PREPARATION AND CHARACTERISATION OF CHITOSAN-GRAPHENE OXIDE NANOCOMPOSITES AS WATER-SOLUBILISING AGENTS FOR ROTENONE

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PREPARATION AND CHARACTERISATION OF CHITOSAN-GRAPHENE OXIDE NANOCOMPOSITES AS WATER-SOLUBILISING AGENTS FOR ROTENONE

MOHD SAHLI BIN MUDA

THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE
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ABSTRACT

This research aimed to prepare and characterise chitosan-graphene oxide (CS-GO) nanocomposites, namely CS-GO 1% (w/w), CS-GO 2% (w/w) and CS-GO 3% (w/w). In this research, the potential of CS-GO nanocomposites as water-solubilising agents for rotenone was evaluated. The CS-GO nanocomposites were characterised by using fourier transform infrared (FTIR) spectrometer, scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) spectrometer and thermogravimetric analyser (TGA). The interactions of nanocomposites with rotenone were carried out through adsorption studies by using Ultraviolet-Visible (UV-Vis) spectrometer, involving several experimental parameters such as solution pH, initial concentration and contact time. The adsorption behaviour of rotenone was studied by using the Freundlich and Langmuir isotherm models. The isotherm models were employed to correlate with the adsorption equilibrium data. The adsorption kinetic data followed the pseudo-first order kinetic model. The interaction between CS-GO nanocomposites and rotenone was assessed through desorption study by using hydrochloric acid and sodium hydroxide as desorption agents. Research findings found that GO nanoparticle aggregates have a spherical shape with size in the range of 1.40 to 34.7 nm. XRD results show that the crystallinity of CS was increased following interaction with GO with a signal counts value more than 3000. Based on Langmuir isotherm model, CS-GO 3% exhibited the highest adsorption capacity for rotenone with Q_{max} value of 92.59 mg/g. The main mechanism for interaction of CS-GO nanocomposites with rotenone was through formation of hydrogen bonding. CS-GO 1%, CS-GO 2% and CS-GO 3% nanocomposites were able to increase the solubility of rotenone in water by 34.40%, 38.80% and 46.30%, respectively. In conclusion, the presence of functional groups such as hydroxyl, carboxyl and amide on CS-GO nanocomposites significantly contributed to water-solubilising mechanism. The implication of CS-GO nanocomposites as water-solubilising agents in pesticide formulations could reduce the amount of organic solvent, producing eco-friendly pesticides for a safer environment.

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT KITOSAN-GRAFIN OKSIDA SEBAGAI EJEN PEMELARUTAN-AIR BAGI ROTENON

ABSTRAK

Kajian ini bertujuan untuk menyediakan dan mencirikan nanokomposit kitosan-grafin oksida (CS-GO), iaitu CS-GO 1% (w/w), CS-GO 2% (w/w) dan CS-GO 3% (w/w). Dalam penyelidikan ini, keupayaan nanokomposit CS-GO sebagai ejen pemelarutan-air bagi rotenon telah dinilai. Nanokomposit CS-GO telah dicirikan menggunakan spektrometer inframerah transformasi Fourier (FTIR), mikroskop pengimbas elektron (SEM), mikroskop penghantaran electron (TEM), spektrometer pembelauan sinar-X (XRD) dan penganalisis termogravimetri (TGA). Interaksi nanokomposit dengan rotenon telah dijalankan melalui kajian penjerapan dengan menggunakan spektrometer Ultralembayung-Nampak (UV-Vis), melibatkan beberapa parameter eksperimen seperti pH larutan, kepekatan awal dan masa sentuh. Perlakuan penjerapan rotenon telah dikaji menggunakan model isoterma Freundlich dan Langmuir. Model isoterma telah digunakan untuk berkolerasi dengan data keseimbangan penjerapan. Data kinetik penjerapan mematuhi model kinetik tertib pseudo-pertama. Interaksi antara nanokomposit CS-GO dan rotenon telah dinilai melalui kajian penyaherapan menggunakan asid hidroklorik dan natrium hidroksida sebagai ejen penyaherapan. Dapatan kajian mendapati bahawa aggregat nanopartikel GO mempunyai bentuk sfera dengan saiz di dalam julat 1.40 hingga 34.7 nm. Keputusan XRD menunjukkan kehabluran CS telah meningkat selepas interaksi dengan GO dengan nilai hitungan isyarat lebih daripada 3000. Berdasarkan model isoterma Langmuir, CS-GO 3% mempamerkan kapasiti penjerapan paling tinggi untuk rotenon dengan nilai $Q_{\max}$ ialah 92.59 mg/g. Mekanisme utama bagi interaksi nanokomposit CS-GO dengan rotenon adalah melalui pembentukan ikatan hidrogen. Nanokomposit CS-GO 1%, CS-GO 2% dan CS-GO 3% mampu untuk meningkatkan keterlarutan rotenon dalam air masing-masing dengan 34.40%, 38.80% dan 46.30%. Kesimpulannya, kehadiran kumpulan berfungsi seperti hidroksil, karboksil dan amida dalam nanokomposit CS-GO telah menyumbang secara signifikan kepada mekanisme pemelarutan-air. Implikasi nanokomposit CS-GO sebagai ejen pemelarutan-air dalam formulasi racun perosak dapat mengurangkan amaun pelarut organik, menghasilkan racun perosak bersifat mesra alam untuk persekitaran yang lebih selamat.

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LIST OF ABBREVIATIONS

AB	Acid Yellow 36
AChE	Acetylcholinsterase
ATP	Adenosine Triphospahte
AY	Acid Blue 74
CS	Chitosan
CPS	Chloripyrifos
CS-GO	Chitosan-Graphene Oxide
CHT-PVA	Chitosan-Poly(vinyl alcohol)
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DOA	Department of Agriculture
DTX	Docetaxel
EC	Emulsified Concentrate
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FTIR	Fourier Transform Infrared
GAP	Good Agriculture Practice
GDP	Gross Domestic Product
GLA	Glutaraldehyde

GO	Graphene Oxide
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
IFS	Integrated Farming System
IPD	Intraparticle Diffusion
LOD	Limit of Detection
LOQ	Limit of Quantification
MLT	Malathion
MPT	Methyl Parathion
MPOB	Malaysian Palm Oil Board
MRLs	Maximum Residue Limits
MRPs	Mailard Reaction Products
NLCs	Nanostructure Lipid Carriers
OCPs	Organochlorine Pesticides
OF	Organic Farming
OP	Organophosphorus
OPPs	Organophosphorus Pesticides
OXPHOS	Oxidative Phosphorylation
P	Phosphorus
PCBs	Polychlorinated Biphenyls

PDA	Poly(p-phenylenediamine)
PEGDA	Poly(ethyleneglycol)
PFO	Pseudo-First Order
PI	Polyimide
POPs	Persistent Organic Pollutants
PSO	Pseudo-Second Order
PVDF	Poly(Vinylidene Fluoride)
PYR	Pyrethroids
SC	Suspension Concentrate
SLNs	Solid Lipid Nanoparticles
SEM	Scanning Electron Microscopy
Tf	Transferin Receptor
TEM	Transmission Electron Microscopy
TPGS-CS	D-α-tocopheryl Polyethlene Glycol Succinate 1000 conjugated Chitosan
TGA	Thermogravimetric Analyses
WDG	Water-dispersible Granules
WHO	World Health Organization
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Crop cultivation system provides basic materials such as wheat, rice, maize, soybean, cotton-fabric, and nuts for human survival and development worldwide. It estimates for 28% of the absolute Egypt's national gains, and become agriculture subsector-dependable for approximately half of the national's work force for its livelihood (Mahmoud et al., 2016). Since 2013, Thailand accounts for 8.4% of the gross domestic product (GDP) in agronomy and utilised the biggest sector of the labour force (39.6%) and major agriculture crops include rice, cassava, rubber, coconut, cotton, sugar cane and oil palm (Fiedler et al., 2015; Nilsson, Backman, Bjerke, & Maniriho, 2019). In 2016, Malaysia has undergo evolution and became the world's second-largest palm oil producer and exporter behind Indonesia when oil palm estate have risen to 5.74 million hectares while the palm oil mills extracted 17.32 million tonnes of crude palm oil (Szulczyk & Rahman, 2018).

Sustainable agriculture is generally considered as a fundamental component of any strategy to fight against poverty and food security issues in developing countries. The World Bank accounts more than 86% of underprivileged people living in developing countries depend on agriculture practices as the source of their self-sufficient and income (Adenle, Sowe, Parayil, & Aginam, 2012; Z. Liu et al., 2019). In Pakistan, the annual production of crops such as wheat is about 24.28 million tonnes and mostly consumed domestically. Meanwhile, rice is grown for domestic utilization and export targets, and enjoys a considerable degree of comparative benefit in international markets, particularly basmati rice. Maize plays the third role as most important cereal after wheat and rice, accounting for 4.8% and 3.5% of the overall cultivated area and agricultural output, respectively for Pakistan (Akhter Ali, Bahadur Rahut, & Behera, 2016).

In 2014, paddy planting activity was specially designated for rice production purposes in Malaysia and about 300,500 ha of land was used in Peninsular Malaysia and another 190,000 ha in East Malaysia (Adnan, Nordin, & Ali, 2018). However, the Milled rice production was only 1.82 million metric tonnes in 2016 with an average yield of 4.03 tonnes per hectare. The rice production was insufficient to support the total consumption for nearly 30.6 million of peoples which accounted as 2.4 million metric tonnes of rice demand (Durand-morat, Nalley, & Thoma, 2018). Thus, the government have to import about 30% of rice including fragrant rice which are Basmati and Jasmine type (H, M, & M, 2014) from different countries such as Thailand, Myanmar, and Vietnam as a solution to overcome the deficit in rice stock from domestic output (Dilipkumar, Seng, Sheng, & Sahid, 2017).

Many factors have been recognised for the low performance in crops production. Pest, insects and weeds are one of the current challenge and draws economic risk to crop systems (ElShafei, El-Said, Attia, & Mohammed, 2010; Mimura, Takahashi, Takanashi, & Deguchi, 2019). For example, Bangladesh encountered vital losses during rice season in 2017/2018. The threat caused by pest problems led to to a 50-percent of price increment in the domestic market due to high demand but less supply of rice. The increasing of rice imports are also reported about one million metric tonnes (Durand-morat et al., 2018). This is supported by Zhang, Zeiss, & Geng (2015) when they reported that approximately of 35% of potential crop output worldwide is lost to pre-harvest pests estimated from 24 to 34% for wheat, 30 to 38% for maize, and 25 to 38% for cotton.

It has been calculated that 30% of agricultural yield encountered lost-possibilities, caused by pathogens or insects. Without chemical treatment, these pathogens and insects are expected to increase even up about 80% in some areas of the world (Rahioui et al., 2014). By 2050, world population is assumed to increase up to 9.2 billion. Hence, there is a projected demand to increase food production by 70%. After outstanding research and development, agrochemical industries have found the key to overcome the crop losses by using pesticide formulation products (Sohni et al., 2018).

1.1.1 Definition and Application of Pesticides

Under the United States' Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), pesticides are termed as substances or mixtures designed purposely to avoid, eradicate, resist or alleviate any pest as well as rodents, insects and weeds (Armenta, Garrigues, & de la Guardia, 2007). In other words, pesticides are designed for crops protection, forests uphold, and ornamental plants security from being damage and disease attacked which is caused by insects, fungi, and other pests (Derbalah, El-Safty, Shenashen, & Abdel Ghany, 2015; Sponsler et al., 2019).

Since the discovery, pesticides are used worldwide to improve plant growth and to advance crop yield for global agricultural output, especially wheat, maize, soybeans and corns since 1940 (Bortolozo et al., 2016). The pesticide market started to nurture during the 1980s. By 1982, the pesticide market matured in the presence of herbicides treatment towards 95% of the cotton, maize and soybean acreage (Plimmer, 2001). The data on annual pesticide consumption in 2005 for selected asian countries are given in Table 1.1. From Table 1.1, it is clear that China consumed 1,000,000 tonnes of pesticides, the largest pesticide user in the whole of Asia in 2005. While, Laos was the country with the least number of tonnes of pesticides application, namely 40 tonnes. Malaysia with a total population of 25,347,000 in 2005 used 204,260,000 tonnes of pesticide with an associated cost of USD 85,020,000 to maintain crop production.

Table 1.1

Annual Pesticide Consumption (tonnes), Associated Cost (USD) and Population for Selected Asian Countries in 2005

Country	Pesticide consumption[a] (tonnes)	Associated cost[a] (USD '000)	Population[b] (millions)
Bangladesh	22,100	75,000	144.2
Cambodia	198	226	13.3
China	1,000,000	5,670,000	1,303.4
North Korea	12,000	60,000	22.9
India	164,080	320,400	1,103.6
South Korea	100000	842,638	48.3
Laos	40	200	5.9
Malaysia	204,260	85,020	26.1
Myanmar	3,030	15,095	50.5
Nepal	580	2,100	25.4
Pakistan	129,589	172,300	162.4
Philippines	31,735	158,675	84.8
Sri Lanka	6,329	49,000	19.7
Thailand	132,509	253,537	65.0
Vietnam	50,000	159,000	83.3

Note. Adapted from *Abhilash & Singh*, 2009[a], *United Nation*, 2014[b]

Based on a statistics data released by National Association of Defense Industry of Agricultural Products, agrochemicals income in Brazil has increased by over 72% from 2006 to 2012. The income generated from these products has contributed almost USD 8.5 billion in 2011, making it performed as the second largest agrochemicals-supplier in the world, only behind the United States (Goulart, Boyle, & Souza, 2015). As discussed by Chakrabort, Zhang Li, Sivakumar & Jones (2015), approximately 70% of the overall Indian workforce rely on agriculture for survival. Hence, the protection of commercial crops by pesticide application is an essential practice. By systematic and precise usage of pesticides, it can contribute to significant advantages to society: improved accessibility of good quality crops; reasonably costs for foodstuffs particularly fruits and vegetables; and clean urban environments (Cha et al., 2015).

Table 1.2 lists the benefit of the pesticide application for the worldwide. Based on the Table 1.2, there is a variety of positive benefits from different sorts of pesticide use. Farmers and growers changed their farming techniques including comprehensive use of pesticide to prevent agricultural losses to pests, weeds and rodents. For example Russia in 2003, the usage of pesticide killed apple worm population in fruits down to 1–2%, attributed to the increment of 1.5–2.0 times of orchard yield and enhanced the marketable percentage to 80–90% of production (Liberale et al., 2004). In health sector, the vectors such as mosquitoes, cockroaches and houseflies can cause infection by spreading devastating human disease such as malaria, filariasis and dengue fever especially in warmer climates. According to World Health Organization (WHO), nearly 93% of those peoples who are at moderately-high risk of malaria infection are living in India, Peninsular Malaysia, Bangladesh, Myanmar, Thailand, Indonesia and Timor Leste. which including 95% of confirmed malaria cases and deaths (Corbel et al., 2013). High-risk exposure to Malaria, children who are younger than 5 years of age accounted as vulnerable and nearly 8% of all malaria deaths reported. It is estimated that every tenth child died of malaria in 2016 (W. Y. Chang & Wei, 2018).

Table 1.2

The Benefit of Pesticide Application

Sector	Use
Agriculture	For weeds, pests, and rodents managements
Domestic personal	For garden spray and household usage including the control of animals, birds and ecto-parasites.
Material building	For protection and sheeting by incorporation of glues, plastic and paints.
Personal material	For clothing and skin care application (Example: Pediculicdes and Scabicides)
Public health	For controlling of spread disease. (Example: malaria, dengue fever, louse-borne typhus, cholera, *Japanese encephalitis*, and filariasis)
Other than agriculture and public health sector	For Controlling of vegetation and fumigation in forests, factory sites, ships and buildings.

Note. Adapted from *Abhilash & Singh*, 2009

1.1.2 History of Pesticides

The pioneer of pesticide history, dichlorodiphenyltrichloroethane (DDT) is a types of insecticide discovered by Paul Müller in 1939. It has draws a great effect in pesticide industry (Jarman & Ballschmiter, 2012). This type of organochlorine pesticides (OCPs) became the major pesticides uses after the Second World War (Grung et al., 2015). DDT was designed for agricultural purpose in the United States in 1946, and its production obtained highest demand in 1963, reaching approximately 80,000 tonnes per year in the United States (Venier & Hites, 2014). In Kenya, OCPs have been introduced since the 1940s when they were imported for animal farms application while DDT and dieldrin were widely used in Uganda to control flies, mosquitoes, banana weevils and termites (Arinaitwe et al., 2016). In Nepal, the primary usage of OCPs was reported as DDT in 1956 followed by organophosphates in the 1960s, carbamates in 1970s and synthetic pyrethroids in the 1980s (U. Ali et al., 2014).

At that period of time, pesticides became popular and had a good reputation mainly due to the successful of controlling the diseases like malaria and bubonic plague spread by mosquitoes and fleas, which had killed millions of people over time (Chowdhary, Kumar, Sharma, Pathak & Jangir, 2018). Nonetheless, this belief had changed after acknowledging the effects of DDT toxicity on birds. DDT has interrupted and caused the disorder of calcium metabolism in birds and resulted to thinner eggshells among higher trophic-order birds, such as eagles and other raptors (Al-Saleh, Al-Doush, Alsabbaheen, Mohamed & Rabbah, 2012). Since then, pesticide ordinance and rules were implemented in 1971 (U. Ali et al., 2014) and DDT was prohibited for agricultural practices in the United States in 1972 (Venier & Hites, 2014).

As a matter of fact, the application of pesticides is not ended with restriction. Instead, pesticides are slowly transformed into a more stable and persistent metabolites (Al-Saleh et al., 2012). Many countries have put effort to stimulate growth in agricultural practices by granting economic incentives to the farmers, such as reduce the tax burden by charging zero rate or very low taxes on pesticides, providing pesticide subsidies and offering free pesticides during major pest outbreaks (Schreinemachers & Tipraqsa, 2012).

Development of Pyrethroid (PYR) and Organophosphorus pesticides (OPPs) begun in 1980s to imitate the insecticidal activity of the natural pyrethrum (Wu et al., 2015; Zheng et al., 2016). For example, Thailand has implemented OPPs and PYR as the major pesticide classes used for crop protection since 2000 (Fiedler et al., 2015). Dilipkumar, Seng, Sheng & Sahid (2017) reported about the ingredients of pesticide in Malaysia. In their findings, they noted about 39,407 and 49,199 tonnes of active pesticide ingredients were used during 2006 and 2014, respectively. The data depicted an annual average growth rate of 3.1% over the past 8 years period for the minimal amount of agricultural pesticides applied in the country.

1.2 Types of Pesticide

Pesticides can be classified either based on their chemical structure or their target behaviour (Zanardi et al., 2015). Table 1.3 lists the commonly used chemical structure-based pesticides which include carbamates, organophosphates, organochlorines, and pyrethroids. As shown in Table 1.3, organophosphate was the most commonly used pesticide group followed by the organochlorine group. Organophosphate compounds usually applied in agricultural pest control programmes (Chiapella, Genti-Raimondi, & Magnarelli, 2014). Their non-persistence in environmental makes them an exquisite alternative to replace the former category of organochlorine pesticides (Furlong, Engel, Barr, & Wolff, 2014). Meanwhile, insecticides, herbicides, fungicides, rodenticides, molluscicides, nematicides and acaricides are examples for target behaviour-based pesticides (Collotta, Bertazzi, & Bollati, 2013).

Similarly, farmers and smallholders in Malaysia applied common agricultural chemicals such as herbicides, insecticides and fungicides (Alizah Ali, Noah, & Malik, 2012; Ho & Tang, 2019). In addition, the tropical countries with the nature of evergreen lustre and warm-humid climate has boost the growing progress of undergrowth and the hatching cycles of farm insects (Ern, Mokhtar, Ta, Singh, & Wan, 2015). Therefore, the practices of agrochemicals is the only way to solve the farm insects-related problems (Ibrahim, 2007; Elahi, Weijun, Zhang, & Nazeer, 2019). Figure 1.1 shows the distribution percentage of pesticide use in Malaysia in 2014. From Figure 1.1, it is clear that the contents of insecticides contributed the largest share which is 51% of the overall pesticides used by the farmers. Meanwhile, herbicides contributed 33% of the total pesticides used by the farmers and fungicides has contributed 16% of the total pesticides the most less chemical pesticides consumed by the farmers in the Malaysian agricultural region (Muazu, Yahya, & Ishak, 2015).

Table 1.3

The Commonly used Pesticides

Active compound	Chemical group
Chlorypyrifos	OPPs
Dimethoate	OPPs
Fenamiphos	OPPs
Fenitrothion	OPPs
Malathion	OPPs
Parathion	OPPs
Aldrin	OCPs
Dicofol	OCPs
Endosulfan	OCPs
Carbofuran	Carbamate
Methomyl	Carbamate
Deltamethrin	Pyrethoid
λ cyhalothrin	Pyrethoid

Note. Adapted from *Diop et al.*, 2006

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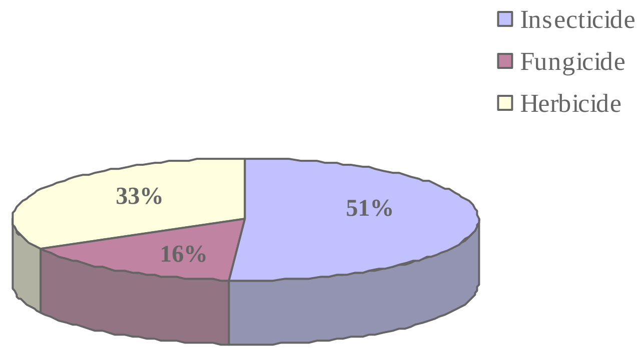

Figure 1.1. Distribution of Pesticides Use in Malaysia in 2014. (Muazu, Yahya & Ishak, 2015)

Similarly with other pesticides, OCPs have been design to protect crop and to control of vector-borne diseases such as malaria and typhus (Qu, Xu, Ai, Liu, & Liu, 2015). OCPs have been extensively used from the 1940s through 1970 as insecticides. This type of pesticides is less soluble in water, but highly soluble in organic solvents and fats (Lovecka et al., 2015). OCPs includes polychlorinated biphenyls (PCBs), cyclodienes, hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), dichlorodiphenyl dichloroethylene (DDE), dichlorodiphenyltrichloroethane (DDT) and malathion (K. Kim, Lee, Lee, Jacobs, & Lee, 2015).

The main behaviour of OCPs are environmental persistence, strong lipophilicity, and bioaccumulation in food webs and living organisms (K. Kim et al., 2015). The first artificial pesticide introduced in Sri Lanka was DDT after World War II to control malaria disease. Compared to OCPs, DDT has high chemical stability, due to the chlorinated aliphatic structure (Qu et al., 2015). In China, nearly 400,000 tonnes of DDT and 4,900,000 tonnes of HCH were released from 1950s to 1983, contributed for 20% and 33% of the world total pesticides production, respectively (L. Yuan et al., 2013).

However, due to their resistance to environmental degradation, OCPs had assembled in the food chain and caused potential consequences towards wild animals and adverse effects on human health. Particularly, OCPs are potential to interfere with hormone related to reproductive system, resulted to pre-term birth, birth defect like hypospadias, intra uterine growth retardation and cancer (T. Sharma et al., 2015). As a result, early 1970, OCPs were severely illegal in many countries including Malaysia (Karaca, Varıs, Korkmaz, Özaydın, & Perc, 2014; Qiu, Qiu, Zhang, & Li, 2019). The restriction usage of environmental persistent pesticides had stimulate the development of non-persistent pesticides, such as organophosphates (OPs), N-methyl carbamate and pyrethoid (González-Alzaga et al., 2015).

Since the application of DDT and other organochlorine pesticides is banned by many countries, organophosphorus (OP) compounds are well-known as effective control to manage multiple insects throughout the cultivation of numerous tropical fruits, rice, vegetable and legumes (Naksen et al., 2015) and become the most commonly applied chemical in agricultural pest control programmes (Melgarejo et al., 2015). Kamel et al., (2009) reported that nearly 33 million kg (73 million pounds) of active ingredient known as OP pesticides were sprayed in the United States in 2001, represented as 70% of all pesticides consumed in that country.

The OP pesticides such as methyl parathion (MPT), chlorpyrifos (CPF) and malathion (MLT) are also used in some countries for hygiene application (Ojha & Srivastava, 2014). Their widespread use are mainly due to their economical perspective, broad spectrum performances, multi-pest control efficiency and lack of targeted pest resistance (Verstappen, Hulst, Fidder, Vermeulen, & Noort, 2012). OP pesticides consist of inhibitor characteristics which is known as acetylcholinesterase (AChE) inhibitors. The enzyme can stabilise the levels of the neurotransmitter acetylcholine by catalysing the hydrolysis of acetylcholine to thiocholine (J. Yan, Guan, Yu, & Chi, 2013). Which means, OP pesticide avoid the disruption of the neurotransmitter acetylcholine, enhanced its concentration and duration of action in the body system (Munoz-Quezada et al., 2013).

Carbamates, the esters of carbamic acids are one of the main category of synthetic pesticides and are employed on a large scale worldwide owing to their broad biological activity (Berman et al., 2016). Carbamates pesticides have been widely used for 50 years ago as insecticides, herbicides, fungicides or nematocides (Li, Li, Li, & Jen, 2004; A. X. Wang, Meng, Wu, & Wang, 2019). Carbamates have gained popularity due to their rather broad spectrum of insect control, weak bio-accumulation potentials and least mammalian toxicities (Song, Shi, & Chen, 2013). Carbaryl, carbofuran and methomyl were ordinarily used carbamates (X. Yan et al., 2019). The half-life of methomyl in water was estimated as 20.8, 27.9 and 15.8 days at pH 4, 7 and 9, respectively. Unlike other non-persistence environmental pesticides, Carbaryl was highly degradable and only shows resistance in 2 to 3 weeks at 10 °C and of 1 to 5 days at 25 °C. Carbofuran was degraded in water by hydrolysis process, with a half-life 5.00, 6.60 and 8.60 days in water when exposed to sunlight (Tien, Lin, Chiu, & Chen, 2013).

Carbamates are regularly used as insecticides owing to their neurotoxic inhibitors called as enzyme acetylcholinesterase, which is competence for the transmission of nervous impulses (Denghel & Göen, 2018). In addition, industrial used carbamates as biocides and other functions such as surface sprays in garden or as baits in home products for the household pests-control management (Soloneski, Kujawski, Scuto, & Larramendy, 2015). Since 1990s, carbamate pesticides were slowly replaced by pyrethroids (Zheng et al., 2016).

1.3 Issues Related to the Improper Pesticide Application

It is known that small doses of pesticides would help to minimise pests for a good agriculture production. However, most of the farmers do not fulfill and disobey the recommended utilisation practices for pesticides when they often apply extensive use of highly toxic pesticides (Abadi, 2018). The large quantities of pesticides used purposely to exploit the speedy action in an attempt to notice full control of pests (M. Khan, Mahmood, & Damalas, 2015).

Table 1.4 shows the value of pesticide consumption by the various countries in 2014. Based on the Table 1.4, China dominated with the usage of pesticide in 2014 and was reported to use 1,807,000 tonnes of active ingredients. Meanwhile, Argentina plays as second major consumer of the pesticides which was 207,706 tonnes of active ingredients consumed in the same year. Following China and Argentina, other countries such as United States, India and Mexico were in the line with 125175, 110100 and 98814 tonnes of active ingredients consumed, respectively. United Kingdom noted as the least consumer of pesticides accounting as 18,392 tonnes of active ingredients consumed.

Table 1.4

Worlwide Scenario of Dietry Exposure to Pesticide from Major Countries

Country	Value of Active Ingredient (Tonnes)
Argentina	207,706
China	1,807,000
Germany	45,836
Italy	58,825
Japan	53,544
Malaysia	49,199
Mexico	98,814
Turkey	39,723
Ukraine	78,201
United Kingdom	18,392
India	110,100
United States	125,175

Note. Adapted from (Chawla, Kaushik, Shiva Swaraj, & Kumar, 2018)

1.3.1 Environmental Pollution

Chemical pesticides are non-friendly to environment because of their physicochemical characteristics which are tenacity to degrade, agglomerate in water surface, accumulate in plants and soils, and assemble in the bodies of shellfish and animals. As the food sources for humans, pesticides that are accumulated are recycled via the food chain, which in turn endanger human's health (Cha et al., 2015; Tsaboula et al., 2019). Chang, Wang, Wang, Li, & Xu, (2016) and X. Yuan et al.,(2019) proved that pesticides are residue in environmental specimen, like water and sediments, food, fish and even human samples.

1.3.1.1 Water

OCPs are example of a pesticide groups of semi volatile persistent organic pollutants (POPs) characterised by their bioaccumulation possibilities and recalcitrance to environmental degradation processes (Cai et al., 2016). Due to their persistent and non-biodegradable behaviour, organochlorine pesticides residues have been found in different area of the lake's environment (Arinaitwe et al., 2016). Generally, the early contamination stages occurred when the application sites has spread via surface overflow to neighboring lakes, rivers and streams. The contaminated surface waters and groundwaters are ultimately consumed as water sources in some community. Subjecting as a drinking water systems, the raw water are treated to different treatment processes in the water purification facilities. However, the treated or final drinking water could possess with the pesticides as the concentrations of the pesticides could change or remain unchanged due to the resistance of environmental degradation properties (Kamel et al., 2009).

For example, solubility of carbofuran in freshwater estimated as 700 mg/L, and therefore leaching and runoff from application sites resulted to the widespread contamination of surface water and ground water. Derbalah et al., (2015) reported that United States Environmental Protection Agency has noted that 3 mg/L for carbofuran is set for quality standard of drinking water. Besides, contamination also occurred when pesticides are transported by wind as dust to a distinct area and infected aquatic systems thousands of miles away (Nagendran, 2011).

1.3.1.2 Food

Although organophosphate pesticides are non-persistent pesticides, their residues pose major threats to food protection and ecosystem due to their acute toxicities (Zheng et al., 2016). Many reports have claimed the concerns to pesticide residues found in milk, grains, fish and vegetables (Y. Liu, Shen, et al., 2016). Fruits are one of the significant food stuffs for human diets. Numerous reports have been made regarding to pesticide residues in fruits (M. Zhang, Zeiss, & Geng, 2015). A Nordic project proved that the pesticides residue remains in the fruits when approximately 12% of the samples (fruit and vegetables imported from Southeast Asia) were above the the EU maximum residue limits (MRLs) (Skretteberg et al., 2015).

Table 1.5 lists the number of pesticide residues that has been found in a several fruits and vegetables (aubergine, mint, basil, peppermint, carambola, chili pepper, coriander leaves, beans with pods, rice, guava, pitaya, chives, sweet corn, broccoli, lychee, rambutan and papaya), as reported by Skretteberg et al., (2015).

Pesticides were detected in over 60% of apple samples in Poland, and the most commonly pesticides were fungicides (Lozowicka, 2015). Besides, the presence of pesticide residues in vegetables (Chen, Dong, Xu, Liu, & Zheng, 2015), tea (Martínez-Domínguez, Romero-González, & Garrido Frenich, 2016) and eggs (R. Ahmad, Salem, & Estaitieh, 2010) have been widely determined in agriculture sector. During 2007-2010 monitoring campaign in Zhejiang Province of China, the percentage of samples in which pesticides were found with chlorpyrifos and cypermethrin residues in various vegetable commodities was 0-22.8% and 4.2-29.3%, and ranging of 0.01-3.47 and 0.01-1.83 mg/kg, respectively. Among them, about 1.4% and 0.3% of vegetable samples above the MRLs for chlorpyrifos and cypermethrin in China, respectively (Y. Liu, Shen, et al., 2016).

Table 1.5

Number of Fruits and Vegetables (sample) Contained Pesticide Residue

Country	Number of samples analysed	Number of samples with residues above MRLs	%	Number of samples with residues at or below MRLs	%	Number of samples without detectable residues	%
Malaysia	45	5	11%	25	56%	15	33%
Pakistan	21	0	0%	4	19%	17	81%
Thailand	575	53	9%	147	26%	375	65%
Vietnam	69	23	33%	27	39%	19	28%
Korea	11	2	18%	1	9%	8	73%
Sum/ % average	721	83	14%	204	30%	434	56%

Note. Adapted from (Skretteberg et al., 2015)

1.3.1.3 Soil

Phosphorus, (P) is the second main of macronutrient in soil required by plant for excellent growth. The role of P in soil attributed to the reaction with calcium, iron or aluminum ions resulted to precipitation or fixation process by microorganism such as phosphate solubilising bacteria. The function of bacteria is to increase the available forms of P to plants (Andrew, Mahugija, Henkelmann, & Schramm, 2014). Meanwhile, photosynthetic microorganism knows as N_2-fixing cyanobacteria (blue-green algae), growth along with the crop lead to the addition of nitrogenous compounds and eventually helps the soil-binding process by cell-death (Adhy & Ath, 2015). However, pesticides have interfered with the nature of microorganism's degradation process and disrupted the sustainability of elements to sustain biogeochemical transformations. Pesticides contaminate the soil when average about one third of the overall pesticide mass use to soil ends up as soil bound residue (Boesten, 2016). Table 1.6 presents the value of DDT pesticide residue in several types of soil. Min, Li & Ping (2015) studied DDT concentration in soil samples collected from several regions. The results noted that the mean concentration of DDTs was high at the rural and urban soil of the region. The urban and rural soil of India contained the highest concentration of DDT residues.

Pesticide transmitted between the plants and their planted soils in two different pathways. Firstly, most of the pesticides could relocate onto the soil when the pesticide is implemented onto the plants. As a consequence, most of the deposited pesticide on the plant potentially washed off to the soil during the rainfall. Secondly, the residues of adsorbed pesticides in soil will remain as contaminants in the environment due to their high persistence capability in nature, and triggered the food contamination again via the plant uptake effect (Y. Liu, Li, et al., 2016). Low concentrations of pesticides could be inadequate to prompt the enzymes involved in the degradation and growing process of microorganisms, while high concentrations of pesticides can draws toxicity to the microorganisms (Lovecka et al., 2015).

Table 1.6

Value of DDT Pesticides Residue in Soil of Various Locations

Area	Land use	ΣDDT (μg/kg)
Tianjin, China	Urban and rural	56
Beijing, China	Park	65.63
Yinchuan, China	Urban and rural	2.24
Harbin, China	Urban and rural	5.43
Shanghai, China	Agricultural	21.41
Hong Kong, China	Rural	6.19
India	Urban and rural	903
Poland	Urban and rural	110
USA	Rural	211
Romania	Rural	226.9
Romania	Urban	113.1

Note. Adapted from (Min, Li, & Ping, 2015)

1.3.2 Health Risks

Water pollution consisted of variety of toxic chemicals that mixed those drinking, cooking and bathing with impure water. In addition, pesticides also pollute the livestock. Several reports have revealed that when pesticides were applied on grain and crops, and then employed to feed livestock, pesticide residues can pollute the livestock by accumulating in the animals’ fatty tissue and milk (Soloneski et al., 2015).

These pesticides accumulate in lipid-rich tissue on account of their strong lipophilic behaviour and slow biodegradability (Mustafa et al., 2015). So, the presence of residues pesticides in natural waters and in foodstuffs is of major concern for public health (Zeliger, 2011). Besides, their toxicity can interfere the neural cell development and altered synaptic formation (Furlong et al., 2014). The impact of exposure to pesticides for extended periods can lead to skin and eye irritation. Critically, These effects can cause severe problems, such as effects in reproductive system, nervous system and even cancer (Bortolozo et al., 2016). Generally, exposure could be happened in three different scenario which are occupational exposure, environmental exposure for communities living in areas with highly potential of agricultural application and dietary exposure of the general population (Cecchi, Rovedatti, Sabino, & Magnarelli, 2012).

1.4 Recent Development in Pesticide Formulation

The global application of synthetic chemicals towards cultivation indiscriminately led to environmental pollution and adverse impact on non-target organisms. Many pesticides of distinct generations live together in the environment and have become a complicated ecological issue, especially for the aquatic eco-systems. Therefore, it is imperative to uncover the alternatives in which ways are efficient in pest control but have less implication on the environment (Gakuya, Itonga, Mbaria, Muthee, & Musau, 2013). As well as they contribute low-residue and high-performance (Mnif & Ghribi, 2015), cost effective, low mammalian toxicity and limited persistence in the environment characteristic (Céspedes et al., 2014).

Biopesticides are currently receiving serious attention from scientists as a promising alternative to chemical pesticide (Murussi et al., 2015; Fawzi, Mfarrej, & Rara, 2019). Biopesticides are commonly categorised as organic products of plant or microbial origin which comprised of pesticide activity or alive microorganisms which are able to monitor pests and plant pathogens (Rousidou et al., 2013). Since biopesticides are originated from natural materials such as plants, animals and bacteria, they are usually degradable within a short time (Brar, Verma, Tyagi, & Valéro, 2006; Pino-otín et al., 2019).

Four common botanical pesticides noted as azadirachtin, celangulin, toosendanin and matrine have been reported to give the least effects on natural enemies, and therefore they have outstanding potency to be applied with biological control for integrated pest management system development (Charleston, Kfir, Dicke, & Vet, 2005). Azadirachtin (neem extract) is the first commercial plant-based pesticides that have dominated on the North American market over the past 20 years with various modes of action (Miresmailli & Isman, 2014). It has an offensive effect in which disrupts moulting by inhibiting ecdysone production and it may disrupt normal mating behavior (Jaastad, Trandem, Hovland, & Mogan, 2009).

Application of essential oils as anti-microbial agent in the vapor form has been investigated to hinder tainting of the product. Additionally, essential oils demonstrate lethal toxicity towards housefly and cockroach, and degrade completely in liquid and soil systems in a short term (Huang, Li, Liu, & Lin, 2014). Besides, vegetable oil sprays which are emulsified with oleic acid that eradicate insect and mite pests by destroying the cell membrane (Jaastad et al., 2009). The beneficial of using botanical pesticides instead of synthetic pesticides are figured in the Table 1.7.

Unfortunately, there is a limitation of the usage of botanical pesticides. Most of the plant origin pesticides is a hydrophobic compound (Holm, Molander, Lundanes, & Greibrokk, 2003; Waidyanatha et al., 2018), which have low solubility in water. Since then, it had been prepared with some formulations that contained large amount of organic solvents that led to the environment pollution once it deposited on soils or in enclosed waters (Lao, Zhang, Xu, & Jiang, 2010). Instead of using organic solvent, water dispersed pesticide formulation is currently seeking serious attention for environmental friendly pesticide development (Feng & Peng, 2012; Sarah et al., 2018).

Table 1.7

The Comparative of Commercial Plant-based Pesticides and Synthethic Pesticides

Comparators	Plant-based pesticides	Synthetic pesticides
Application	Applications restricted in medical, forestry, stored products, urban and large- scale horticulture	Various applications in almost all pest management sectors
Active ingredients	Usually combination of several secondary metabolites with various modes of actions. Concentration of active ingredients in the end product must be applied at certain level (usually set up as higher than synthetic pesticides) to be effective	Usually one or two active ingredients with specific mode of action, for example neurotoxins. Usually small amount of active ingredient is required in the final product for efficient control
Period of validity	Relatively unstable and Limited, can breakdown and / or change over time	Relatively stable and/ or long shelf life
Scalability	Limited, depending on accessibility of biomass; limited chemical standardization	Scalable for mass production; rigorous standards in place
Manufacturing cost	Variable, rely on biomass availability and / or market price	Generally lower than commercial botanical pesticides, especially off patent
Marketing pathways	Limited agriculture and mostly retail	Non-limited and large-scale agriculture, aviation and military

Note. Adapted from (Miresmailli & Isman, 2014)

1.5 Problem Statement

A pesticide product comprises of two compartments namely active and inert ingredients. Active ingredients are chemicals designated for pest control while inert ingredients are basicly solvents that act as the delivery carrier to carry the active ingredients to the target pest (Fan, Chen, Fan, Liu, & Peng, 2015; Sandeep Kumar et al., 2019). Most of the active ingredients in pesticides are hydrophobic compounds. Due to the favourable solubility behaviour of many active ingredients, organic solvents are commonly selected as the solvent of choice in commercial (Q. Zhou et al., 2017). These chemical solvents can enter and contaminate water and sources of food throughout direct application, runoff, and atmospheric deposition (Adams, Brickel, & Bhat, 2019). Based on Abu Dhabi Urban Planning Council from Estidama program, the environment is one of major priorities, importantly to be protected and developed, which in turn contributed positive outcomes in all aspects of our lives such as livestock, human beings, and agriculture (Fawzi, Mfarrej, & Rara, 2018).

When entering the landfilling sites and the land resources, organic solvents contaminated the environment by disturbing the soil composition and affect the nearby water resources. The evaporation of organic solvents will generates gases like hydrogen and ammonia, and become toxic upon contact with water (Justyna, Owczarek, Tobiszewski, & Namie, 2017). This ultimately harms the flora and fauna of the environment (Meshram et al., 2019). Hence, the implication of green solvent must be implied in order to reduce the environmental impact. In this sense, water can be considered as a potentially green solvent since is non-toxic to health and the environment. Moreover, it is the safest and least expensive solvent (Castro-puyana, Marina, & Plaza, 2017).

Therefore, it is important to develop and promote water-based pesticide formulations. Like other countries, Malaysia is committed to develop water dispersed pesticide formulation. In this study, chitosan-graphene oxide nanocomposites will act as water-solubilising agents to improve the solubility of hydrophobic rotenone. The Amount of organic solvents in pesticide production will be reduced and therefore will solve the environmental issues highlighted by Malaysian government.

1.6 Research Gap

1. Researchers have reported the potential of chitosan-coated polylactide nanoparticles as water-solubilising agents that can interact with hydrophobic pesticide active ingredients and adsorb them onto the particles. There is a need to compare with another potential of hybrid-chitosan nanoparticles as water-solubilising agents. In this study, chitosan will be used to disperse graphene oxide and provide excellent microenvironment as a water-solubilising agent for rotenone.
2. Researchers normally used chitosan-graphene oxide nanocomposites as highly effectual adsorbent materials for the dyes adsorption, heavy metals and other contaminants applications. There is a need to study several other performances of

chitosan-graphene oxide nanocomposites. In this study, the capability of chitosan-graphene oxide nanocomposites to adsorb a plant derived active ingredient namely rotenone will be evaluated, as well as it is important to elucidate the possible adsorption mechanism(s) involved.

3. Researchers have doped graphene oxide with various matrices including chitosan to produce functional biopolymer based nanocomposites with enhanced electrical, thermal and mechanical characteristics. It is significant to study the solubility behaviour of these nanocomposites. In this study, the water-solubility of chitosan-graphene oxide nanocomposites will be investigated in order to reduce the usage of organic solvent in pesticide formulation.

1.7 Research Aim

The overall aim of this study is to synthesise and utilise chitosan-graphene oxide nanocomposites as water-solubilising agents for rotenone.

1.8 Research Objectives

The objectives of this research are:

1. To synthesise chitosan-graphene oxide nanocomposites.

2. To characterise the physical and chemical properties of chitosan- graphene oxide nanocomposites.
3. To elucidate the mechanism(s) involved for interaction between chitosan-graphene oxide and rotenone.

1.9 Research Significance

This research emphasises the significant of development of water-solubilising agent as alternative way to decrease the usage of organic solvents in pecticide industry. Moreover, this research highlights the efficacy of chitosan derivative to interact with plant derived active ingredient for the improvement of pesticide performance in water-based solution.

1.10 Thesis Organisation

Chapter 1 provides introduction of the study. In this chapter, several topics such as research background, definition and application of pesticides, history of pesticides, types of pesticides, issues related to the improper use of pesticides and recent development related to pesticides are outlined for the purpose to provide a better definition of the importance of development and promotion of water-based pesticides formulation. Chapter 2 explains the chitosan, graphene oxide, rotenone and application of chitosan derivatives and graphene oxide derivatives in various fields.

Chapter 3 describes the methodology involved in the synthesis of chitosan functionalised graphene oxide nanocomposites and characterisation techniques to determine the chemical and physical properties of the nanocomposites. Chapter 4 explains and discusses the finding of this research. The results include the chemical and physical characterisations, and performance study of the chitosan-graphene oxide nanocomposites when interacting with rotenone. Conclusion from this research and suggestion for future research are described in Chapter 5.

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