is considered one of the latest advanced agricultural practices for improving productivity and product quality. This field includes the development of more effective and nonpersistent pesticides and new techniques including CRFs. Over the last decade, the intensified research growth and promising application of nanotechnology in agriculture, specifically in pesticide delivery, indicate its ability to revolutionise the pesticide sector by formulating controlled-release nanopesticide formulations along with existing microencapsulated pesticides.

3.2 THE SUGARCANE INDUSTRY AND PESTICIDE USAGE

The project team engaged with farmers from the sugarcane industry to identify the issues faced with the application of imidacloprid in 2019, which supported the understanding of the targeted release of imidacloprid required for sugarcane farming systems.

1.3.1 Imidacloprid

Amongst the pesticides, neonicotinoids have been the fastest growing in the global market compared to other insecticides such as carbamates, organophosphates and pyrethroids for the last two decades (Jeschke, Nauen et al. 2011). Neonicotinoids are registered in more than 120 countries for commercial use in controlling a wide range of sucking and chewing insect pests in both agricultural and household scenarios (Jeschke, Nauen et al. 2011). The first neonicotinoid insecticide, namely, imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine), was introduced on the market in 1991 and is a representative neonicotinoid insecticide (Tomizawa and Casida 2011). Moreover, imidacloprid has become the most successful, efficacious and best-selling insecticide worldwide due to its unique chemical and biological properties (Jeschke and Nauen 2008). Imidacloprid possesses broad-spectrum insecticidal activity with low application rates, excellent systemic characteristics related to plant uptake and translocation, and adaptability to various application methods. The application methods include, for example, irrigation systems, furrow application, granular application or seed treatment (Jeschke and Nauen 2008). The chemical structure and physicochemical properties of imidacloprid are illustrated in Figure 4 and Table 2. Figure 5 shows the Fourier transform infrared spectroscopy (FTIR) spectrum of imidacloprid.

Its mode of action and selective toxicity toward insects have generated much attention regarding the safety profile of insecticides (Tomizawa and Casida 2005). Imidacloprid mainly acts on the central nervous system (CNS) of insects through binding with nicotinic

acetylcholine receptors (nAChRs), blocking the nicotinergic neuronal pathway. Compared with mammals, imidacloprid has a high binding affinity for insect nAChRs and consequently is more toxic to insects than mammals (Tomizawa and Casida 2005, Jeschke and Nauen 2008). Thus, the application of imidacloprid is not limited to agricultural crop fields but extends to widespread applications for controlling household and garden pests (e.g. termites, cockroaches, aphids, thrips, turf beetles) and even for controlling fleas on domestic animals (Jeschke, Nauen et al. 2011). However, their massive application and physico-chemical properties related to solubility and stability have made them potential contaminants of surface and ground water, especially by leaching (Gupta, Gajbhiye et al. 2002).

It was observed that global contamination of surface water with neonicotinoids has been very evident during the last decade, and among the neonicotinoids, imidacloprid was the most common contaminant found in Australia, Canada, Germany, Spain and the United States (Sadaria, Supowit et al. 2016). Thus, this pesticide can become a major threat to aquatic organisms. Recent studies have documented the toxic effects of imidacloprid and its metabolites on aquatic organisms such as algae, crustaceans, invertebrates and fish (Pestana, Alexander et al. 2009, Tišler, Jemec et al. 2009, Chen, Culbert et al. 2010, Hayasaka, Korenaga et al. 2012, Malev, Klobučar et al. 2012, Mohr, Berghahn et al. 2012). Similarly, glyphosate, the bestselling herbicide worldwide, has been reported to cause resistance in weeds. In Australia, rigid ryegrass (*Lolium rigidum)* has become resistant to this herbicide (Powles, Debrah et al. 1998). Another widely used anionic herbicide, 2,4-D (2,4-dichlorophenoxy acetic acid), is prone to loss by leaching.

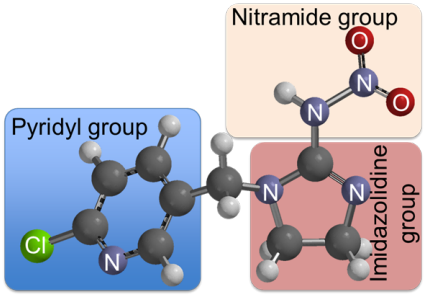


Figure 4. Chemical structure of imidacloprid.

Table 2. Physicochemical properties of imidacloprid.

Parameters	**Properties**	**Parameters**	**Properties**
Chemical formula	$C_9H_{10}ClN_5O_2$	log K_{ow}	0.57 (at 21 °C)
Molecular weight	255.662 g mol^{-1}	Dissociation constants	pKa_1 = 1.56 pKa_2 = 11.12
Appearance	Colorless crystals		
Melting point	143–144 °C	K_{oc}	156-960
Solubility (in water)	0.61 g L^{-1} (at 20°C)	Henry's constant	1.7 x 10^{-10} Pa·m^3 mol^{-1}
Density	1.54 g L^{-1}		
Stability	pH 5-11 (Stable to hydrolysis)	Vapour pressure	3 x 10^{-12} mmHg (at 20)

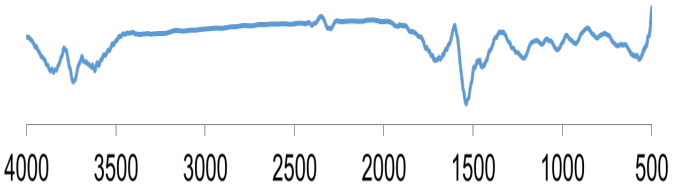


Figure 5. ATR-FTIR spectrum of imidacloprid.

1.3.2 Sugarcane industry and issues

Australian sugarcane is grown in areas with high rainfall and irrigation along coastal plains and river valleys on 2,100 km of the Australian eastern coastline between Mossman in the far northern region of Queensland and Grafton in New South Wales (Figure 6). Queensland accounts for approximately 95% of Australia's raw sugar production. More than 80% of all sugar produced in Australia is exported as bulk raw sugar, making Australia the second largest raw sugar exporter in the world (Department of Agriculture, Fisheries and Forestry, n.d.). The major regions for sugarcane farming include the Burdekin region (QLD), Herbert region (QLD), Northern region (QLD), Central region (QLD), Southern region (QLD) and NSW region. This project engaged farmer groups from the Herbert and Burdekin regions.

Canegrubs are currently the most significant economic pest of sugarcane in Australia. Sugar Research Australia (SRA) illustrates the issue of canegrubs in detail, including their species, biological life cycle and control options. The information below is mainly cited from the SRA website (Sugar Research Australia, n.d.). Canegrubs are the larvae of several types of cane beetles. There are 19 endemic and one introduced species of canegrub in Australia (Table 3). Larvae, or grubs, damage sugarcane plants through their feeding action on plant roots. The cane beetle undergoes complete metamorphosis (e.g., egg, larva/grub and pupa/adult) (Figure 6), during its life which takes one year or two years (Figure 6 and 7).

The cycle begins when eggs are laid between October and February. The timing of egg laying may differ slightly between species and from year to year, depending on climatic conditions. Seasonal weather conditions also influence the timing of lifecycles. The rapid emergence of adults results in concentrated beetle flights and subsequent egg laying. At other times, weather conditions may result in a staggered emergence of adults, resulting in beetle flights and egg laying spread over a longer time period. This often results in a mix of instars being present in cane blocks.

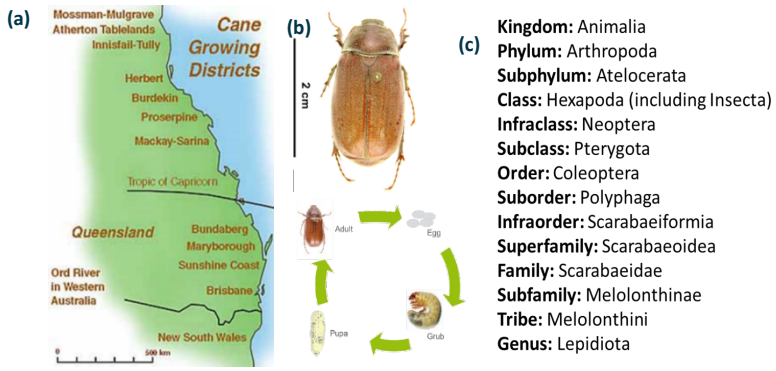


Figure 6. (a) Sugarcane growing region in Australia (source: https://www.zelmeroz.com/canesig/industry/industry-01.html). (b) The canegrub adult (beetle) and life cycle of canegrub. (c) Taxonomy of canegrub (CaneSIG).

Table 3. List of canegrubs in Australia (SRA, n.d.).

Sl. No.	Common Name	Scientific Name	Regions of distribution
1.	Childers canegrub	*Antitrogus parvulus*	Southern
2.	Southern one-year	*Antitrogus consanguinies*	Southern
3.	Planiceps canegrub	*Antitrogus planiceps*	NSW
4.	Nambour canegrub	*Antitrogus rugulosus*	NSW
5.	Greyback canegrub	*Dermolepida albohirtum*	Burdekin, Central, Herbert, Northern
6.	Negatoria canegrub	*Lepidiota negatoria*	Central, Southern
7.	Bundaberg canegrub	*Lepidiota crinita*	Southern
8.	Consobrina canegrub	*Lepidiota consobrina*	Northern
9.	Squamulata canegrub	*Lepidiota squamulata*	Burdekin, Central, Herbert, Southern
10.	Grata canegrub	*Lepidiota grata*	Burdekin, Central, Herbert, Northern, Southern
11.	Rothe's canegrub	*Lepidiota rothei*	Burdekin, Herbert, Northern
12.	Sororia canegrub	*Lepidiota sororia*	Herbert, Northern
13.	Grisea canegrub	*Lepidiota grisea*	Northern
14.	Froggatt's canegrub	*Lepidiota froggatti*	Northern
15.	Caudata canegrub	*Lepidiota caudate*	Northern
16.	Noxia canegrub	*Lepidiota noxia*	Southern
17.	Picticollis canegrub	*Lepidiota picticollis*	Southern
18.	French's canegrub	*Lepidiota frenchi*	Burdekin, Central, Herbert, Northern, Southern
19.	Plectris canegrub	*Plectris aliena*	NSW
20.	Rhopaea canegrub	*Rhopaea magnicornis*	NSW

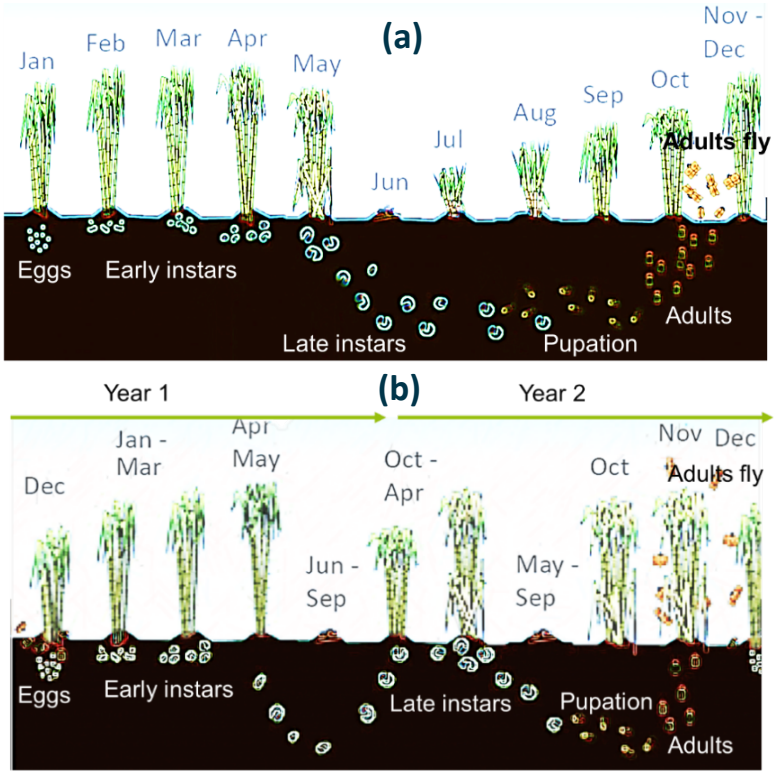


Figure 7. Canegrub life cycle: (a) 1 year and (b) 2 years (Source: https://sugarresearch.com.au/pests/canegrubs/)

Table 4. Feeding period.

Regions	Egg laying	Aggressive feeding
Northern to Central	December – January	March – May
Southern	September – October	January – April

Considering the behaviour of current pesticide formulations, the life cycle of canegrubs and the cropping pattern of sugarcane, the research hypothesis was slightly changed. The initial target was the preparation of a stimuli-responsive formulation that is triggered by different environmental factors, such as soil pH, temperature and ionic strength. According to discussions with farmers, the sustained and delayed release of active ingredients is highly important for actual sugarcane growing region scenarios. The soil pH ranged from 4.5–8.7, the field temperature remained > 16.5 °C, the cation exchange capacity ranged from 5–25 cmol(-)/kg, and the organic carbon (OC) concentration ranged from 0.5–2.5 %. Thus, the detailed research activities have been modified to achieve the desired products.

Based on the farmers' perspective, the product(s) need to achieve the following potential characteristics:

- The product should be free from controlled release, influenced by soil pH and temperature because of the wide range of soil types; therefore, soil pH and soil temperature vary from region to region. The application of these new formulated products requires consistent results among a wide range of soil types.
- Based on the nature of the pesticide, the canegrub life cycle and the cropping system of sugarcane, a special arrangement is required in pesticide formulation. The pesticide

formulation should have sustained release properties for 5–7 months, with an initial lag time of 2–3 months.

3.3 PROJECT AIMS AND OBJECTIVES

Pesticide utilisation is crucial for food security given the increasing demand for food quality and quantity both in Australia and globally. Approximately 90% of the pesticides are either lost in the environment or do not reach the target area required for effective pest control, potentially polluting the environment. Nanoporous materials have the potential to encapsulate pesticides and improve their efficiency by controlling the release of the active ingredient of the pesticide. This project aimed to evaluate nanoporous materials (either clay- or carbon-based) as potential carriers to improve pesticide delivery at the field level. This study will lead to the development of a controllable system to deliver one neonicotinoid insecticide (imidacloprid) for canegrub control. It is expected that the encapsulated pesticide active ingredients will be released in a sustained way for a longer period of targeted pest control. This approach will increase the pest control efficiency, increase productivity and reduce pesticide residues in the environment.

The main aim of this project is to develop a controlled release pesticide delivery system through the development of materials and loading and release mechanisms and to evaluate its efficacy. A controllable delivery system can be achieved by loading the active ingredients via encapsulation or entrapment into nanoporous carrier materials. The total amount of pesticide applied will decrease as the efficiency increases.

The specific objectives include:

- Potential of nanocarrier materials for encapsulating imidacloprid
- Investigate the loading techniques and mechanism for imidacloprid encapsulation
- Investigate the pattern of pesticide release from carrier materials
- Evaluation of the efficacy of encapsulated insecticides for canegrub control.

The research results obtained in this study could contribute to long-term objectives, including:

- Validation of the materials developed for other active ingredients
- Pilot-scale production and application of nanoencapulated pesticides
- Field trials of nanoencapsulated pesticides for various insects.

This report outlines the main findings from the review and experimental results to develop existing pesticide formulations for pesticide delivery of particular interest to Soil CRC members and participants through research, consultations and discussion. The following main aspects are presented in the final report:

- Literature review
- Synthesis, structural development, and characterisation of nanoporous materials
- Loading and release of pesticides onto nanoporous materials.

Research related to the evaluation of the efficacy and environmental behaviour of the products obtained is not part of this report.

BACKGROUND

2.1 PREVIOUS RESEARCH AND LITERATURE

2.1.1 Pesticide delivery and the role of nanotechnology

The use of nanotechnology in agricultural practices has been considered one of the most promising practices in recent years. The design, fabrication and utilisation of materials, structures, devices and systems involve the control of a nanometre length scale (1–100 nm) and the exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale in at least one dimension (Li, Lu et al. 2010). There are investigations in the literature related to the utilisation of nanotechnology in various agricultural practices, such as seed treatment, germination, plant growth and development, pest control, pesticide delivery, fertiliser delivery, genetic material delivery, toxic agrochemical detection, and pathogen detection (Scott, Chen et al. 2003, Nair, Varghese et al. 2010, Ghormade, Deshpande et al. 2011, Gogos, Knauer et al. 2012, Goswami and Bandyopadh 2012, Khot, Sankaran et al. 2012, Rai and Ingle 2012, Sekhon 2014, Nuruzzaman, Rahman et al. 2016). In terms of pest management, nanomaterials have novel properties that can increase the efficiency of agrochemicals (e.g. pesticide, fertiliser, growth hormone) and make the delivery system 'smart' (Nair, Varghese et al. 2010). In pest management, pesticides can be delivered via a smart delivery system in a controlled and targeted manner which has been postulated for drug delivery to humans (Roco 2003). Notably, various nanomaterials have exhibited potential as carriers for pesticide delivery. Moreover, some nanoparticles are also capable of controlling agricultural pests.

Nanopesticides

Considering the definition of nanotechnology, the addition of the prefix 'nano' with pesticide may differentiate them from conventional pesticide on the basis of size and structure in a simplistic way. According to Bergeson (2010), very small particles of active ingredients or other small, engineered structures that can prevent, destroy, repel or mitigate pests are considered nanopesticides. However, based on the purpose of nanomaterial utilisation, nanopesticides can be categorised as nanocide or nano-delivered pesticides.

Nanocides

Nanoscale materials or nanoparticles that have pesticidal effects and thus act as active ingredients are known as nanocides and include nonmetal and metal oxides (Barik, Sahu et al. 2008, Barik, Kamaraju et al. 2012, Gogos, Knauer et al. 2012, Kah and Hofmann 2014).

Nano-delivered pesticides

Nanomaterials are utilised as carrier materials for the delivery of conventional pesticides. In this context, nanomaterials provide support to conventional pesticide AIs for the preparation of nanostructured pesticide formulations through adsorption, ligand-mediated attachment, entrapment and encapsulation (Ghormade, Deshpande et al. 2011). The use of nanomaterials such as nano-encapsulates, nano-containers and nano-cages for pesticide delivery and the utilisation of these nanomaterials are good techniques for the preparation of CRFs. These nanomaterials also protect active ingredients from premature degradation, increase stability and pest control efficacy, and reduce the amount of pesticide applied (Nuruzzaman, Rahman et al. 2016). In some cases, nanomaterials are

introduced into composite materials such as polymeric matrices to enhance the efficacy of the system as carriers for pesticide delivery. Recently, emulsion-based pesticide formulations have been formulated more effectively via the beneficial aspects of nanotechnology. Using this technology, emulsions such as microemulsions and nanoemulsions are prepared where the droplet sizes are maintained below 100 nm. Thus, microemulsion- and nanoemulsion-based pesticide formulations show better stability than conventional emulsion-based formulations.

Despite the pest control efficiency of various nanoparticles, the main aspect of this report is improving conventional pesticide formulations with the help of nanotechnology. Hence, this report has focused mainly on the potential application of nano delivered pesticides.

2.1.2 Goals of nanopesticides

Nanopesticide formulations are prepared by loading AIs in nanocarriers or nanoencapsulation materials to increase the bioavailability of active substances and reduce toxicity, improve the timed release of active substances and enable the precise targeting of active substances (Sasson, Levy-Ruso et al. 2007). Nanoencapsulation technology has been introduced for crop protection chemicals to achieve either of these outcomes or to be nanosized, which reduces the amount of nanoencapsulated materials being applied due to the high surface area of the nanomaterials.

The utilisation of novel techniques aims to achieve the following effects:

- increasing the apparent solubility of poorly soluble active ingredients
- releasing active ingredients in a slow/targeted manner
- protecting the active ingredient against premature degradation
- reduce the amount of pesticide applied
- increasing the stability of the pesticide.

2.1.3 Nanoporous materials for pesticide delivery

The application of nanotechnology in pesticide delivery involves the use of nanomaterials. Before investigating the potential of different nanoporous materials, it is important to clarify the various types of nanomaterials discussed in this report. Most often, the terms related to nanomaterials found in the literature conflict with each other. Generally, a nanomaterial is a generic term that indicates a material with any external dimension at the nanoscale or an internal structure at the nanoscale. Accordingly, nanomaterials can be grouped into nanostructure materials and nano-objects. Materials with internal nanostructures or surface nanostructures are composed of interrelated constituent parts, in which one or more of those parts within the nanoscale region are considered nanostructured materials. In contrast, if at least one external dimension of a nanostructured material is within the nanoscale, the material is known as a nano-object. Furthermore, depending on the external dimensions of the nano-objects, they are further known as nanoparticles, nanorods, nanotubes, nanoplates, nanofibres, etc.

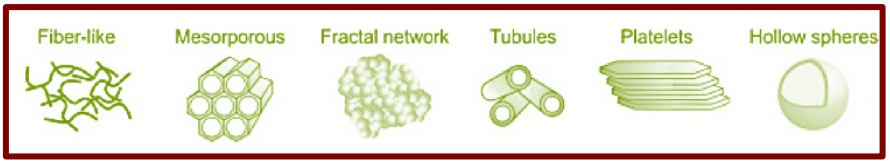


Figure 8. Different types of nano-objects.

From this scenario, one can obtain information about the formation and structure of a wide range of nanoporous materials. The materials can be built with either an organic or inorganic framework. Nanoporous materials can be classified into two groups: bulk materials and membranes. For example, zeolites are representative of natural bulk nanoporous materials, whereas cell membranes are examples of nanoporous membranes. Thus, a wide range of natural and synthetic organic or inorganic-based bulk nanoporous materials, as well as polymer or polymeric membrane-based materials, could be utilised as encapsulation or carrier materials for the effective delivery of pesticides. Depending on the pore size, the International Union of Pure and Applied Chemistry (IUPAC) has classified nanoporous materials as microporous materials (pore size 0.2–2 nm), mesoporous materials (pore size 2–50 nm) or macroporous materials (pore size > 50 nm). In terms of controlled release formulations, pore size is very important because of its significant influence on pesticide loading and release behaviour. The currently available nanoporous materials investigated for pesticide delivery are summarised in the following sections.

2.1.3.1 Organic Nanoporous Materials

2.1.3.1.1 Polymer-based nanomaterials

Different polymeric nanomaterials thus far have exhibited potential for use in a wide range of applications as carriers for bioactive molecule delivery, such as drug delivery to humans. In the case of pesticide delivery, nano-delivered pesticide formulations were first introduced through the preparation of nanosized polymeric vesicles where pesticide AIs were coated with biodegradable polymers. To date, various polymeric nanomaterials, such as nanocapsules, nanospheres, polymeric micelles, and nanogels, have been utilised to deliver pesticides (Figure 9).

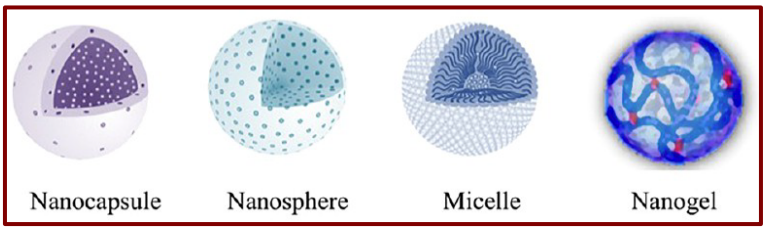


Figure 9. Different morphological forms of polymeric nanodelivered pesticides. Adapted from (Nuruzzaman, Rahman et al. 2016).

However, these polymer-coated nanopesticides suffer from various limitations, such as poor thermal and chemical stability, rapid elimination by the plant enzyme system, and degradation of some polymers, resulting in the formation of acidic monomers and decreased pH within the polymer matrix (Wen, Kim et al. 2003). Currently, their use is

increasing gradually due to the number of available sources, easy modification of surfaces, and simple synthesis techniques, such as the self-assembly of amphiphilic block copolymers.

Among the polymer-based nanocarriers, nanocapsules are the most commonly used vehicles for pesticide delivery. Nanocapsules are vesicular systems that are made up of a polymeric membrane encapsulating active compounds as an inner core at the nanoscale level (Mora-Huertas, Fessi et al. 2010, Ezhilarasi, Karthik et al. 2013). Hence, the nanocapsule structure is built with a core−shell arrangement of pesticide-active compounds and a polymeric membrane or coating. The active ingredients are arranged in the core in various ways. The active substances are usually dissolved in the solvent to form an inner liquid core and solidified to evaporate the solvent. The inner core is also structured with pesticide formulations or a polymeric matrix. Sometimes the polymeric shell may also absorb AIs. In this way, the active substances are encapsulated by nanocapsules spontaneously during the formation of nanocapsules. Polymeric nanocapsules are widely applied, and subsequently, additional studies have been conducted to determine their effective synthesis. The availability of different polymers and their inherent properties have given researchers the option to synthesise nanocapsules through different methods. The most developed strategies are nanoprecipitation, emulsion diffusion, solvent evaporation, double emulsification, emulsification coacervation and layer-by-layer deposition.

Nevertheless, various other methods, such as melt dispersion, emulsion polymerisation, interfacial polymerisation, interfacial deposition, solvent displacement and emulsion evaporation, have been described in the literature in combination with modifications of the abovementioned methods.

A wide range of synthetic and natural polymers have been utilised for the synthesis of nanocapsules. For instance, Yang et al. (2009) synthesised nanocapsules using polyethylene glycol (PEG) loaded with garlic essential oil. In another study, PEG-400 was utilised to encapsulate the neurotoxic organophosphate pesticide acephate (Choudhury, Pradhan et al. 2012). A polymer such as poly-ε-caprolactone (PCL) is considered to be a good synthesis material for preparing nanocapsules due to its water insolubility and slow degradation while remaining harmless to the environment. In their study, Grillo et al. (2012) prepared nanocapsules using PCL for encapsulating herbicides such as ametryn, atrazine, and simazine by employing the interfacial deposition method (Grillo, dos Santos et al. 2012, Pereira, Grillo et al. 2014). The nanoencapsulated herbicides could control the target species, and the formulation was safe for nontarget species. This formulation also remained stable over time and reduced the mobility of atrazine (Pereira, Grillo et al. 2014). These properties demonstrated the potential of utilising nanotechnology in agriculture.

Considering the environmental benefits of natural polysaccharides such as chitosan, sodium alginate, and starch, they have become more popular due to their nontoxic, biodegradable and biocompatible properties (Campos, de Oliveira et al. 2014). The neonicotinoid pesticide imidacloprid was successfully loaded in alginate-based nanocapsules (Guan, Chi et al. 2008, Kumar, Bhanjana et al. 2014). The ability of different polymers to form amphiphilic block copolymers also facilitated the synthesis of nanocapsules. Amphiphilic copolymers can form nanosized micelles in aqueous solution that entrap pesticides in the interior region of micelles. A diblock copolymer, namely, chitosan−poly(lactide) (chitosan-co-PLA), was used to encapsulate imidacloprid via the formation of nanocapsules (Li, Huang et al. 2011). Similarly, the organophosphate pesticide chlorpyrifos was encapsulated in nanocapsules synthesized using an amphiphilic chitosan copolymer (chitosan-co-PLA-DPPE) (Zhang, Li et al. 2013). In another study, the

readily available copolymer known as poly(lactic-co-glycolic) acid (PLGA), which originates from polylactic acid (PLA) and polyglycolic acid (PGA), was used for the first time as a nanocarrier material in a plant protection system (Zhang, Li et al. 2013).

Amphiphilic triblock copolymers have also received special attention for synthesising polymeric nanocapsules. Memarizadeh et al. (2014) prepared amphiphilic ABA tri-block linear dendritic copolymers composed of poly(citric acid) (PCA) as block A and PEG as block B. They encapsulated the pesticide imidacloprid using the self-assembling ability of the copolymers. The triblock copolymer polyethylene glycol–polybutyleneadipate–polyethylene glycol (PEG–PBA–PEG) also exhibited efficacy in encasing plant extracts in the form of nanocapsules (Esmaeili and Saremnia 2012). The micelles of the block copolymers could also be used as vehicles for pesticide delivery. Generally, direct dissolution and film casting methods are employed to determine the influence of micelle formation, polymer weight and the CMC on the radius of gyration. To date, a number of studies have attempted to encapsulate commercial and biological pesticides into nanomicellar aggregates using PEG-originated amphiphilic block copolymers (Kumar, Shakil et al. 2010, Shakil, Singh et al. 2010, Loha, Shakil et al. 2011, Adak, Kumar et al. 2012, Pankaj, Shakil et al. 2012, Sarkar, Kumar et al. 2012, Kaushik, Shakil et al. 2013). The micellar characteristics depend on the nature of the block copolymers and the structure of the hydrophilic block. The radius of gyration increased when the size of the hydrophilic segment increased.

The copolymer of chitosan was conjugated with polylactide, namely, chitosan-co-(D, L-lactide) or chitosan−PLA. This copolymer was designed to achieve the amphiphilic nature of the polymer so that the micelle structure could be easily formed in aqueous media. The pesticide imidacloprid was encapsulated within the core of the micelle via the nanoprecipitation method (Li, Huang et al. 2011). Feng and Peng (Feng and Peng 2012) prepared another amphiphilic chitosan derivative, namely, 6-O-carboxymethylated chitosan with ricinoleic acid (R-CM-chitosan), to encapsulate biocides such as azadirachtin. The particle size of the encapsulated azadirachtin−(R-CM-chitosan) was reported to be 200–500 nm, with a loading efficiency of up to 56%.

Other polymeric nanocarriers, such as nanospheres and nanogels, could also be utilised as carriers for pesticide delivery. In a nanosphere, the AIs are uniformly distributed within the polymeric matrix (Ezhilarasi, Karthik et al. 2013, Perlatti, de Souza Bergo et al. 2013). The synthesis processes of nanospheres are similar to those of nanocapsule synthesis (e.g. emulsion or interfacial polymerisation). However, nanogels are aqueous dispersions of hydrogel particles formed by physically or chemically crosslinked polymer networks at the nanoscale. Nanogels are formed through the controlled aggregation of interactive polymers due to their self-assembly properties in aqueous media. The polymers are hydrophobically modified to generate self-assembly properties. The nanogels remain swollen due to the presence of an ample amount of water, which facilitates the loading of active compounds spontaneously through electrostatic, van der Waals, and/or hydrophobic interactions between the active compounds and the polymer matrix. In this way, the active compounds are trapped in the polymer matrix while stable nanogel particles are formed.

Employing nanogels as media to deliver pesticides is a very recent phenomenon, and only a few related studies have been published. From the available literature, it was observed that nanogels were synthesised from natural polymers, which is a very good sign of establishing an eco-friendly approach for pest control with the help of nanotechnology. Abreu et al. (2012) synthesised nanogels from a mixture of chitosan and cashew gum to

encapsulate *Lippia sidoides* oil. The essential oil was loaded into the nanogels via the spray–drying method. In another analysis, nanogels were prepared from a mixture of myristic acid and chitosan to encapsulate *Carum copticum* oil (Ziaee, Moharramipour et al. 2014). The oil-loaded nanogels exhibited greater fumigant toxicity than did the free oil over a longer period of time. To increase the sustained release of pheromones for longer periods, nanogels were prepared from a low-molecular-mass gelator (Bhagat, Samanta et al. 2013).

2.1.3.1.2 Lipid-based nanomaterials

In addition to polymeric vehicles, lipid-based nanocarriers could be potential delivery systems for bioactive substances with better encapsulating efficiency and low toxicity (Fathi, Mozafari et al. 2012, Tamjidi, Shahedi et al. 2013). Lipid-based nanocarriers are able to encapsulate both hydrophilic and hydrophobic or lipophilic active ingredients. For instance, nanoliposomes are vesicles consisting of a bilayer lipid with a watery interior at the nanoscale. Colloidal structures are formed by the arrangement of lipids, most commonly phospholipids, in an aqueous solution (Mozafari, Johnson et al. 2008). Generally, a high-energy input is required to form bilayer vesicles; otherwise, they may form flat membrane-like layered structures (Lasic, Joannic et al. 2001). Most often, cholesterols are incorporated into the phospholipid membrane to increase the shape stability of liposomal vesicles by modulating the fluidity of the lipid bilayer. The impregnated cholesterol prevents the crystallisation of the acyl chains of phospholipids and provides steric hindrance to their movement, hence reducing the permeability of the lipid membrane to the solutes. Cholesterol also prevents peroxidation and acyl-ester hydrolysis of the liposome membrane by drying the lipid−water interface (Grit and Crommelin 1993, Samuni, Lipman et al. 2000). In the absence of stabilising agents, the structures of liposomes or nanoliposomes are not stable due to their geometrical constraints. To date, various methods have been investigated for stabilising nanosized liposomes to prolong their shelf life. These include lyophilisation/freeze-drying, spray-drying and supercritical fluid (SCF) technology, where lyophilisation has been proven to be the best method for stabilization (Lo, Tsai et al. 2004, Sankar Kadimi, Balasubramanian et al. 2007, Mishima 2008, Stark, Pabst et al. 2010). Phase transition can be avoided by adding lyoprotectants (Chen, Han et al. 2010). Sugars such as monosaccharides, disaccharides, polysaccharides, or even synthetic saccharides can be used as lyoprotectants; however, among the disaccharides, trehalose has been proven to be the most effective (Kawai and Suzuki 2007).

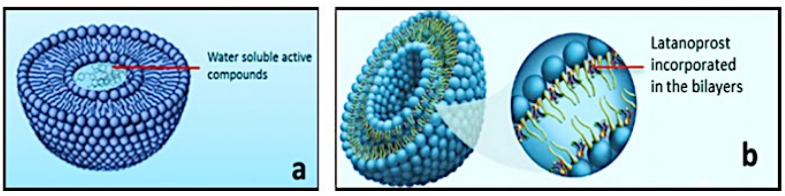


Figure 10. Schematic representation of (a) water-soluble active compounds at the inner core of liposomes and (b) liposomes with the drug latanoprost incorporated into the lipid bilayer. Adapted from (Natarajan, Darwitan et al. 2014).

Along with other applications, nanoliposomes are considered to be very efficient at encapsulating and delivering bioactive substances to targets of biological, biochemical,

pharmacological, and agricultural interest (Taylor, Weiss et al. 2005). In terms of pesticide loading, nanoliposomes are flexible in nature and able to encapsulate hydrophilic (or water-soluble) molecules during vesicle formation trapping in combination with aqueous media in the inner core of vesicles, and hydrophobic or lipophilic molecules are incorporated into liposomal bilayers. Notably, due to the lipophilic characteristics of nanoliposomes, they are potential carriers of contact insecticides and allow bioactive compounds to be absorbed through the cuticle of the insect body. They also regularly facilitate the dispersion of hydrophobic AIs in aqueous solutions. Thus, both water-soluble and water-insoluble active ingredients can be delivered simultaneously. This approach may facilitate the application of multi-pesticide application (both contact and systemic), which can combat a wide range of agricultural pests.

However, the high cost, low payload, and comparatively faster release of active ingredients are the disadvantages of this carrier material (Tamjidi, Shahedi et al. 2013). To delay release, coatings with polymers and various parameters during synthesis can significantly affect the size, surface charge, dispersibility and even encapsulation efficacy. For instance, Bang et al. (2009) utilised lecithin (phosphatidylcholine) and cholesterol for the synthesis of nanosized liposomes to encapsulate the pesticide etofenprox. The size of the prepared liposomes was reduced (up to 150 nm) by increasing the ratio of lecithin and extending the homogenisation time (2−6 min). The surface charge was positive (10.3 mV), whereas the low-molecular-weight chitosan (0.1%, w/v)-coated nanoliposomes had a lower absolute zeta potential than the high-molecular-weight chitosan (0.1%, w/v)-coated nanoliposomes. The surface charge changed from positive to negative due to secondary coating with alginic acid (−21.8 mV). The size also changed remarkably in the ± 30 nm range after secondary coating with alginic acid (0.1, 0.3, and 0.5%, w/v). However, their pesticide encapsulation efficacy decreased slightly with increasing concentrations of chitosan (0.1−0.5%, w/v) (Bang, Yu et al. 2009). In another study, Hwang et al. (2011) reported that the nanoliposome size varied with the ratio and molecular weight of the coating material (chitosan). Recently, other vesicles, namely, niosomes, were introduced that have similar structures to liposomes but are able to avoid limitations related to the stability and complexity of liposomes. Niosomes are vesicles consisting of a bilayer of nonionic surfactant and cholesterol with a watery interior. Alkyl or dialkyl polyglycerol ether-based non-ionic surfactants are commonly used and could be prospective alternatives to nanoliposomes for pesticide delivery.

In addition to lipid-based vesicles, nonporous solid lipid nanomatrices or nanoparticles (SLNs) have been reported to be superior carrier materials to other nanocarrier materials, such as polymeric nanoparticles, liposomes/nanoliposomes, nanoemulsions, and nanosuspensions, in colloidal systems (Müller, Mäder et al. 2000, Mehnert and Mäder 2001, Müller, Radtke et al. 2002, Saupe and Rades 2006). It has been reported that SLNs can retain the beneficial properties of other colloidal carriers and have no disadvantages in terms of physical or chemical storage stability, toxicity, loading capacity, production scale, target-oriented release properties, feasibility, etc. (Mehnert and Mäder 2001). Thus, SLNs are considered to be promising colloidal carrier materials in controlled-delivery systems. The SLNs may be either semicrystalline or crystalline, solid lipid spherical nanostructure substances, which are stabilised by surfactants. However, the main requirements of SLNs synthesis are lipids that are solid at room and physiological temperatures, surfactant(s)/emulsifier(s) and water. The lipids included triglycerides, partial glycerides, fatty acids, steroids and waxes. The choice of emulsifiers or surfactants needed to stabilise aqueous lipid dispersion depends on the type of lipid utilised for the synthesis of SLNs. Various emulsifiers that differ in terms of charge and molecular weight

can be used, but phospholipids may be one of the best choices (e.g. soybean lecithin or egg lecithin). Various methods, such as high-pressure homogenization microemulsion and nanoprecipitation, have been developed for the synthesis of SLNs. High-pressure homogenisation is the most commonly used technique for large-scale production where this process involves either hot homogenisation or cold homogenisation.

Achieving physical stability in colloidal suspensions of SLNs requires a specific surface charge as well as storage at low temperatures (Helgason, Awad et al. 2009). The aggregation of charged nanoparticles is prevented due to electric repulsion. A zeta potential > 8−9 mV is required for proper stabilisation of the material. However, the application of SLNs in pesticide delivery has not been well managed and is still in its infancy. Only a few studies were found in which the pesticidal active ingredients were successfully loaded into the SLNs. For example, Lai et al. (2006) prepared SLN-based pesticide formulations by applying the high-pressure homogenization technique. The essential oils of the ecological pesticide *Artemisia arborescens* L. were loaded into lipids as Compritol 888 ATO and stabilised by surfactants such as Poloxamer 188 or Miranol Ultra C32.

2.1.3.2 Inorganic nanoporous materials

The synthesis of inorganic porous nanomaterials with interesting hierarchical morphologies and their utilisation have attracted much attention for enhancing the sustainability of nano-delivered pesticide systems. Along with biodegradable polymer- and lipid-based nanocarriers, various inorganic nanomaterials have also been developed as nontoxic, biocompatible and stable alternatives and have been used for controlled-release applications. Additionally, various inorganic nanoparticles have also exhibited potential as AIs for controlling a wide range of agricultural and stored grain pests. However, the available literature reveals that of the various inorganic nano/macron-sized materials, nanoporous materials are highly significant for the preparation of CRFs for pesticides. To date, various nanoporous materials have been synthesised; however, in terms of pesticide delivery, silica-based porous nanomaterials and calcium carbonate nanospheres have been found to be promising inorganic nanoporous carriers. These nanomaterials also have beneficial effects on agricultural applications, providing support to plants against abiotic stress and soil amendments.

2.1.3.2.1 Silica-based porous nanomaterials

The synthesis of different porous silica materials has advanced rapidly for active ingredient delivery due to their controllable morphologies, mesostructures and porosities, high level of biocompatibility, and ease of functionalisation (Popat, Liu et al. 2012). Depending on their surface structure and interior design, porous silica nanoparticles are grouped as mesoporous silica nanoparticles (MSNs) or porous hollow silica nanoparticles (PHSNs or HSNs). The pesticides are encapsulated by MSNs or HSNs without forming any noncovalent bonds between the active compounds and silica (SiO_2) nanoparticles. This process involves either the adsorption of active compounds within the mesopores of silica nanoparticles or entrapment within capillary pores. To deliver the pesticide as part of this process, the synthesis of porous silica is first needed. Both MSNs and HSNs have exhibited potential as carriers for pesticide delivery. Nonetheless, the efficacy of these materials varies according to their structural properties, such as pore size, particle size, morphology, and porous structure. Generally, the sol-gel process is most commonly used for the synthesis of silica nanoparticles. In the case of MSNs, amphiphilic surfactants play a vital role in providing basic structures. In contrast, for HSN synthesis, a template is needed which is mainly responsible for the hollow space.

The synthesis of silica-based porous materials began with the successful production of mesoporous silica nanoparticles (MSNs), known as 'MCM-41'. Over the last two decades, the synthesis of various types of MSNs has fortified the use of MSNs as a vehicle for pesticide delivery. The morphology, structural arrangement, pore size and channel structure of the MSNs, such as MCM-41, MCM-48, IBN-1, SBA-1, SBA-3, SBA-15, SBA-16, FDU-12, and HMS, differ. The properties of the different MSNs are summarised in Table 2. The porous structures of the various MSNs are presented in Figure 7. Thus, it is apparent that the pesticide-loading capacities of the MSNs will significantly differ from each other (Table 5).

Table 5. Pore size and structure of MSNs.

Mesoporous silica	**Space group**	**Pore diameter (nm)**	**Channel structure**
MCM-41	P6 mm	2-50	Hexagonal 1D/2D
MCM-48	Ia3d	2-5	Bicontinuous/cubic 3D
IBN-1		2	Cubic 3D
SBA-1	Pm3n	2-4	Cubic 3D
SBA-3	P6 mm	2-4	Hexagonal 2D
SBA-15	P6 mm	5-10	Hexagonal 1D/2D
SBA-16	Im3m	Min 1-6; max. 4-9	Body centred arrangement of cages
FDU-12	Fm3m	Min 4-9; max 10-12	Face centered cubic arrangement of cages
HMS	P6 mm	2-5	Hexagonal

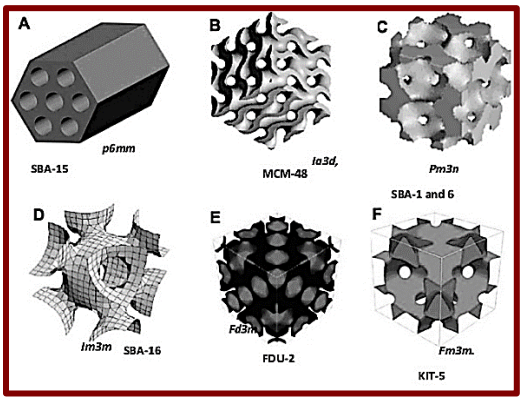


Figure 11. Structures of several ordered mesoporous silica materials.

Table 6. Pesticide loading efficacy of different MSNs.

Mesoporous silica	Target pesticide	Particle size (nm)	Surface area (m^2g^{-1})	Pore diameter (nm)	Pore volume (cm^3g^{-1})	Loading method	Loading/adsorption capacity (mg g^{-1})	Reference
MCM-41		150	1020.00	2.40	1.03	Adsorption		
MCM-41 (Imi)	Imidacloprid		754.00	2.00	0.50	(Diffusion)	3	
MCM-48		120	1250.00	2.00	1.35			(Popat, Liu et al. 2012)
MCM-48 (Imi)	Imidacloprid		650.00	1.80	0.50		16	
SBA-15		200 (dia)	505.00	6.50	0.84			
SBA-15 (Imi)	Imidacloprid		415.00	5.10	0.75		4	
IBN-1		100	919.00	11.00	0.86			
IBN-1 (Imi)	Imidacloprid		700.00	10.20	0.70		7	
MSN		~160	810.00	3.20	0.67	Solvent		
RMSN	Metalaxyl	~162	766.00	2.90	0.58	Evaporation	14%	(Wanyika 2013)
MSNs		288	1138.73	3.73	1.28			
Py@MSNs	Pyraclostrobin	--	543.45	3.48	0.59		26.7%	(Zhao, Cao et al. 2018)
Py@MSNs-HTCC	Pyraclostrobin	299	29.02	59.79	0.22		28.5-41.6%	
Py@MSNs-HTCC (calcined)	-		960.17	3.88	1.14			
MSNs	--	200-300	808.90					
Py-MSNs	Pyrimethanil		9.47			Simple immersion	29.77% (toluene)	(Zhao, Cao et al. 2017)
P-MSN	--		1356.00	3.75	1.65		1.5%	
MSN-TA			956.40	2.31	0.59			(Cao, Zhou et al. 2017)
2,4-D@MSN-TA	2,4-D		454.80	--	0.03		21.7%	

TA-Trimethyl ammonium

The structural differences in MSNs also have significant effects on the release behaviour of pesticides. For instance, Popat et al. (2012) reported that 40% of imidacloprid was released from all the experimental MSNs into water within a few hours, but MCM-41 and SBA-15 exhibited a slightly slower release pattern due to their 2D channel structure compared to MCM-48 and IBN-1, which were structured with 3D channels. The initial burst release was observed due to diffusion of imidacloprid from hydrophilic mesopores and dissolution of silica in the medium (water). In their study, Wanyika (2013) reported that 76% of free metalaxyl was released into soil, whereas only 11.5% of the metalaxyl was released from MSNs into soil after 30 days. The release of metalaxyl from MSNs in water was faster than that in soil, and approximately 47% of the metalaxyl was released within 30 days. Adsorption–desorption isotherms showed hysteresis (H = 3.059). The release rate of AIs from MSNs can also increase with surface modification. It was observed that less than 40% of the free pyraclostrobin was released into a 30% aqueous methanol solution containing 0.5% Tween 80 emulsifier after 10 h. In contrast, 55% of the pyraclostrobin was released from bare MSNs, whereas 72% of the pyraclostrobin was released from chitosan-caped MSNs within 2 h. This release was due to changes in the crystalline structure of pyraclostrobin, whereas chitosan was adsorbed on water that also made the AIs ready to release (Zhao, Cao et al. 2018). The conditions of the release medium, such as pH, temperature and ionic strength, can also affect the release rate. It was observed that 56% pyrimethanil was released into phosphate buffer solution at pH 6.13, 6.93 and 8.06 after 30 h. After 30 h, the release of pyrimethanil was faster at low pH (6.13), and approximately 99% pyrimethanil was released after 60 h. In contrast, 93% and 91% pyrimethanil were released at pH 6.93 and 8.06, respectively, after 80 h (Zhao, Cao et al. 2017). Similarly, the pH of the release medium significantly affects the release of 2,4-D from trimethyl ammonium-modified MSNs (MSN-TAs). Sixteen percent of the pesticide was released into the water at pH 3.0 within the first 2 h, while 43% of the pesticide was released at pH 10.0. The ionic strength of the release medium enhanced the release rate of 2,4-D. At approximately neutral pH, 40% of the pesticide was released from 2,4-D@MSN-TA, while at 0.1 M NaCl, 90% of the pesticide was released over 5 h. A temperature-dependent release of 2,4-D was also observed from 2,4-D@MSN-TA. Overall, 96%, 75% and 52% of the pesticide was released at 40, 30 and 20 °C, respectively, after 900 min (Cao, Zhou et al. 2017).

HSNs act as carrier materials for both oil-soluble and water-soluble pesticides, and their loading efficiency depends on their morphological features. Both oil-soluble and water-soluble pesticides, namely, avermectin and validamycin, were loaded in HSNs (Wen, Li et al. 2005, Liu, Wen et al. 2006). However, pesticide-loading efficacy is often controlled by pore size which can be increased by improving the loading methods. For instance, the pesticide avermectin was loaded into HSNs employing the simple immersion method, and the amount of pesticide loading reached 58.3% (w/w) (Wen, Li et al. 2005). Pesticide loading by simple immersion takes longer to reach adsorption saturation; for example, for avermectin, this process took 2 weeks due to the tiny nanosized pores (approximately 5 nm) in the shell of the silica nanoparticles. The open-pore network and hollow interior of PHSNs are expected to facilitate the transport of vapours and gases through the entire volume of the material, and pressure can be an important variable that enhances adsorption (Domingo, García-Carmona et al. 2002). On the basis of this mechanism, Liu et al. (2006) loaded the pesticide validamycin using the supercritical fluid drug loading (SFDL) process. This process improved the loading capacity and decreased the adsorption saturation period compared to those of the simple immersion method. At a

weight ratio of validamycin to PHSNs of 2:1, ~ 36 wt.% of validamycin was loaded within 9 h via SFDL, whereas 14 days were required to load only 25% wt with the simple immersing method.

The pesticidal active compounds can also be encapsulated by porous silica nanoparticles during the synthesis of HSNs. Different soft templates, including emulsion droplets, are utilised to decorate porous silica with a hollow structure. Generally, pesticides are dissolved in the water or oil phase during synthesis and then directly encapsulated into the hollow interior during synthesis. Qian et al. (2013) encapsulated tebuconazole (fungicide) into porous hollow silica nanospheres during synthesis through the formation of a mini-emulsion, where the emulsion droplets functioned as a soft template for the synthesis of HSNs. Furthermore, surface functionalisation of HSNs can be an effective tool for improving adsorption capacity, where the active compounds are absorbed by the surface of silica nanoparticles (Sasidharan, Zenibana et al. 2013). However, in the presynthesis-loading process, the release of AIs is controlled by the shell thickness of the HSNs, whereas the release is controlled by the pore diameter while pesticides are loaded into the HSNs after synthesis (Wibowo, Zhao et al. 2014).

2.1.3.2.2 Porous calcium carbonate nanospheres

Calcium carbonate ($CaCO_3$) is considered one of the most abundant inorganic biominerals. The utilisation of these nanomaterials as carriers for biomolecule delivery is attracting increasing attention because they are inexpensive, environmentally friendly and highly stable. Its application in drug delivery to humans further ensures its biocompatibility (Maleki Dizaj, Barzegar-Jalali et al. 2015). The application of nano-$CaCO_3$ is not limited to drug delivery. Moreover, the porous structure of these nanomaterials has been used as a potential nanocarrier for pesticide delivery, where the pesticide can be loaded easily via electrostatic interactions as well as hydrogen bonding interactions (Qian, Shi et al. 2011, Qian, Shi et al. 2013, Xiang, Han et al. 2018). Hua et al. (2015) reported that $CaCO_3$ nanoparticles not only provide nutrients to plants but also enhance their pest tolerance.

2.1.3.3 Natural Nanoporous Materials

In search of nanoporous materials as carriers for pesticide delivery those are crucial for the development of new, targeted and low residual delivery systems. Some nature-based porous mineral materials are considered ready to use due to their worldwide natural deposition, low cost, availability and biocompatibility.

2.1.3.3.1 Nanoclays

The application of clay materials has a long pedigree record even before their structure was determined and understood. The use of clays as carriers for pesticide delivery is considered one of the most suitable environmentally benign approaches due to their natural sources. It is expected that clays will not add additional threats to the environment. The physicochemical properties of clays, such as biocompatibility, thermal stability, natural abundance, low cost, and other environmentally friendly characteristics, have made them excellent candidates for carriers of pesticides.

Nanoclays are a wide group of minerals that are commonly described as aluminium silicates or hydrous silicates with sheet-like structures. Sheet-structured hydrous silicates are generally termed phyllosilicates and are very important because they build the structures of individual clay minerals (Majeed, Jawaid et al. 2013). The phyllosilicates constituted a layered structure of two types of sheets, specifically tetrahedral silicate and octahedral alumina. The diversity of clay minerals depends on the arrangement of these

sheets in the layer, which include a 1:1 type of clay (e.g. kaolinite), 2:1 type of clay (e.g. montmorillonite), and 2:1:1 type of clay (e.g. chlorite).

The thickness of the layers of primary clay particles is in the nanometre range; consequently, clay and clay minerals may be regarded as nanomaterials of geological and pedological origins, although their length varies in the millimetre range (Yuan and Wu 2007). For instance, the thickness of the elementary layers of smectites can vary from 0.96 to 1.50 nm but can vary from a few tenths to hundreds of nanometres in length and width (Schoonheydt 2002). However, the thickness of the elementary layers varies from clay to clay minerals. The clay layers are attracted by each other and may join together in a clay crystallite due to van der Waals forces, interlayer cations, electrostatic forces or hydrogen bonding (Uddin 2008), leaving an interlayer space known as the gallery (Figure 8). The active compounds are mainly encapsulated in this interlayer space or gallery. The penetration of active compounds into the interlayer space is also denoted as intercalation (Khajeh, Laurent et al. 2013).

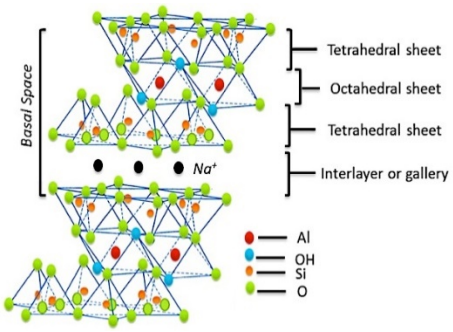


Figure 12. Structure of sodium montmorillonite (2:1 type) of clay minerals. Adapted from (Nuruzzaman, Rahman et al. 2016).

Clay or organoclay minerals can be modified with polymers to form polymer−clay nanocomposites. Depending on the state of the layered silicate material, polymer−clay nanocomposites can be formed as conventional nanocomposites, intercalated nanocomposites, or exfoliated nanocomposites. The formation of polymer−clay nanocomposites is influenced by their preparation methods. Chen et al. (2008) reported that exfoliated nanocomposites are synthesised mainly via in situ polymerisation and solution methods, whereas it is easier to synthesise intercalated nanocomposites via melt processing. For instance, a molten low-polarity polymer such as polystyrene can be directly intercalated into alkyl-ammonium-modified smectites (Vaia, Ishii et al. 1993). The coexistence of exfoliated and intercalated nanocomposites can also be observed. Other methods for polymer–clay nanocomposite formation include covulcanisation, solid-state intercalation, sol-gel, emulsion, and supercritical CO_2 fluid methods (Chen, Evans et al. 2008). When the polymers originate from a natural source such as starch, cellulose, or their derivatives, such as chitosan or gelatine, the composites are termed bionanocomposites. Biopolymers are considered to be eco-friendly polymers and can be used as alternatives to conventional polymers for environmental application. They are able to synthesise nanocomposites similarly to conventional polymers. For example, Chevillard et al. (2012) prepared new pesticide formulations by combining ethofumesate (a model pesticide) and polymer−clay nanocomposites via the bivis extrusion process. The nanocomposites were designed with wheat gluten and three montmorillonites (MMT), that

is, unmodified MMT (HPS) and two surfactant-modified MMTs (C30B and D72T). In their investigation, well-dispersed nanoclays were observed, which indicated that wheat gluten was able to interact with modified and unmodified MMT, and a well-intercalated−exfoliated nanocomposite structure was formed.

The hydrophilicity of the clay mineral surface can be achieved through the hydration of exchangeable cations and the presence of Si−OH clay mineral groups. When water is absent, clay minerals have a greater affinity for hydrophobic compounds (Patel, Somani et al. 2006). The hydrophilic surface of clay minerals can become hydrophobic during the modification of clay minerals as 'pillared clay with a suitable pillaring agent. Both inorganic and organic compounds can be used as pillars. Pillared clays can be prepared according to a simple procedure of replacing exchangeable cations (Ca^{2+} or Na^{+}) in the interlayer space with large polyoxocations of multivalent metals, such as Al, Si, Cr, or Zr, in which hydroxy-oxide pillars separate the platelets from each other. In this way, pillared clays possess a porous structure with a high surface area (Gerstl, Nasser et al. 1998). In their analysis, Gerstl et al. (1998) prepared pillared clay by modifying sodium-montmorillonite with $Al(OH)_{x,}$ and the herbicide alachlor was successfully loaded into the interlayer of pillared clays. Clay materials can also be modified with heat treatment or acid treatment. In their analysis, Bojemueller et al. (2001) investigated the morphology of thermally modified bentonite and its interaction with pesticides. They found that the mesopore (diameter = 2−50 nm) volume of calcinated bentonite increased above 450 °C, whereas the micropore volume decreased. Pesticide molecules interact with aluminium ions or oligomeric hydroxoaluminum cations, which are enriched at the edges of silicates due to heat treatment.

2.1.3.3.2 Layered double hydroxides

The utilisation of layer double hydroxides (LDHs) has attracted much attention for the preparation of controlled/slow-release pesticide formulations due to their high buffering capacity, high water-retention ability, acid-neutralising potential, and high affinity for ubiquitous carbonate ions which may facilitate the preparation of complete and controlled release pesticide formulations through the intercalation of pesticide molecules. Generally, LDHs are anionic lamellar compounds made up of positively charged brucite ($Mg(OH)_2$)-type layers of mixed metal hydroxides (Figure 9). The brucite layer mainly consists of shared octahedra of hexacoordinated Mg^{2+} cations with hydroxide groups; thus, these octahedra play a key role in the formation of infinite 2-dimensional nanosheets. The thickness of the nanosheets is approximately 1 nm, and the lateral size ranges from sub-micrometre to several tens of micrometres. In the octahedron, the hydroxide ions remain at the vertex positions, whereas the metal cations occupy the central position. However, LDHs are produced due to partial isomorphic substitution of Mg^{2+} ions by a trivalent cation with a similar ionic radius, such as Al^{3+}. The positive charge in LDHs is also generated by this substitution. To compensate for the positive layer charge, the anions occupy the interlayer positions. The generic formula of LDHs has been described in the literature as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$, where M^{2+} and M^{3+} denote as divalent and trivalent metal cations, respectively; M^{2+}= Mg^{2+}, Zn^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+} or $Ni^{2+;}$ M^{3+}= Al^{3+}, Ga^{3+}, Fe^{3+}, or Mn^{3+}; and A^{n-} is the non-framework charge compensating for inorganic or organic anions. The most common anions present in the interlayer are CO_3^{2-}, NO_3^{-}, Cl^{-}, and SO_4^{2-}, or they can be replaced by RCO^{2-} in combination with water in a hydrated form; moreover, x is the mole fraction of M^{3+} and normally ranges between 0.2 and 0.4. For instance, hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$), a naturally occurring layered mineral, is the true representative of the carbonate phase of MgAl-LDH, where the M^{2+}:M^{3+} ratio is 3:1. Thus, the cationic ratio of divalent to trivalent metals significantly affects the charge density of LDHs.

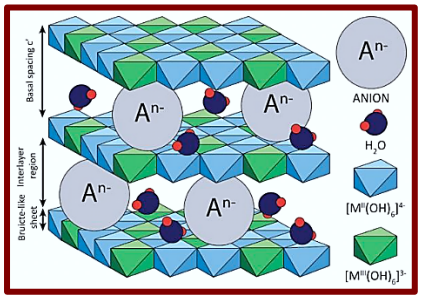


Figure 13. Schematic representation of the LDH (hydrotalcite) structure. Adapted and modified from (Dębek, Motak et al. 2017).

Thus, LDHs are good carriers for anionic pesticides. In their investigation, Cardoso et al. (2006) intercalated the anionic herbicides 2,4-D, MCPA, and picloram into MgAl-LDH, where LDHs were found to be effective at encapsulating natural bioactive compounds. Park et al. (2010) evaluated the potential of LDHs as an encapsulated material for the natural antibiotic cinnamate, which also serves as a fungicide. Cinnamate was intercalated using the coprecipitation method, where the intercalation amount was 42 wt.%.

2.1.3.3.3 Clay nanotubes

In addition to layered structured clays and LDHs, hollow tubular structured clays such as halloysite clay have added new dimensions to utilise natural clays as carriers for pesticide delivery. Halloysite nanoclays are considered natural wonders and true representatives of nature-based nanomaterials not only because of their nanosize diameter but also because of their nanosized lumen structure. The halloysite is mainly an aluminosilicate clay mineral with an external diameter of ~50 nm and an inner diameter of ~10–15 nm but varies in length from 500 nm to 1000 nm (Lvov, Shchukin et al. 2008). Due to their nanosized tubular structure, halloysite clay is known as halloysite nanotube (HNT) (Yuan, Tan et al. 2015). It has a similar structure to kaolinite but possesses a significant difference in the presence of an additional water monolayer between adjacent clay layers. The chemical formula of halloysite nanotubes is $Al_2SiO_5(OH)_4.nH2O$, where 'n' indicates the presence or absence of water. The space between the inner and outer layers of aluminium hydroxide is 10 Å in the hydrated form (n=2) and 7 Å in the anhydrous form (n=0) (Joussein, Petit et al. 2005). The external surface of HNTs consists of mainly siloxane groups (Si−O−Si), whereas the inner lumen is structured with aluminol groups (Al−OH). Al-OH and Si-OH can also be found at the edges and at the defects of the aluminosilicate layers. Normally, pure halloysite is white in colour, but those obtained from natural deposits vary from yellowish to brown and some greenish in colour due to the presence of different impurities. The size, diameter, pore size, surface area and morphology also vary among their natural sources. In some natural deposits, platy and spheroidal structured halloysite has also been found. However, hollow tubular-structured halloysite nanoclays are the most attractive form of nanoclay used in current research because of their large surface area, low density, mechanical and thermal stability, and surface permeability (Caruso 2001).

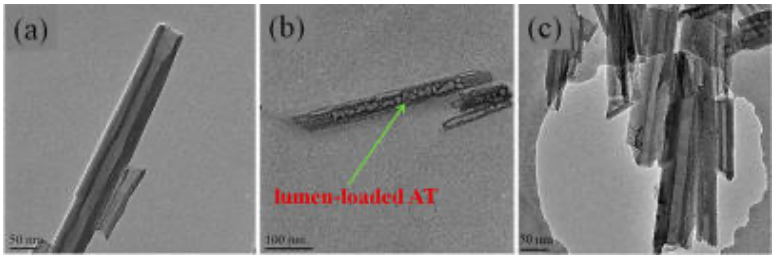


Figure 14. TEM images of (a) pristine HNTs, (b) HNTs-AT before the deloading of AT and (c) HNTs-AT after the deloading of AT (Zhong, Wang et al. 2017).

To date, the application of HNTs as carrier materials has been investigated for the delivery of a wide range of chemicals and bioactive agents (Lvov, Wang et al. 2016). Recently, the application of HNTs as carriers for pesticide delivery was also reported in the literature (Tan, Yuan et al. 2015, Scarfato, Avallone et al. 2016, Zhong, Wang et al. 2017). In a comparison study, HNT showed better loading efficiency for the herbicide amitrol than for kaolinite. The loading capacity of HNTs was also enhanced by surface modification with methoxy groups due to expansion of the coiled interlayer space. However, the herbicide release was much slower for surface-modified kaolinite than for HNT because of the lower amount of intercalated herbicide in HNT than in kaolinite (Tan, Yuan et al. 2015). Additionally, in comparison with other tubular nanomaterials, such as carbon nanotubes, HNTs are also considerably cheaper and have potential for use in multiple applications (Lvov, Shchukin et al. 2008).

Similarly, other tubular-structured clay nanomaterials, such as imogolite nanotubes (INTs), chrysotile nanotubes and antigorite nanotubes, could be used as carriers for pesticide delivery. However, the lumen diameter of imogolite nanotubes is approximately 1–5 nm; thus, these nanotubes are suitable only for smaller pesticide molecules, whereas the environmental application of chrysotile nanotubes and antigorite nanotubes is controversial.

2.1.3.3.4 Zeolites

Natural zeolites are considered as one of the bestowed materials of nature. Naturally, zeolites are formed in the areas of volcanic rocks and ash layers and react with alkaline ground water. With respect to their widespread applications, researchers and mineralogists have referred to these rocks as ‘the magic rock’ (Mumpton 1999). To date, massive applications of these materials have been observed in chemical, biotechnology, environmental pollution control, and pesticide and medical industries because of their attractive physical and chemical properties, especially high cation exchange capacity, hydration-rehydration features and catalytic activities (Mumpton 1999). In agriculture, zeolites are used as soil enhancers, soil conditioners, livestock feed additives, pesticide active ingredients, hydroponic growing media and so on (Adamović, Stojanović et al. 2011, Eroglu, Emekci et al. 2017). They are also used for fertiliser management, mycotoxin control and environmental pollution control (Adamović, Stojanović et al. 2011). Zeolites are similar to other clay minerals and are structured with tectosilicate aluminosilicates instead of phyllosilicates. In terms of plant protection, zeolite itself has exhibited pest control efficacy against a wide range of agricultural pests, including fungi and various insect pests (Rumbos, Sakka et al. 2016, Lü, Sehgal et al. 2017).

The zeolite structure may be represented by the formula $M_{x/n}[(AlO_2)_x.(SiO_2)_y].wH_2O$, where M is an alkali or alkaline-earth cation (Na^+, K^+, Li^+ and/or Ca^{2+}, Mg^{2+}, Ba, Sr), n is the cation charge, w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and the ratio y/x usually has values ranging from 1 to ∞ (Smedt, Someus et al. 2015). According to Valtchev and Tosheva (2013):

> Zeolite is a crystalline aluminosilicate built of oxygen-linked tetrahedral silicon and aluminum atoms that form a 3-dimensional microporous structure comprising channels and voids occupied by alkali or alkali-earth cations and water molecules.

According to this definition, the basic building units (BBUs) or primary building units (PBUs) of zeolite are considered to consist of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, commonly denoted as TO_4 (T is mainly tetrahedrally coordinated Si or Al) (Smedt, Someus et al. 2015). Thus, the framework of zeolite is built by interlinked tetrahedra. In this case, each tetrahedron is connected with 4 neighbours by sharing the vertex O atoms, forming the 3-dimensional framework. The zeolite framework is complex because of the wide arrangement abilities of BBUs, which can lead to the formation of chains or layer-like structures known as secondary building units (SBUs). A more complex building unit termed the composite building unit (CBU) is further structured with different combinations of BBUs that usually reflect the characteristics of the zeolite framework. Every zeolite is generally classified based on the CBU type. The structural commission of international zeolite association (IZA-SC) has assigned a three lowercase letter to each of these CBUs. CBUs are interconnected with each other, leaving cages and cavities/supercages (Figure 15) in the zeolite framework, which is the most important phenomenon of zeolite in relation to pesticide delivery and accommodates guest molecules (i.e. pesticide AIs).

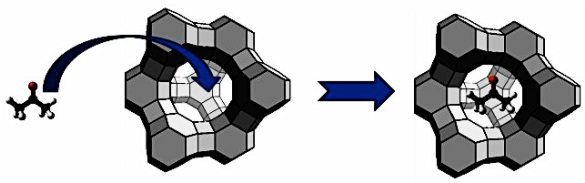


Figure 15. Adsorption of an acetone molecule into a zeolite Y supercage (window 7.4 Å, cage 13.2 Å). Adapted from (Zheng, Li et al. 2012).

The application of zeolites as carriers for pesticide delivery is promising due to their porous structure, but limited work has been conducted in the literature (Zhang, Kim et al. 2006). The available literature also reports that most often, the pore size (< 2 nm) of zeolite is too small to penetrate large pesticide molecules when the AIs are larger than 20 °A. Zhang et al. (2006) prepared controlled-release formulations of paraquat by loading them into surface-modified zeolite Y (carbide, LZY-52). Paraquat was loaded onto zeolite via adsorption following an ion exchange process. It was assumed that paraquat (13.4 X 6.4 X 3.4 °A) would easily ion exchange with zeolite Y through its supercages (13°A diameter) only (Zhang, Kim et al. 2006). Despite pore size limitations, the physicochemical properties of zeolite mentioned earlier make it an excellent adsorbent for removing pesticides from aqueous solution, and related research has been maximised in this area. Surface modification with polymers, surfactants or different silylation agents was found to be a promising approach for enhancing the sorption capacity. Surface modifications or functionalization also delay the release of AIs from pesticide-adsorbed zeolite by creating

a film barrier. In this case, the pesticides are released via diffusion via two steps: first, intrazeolitic diffusion of ions within the zeolite framework and second, diffusion out of the surface-modified zeolite framework (Zhang, Kim et al. 2006). However, layered-structured montmorillonite clay showed a higher 2,4-D sorption capacity than zeolite (clinoptilolite and zeolite Y), whereas zeolite Y exhibited a higher sorption capacity than clinoptilolite (Bhardwaj, Sharma et al. 2014). Thus, it could be assumed that structural differences in zeolites, including pore size, are influential factors on their sorption capacity.

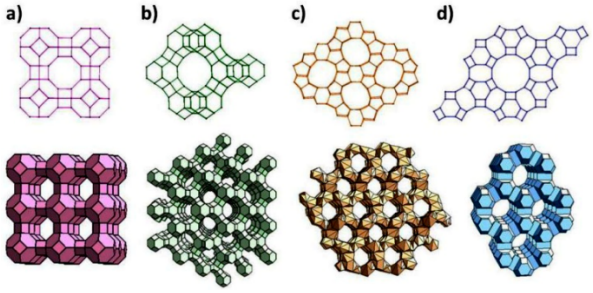


Figure 16. Representative zeolite frameworks (with sodalite pore openings). (a) Zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D, 5.3 × 5.6 Å, 5.1 × 5.5 Å) D—dimensions of the channel system. Adapted from (Zheng, Li et al. 2012).

Owing to the potential application of zeolites, their synthesis has received much attention. To date, 235 zeolite frameworks have been described by IZA-SC, including more than 40 natural zeolites (http://www.iza-structure.org/databases/). The different zeolite frameworks are presented in Figure 16. The synthesis of micromesoporous zeolites, micromacroporous structured zeolites and micromeso-macroporous structured zeolites is a promising aspect of recent studies for enhancing the mass transport properties of zeolites (Chen, Li et al. 2012). For example, Ramos et al. (2017) reported the synthesis of mesoporous zeolites (pore diameter >50 nm) while evaluating their potential as carriers for the insect pheromone rhychophorol. The synthesis of nanocrystalline zeolites is also supposed to be an effective approach for accessing nanoscale materials (Mintova, Jaber et al. 2015). For instance, a nanocrystalline zeolite with a crystal size of 50 nm has an external surface area > 100 $m^2\ g^{-1,}$ whereas a 500 nm zeolite crystal has an external surface area less than 10 $m^2\ g^{-1}$. Various green synthesis routes of zeolite have enhanced its possible ecofriendly application (Lehman and Larsen 2014, Meng and Xiao 2014).

2.1.4.1 Other Nanoporous Materials

Some other nanoporous materials that could be promising for controlled release pesticide delivery include the following:

- Carbon nanotubes
- Carbon nanosphere
- Dendrimers
- Porous calcium carbonate nanoparticles
- Polymerosomes
- Nanostructured lipids

2.1.4 Gaps in Current Knowledge

Various nanoporous materials for the development of pesticide delivery have been reviewed. These materials possess various properties, advantages and disadvantages for achieving targeted delivery. The following criteria for selecting precursor materials for this project were considered: nanoporous, biocompatible, economical and ecofriendly.

Among the various nanoporous carrier materials for pesticide delivery, inorganic porous nanomaterials with interesting hierarchical morphologies have attracted much attention for enhancing the sustainability of nano-delivered pesticide systems. Inorganic nanoporous materials can offer nontoxic, biocompatible and stable alternatives for controlled-release applications. Based on the selection criteria, naturally available clay-based nanoporous materials were selected for this project. Moreover, structural variation could also affect the performance of pesticide formulations. Thus, in this project, hollow tubular-structured halloysite nanoclays and platy-structured montmorillonite nanoclays were selected as potential carriers, halloysite clay nanotubes and montmorillonite nanoclays.

METHODOLOGY

3.1 MATERIALS AND REAGENTS

In this project, pristine HNTs were purchased from Sigma and sourced from SA and New Zealand Mineral Co. for the preparation of carrier materials. Chemicals, including acid, imidacloprid standards, solvent and liquid chromatography-mass spectrometry (LC-MS) grade water, were purchased from Sigma and Thermo Fisher Scientific. The materials and chemicals used were sourced directly without further treatment for the experiments mentioned below.

Imidacloprid is the main active ingredient used for the development of carrier materials. This was largely supported by the farmers' group, where they identified imidacloprid issues for agricultural practices. The imidacloprid used for loading experiments were technical grade at 97% purity. The imidacloprid used for analysis is analytical standard. The commercial slow-release pesticide contains 50 g/kg imidacloprid as active ingredients.

3.2 MATERIAL SYNTHESIS

Modification methods were performed for the raw clay minerals, including acid treatment and organic modification, followed by preparation of polymer beads that incorporated the clay minerals.

3.3.1 Acid treatment

In this project, pristine HNTs were purchased from Sigma Aldrich, Australia. To enlarge the lumen structure, HNTs were etched with acid by a dealumination process. The dealumination process was performed by etching the HNTs with sulfuric acid as per methodology described in the literature (Abdullayev, Joshi et al. 2012). The dealumination process occurs in three steps: (1) diffusion of hydrogen ions into the inner tube, (2) chemical reaction with alumina and (3) transport of the reaction products out of the lumen (Abdullayev, Joshi et al. 2012). In brief, a certain amount (10 g) of HNTs was dispersed in 400 mL of 1.0 M sulfuric acid. The suspension was magnetically stirred on a hot plate for

48 h at 50 °C, and the HNTs were denoted as H_{ac}. The resulting mixtures were washed with Milli-Q (MQ) water until the pH of the supernatant from the washing stage reached between 6 and 7, similar to that of MQ water. The sample was subsequently dried in an oven at 60 °C. Finally, the sample was a white solid that was easily crushed into powder using a mortar. In this study, pristine halloysite was denoted as H_0.

3.3.2 Organic modification

The HNTs were also modified for surface function using 3-amonopropyltriethoxy silane (APTES) to achieve the desired performance (e.g. to achieve the desired percentage of pesticide loading). The clay minerals were also modified using 4,4'-Oxydianiline (ODA).

3.3.3 Loading of imidacloprid onto clays and modified clays

HNTs are natural clays with tubular structures (with external diameters within the nanoscale (<100 nm)) and internal diameters ranging between 10 and 80 nm depending on their origin and source (Tan, Yuan et al. 2015, Scarfato, Avallone et al. 2016). The loading of active ingredients can be achieved by immersion or entrapment. The interactions among pesticides and carriers play vital roles in loading and releasing active ingredients. Various processes, such as enlarging the lumen diameter, enlarging the interlayer space, surface functionalisation, surface modification and thermal treatment, influence the interactions. The sorption method was used to load imidacloprid upon various treatments.

Moreover, entrapment under vacuum was applied to trap the imidacloprid in the porous structure. A vacuum desiccator was used to evaporate the solvents from the clay minerals. Clay and modified clays were immersed in various solvents containing imidacloprid and then evaporated under vacuum to allow the release of air in the porous structure of clay minerals.

3.3.4 Synthesis of clay-polymer composites

Polymers, such as alginate, polylactic acid and polyacrylonitrile, were used for the preparation of bead composites. The pristine and treated clays were loaded with imidacloprid and then incorporated into the polymer beads. The solution was dropped into a polymer solution where clay and imidacloprid were incorporated into the composite. The system was stirred under constant pressure, and the composites were collected through filtration/sieving. The fresh composites were dried at room temperature, freeze-dried and oven-dried. The structure could be lost during the drying process. The materials were then characterised and tested for release.

3.3 METHODS FOR MATERIAL CHARACTERISATION

The raw materials, modified materials and pesticide-loaded materials were characterised to understand the properties and loading effects. The following methods were used for characterisation.

BET surface area

The specific Brunauer−Emmett−Teller (BET) surface area were analysed using an N2 adsorption−desorption instrument (Micromeritics Tristar II 3020, USA).

XRD analysis

A PANalytical X-ray diffractometer (The Netherlands) was used for X-ray diffraction (XRD) using a copper (Cu) anode at 40 mA and 40 kV. This helps identify any changes in the mineral structure of the samples.

Thermogravimetric analysis (TGA)

TGA was performed with a Q600 SDT (TA Instruments). Approximately 6 mg of the sample was heated from 50 to 800 °C in a 40 µL platinum crucible. The heating rate was 10 °C min^{-1} under an atmosphere of high-purity continuous N gas flow at 120 mL min^{-1}.

Scanning electron microscopy (SEM)

A field emission scanning electron microscope (FESEM, Zeiss Supra 55VP, Carl Zeiss AG) fitted with an energy dispersive X-ray spectroscopy (EDAX) facility was used for SEM analysis. The dried powdered samples were placed on a sample holder and subsequently coated with Au–Pd (8.5 nm) by using a Leica EM ACE600 high-vacuum coater for high-resolution imaging. The SEM images were obtained at an accelerating voltage of 4.5 kV, and multiple image magnifications at various areas were obtained.

TEM (transmission electron microscope)

The materials before and after loading with imidacloprid were investigated by using a transmission electron microscope (TEM, Tecnai T20, FEI Tecnai (LaB6)). The samples were dispersed in ethanol, after which one drop of the suspension was dried on a copper grid (Ted Pella, Inc., Redding, CA). The TEM images were generated at an accelerating voltage of 120 kV. Changes in the shell thickness and void space of the BHSNs were evaluated through image analysis using ImageJ software (NIH, free downloaded).

FTIR spectroscopy

The loading of imidacloprid in the nanocomposites was investigated by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, IR Affinity-1, Shimadzu, Japan). FTIR analysis was performed from 4000 to 400 cm^{-1} with a signal resolution of 4 cm^{-1}. Each sample was scanned 32 times to obtain a good signal-to-noise ratio.

UV–VIS

To measure the concentration of imidacloprid present in the mixed solution, all the solutions were collected and measured by a UV−vis spectrophotometer (Shimadzu, UV-1700 PharmaSpec) at a λmax of 270 nm. Standard curves were determined from 0–25 mg/L.

LC–MS

IMI was also measured using an LC–MS (Agilent 1260 pump and 6150 single quadrupole mass spectrometer). Standard solutions were prepared in acetonitrile (ACN) and stored in amber vials at 4 °C in a refrigerator. Calibration solutions were prepared from these standard solutions in a 50/50 (v/v) mixture of ACN/H2O. Quality control samples were also used to test the reproducibility within a run. A 20 µL aliquot of sample was injected into the instrument, and separations were carried out at 40 °C using a Zorbax Eclipse Plus C18 column (3.5 µm, 4.6 × 150 mm). The mobile phase consisted of a mixture of ACN/H2O (40/60) and 0.2% acetic acid. The separation was optimized for the soil matrix samples, and the flow rate was set at 0.6 mL/min. The MS instrument was operated in positive mode

under the following conditions: 350 °C for the gas temperature in the nebuliser, 10 L min-1 for the drying gas flow and 4500 V for the capillary voltage. LC–MS chromatograms were obtained by scanning from 50 to 500 m/z. Selected-ion monitoring (SIM) of the most abundant ion (256 m/z) was used for quantification.

3.4 METHODS FOR THE RELEASE STUDY

The release of active ingredients from the loaded beads was investigated using sequential extraction. Approximately 50 mg of sample was immersed in 50 mL of water for the release study. The water was replaced every 1–3 days to achieve new equilibration for the release of imidacloprid. The solution was then analysed using LC–MS to determine the release pattern.

The release of imidacloprid was also investigated in two types of soils after incubation for 8 weeks. The two soils were spiked with various amounts of beads (according to the loading amount of imidacloprid), which was calculated using the target concentration of 1.125 mg imidacloprid/g soil. The imidacloprid in the soil pore water was extracted using a high-speed centrifuge method followed by dilution and analysis using the LC–MS method (with a calibration range of 0 ~ 100 µg/L).

RESULTS

4.1 THE EFFECT OF MODIFICATION ON THE CHARACTERISTICS OF CLAY MATERIALS

4.1.1 Physicochemical properties of halloysite clay nanotubes

Naturally, halloysite remains as hydrated mineral, and the chemical structure of HNTs is similar to that of platy clay kaolinite except that the unit layer is separated by a monolayer of water molecules. The chemical structure of the HNTs is $Al_2SiO_2O_5(OH)_4.nH_2O$; when n = 2, the mineral is known as halloysite-10 A°, and when n = 0, the halloysite is known as halloysite-7 A° (Joussein, Petit et al. 2005). The 10 A° indicates the layer periodicity or d_{001}-value of the layers. A dehydrated structure is obtained through the loss of interlayer water from hydrated halloysite by heating or keeping the mixture under vacuum (Joussein, et al. 2005).

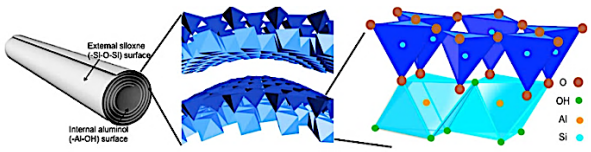


Figure 17. Schematic structure of HNTs. Adapted and modified from (Rachel et al. 2012).

In general, pure halloysite is white in colour, whereas the colour of halloysite obtained from natural deposits varies from yellowish to brown, sometimes greenish, due to the presence of different types of impurities (Abdullayev and Lvov 2013). The morphology and porosity

also vary due to their natural sources (Pasbakhsh et al. 2013). To date, HNTs have been reported to be of various dimensions, and the length of HNTs varies from submicron to several microns, while the diameter of the tube varies from 30 to 190 nm (Joussein et al. 2005). Similarly, the lumen diameter also changes with tube diameter and varies from 10 to 100 nm (Yuan et al. 2008; Yuan et al. 2015). Most likely, the dimensions of HNTs depend on the source of HNTs (natural deposits). However, in this project, we considered fine/ultrafine halloysite powder with a tubular morphology that was purchased from Sigma Aldrich, Australia. According to the supplier, some of the physicochemical properties are given below.

Table 7. Properties of the used halloysite nanoclay.

Parameters	Properties
Shape	Nanotube
Diameter × Length	30–70 nm × 1-3 µm
Pore size	1.26–1.34 mL/g pore volume
Colour	75-96, Hunter Brightness
Refractive index	n20/D 1.54
Surface area	64 m^2/g
Cation exchange capacity	8.0 meq/g
Density	2.53 (true specific gravity)

4.1.2 Physicochemical properties of montmorillonite nanoclay

Among the various clay minerals, montmorillonite (MMT) clay is considered to be the most promising material due to its low cost, availability, swelling ability/layer expansion capacity, high surface area, cation exchange capacity, etc. (Zhu et al. 2016). However, natural clays have several limitations due to the presence of inorganic cations. Generally, inorganic cations are strongly hydrated in aqueous media and have hydrophilic surface properties (Xi et al. 2010). Hence, while they are good adsorbents of ionic or polar compounds, they are not ideal for accessing non-ionic or hydrophobic organic compounds (Sanchez-Martin, et al. 2006). These properties make it possible to modify surfaces with quaternary ammonium or phosphonium cations containing alkyl, phenyl, benzyl and pyridyl groups via ion exchange and adsorption processes as well as by grafting with different organic silanes (Ganguly et al. 2011). Such modifications also enhance organophilicity and/or hydrophobicity, expand interlayer spaces and ultimately enhance sorption capacity (Shattar et al. 2016). Organically modified MMT nanoclays have already exhibited potential for use in developing CRFs as well as adsorbing pesticide molecules from contaminated water bodies (Celis et al. 2007; Chevillard et al. 2012; Shattar, Zakaria et al. 2016).

Prior to the commencement of this project, we investigated the interactions and sorption capacity of MMT nanoclays for imidacloprid. The MMT nanoclay was purchased from Sigma Aldrich (Australia), and its properties are presented in Table 8.

Table 8 Properties of the experimental MMT nanoclay.

Specification	Properties	Remarks
Surface modification	0.5–5 wt.% aminopropyltriethoxysilane 15-35 wt.% octadecylamine	As per supplier
Colour	Off white	As per supplier
Appearance	Powder	As per supplier
Weight loss in drying	≤ 3%	As per supplier
Size	≤ 20 micron	As per supplier
Bulk density	200–500 kg m^{-3}	As per supplier
Organic carbon content	19.2%	Determined
pH in water	4.15–4.45 (2- 4 g L^{-1})	Determined

The MMT nanoclay showed an adsorption capacity of 196 mg $g^{-1,}$ where the sorption capacity was 84 mg g^{-1} with an initial pesticide concentration of 500 mg L^{-1}. During sorption, hydrophobic interactions followed by hydrogen-bonding interactions play a vital role. Pristine MMT K10 was modified in this project using more biocompatible agents, especially amino acids, to prepare completely eco-friendly carriers.

4.1.3 Characterisation of acid-treated HNTs

X-ray diffraction pattern analysis of HNTs

The crystalline phases of HNTs and acid-treated HNTs were evaluated via X-ray diffraction (XRD) pattern analysis. The XRD patterns were obtained using a Bruker D8 Discover diffractometer equipped with Cu-Kα radiation (λ = 0.154 nm) generated at 40 kV and 40 mA. The scanning rate was 1 ° (2θ) min^{-1} in the range of 5–80 ° with a step size of 0.04 °. Figure 18 shows a sharp peak at a 2θ of 12.34 ° with a corresponding d value of ~7.3 A°, which is the characteristic (001) peak of halloysite and indicates multilayer packing (Abdullayev, Joshi et al. 2012). The d value (7.3 A°) at this 2θ position also indicates a dehydrated structure of halloysite (Yuan et al. 2015). The most prominent peak appeared at a 2θ of $^{\sim 20^{\circ},}$ with a corresponding d value of 4.5 A°, which is an indication of the tubular structure of halloysite (Tazaki 2005). The d_{002} peak at 3.6 A° at a 2θ of ~24.5° supports the presence of a multilayer tubular structure. In addition, a sharp peak was observed at a 2θ of ~26.62 °, indicating that the halloysite was structured with crystalline silica or quartz. This result indicated that with acid treatment, the HNTs did not lose their tubular structure. In addition, Figure 19 indicates that the peak representing SiO_2 increased after acid treatment.

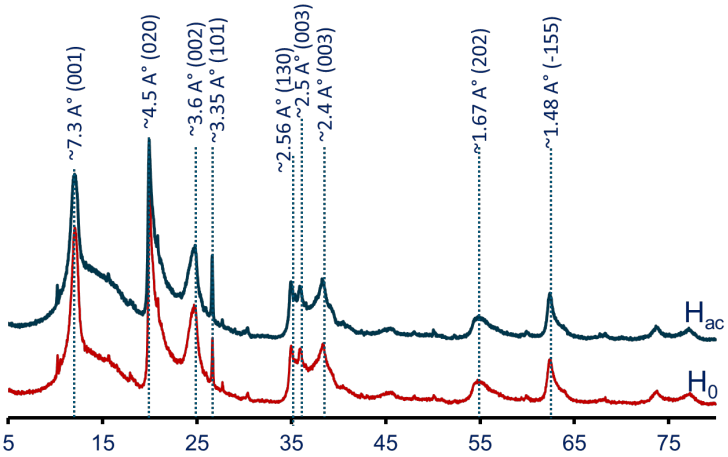


Figure 18. XRD patterns of pristine and acid treated HNTs.

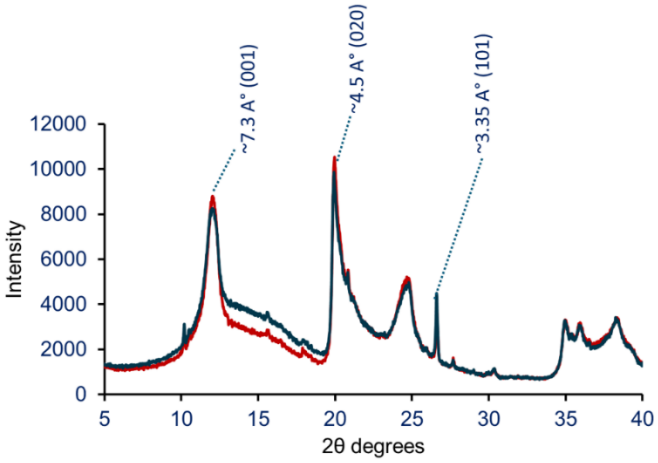


Figure 19. XRD patterns of pristine and acid treated HNTs.

Morphological analysis

The external surface morphologies of the pristine and acid-treated HNTs were evaluated by using a field emission scanning electron microscope (FESEM, Zeiss Supra 55VP, Carl Zeiss AG). For SEM analysis, one drop of dispersed HNT suspension (in acetone) was placed on a sample holder and then dried under vacuum. Prior to SEM analysis, the samples were coated with Au-Pd (8.5 nm) using a Leica EM ACE600 High Vacuum Coater for high-resolution imaging. The SEM images were obtained at an accelerating voltage of 5 kV, and multiple image magnifications at various areas were obtained for each sample. The internal surface morphologies of the pristine and acid-treated HNTs were evaluated by using a transmission electron microscope (TEM, Tecnai T20, FEI Tecnai (LaB6)). Before TEM analysis, the HNT powder sample was dispersed in ethanol, after which one drop of HNT suspension was dried and placed on a copper grid (Ted Pella, Inc., CA, USA). The TEM images were taken at an accelerating voltage of 120 kV.

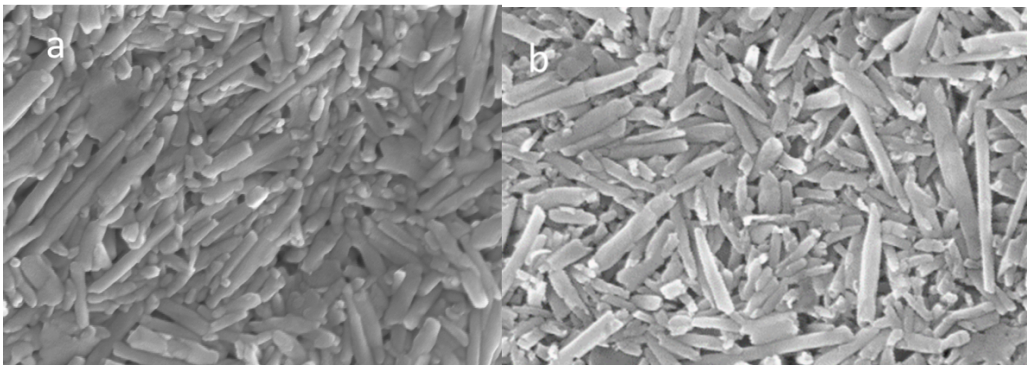


Figure 20. SEM images of (a) pristine HNTs and (b) acid-treated HNTs.

The diameter of the HNTs is much less than 100 nm, and the nanotubes have a wide range of lengths. This result was supported by the information provided by the supplier (Sigma–Aldrich) (i.e. the diameter and length of the pristine HNTs were 30–70 nm × 1–3 μm with a tubular structure). It was also observed that the HNTs preserved their cylindrical morphology even after acid treatment. In addition, some broken particles were observed in the acid-treated samples which resulted in the average length less than that of the pristine HNTs (Figure 20). Similar observations were reported by Wang et al. (2014) who treated HNTs with HCl. The broken HNTs may be due to continuous mechanical stirring in the presence of acid (Wang et al. 2014).

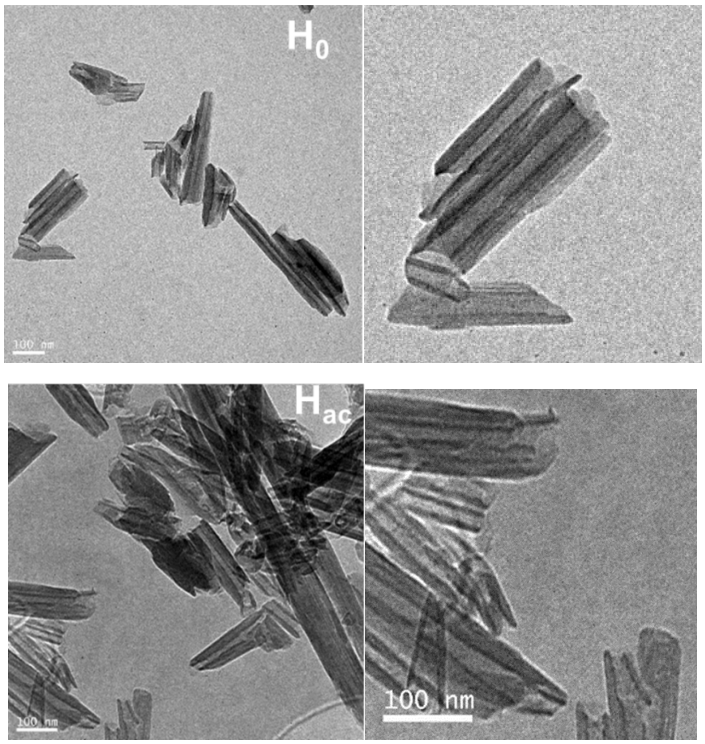


Figure 21. TEM images of (a) pristine and (b) acid-treated HNTs.

Figure 21 shows that HNTs had a hollow tubular structure even after acid treatment. However, after acid treatment, the pristine HNTs exhibited a smooth inner surface,

whereas a rough surface was observed for the sample (Figure 22). This result indicated that the acid treatment mainly etched the inner surface, facilitating the increase in the diameter of the lumen.

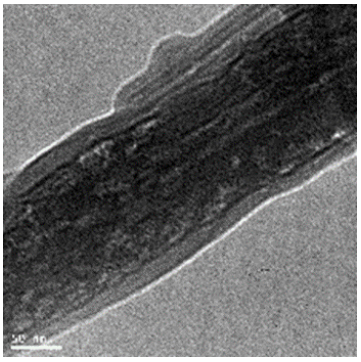


Figure 22. TEM image of acid-treated HNTs showing the inner surface.

Elemental analysis

Energy-dispersive X-ray spectroscopy (EDAX) was utilised to investigate the elemental composition of the HNTs before and after acid treatment. The elemental analysis of the HNTs before and after acid treatment strongly supported the results obtained by XRD analysis considering the three major elements (i.e. C, O, Al and Si) (Figure 23). The EDAX spectra revealed that the amount of Si increased after acid treatment. However, the atomic ratio (%) of Al to Si was ~ 1 but was reduced in acid-treated HNTs (Figure 24). This result indicated that the amount of Al in the acid-treated HNTs was lower than that in the pristine HNTs.

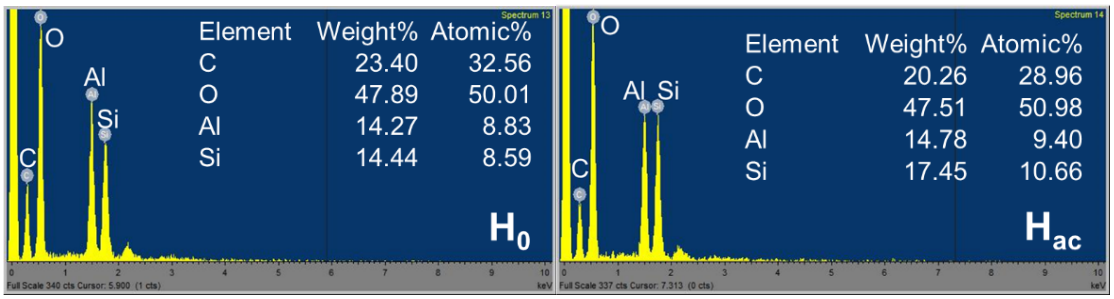


Figure 23. EDAX spectra and elemental composition of the pristine and acid-treated HNTs.

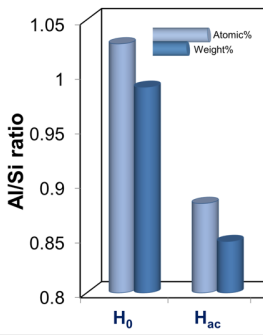


Figure 24. Al/Si ratios of pristine and acid-treated HNTs.

FTIR analysis

Both pristine and acid-treated HNTs were characterised by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, IR Afinity-1, Shimadzu, Japan). FTIR analysis was carried out from 3800 to 600 cm^{-1} with a signal resolution of 4 cm^{-1}. For each sample, 32 scans were taken to obtain a better signal-to-noise ratio. The band vibrational peaks corresponding to these chemical bonds were observed in the FTIR spectra of both the pristine and acid-treated HNTs in the spectral range of 600 to 3800 $cm^{-1,}$ as shown in Figure 25. The structural -OH stretching vibrations at 3692 cm^{-1} and 3622 cm^{-1} were attributed to Al-OH groups because these peaks disappeared after 100% dealumination (Abdullayev et al. 2012, Joo et al. 2012). An indicative change was observed for the peak at 3622 cm^{-1}. Two distinct peaks were observed at this peak position (3624 cm^{-1} and 3620 $cm^{-1)}$ when HNTs were treated with acid for 48 h (Figure 25a inset). This indicates that the deformation of Al-OH and the formation of new bond structures, most likely Si-OH, were influenced by acid treatment. As silica tetrahedrons and alumina octahedra are attached to each other by shearing an O atom with an Al-O-Si bond structure, when Al^{3+} is released from the structure, the diffused H^+ (from H_2SO_4) binds with Si-O- and forms Si-O-H. The transformation of Al-OSi and Si-OAl into Si-OH resulted in the hydrophilic nature of the acid-treated HNTs. The stretching vibration of the deformed water was observed at 1640 cm^{-1}, which was affected by the duration of acid treatment.

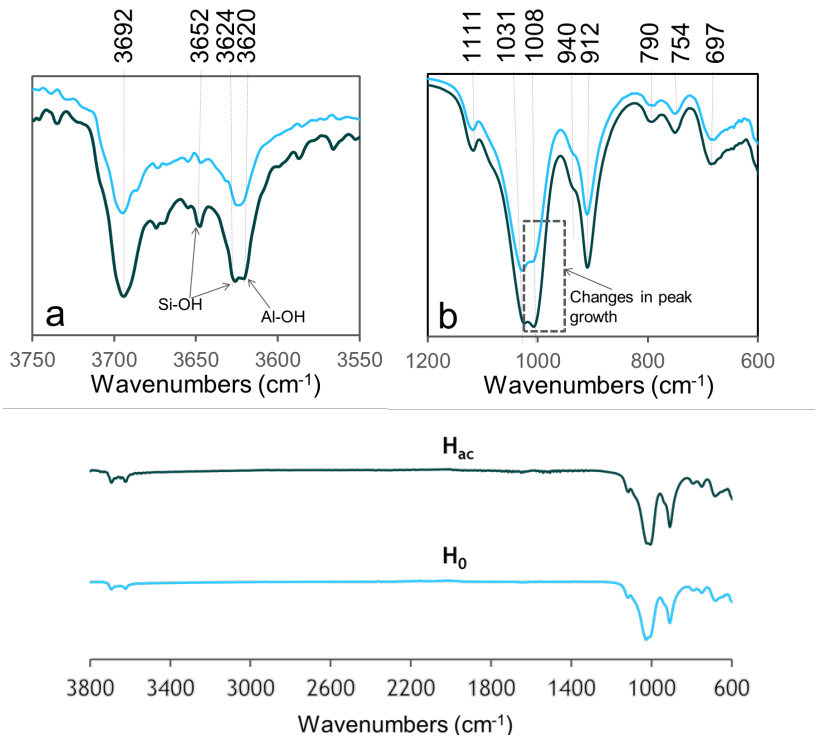


Figure 25. FTIR analysis of pristine and acid-treated HNTs.

On the other hand, the bands at 1031 cm^{-1} and 1111 cm^{-1} are assigned to the in-plane stretching vibrations of the Si-O network (Si-O-Si and O-Si-O), respectively, and perpendicular/apical Si-O stretching vibrations may be present at the surfaces of HNTs (Yuan, Southon et al. 2008, Zhang, He et al. 2013). Therefore, no changes were observed in the FTIR spectra of the acid-treated HNTs (Figure 25b inset). Peaks at 940 cm^{-1} and 912 cm^{-1} indicate O-H deformation vibrations present at the inner surface as well as in the intersheet, respectively (Yuan, Southon et al. 2008, Zhang, He et al. 2013). In addition, the peak at 790 cm^{-1} represents the symmetric stretching of Si-O-Si, whereas the peaks at 754 cm^{-1} and 697 cm^{-1} represent perpendicular Si-O-Al stretching (Yuan et al. 2008).

Thermogravimetric analysis

Thermogravimetric analysis of the HNT powder samples was carried out using a Q600 SDT (TA Instruments). Approximately 6 mg of each sample was heated from 50 to 800 °C in a 40 µl platinum crucible. The heating rate was 10 °C min^{-1} under an atmosphere of high purity continuous N gas flow at 120 mL min^{-1}. Figure 26 shows the thermal decomposition properties of both the pristine and acid-treated HNTs. Among the samples, ~15% weight loss was observed for acid-treated HNTs, whereas approximately 13.95% weight loss was observed for the pristine HNTs. The weight loss (TGA) and derivative weight loss (DTG) curves obtained via thermogravimetric analysis exhibited two-step weight loss up to 580 °C. In the first step, a minute weight loss was observed in the range of 30–150 °C due to the physically adsorbed water. The corresponding DTG peaks showed a maximum degradation temperature of 129.76 °C for pristine HNTs, whereas the temperature tended to increase for acid-treated HNTs (138.83 °C).

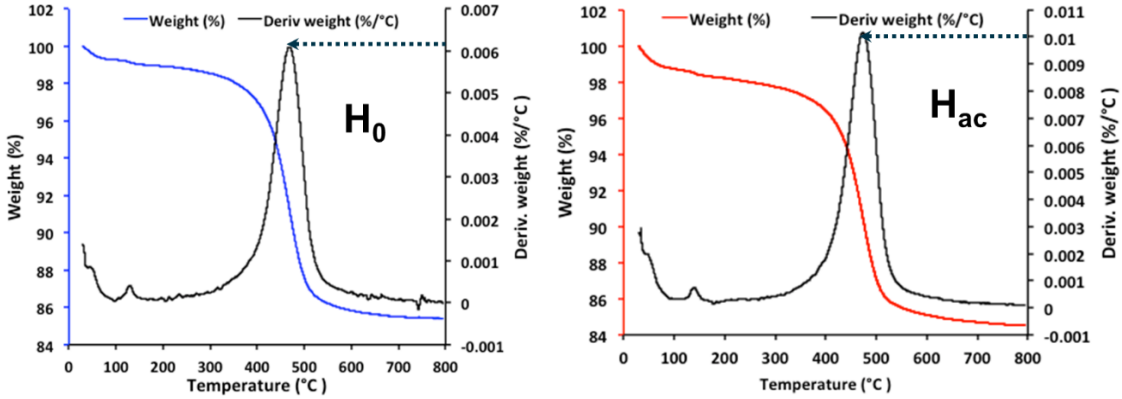


Figure 26. Thermogravimetric analysis of pristine and acid-treated HNTs.

Zeta potential analysis

The surface ζ-potential of the experimental HNTs was measured by using a Zetasizer (model Nano-ZS90; Malvern Instruments, Worcestershire, United Kingdom). For zeta potential analysis, 0.1 wt.% HNT suspensions were prepared, and the zeta potential (mV) was measured between pH 3 and 11 (Figure 27). For each pH, the zeta values were recorded three times, and the means are presented. The zeta potential plot shows that the surface charge of the HNTs is slightly negative at lower pH values (3–5), whereas it gradually increases with increasing pH and becomes highly negative at higher pH values (~45 mV). The negative surface charge with increasing pH was due to the tubular morphology of the material, especially its specific surface structure. The outer surface of the HNTs is built mainly of silica, and alumina is present mainly on the inner surface.

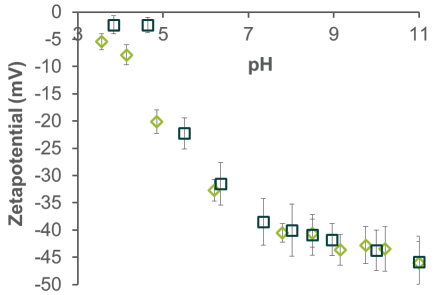


Figure 27. Zeta potential of HNTs at various pH values (◊ pristine HNTs and ▫ acid-treated HNTs).

Stability of HNTs

The effects of zeta potential on the stability of the HNTs were tested at pH 4.9, 7.8 and 9.0. At pH 4.9, the acid-treated HNTs were deposited faster than the pristine HNTs, while at higher pH values, all the HNTs held their suspension stable for a longer period (Figure 28).

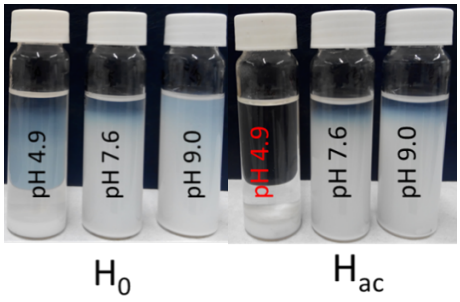


Figure 28. Physical stability of pristine and acid-treated HNTs at various pH values after 24 h.

Surface area and porosity

The surface area and pore size analysis of the sample were carried out by N adsorption and desorption isotherms at 77.350 K using a Micromeritics Tristar II 3020 surface area and porosity analyser. Before analysis, the samples were degassed at 180 °C for 20 h. The specific surface area was calculated on the basis of the Brunauer–Emmett–Teller (BET) equation and Langmuir equation. The pore size distribution plot was obtained by the Barrett–Joyner–Halenda (BJH) method. The adsorption/desorption isotherms of N_2 and the pore size distributions of the HNTs are shown in Figure 29. From the BET equation, the single-point surface area was measured at a relative pressure $P/P_0 = 0.299$ as 49.24 $m^2 g^{-1}$ for pristine HNTs but increased to 70.51 $m^2 g^{-1}$ when the HNTs were treated with acid for 48 h. Additionally, the Langmuir surface area was measured as 121.77 $m^2 g^{-1}$ for pristine HNTs but increased to 169.16 $m^2 g^{-1}$ for acid-treated HNTs.

Nitrogen adsorption and desorption isotherms were also recorded for the HNTs to characterise the pore volume distribution and, decisively, the porosity of the HNTs. From the adsorption isotherm, it was observed that N_2 adsorbed rapidly at higher relative pressures ($P/P_0 > 0.8$) because of the requirement of N_2 to fill the inner cavities. However, the desorption process showed hysteresis with a sharp capillary condensation step in the relative pressure range of 0.95–0.85, indicating the presence of large mesopores. However, the hysteresis of the isotherms followed a similar pattern, which indicated no blockage of N_2 gas within the pores. Furthermore, the BJH pore size distribution also clearly represents the changes in porosity of the HNT structure. The average BJH adsorption pore width of the pristine HNTs was 3.74 nm, and that of the acid-treated HNTs was 3.89 nm. However, the average volume of pores between 1.7 and 300 nm was 0.074 $cm^3 g^{-1}$ for pristine HNTs but increased to 0.102 $cm^3 g^{-1}$ for acid-treated HNTs.

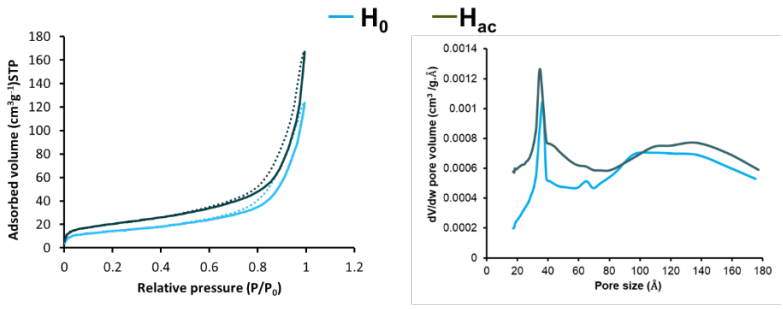


Figure 29. (a) Nitrogen adsorption-desorption isotherms and (b) corresponding pore size distributions of the pristine and acid-treated HNTs.

To optimise the lumen and etching conditions, HNTs were treated with acid for 24, 48, 72, 96, 120 and 144 h, and the HNTs were denoted as H_1, H_2, H_3, H_4, H_5, and H_6, respectively, while the pristine HNTs were denoted as H_0.

X-ray diffraction pattern analysis of HNTs

The XRD patterns of the pristine and acid-treated HNTs at various concentrations are presented in Figure 30. All the acid-treated HNTs exhibited characteristic peaks of pristine halloysite (i.e. a hollow tubular structure).

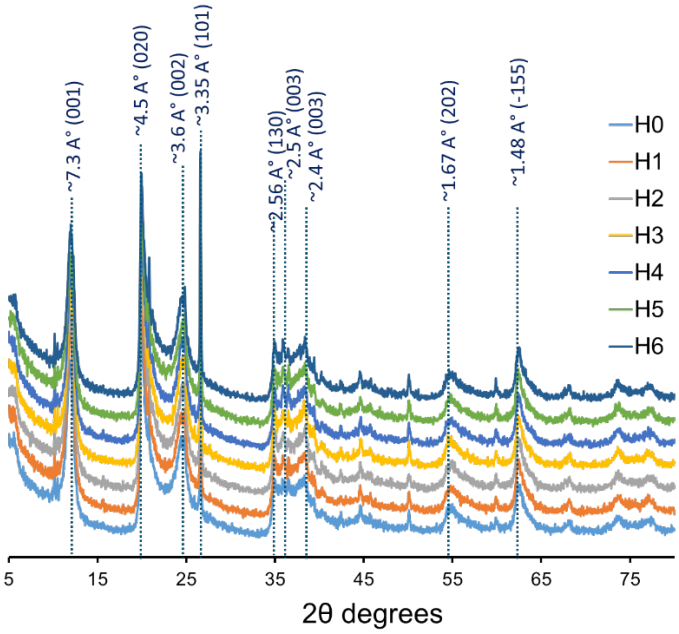


Figure 30. XRD patterns of pristine and acid-treated HNTs at various treatment.

Morphological analysis

TEM images of HNTs treated with acid for 0, 48, 96 and 144 h are presented in Figure 31. The etching level increased with increasing acid treatment time. More broken HNT particles were observed with increasing treatment time.

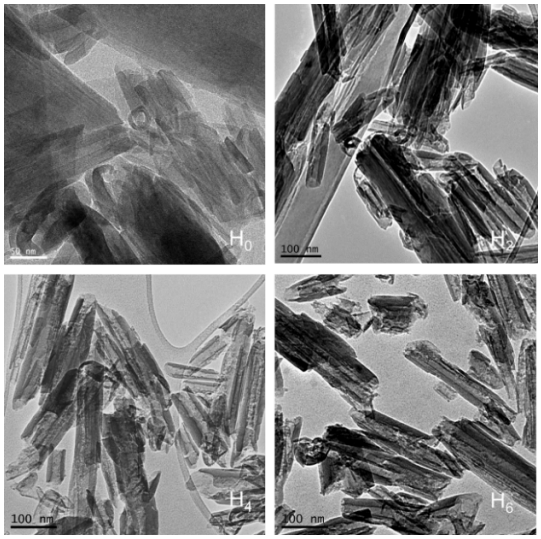


Figure 31. TEM images of pristine and acid-treated HNTs.

Surface area

Table 9 shows the surface areas of the different acid-treated HNTs. The duration of acid treatment affected the surface area of the HNTs. From the N adsorption–desorption isotherms, it was observed that the tubular structure of the HNTs was not altered. An increase in the surface area of HNTs is expected to facilitate the enhancement of pesticide loading into the lumen.

Table 9. Surface areas of the various HNTs.

HNTs	**Single point surface area at p/p° = 0.29 (m^2g^{-1})**
H_0	52.73
H_1	62.99
H_2	70.51
H_3	78.05
H_4	93.23
H_5	102.46
H_6	100.73

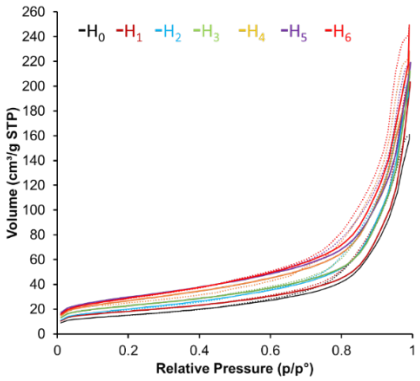
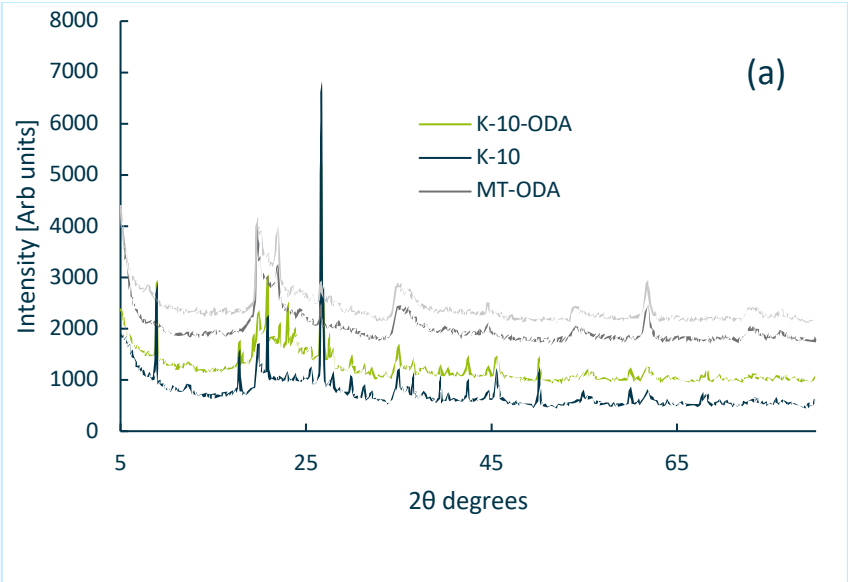


Figure 32. Nitrogen adsorption–desorption isotherms.

4.1.4 Characterisation of functionalised HNTs

XRD analysis

The organic-treated clays, including HNTs and MMTs, were characterised using XRD (Figure 33). The main structure of MMT is not changed upon modification with organic compounds. The basal spaces might increase upon further incorporation of APTES. The presence of peaks for organic compounds was found in the modified HNT minerals.



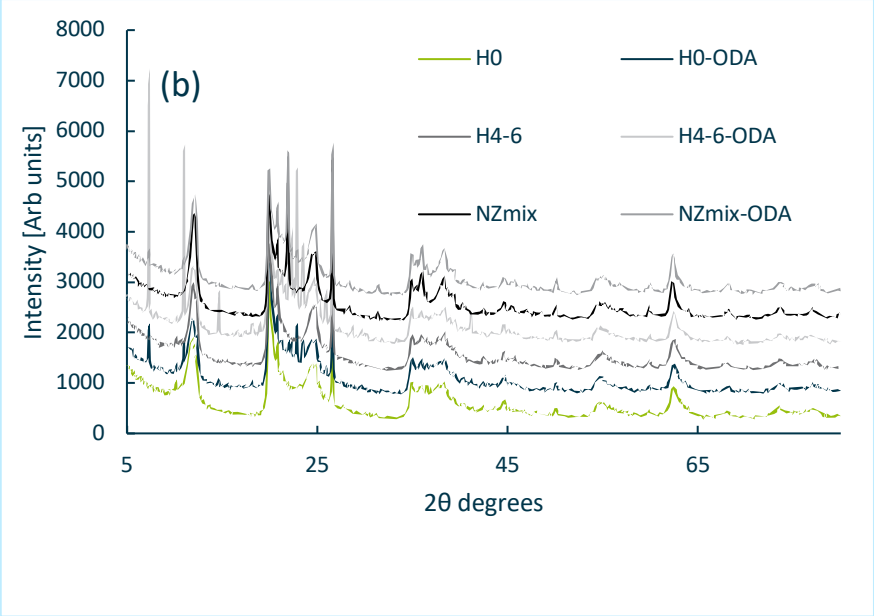


Figure 33. XRD patterns of the organic modified clays (a) montmorillonite (b) halloysite.

Surface area

The surface areas of the organic-modified samples are shown in Table 10. Generally, organic modification decreased the surface area of HNTs and MMTs. The organic compounds could occupy the surface and porous structure of the clay particles.

Table 10. Surface area of the organic modified clays.

Samples	**Surface area (m^2 g^{-1})**		
	Single point at *p/p°*= 0.29	BET	Langmuir
H0-ODA	26.77	30.24	44.82
Hmix-ODA	16.90	19.26	66.80
NZmix-ODA	14.29	15.90	50.34
K10-ODA	1.61	1.72	3.07
K10-ODAbottom	1.63	1.74	2.25
K10-ODA foam	0.53	0.59	0.12
MT-ODA			
MT-ODA+APTES			
NZmix			

TGA analysis

TGA was also conducted for the MMT, HNTs and their modified materials, and the results are shown in Figure 34. The incorporation of organic compounds in the clay minerals was verified by weight loss in the 200–300 and 350–450 ranges, where the organic modifier underwent combustion and weight loss. This effect is more obvious for HNTs and their modified samples. The pristine clays only showed initial weight losses of approximately 100 and 500 degrees for MMT and HNTs, respectively.

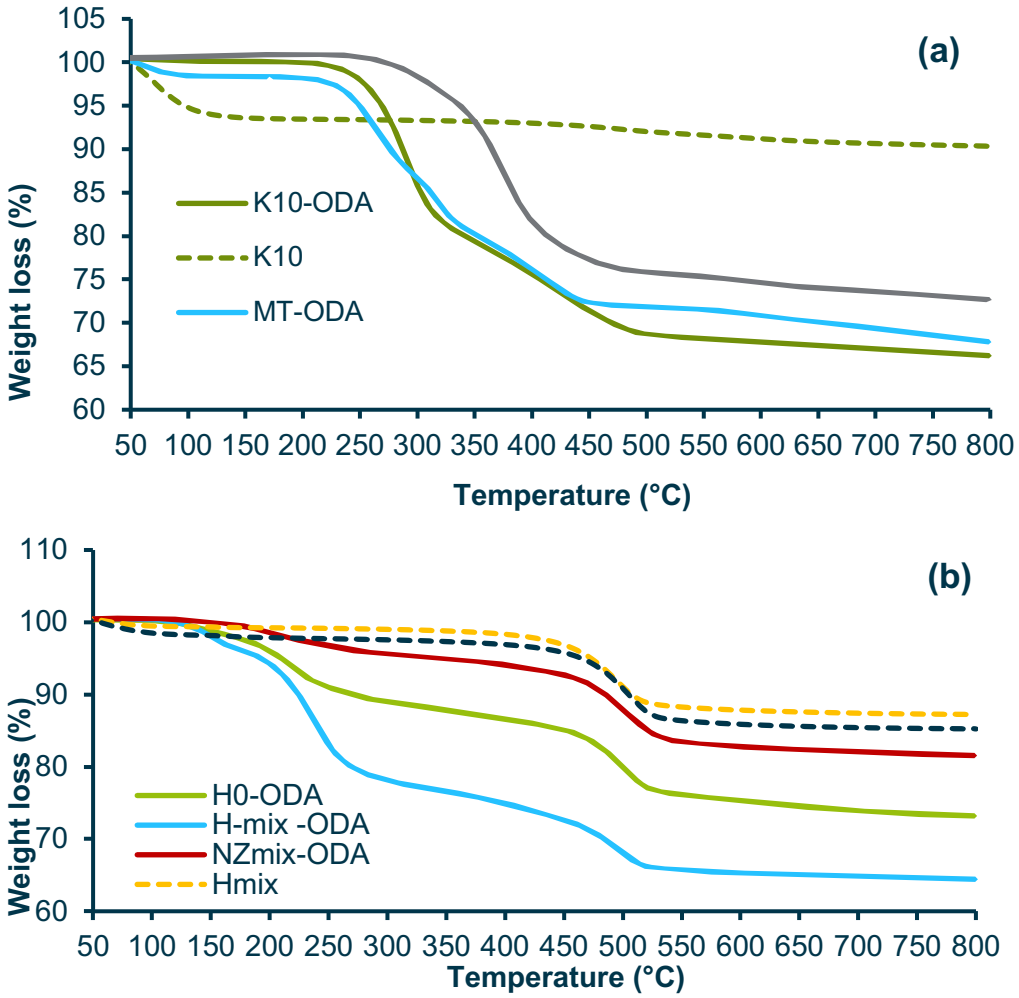


Figure 34. TGA of organic modified clay minerals (a) montmorillonite (b) halloysite.

Morphological analysis

The ODA-modified halloysite and montmorillonite were analysed via SEM, as shown in Figure 35. There was no obvious change in morphological characteristics before or after modification. There might be additional aggregated particles after modification with organic compounds.

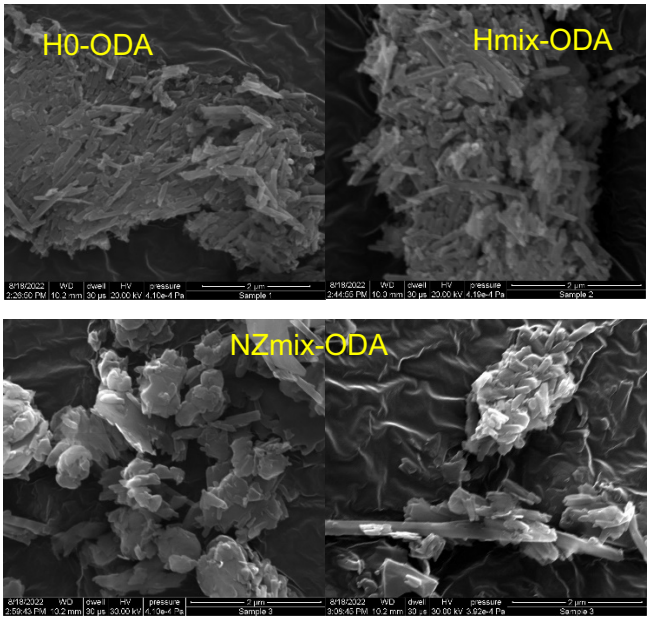


Figure 35. SEM analysis of halloysite after organic modification.

4.2 THE EFFECT OF MODIFICATION ON THE SORPTION LOADING OF IMIDACLOPRID ON CLAY MATERIALS

4.2.1 Adsorption of imidacloprid to HNTs

To investigate the interactions between imidacloprid and HNTs, a batch adsorption study was carried out. The desired amounts of HNT clay powders were added to 20 mL of pesticide solution and shaken at 25 ± 1 °C using an overhead thermostat shaker at 150 rpm. All the experiments were carried out for 24 h to reach equilibrium. The time required to reach adsorption equilibrium was determined prior to the batch experiments. After adsorption, the solution was filtered to determine the pesticide concentration in the solution. The concentration of imidacloprid was calculated from the absorbance obtained from a UV–VIS spectrophotometer (Shimadzu UV1700 PharmaSpec) at a λ_{max} of 270 nm. There was no significant loss of solute material due to degradation or adsorption onto the glass vial walls. The specific experimental conditions or states are captioned in the respective figures. The adsorption efficiency (A, %), the amount of imidacloprid adsorbed at time t (Q_t, mg g^{-1}) and at equilibrium (Q_e, mg g^{-1}) were calculated using the following equations:

$$\% A = \frac{100(C_0 - C_e)}{C_0} \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where C_0, C_t and C_e are the initial concentration at time t and the equilibrium solution concentration (mg/L), respectively, Q_t and Q_e are the amounts of pesticide adsorbed at time t and per gram of adsorbent (mg/g) at equilibrium, respectively, V is the volume of solution (L) and m is the mass of the adsorbent (g).

The system pH and/or initial solution pH can affect the chemical properties of solutes and sorbents, which play vital roles in adsorption. Thus, before the batch adsorption study, the effect of the initial system pH on imidacloprid adsorption to MMT nanoclays was investigated over a pH range between 4 and 10 (Figure 36). The adsorption of imidacloprid to HNTs was strongly influenced by the initial system pH. An increasing trend in imidacloprid adsorption to HNTs was observed with increasing initial pH of the suspension up to pH 9.0, after which the adsorption tended to decrease. At pH 9.0, the formation of Al-OH and Si-OH is maximised, while further increasing the pH of Si-OH tends to generate $Si\text{-}O^-$; therefore, the adsorption of imidacloprid decreases with increasing pH 9.0.

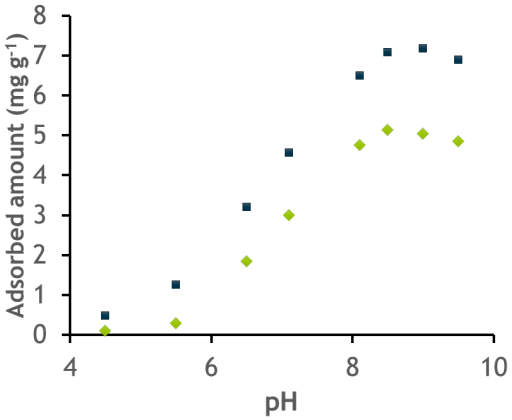


Figure 36. Adsorption of imidacloprid on HNTs at various pH values.

From the physicochemical properties of imidacloprid, it was observed that it can interact with other materials via hydrophobic interactions as well as hydrogen bonding interactions. Notably, HNTs are hydrophilic in nature because they contain very little organic carbon. Thus, hydrogen bonding interactions remained the main interaction mechanism. As acid treatment facilitated the formation of more –OH groups, the adsorption of imidacloprid to acid-treated HNTs was greater than that to pristine HNTs. Furthermore, the interaction was investigated via FTIR (Figure 37). The FTIR spectra showed that imidacloprid interacted with –OH groups as well as interlayers by interacting with physiosorbed H_2O molecules.

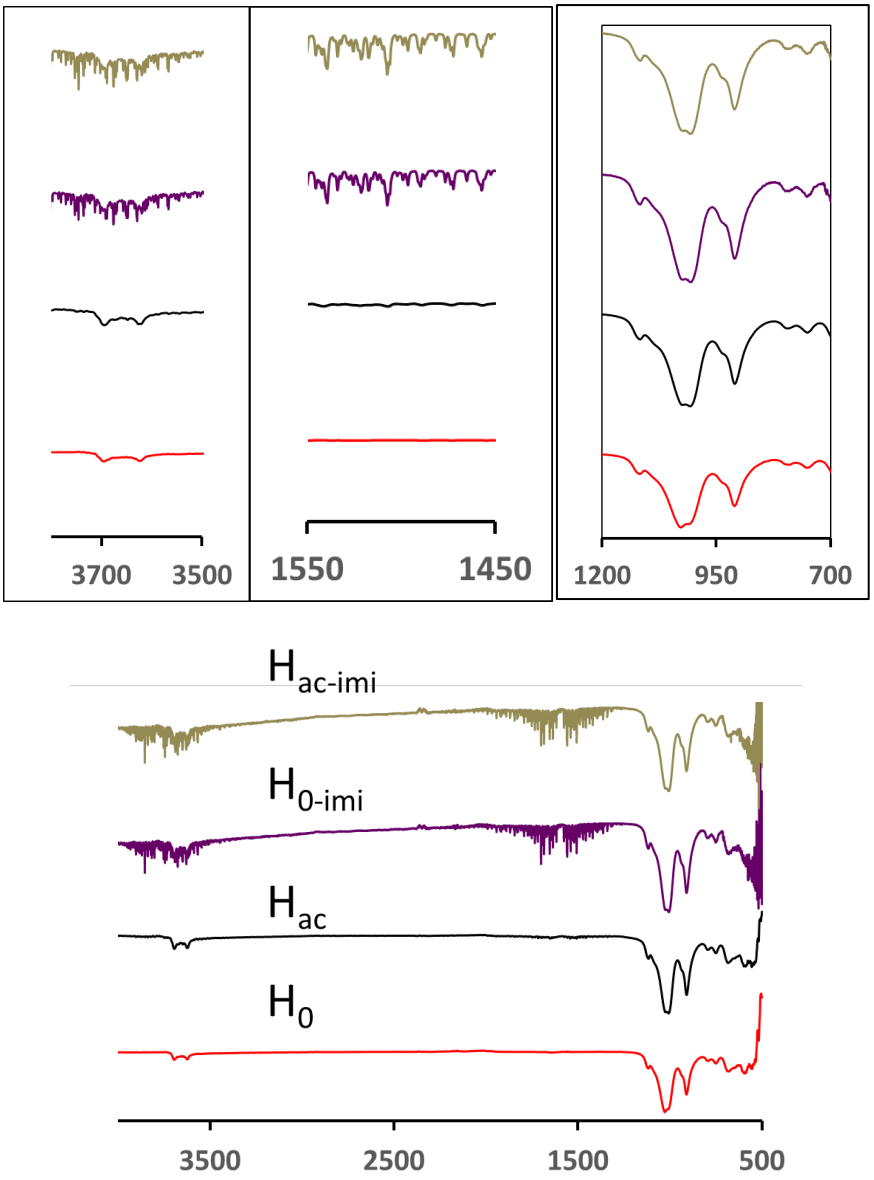


Figure 37. FTIR spectra showing the interaction of imidacloprid with HNTs.

Finally, we measured the sorption capacity of both HNTs. To determine the maximum adsorption capacity, the equilibrium data obtained from various initial pesticide concentrations were plotted with the Langmuir equation. The linear form of the Langmuir equation can be expressed as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \qquad (3)$$

where C_e (mg L^{-1}) is the concentration of imidacloprid at equilibrium, Q_e (mg g^{-1}) is the amount of imidacloprid adsorbed by the HNTs at equilibrium, Qm (mg g^{-1}) is the maximum adsorption capacity corresponding to monolayer coverage and K_L (L mg^{-1}) is the Langmuir constant.

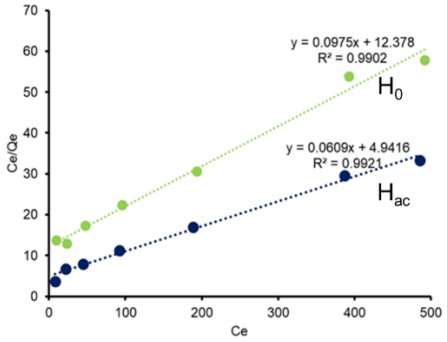


Figure 38. Langmuir isotherms for imidacloprid adsorption to HNTs.

The adsorption capacity was also described by the nonlinear Freundlich equation expressed as:

$$Q_e = K_f C_e^{1/n} \quad (4)$$

where Q_e (mg g^{-1}) is the imidacloprid concentration on MMTs at equilibrium, C_e (mg L^{-1}) is the concentration of imidacloprid in solution at equilibrium, K_f is the Freundlich distribution coefficient (coefficient of adsorption-desorption capacity, (mg g^{-1})/(mgL^{-1})$^{1/n}$) and 1/n is the Freundlich exponent (coefficient of nonlinearity).

K_f and 1/n are also denoted as Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. A higher K_f indicates a greater affinity for the adsorbate, and the values of the empirical parameter 1/n lie between 0.1 < 1/n < 1, indicating favourable adsorption.

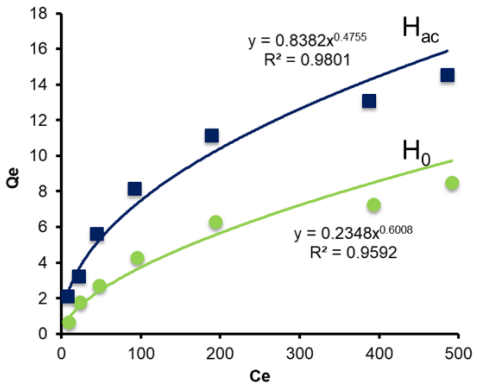


Figure 39. Freundlich isotherms for imidacloprid adsorption to HNTs.

The correlation coefficient (R^2) indicates that the experimental data agree well with the Langmuir rather than the Freundlich isotherm model. Therefore, it could be assumed that the sorption of imidacloprid to HNTs was mostly supported by a homogeneously distributed active surface for monolayer adsorption (i.e. the active sites for imidacloprid

adsorption are energetically homogeneous). With acid treatment, the adsorption of imidacloprid to HNTs increased almost 60%.

Table 11. Parameters of the Langmuir and Freundlich equations describing the adsorption of imidacloprid to HNTs

Langmuir equation			**Freundlich equation**		
	H_{ac}	H_0		H_{ac}	H_0
Q_{max} (mg g^{-1})	16.42	10.26	K_f (L g^{-1})	0.8382	0.2348
K_L	0.014	0.007	1/n	0.4755	0.6008
R^2	0.9921	0.9902	R^2	0.9801	0.9592

4.2.2 Adsorption of imidacloprid to ODA-modified HNTs and MMT

The adsorption of imidacloprid to acid-treated and pristine halloysite samples (sourced from Sigma and clay companies) is shown in Figure 40. The acid-treated sigma acid sample (SIG4) exhibited the highest sorption with the pH adjusted, while the clay sourced from South Australia (sample 2) exhibited higher sorption at pristine pH. Further modification using ODA was determined for its sorption ability (Figure 41). The sorption study was conducted at a constant pH of approximately 8.5–9. Sorption was performed for 72 h to ensure equilibration. The results indicated that the ODA-modified clays exhibited greater sorption than did the pristine clays. Further modification of APTES for MMT decreased the sorption amount compared to that of MMT–ODA. Conversely, the sorption of imidacloprid by ODA and acid-modified halloysite was greater than that by other treatments and other sources of HNTs. These results further verified the effect of acid treatment and organic modification on the clay particles.

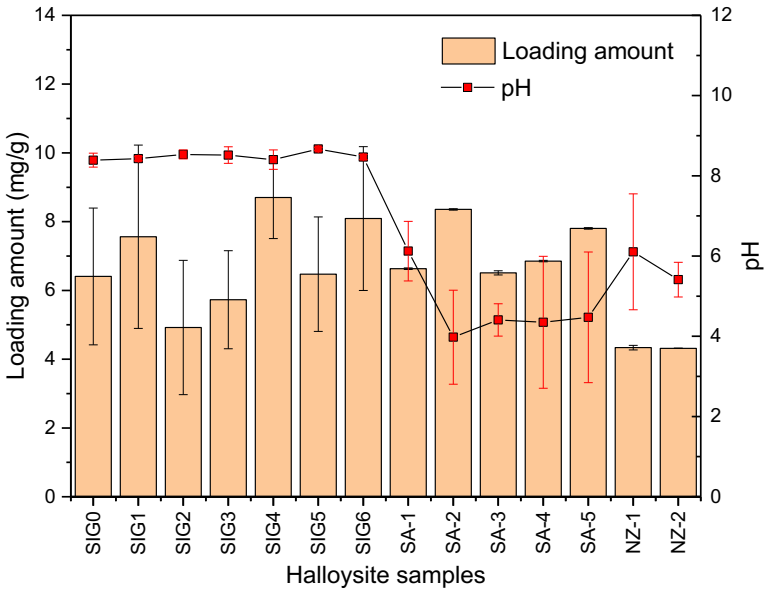


Figure 40. Sorption of imidacloprid by pristine and acid-treated halloysites.

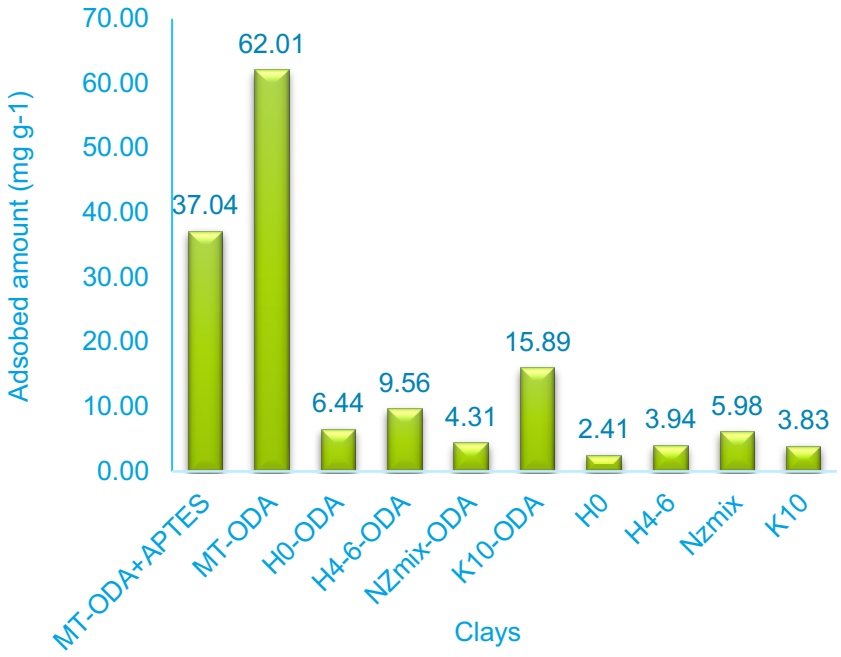


Figure 41. Sorption of imidacloprid by ODA-modified clays.

4.2.3 Entrapment of IMI with pristine and modified HNTs

In this project, along with adsorption, the lumen space of HNTs was also used for pesticide loading via entrapment to achieve 5–10 wt.%. Figure 42 shows that the pesticide was loaded via entrapment.

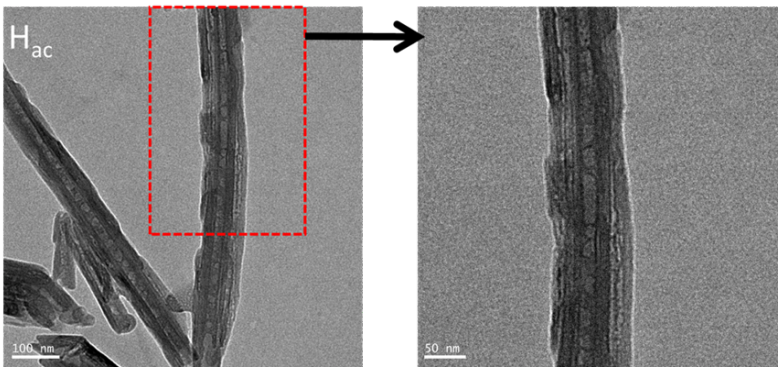


Figure 42. TEM images of pesticide-loaded acid-treated HNTs.

4.3 CHARACTERISATION OF THE POLYMER BEADS

Biodegradable alginate-based halloysite microbeads (Figure 43) were prepared. Several combinations of beads were prepared. The beads are spherical and the strength of the beads is enhanced upon incorporation of clay particles during preparation. Additional imidacloprid was loaded while preparing the beads. The highest loading achieved was ~40% (Figure 44) which was obtained through extraction of the beads with acetonitrile. The high loading was also due to the light polymer weight and high porous structure for

the polymer beads. The incorporation of clay minerals decreased the total loading of imidacloprid due to the high density of clay particles. Freeze drying of the beads helped maintain the shape and porous structure of the beads (Figure 45) compared to those of the oven-dried beads. The drying process can be critical for the entrapment of imidacloprid, as the amount of imidacloprid loaded on the oven-dried samples could be influenced.

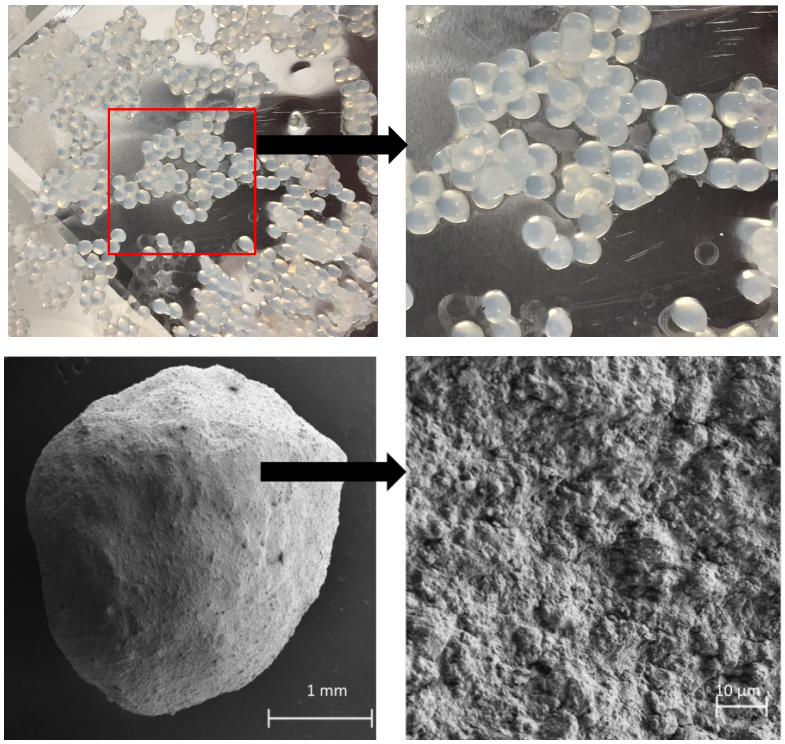


Figure 43. Alginate-based halloysite microbeads.

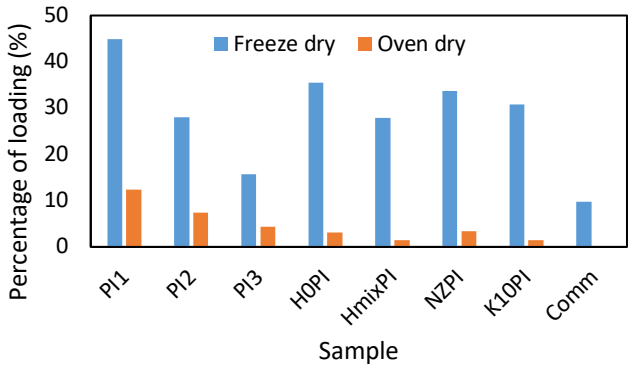


Figure 44. Loading percentage for different drying procedures during preparation.

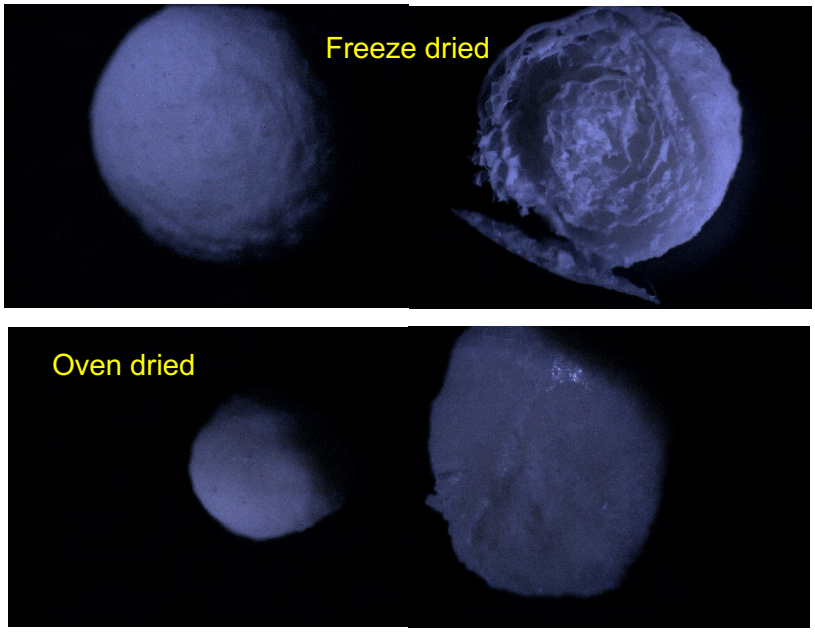


Figure 45. The morphology of imidacloprid-loaded beads (clay incorporated).

SEM was used to investigate the surface of the beads before and after loading of imidacloprid in greater detail (Figure 46). The blank polymer beads had smooth surfaces and porous structures. A detailed look at the surface reveals the deposition of salts on the surface which are due to the use of salts during preparation. The porous structure remained unchanged after loading imidacloprid on the beads. EDS analysis revealed the presence of N on the surface which was due to the molecular structure of the imidacloprid. Further incorporation of clay minerals and imidacloprid-loaded clay minerals in the beads supported the preparation of composites consisting of clay and polymer. The surface became rough and clay particles could be observed either attached to the surface or embedded with the polymer. The EDS analysis showed the presence of N and Si, which are due to the incorporation of imidacloprid and clay minerals in the polymer beads.

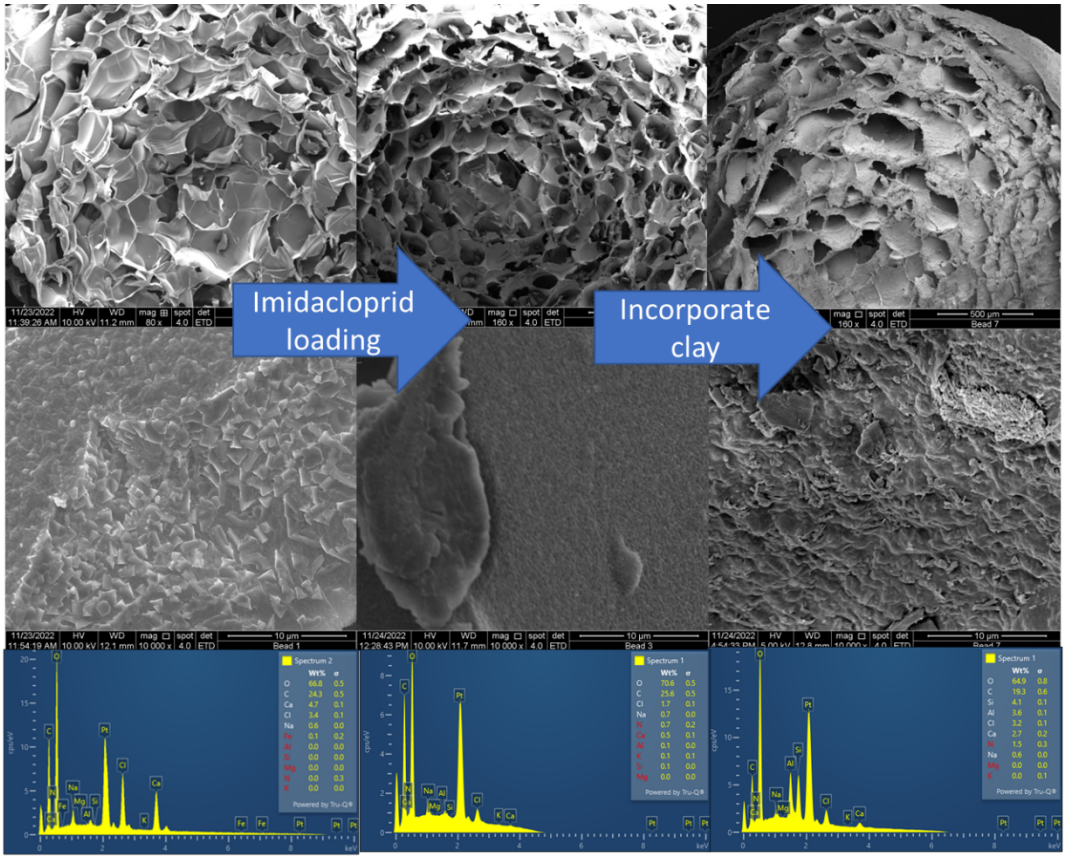


Figure 46. SEM images of the polymer beads.

TGA was performed for the imidacloprid-loaded composites (Figure 47). The weight loss of the imidacloprid-loaded polymer composite was similar to that of blank beads, which showed weight loss at approximately 230 °C, 287 °C, and 413–428 °C. The blank beads also showed small weight loss at approximately 685 °C and 760 °C. However, the percentage of weight loss decreased after the incorporation of clay minerals. The main weight loss occurred at approximately 271 °C, 426 °C and 535 °C.

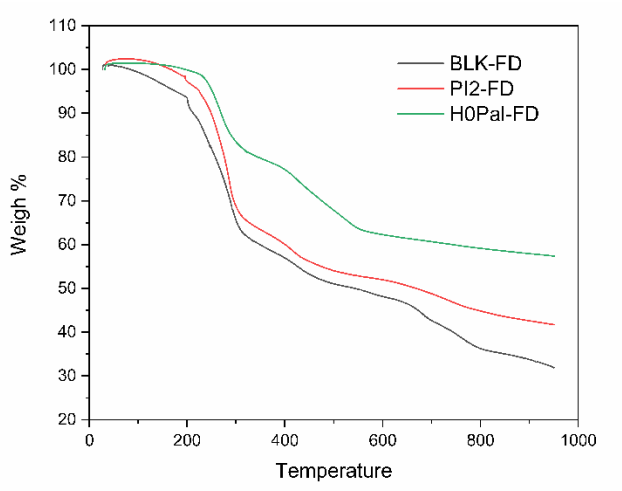


Figure 47. TGA analysis of the polymer composites.

4.4 THE RELEASE BEHAVIOUR OF IMIDACLOPRID FROM POLYMER BEADS

The release of imidacloprid from the prepared beads was investigated under aqueous conditions. The beads have different initial loading concentration as indicated in Figure 44. The beads were submerged in water for a period of time, and the amount of released imidacloprid was analysed using LC–MS. The release of imidacloprid from the freeze-dried and oven-dried beads is shown in Figure 48. A high amount of imidacloprid was released in the initial cycle, after which the amount of imidacloprid released decreased with increasing release cycles. The released concentrations were well below the solubility of imidacloprid (610 mg/L), indicating that other factors limit the release of imidacloprid. The prepared beads all showed greater release than did the commercial product. The cycle continued for 15 rounds, during which most of the samples showed a minimal amount of release (< 100 µg/L). The commercial product was released in a longer time from the freeze-dried beads. Comparative release was achieved for the products prepared and commercial samples for oven-dried samples. A significant decrease in the initial release of imidacloprid was observed, which could be due to the decreased loading amount and the difficulty in releasing from the nonporous structure from the oven-dried samples.

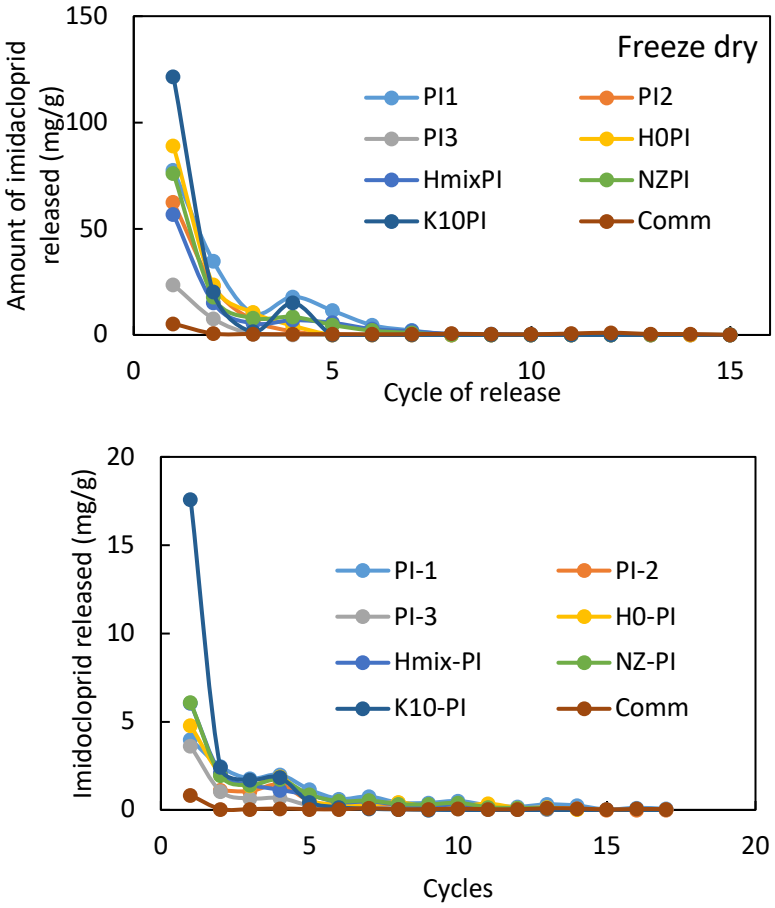
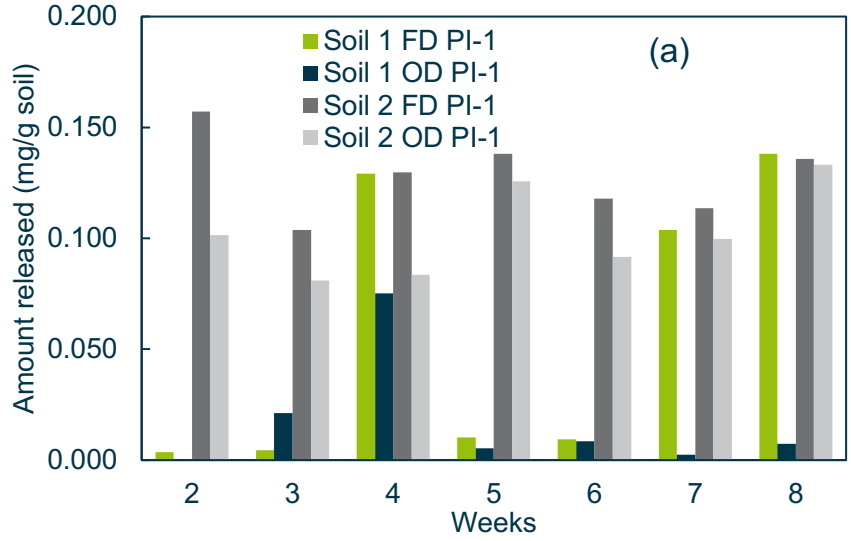
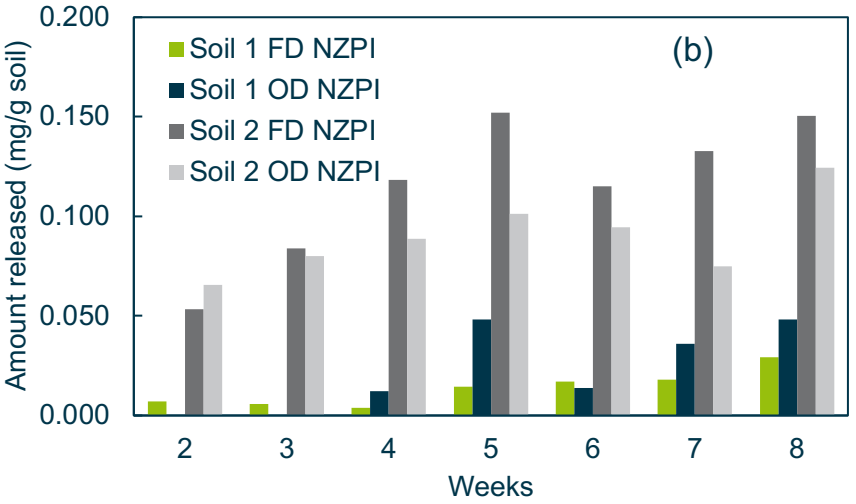


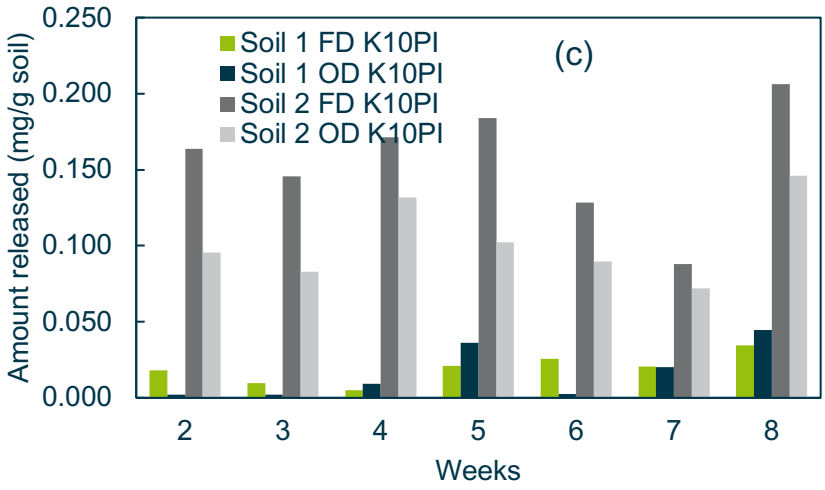
Figure 48. Release of imidacloprid from various beads.

The release of imidacloprid from the beads in the soils was investigated. The beads (PI, NZPI, K10PI, commercial product) were spiked in two soils with moisture maintained under field conditions (i.e. 20% and 23% water content for Soil 1 and Soil 2, respectively). Soil 1 and Soil 2 were sampled from sugarcane farmland with support from farmer groups which had no detectable residue imidacloprid concentrations. Soil 1 had higher pH (7.41) and EC (8.1 mS/cm) values than did Soil 2 (5.19 and 31.9 µS/cm, respectively).

The release of imidacloprid from freeze-dried and oven-dried beads in soils is shown in Figure 49. There was no imidacloprid detected in the control soils over the 8 week period. The released amount fluctuated during the 8 weeks for the composite samples which were mostly less than 10% of the total amount of theoretical amount added to the soil. A general increasing trend was shown with increasing incubation time. More imidacloprid was detected in the Soil 2 samples than in the Soil 1 samples for all the composites, indicating influences from soil types. Soil 2 is a sandy soil, while Soil 1 is a more clayey soil. This was also observed for the commercial product. Oven-dried composites generally released less imidacloprid than freeze-dried samples did which is consistent with the release behaviour in water conditions. This was particularly evident in the Soil 2 samples and early-stage Soil 1 samples. K10PI FD in Soil 2 showed greater release than that in the other samples, while the release in the commercial product was the lowest among the samples. This is consistent with the lower release of imidacloprid in water for commercial products and K10PI exhibited high release in the first several cycles in water. The PI, NZPI and K10PI OD samples exhibited comparable releases in Soil 2. These findings indicate that soil type and sample preparation procedure could influence the release of loaded imidacloprid in soils.


0.200
0.150
0.100
0.050
0.000
Amount released (mg/g soil)
Soil 1 FD PI-1
Soil 1 OD PI-1
Soil 2 FD PI-1
Soil 2 OD PI-1
(a)
2
3
4
5
6
7
8
Weeks


0.200
0.150
0.100
0.050
0.000
Amount released (mg/g soil)
Soil 1 FD NZPI
Soil 1 OD NZPI
Soil 2 FD NZPI
Soil 2 OD NZPI
(b)
2
3
4
5
6
7
8
Weeks


0.250
0.200
0.150
0.100
0.050
0.000
Amount released (mg/g soil)
Soil 1 FD K10PI
Soil 1 OD K10PI
Soil 2 FD K10PI
Soil 2 OD K10PI
(c)
2
3
4
5
6
7
8
Weeks

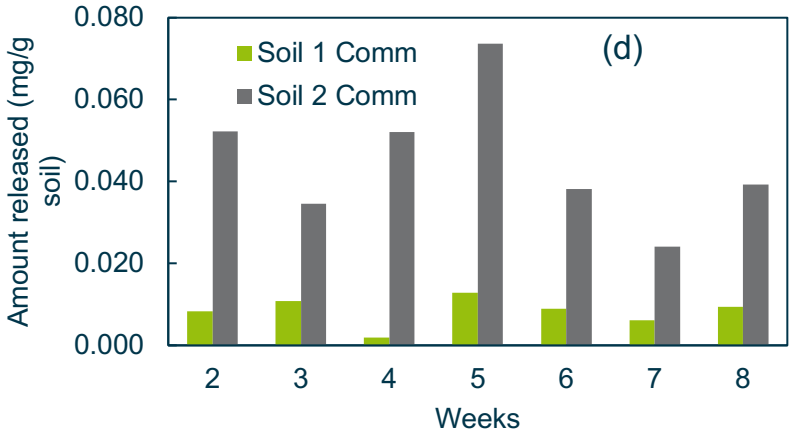


Figure 49. The release of imidacloprid from beads prepared and commercial products in two types of soils over the 8-week period. (a) freeze dried and oven dried polymer beads (b) freeze dried and oven dried halloysite polymer beads (c) freeze dried and oven dried montmorillonite polymer beads (d) commercial products

DISCUSSION

The delivery of pesticides using various materials has promising potential in the agriculture sector. The technique could provide important economic, social and environmental benefits to farmers in Australia and other countries. This technique enables the controlled release of pesticides as active ingredients to target plants and farming or agricultural areas which could significantly reduce the losses incurred by pesticides and any of their residual effects. If fewer pesticides are applied in the field, then any adverse effects of pesticides on the environment and soil functions could be significantly reduced. The utilisation of cost-effective precursor materials could reduce the cost of pesticide application. Overall, the technique is promising for the development of controlled release pesticide formulations which have the potential to greatly improve agricultural practices and not damage the environment.

However, the development of cost-effective and fit-for-purpose carrier materials and pesticide delivery systems depends on understanding the interaction mechanisms of active ingredients and carrier materials. Various carrier materials with different functional groups could provide interaction mechanisms that potentially control the release of pesticides from carrier materials. A review of various carrier materials was undertaken in this project to determine the key aspects that are vital for the development of controlled release pesticides. The porous structure and surface functional groups are critical for the interaction mechanism and entrapment of pesticides. Materials with carrier potentials include but are not limited to polymer-based nanomaterials, lipid-based nanomaterials, inorganic nanoporous materials (e.g. silica-based materials) and natural nanoporous materials (e.g. clays). These materials possess various properties, advantages and disadvantages for achieving targeted delivery. The criteria for selecting carrier materials include qualities of being nanoporous, biocompatible, economical and ecofriendly. This review provided state-of-the-art information on the carrier materials.

Among the materials discussed, inorganic nanoporous materials can offer a nontoxic, biocompatible and stable alternative for controlled-release applications. In particular, naturally available clay-based nanoporous materials can provide multiple benefits for delivery systems.

In this project, hollow tubular-structured halloysite nanoclays and platy-structured montmorillonite nanoclays were selected as potential carriers because they provide two different structures for the delivery of pesticides. The other major consideration for the utilisation of clay minerals is also linked to the abundance, low cost and local availability of resources. These features provide potential for the development of local clay minerals as integral aspects of value-added products.

The development of carrier materials also involves physicochemical treatment which can help enhance the loading capacity of the materials. In such cases, various methods, including acid treatment, thermal treatment, surface functionalisation, interpolation and composites, are reviewed during the project for clay minerals. This project focuses on two main research activities, namely (1) utilising acid to treat the surface of clay nanotubes to enlarge the porous structure and (2) incorporating organic molecules into the clay mineral surface for enhanced sorption of imidacloprid. The methods were applied to clay minerals. The results indicated higher surface functionability for clay nanotubes which are favourable for the interaction between nanoclay and imidacloprid. The incorporation of organic matter into platy-clays also enhanced how much imidacloprid was sorbed through the interaction process. Various characterisation techniques are used to understand the changes in treatment and interaction mechanisms.

The treated and untreated clay minerals were investigated for their capacity to load imidacloprid. Two methods were involved in the project, specifically vacuum entrapment and sorption immersion experiments. These two techniques were executed so that we better understand the loading of imidacloprid on clay minerals, particularly at different locations on the particles. Vacuum entrapment aimed to displace voids in nanotubes through the usage of different solvents. The sorption loading made possible the distribution of imidacloprid on active functional sites upon modification. Furthermore, the results indicated the loading of imidacloprid in modified clays which could be released from clay minerals while incorporating it into polymer beads for pesticide delivery.

The pristine and treated clay particles were all incorporated into the preparation of polymer beads where more imidacloprid was loaded. The composite materials were prepared to increase the loading of imidacloprid and improve the strength of the carrier product. Such composite materials are also being increasingly investigated for other applications (e.g. environmental remediation). In this project, a large amount of imidacloprid could be incorporated into polymer beads which could then be manipulated so that it was fit for purpose. This strategy provides flexibility for the application of products to various scenarios requiring different amounts of imidacloprid. The porous structure of fresh beads could be maintained through a freeze-drying process, which firstly enabled the internal release of imidacloprid into the pores, and secondly, resulted in more release during the initial stage. However, the loading amount could be significantly reduced if an oven-drying process was incorporated during preparation.

This also enables both the stronger entrapment of imidacloprid in the beads and elongated release. However, the overall incorporation of clay particles enhanced the strength and sustainability of the beads under water conditions. The release procedure was compared with that of the currently available commercial product. The release patterns were similar for these products. However, much greater amounts and greater releases were observed for the products than for the commercial products, given the greater amount of imidacloprid loaded. The cycle-release methods enable the estimation of longer-term release behaviour. The release pattern in the soil suggested more fluctuation data and similar results under water conditions. Soil type could influence the release amount over time.

Research results based on clay minerals for the delivery of imidacloprid are useful for the development and commercialisation of potential controlled-release products. As an emerging area of research, many decades may be needed before the more mature application of controlled-release formulas in agricultural practices is viable. Nonetheless the utilisation of low-cost clay minerals provides opportunities to reduce the cost and provide benefits to farmers and the wider society. Further research is required to identify more mature products that can be sold on the market, are economically cost-effective and environmentally friendly.

CONCLUSION

This project focused on the development of controlled-release pesticides for agricultural application and it received significant support from the sugarcane industry. Imidacloprid is widely used in the sugarcane industry and has residual effects on the surroundings and soil functions. The project included several research activities, namely the literature review, synthesis and characterisation, and the loading and releasing of imidacloprid from materials. The key findings are listed below.

1. Porous structure carrier materials with low-cost, biocompatible and ecofriendly properties are promising for the development of controlled-release pesticides. Various organic and inorganic materials could be used, while natural clay minerals were selected for this project given their low cost, abundance, local availability, environmental friendliness and manipulatable properties.
2. Chemical treatment of clay minerals enhanced the entrapment and sorption of imidacloprid on the materials. These outcomes were achieved through acid erosion and organic functionalisation which improved the active surface properties. The sorption-loading method was more feasible and easier to scale up under the pilot study conditions.
3. The incorporation of clay and modified clay minerals in the polymer product enhanced the strength of the product. More imidacloprid was loaded on the product than on the commercial product. The releasing patterns were similar for these products with commercial products demonstrating lower release during the testing period.

The research results are useful and have important implications for the further development of controlled-release pesticides for commercialisation in agriculture. This research project represents an opportunity for future detailed research in this sector of the economy.

RECOMMENDATIONS

The research project intended to prepare potential products and evaluate their release behaviour and efficacy. The milestones related to pest control efficacy have not been investigated given the challenges encountered during the project. However, the following recommendations are made should any further research or activities be conducted to enable future development and commercialisation.

- **Further research on the efficacy is needed to understand the cost-effectiveness of the products.** More imidacloprid is loaded in the products than in the current commercial product. The efficacy of these products for pest control needs to be investigated and compared with that of other commercial products, so that the cost-effectiveness and

competitiveness of the potential products can be determined. This information will be critical for evaluating potential commercialisation of any products.

- **Pilot-scale application in the field for efficacy and behaviour tests.** The products optimised upon determination of the above items can be selected for pilot-scale field application in order to determine the feasibility of commercialisation and utilisation. Various soil conditions are recommended for these tests.

The above recommendations are required to pave the way for the potential commercialisation of controlled-release products for pesticide delivery. It is recognised that potential commercialisation will require much more work being done with efforts from research institutes, government, regulatory, industry and end-users. Undoubtedly, further research and related efforts are required to realise the commercialisation potential.

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