DEVELOPMENT OF NEW GREEN CHITOSAN-NATURAL RUBBER AND CHITOSAN-BANANA TRUNK FIBRES BIOCOMPOSITES AS RELEASE MATRICES

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UNIVERSITI SAINS MALAYSIA
2017

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by

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Thesis submitted in fulfilment of the requirements

for the degree of

Doctor of Philosophy

January 2017

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A THESIS

Presented in Partial Fulfilment of the Requirements for
The Degree of Doctor of Philosophy in the
School of Chemical Sciences,
Universiti Sains Malaysia

By

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Universiti Sains Malaysia

2017

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DEDICATION

To

MY GRANDMOTHER (Late)

She was a special person. She always made me feel loved, wanted and special. Some of my best memories are with her. I know she made my childhood very special. It didn't matter what she was doing, she always had time for me.

To

MY MOTHER

For

Leading me into intellectual pursuits and unconditional support throughout my life

To

MY FATHER

For

Their uncompromising principles that guided me throughout my life

To

MY BROTHER, SISTERS & RELATIVES

For

Their kindness and to create a friendly environment.

To

MY WIFE

For

No issues, no drama except her dressing.

To

MY KID

When he opens his eyes, I feel alive.

To

MY SUPERVISOR & TEACHERS

For

Their guidance and kind patronage throughout my educational pursuits.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor Assoc. Prof. Dr. Mas Rosemal Hakim Mas Haris for his guidance, insightful comments, encouragement, consistent and endless support throughout my research work. I have been extremely lucky to have a supervisor who cared so much about my work, and who responded to my questions and queries so promptly. It was a real privilege and an honour for me to share of his exceptional scientific knowledge but also of his extraordinary human qualities.

I must express my gratitude to my parents, family members and relatives who experienced all of the ups and downs of my life. An especially warm and sincere thank you goes to my mother and father for their constant encouragement, love and prayers, moral and spiritual support.

I would like to thank my lab-fellow Dr. Luqman Idrees for his support and guidence, and I can't forget his valuable conversation and suggestions. I would like to thank all the members of staff at Universiti Sains Malaysia who helped me in my supervisor's absence.

Finally, I would like to thank the The World Academy of Sciences (TWAS) and Universiti Sains Malaysia (USM) for the award of 2012-TWAS-USM-Postgraduate-Fellowship (FR number: 3240268485) which allowed me to undertake this research.

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LIST OF ABBREVIATIONS

µg/mL	Microgram per millilitre
µm	Micrometre (10^{-6} meter)
AAS	Atomic Absorption Spectroscopy
AC	Activated carbon
BET	Brunauer-Emmett-Teller
BTF	Banana trunk fibres
BTF-i-CTS_{AC}	Banana trunk fibres immobilized in acidified chitosan
CRF	Controlled-release formulation
CTS	Chitosan
CTS_{AC}	Acidified chitosan
CTS_{AC}-d-NR	Acidified CTS dispersed in partially cross-linked natural rubber
ENR	Epoxidized natural rubber
EPA	Environmental Protection Agency
FT-IR	Fourier Transform Infrared
g/mol	gram per mole
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
LD_{50}	Lethal dose, the amount of a substance that kills 50% of the test organisms
mg/g	Milligram per gram
mg/L	Milligram per litre
$M\bar{w}$	Relative average weight molecular weight
ng/mL	Nanogram per millilitre

nm	Nanometre (10^{-9} metre)
NMR	Nuclear Magnetic Resonance
NPK	Nitrogen, phosphorus and potassium
NR	Natural Rubber
phr	Part per hundred
rpm	Round per minute
SDS	Sodium dodecyl sulphate
SEM	Scanning Electron Microscopy
STP	Standard temperature and pressure
TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet–Visible
v/v	Volume by volume
WHO	World Health Organisation

PEMBANGUNAN BIOKOMPOSIT HIJAU BAHARU KITOSAN-GETAH ASLI DAN KITOSAN-SERAT BATANG PISANG SEBAGAI MATRIKS PELEPASAN

ABSTRAK

Sejenis biokomposit hijau baru terdiri daripada (i) kitosan berasid (CTS_{AC}) tersebar dalam matrik getah asli (NR) tersambung-silang separa ($\overline{x}CTS_{AC}$-d-NR) di mana $\overline{x}$ = 2.5, 5, 10, 20 dan 40-phr, dan (ii) serat batang pisang (BTF) terperangkap dalam CTS_{AC} (BTF-i-CTS_{AC}) disediakan dan dicirikan dengan kaedah spektroskopi FT-IR, TGA, SEM dan BET. Keputusan analisis FT-IR dan TGA menunjukkan bahawa, dalam $\overline{x}CTS_{AC}$-d-NR, CTS_{AC} tidak tercantum tetapi tersebar dalam matrik getah asli, dan dalam BTF-i-CTS_{AC}, BTF hanyalah terperangkap di CTS_{AC}. $\overline{x}CTS_{AC}$-d-NR ($\overline{x}$ = 2.5, 5, 10, 20 dan 40-phr) digunakan sebagai matriks pelepasan perlahan untuk beberapa racun perosak dan baja, dan BTF-i-CTS_{AC} (BTF = 10%) sebagai pengerap untuk penyingkiran Cd^{2+} dan Cr^{6+} dari media berair. Tingkah laku bengkak NR tersambung-silang separa, BTF, $\overline{x}CTS_{AC}$-d-NR dan BTF-i-CTS_{AC} dalam air dan beberapa pelarut organik dikaji. Bagi $\overline{x}CTS_{AC}$-d-NR, didapati secara amnya bahawa oleh kerana CTS_{AC} bersifat hidrofilik, peningkatan muatan CTS_{AC} akan menyebabkan peningkatan pengambilan air tetapi menyebabkan penurunan pengambilan pelarut-pelarut organik. Hartanah ini boleh dikaitkan dengan lompang dalaman dibentuk oleh pengecutan CTS semasa proses pengeringan. Keputusan kajian kebolehan biodegrad dalam tanah untuk tempoh lapan bulan menunjukkan bahawa biodegradasi 7.85, 19.98, 27.68, 51.67, 62,65 dan 73,55% bagi NR tersambung-silang separa, 2.5phrCTS_{AC}-d-NR, 5phrCTS_{AC}-d-NR, 10phrCTS_{AC}-d-

NR, 20phrCTS_{AC}-d-NR dan 40phrCTS_{AC}-d-NR adalah, masing-masing. Corak pelepasan racun perosak dan baja daripada 5phrCTS_{AC}-d-NR didapati pelahan secara berterusan (secara purata sepanjang tempoh masa yang panjang 300 h) dan berlestari, yang menunjukkan bahawa biokomposit jenis ini adalah sesuai untuk diaplikasikan dalam fomulasi pelepasan secara kawalan. Corak pelepasan racun perosak contoh daripada BTF-i-CTS_{AC} boleh digolongkan sebagai pelepasan ladakan kerana titik kesetaraan purata hanya dicapai dalam lingungan 36 jam. Peratusan penyingkiran Cd^{2+} oleh BTF-i-CTS_{AC}, filem CTS_{AC}, BTF, kitin dan karbon diaktifkan (AC) daripada media akueus yang didapat, masing-masing, adalah 74.97, 60.26, 92.51, 36.91 dan 98.70%; manakala bagi Cr^{6+} adalah 97.74, 97.68, 24.44, 16.25 and 18.52%. Data BET bagi BTF-i-CTS_{AC}, filem CTS_{AC}, BTF, kitin dan AC yang diperolehi, masing-masing, adalah 3.75, 3.66, 7.82, 5.07 and 702.76 m^2/g. Nampaknya, bahawa tiada kaitan secara langsung antara kebolehan serapan yang diperhatikan dan data BET. Tambahan pula, struktur kimia bagi CTS adalah hampir sama dengan struktur kimia kitin dan BTF kecuali kehadiran kumpulan amino primer ($-NH_2$) yang menggantikan, kumpulan asetil ($-CO(CH_3)$) atau hidroksil (-OH). Penemuan ini menunjukkan bahawa penyerapan secara kimia melalui pembentukan ikatan gelang yang melibatkan kumpulan $-NH_2$ adalah faktor yang amat penting bagi penyingkiran Cr^{6+}. Pelbagai model matematik seperti peraturan pertama-pseudo, peraturan kedua-pseudo, Langmuir and isoterma Freundlich diaplikasikan pada data yang diperolehi untuk menentukan kinetik penyerapan dan mekanisme pengambilan ion logam berat tersebut. Keputusan kajian menunjukkan bahawa data yang diperolehi adalah amat bersesuaian dengan peraturan pertama-pseudo dan model

isoterma Freundlich, bermakna kadar langkah penentuan adalah penyerapan secara kimia yang melibatkan penukaran atau pengkongsian elektron antara bahan penjerap dan bahan yang diserap.

DEVELOPMENT OF NEW GREEN CHITOSAN-NATURAL RUBBER AND CHITOSAN-BANANA TRUNK FIBRES BIOCOMPOSITES AS RELEASE MATRICES

ABSTRACT

A new class of green biocomposites comprising of (i) acidified chitosan (CTS_{AC}) dispersed in partially cross-linked NR matrices ($\overline{x}CTS_{AC}$-d-NR) wherein $\overline{x}$ = 2.5, 5, 10, 20 and 40-phr, and (ii) banana trunk fibres (BTF) immobilized in CTS_{AC} (BTF-i-CTS_{AC}) were prepared and characterized by means of Fourier Transform Infrared (FT-IR) spectroscopy, Thermogravimetric Analysis (TGA), Scanning Electron Microscope (SEM) and Brunauer–Emmett–Teller (BET). Results of FT-IR and TGA analyses revealed that, in $\overline{x}CTS_{AC}$-d-NR, the CTS_{AC} was not grafted but dispersed in partially crosslinked NR, and in BTF-i-CTS_{AC}, the BTF were merely immobilized in CTS_{AC}. $\overline{x}CTS_{AC}$-d-NR ($\overline{x}$ = 2.5, 5, 10, 20 and 40-phr) were used as slow release matrices for several pesticides and fertilizers, and BTF-i-CTS_{AC} (BTF = 10 %) as sorbent for the removal of Cd^{2+} and Cr^{6+} from aqueous media. The swelling behaviours of partially cross-linked NR, CTS_{AC} film, BTF, $\overline{x}CTS_{AC}$-d-NR and BTF-i-CTS_{AC} in water and several organic solvents were studied. For $\overline{x}CTS_{AC}$-d-NR, it is found that due to hydrophilic nature of CTS_{AC}, increased in CTS_{AC} loading resulted in the increased water uptake but decreased in organic solvents uptake. These properties can be attributed to the internal voids formed by the shrinkage of CTS during drying process. Results of soil burial biodegradability studies for a period of eight months indicated percentage weight loss of 7.85, 19.98, 27.68, 51.67, 62.65 and 73.55% for partially cross-linked NR, 2.5phrCTS_{AC}-d-NR, 5phrCTS_{AC}-d-NR,

10phrCTS_{AC}-d-NR, 20phrCTS_{AC}-d-NR and 40phrCTS_{AC}-d-NR, respectively. The release behaviours of pesticides and fertilizers from 5phrCTS_{AC}-d-NR were also investigated and found to be consistently slow (on average over a prolonged period of 300 h) and sustainable, suggesting that this type of biocomposites is suitable for application in a controlled-release formulation. The release pattern of model pesticides (naphthols) from BTF-i-CTS_{AC} can be classified as a burst release because the levelling off point was attained within 36 h only. The percentage uptake of Cd^{2+} by BTF-i-CTS_{AC}, CTS_{AC} film, BTF, chitin and activated carbon (AC) from aqueous media is determined to be 74.97, 60.26, 92.51, 36.91 and 98.70%; whereas for Cr^{6+} is 97.74, 97.68, 24.44, 16.25 and 18.52%, respectively. The BET data for BTF-i-CTS_{AC}, CTS_{AC} film, BTF, chitin and AC were found to be 3.75, 3.66, 7.82, 5.07 and 702.76 m^2/g, respectively. Apparently, no direct correlation between the observed sorption capacities and BET data was observed. Furthermore, the chemical structure of CTS is almost similar to that of chitin and BTF except the presence of primary amine group ($-NH_2$) in place of either the acetyl group ($-CO(CH_3)$) or hydroxyl group (-OH), respectively. These findings revealed that chemisorption possibly via chelation involving the $-NH_2$ group was likely a dominant factor for the removal of Cr^{6+}. Various mathematical models such as pseudo-first-order, pseudo-second-order, Langmuir and Freundlich isotherms were applied to the experimental data to find out the sorption kinetic and mechanism of the uptake of metal ions. The results indicated that the data best fitted pseudo-second-order kinetic and Freundlish isotherm, suggesting that the rate-limiting step is chemisorption involving exchange or sharing of electrons between sorbate and sorbent.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Background

Pollution of water resources is a serious and growing problem, as an increasing number of pollutants are entering water supplies from industrialization and human activities [1]. The pollution of aquatic environment by toxic chemical compounds continues to occur, and many pollutants remain to be addressed because unprecedented health hazards are coming to light that did not previously existed [2]. Besides other pollutants, pesticides and fertilizers residues are the major sources of water contamination due to the increasing and repeated application [3]. Pesticides are highly toxic, biomagnify as they move up through the food chain, and persist in the environment for long periods of time [4]. The huge production and usage of these anthropogenic pollutants drawn extensive attention as they can affect the normal function of reproductive and endocrine systems of humans and animals, and classified as persistent organic pollutants [5]. According to the WHO, each year, about three million pesticide poisoning cases occur worldwide with 220,000 (0.22 millions) deaths. Unfortunately, 798,000 and 500,000 people died from self-harm, respectively in the year 1990 and 2000, over 75% of them were from developing countries [6]. According to another survey, on average 300,000 deaths have been estimated from pesticide poisoning every year. Among them, 74% of these deaths were caused by oleander and paraquat in people under the age of 25 years old [7]. Veterinary Diagnostic Laboratory, United States has reported that 0.04% of all the

animal deaths occurred due to the pesticide toxicosis [8]. In the aquatic environment, agricultural runoff and irrigation of water significantly increased the pesticide levels where the aquatic life has been affected badly, and considered to be highly toxic to fishes and other aquatic organisms [9, 10].

Nitrogen, phosphorus and potassium (NPK) are the three essential elements of fertilizers [11]. The world NPK consumption in the year 1998-1999 estimated 81×10^{12}, 14×10^{12} and 18×10^{12} gram, respectively. It has been predicted that more than 70% of the food production will have to depend on fertilizers by the year 2020 due to the increasing population growth [12]. These micronutrients are very essential to the growth and development of plants, although plants utilize these nutrients in very small quantities [13]. Fertilizers potential hazards to the environment have resulted in severe limitation to their repeated applications, due to rainfall the applied fertilizers are rapidly leached below the root zone and are accumulate in acidic subsoils [14]. As such, about 40−70% of nitrogen, 80−90% of phosphorus, and 50−70% of potassium of the applied conventional fertilizers are either decomposed or lost to the environment depending on soil conditions and method of application. Huge application of fertilizers causes large economic and resource losses, resulting in very serious public health and environmental problems [15]. The fertilizers conventional formulations may lead to high concentration levels which may produce undesirable side effects in the surrounding environment, mainly in the target area [16]. Nitrate content in groundwater already exceeds the WHO permissible level (10 mg/L) in some regions, which may cause eutrophication, a serious environmental problem [17]. In order to increase fertilizers efficiency, a suitable method must be

developed to keep the applied fertilizers in the surface soil over a prolonged period of time [18]. In conclusion, controlled-release formulation (CRF) is the only economic method to reduce nutrient losses, and to minimize the potential for negative effects associated with overdosage and repeated applications [19, 20]. CRF demonstrate many advantages over a conventional method of application such as sustained supply of nutrients over prolonged period of time, decreased repeated application, reduced potential hazards and minimized environmental pollution [16].

Due to the industrial revolution, industrial wastes and human activities are continuously contaminating surface and groundwater resources [21]. Heavy metal ions are the major constituent of various industrial wastes, introduced to the water resources by means of various industrial activities such as mining operation, textile, tanneries, batteries, paper, pesticide and fertilizer industries [22]. Most of the heavy metal ions accumulate in the living tissues, induce harmful effects on humans and animals resulting in various diseases and disorders [23]. Among heavy metals cadmium (Cd) and chromium (Cr) are the most toxic metals to many organisms even at very low concentrations [24]. Cd, a ductile lustrous, malleable transition, non-essential poisonous heavy metal with an extremely long half-life (>20 years) is classified as a probable human carcinogen. The threshold range of Cd is continuously increasing in the environment due to man-made activities such as phosphate fertilizers, industrial aqueous wastes and municipal sewage [25]. Upon absorption into human body, Cd is rapidly transported by blood to different organs where its number of physiological consequences such as renal failure, lungs inflammation, immunosuppression, kidney and skeleton damage as well as various types of cancers

have been observed [26]. Cr is considered to have high toxicity in plants, animals, and humans. Shortness of breath, coughing, wheezing, cardiotoxicity, immunotoxicity, hepatotoxicity, nephrotoxicity, irritation of nose and ulceration are the main adverse effects of Cr^{6+} over exposure [27]. In plants, decreased growth, leaf chlorosis, root damage and decreased grain yield are the common adverse effects of Cr^{6+}. It also adversely affects several physiological processes of plants such as seed germination, plant growth, water balance, status of minerals, photosynthesis and nitrogen metabolism [28]. The earlier reports indicated that several technologies have been used to remove metal ions from aqueous wastes, however adsorption, a physicochemical treatment is one of the effective techniques for the removal of metals ions from aqueous medium [29]. Rahim and Mas Haris (2015) have suggested biopolymers such as alginate, microalgal, chitin and chitosan for the removal of heavy metal ions [30].

1.2 Chitosan

Chitosan (CTS) is a linear, biodegradable, biocompatible, non-toxic and eco-friendly natural copolymer widely used in the CRF of drugs, pesticides and fertilizers [31]. In addition to this, CTS is also effective in the removal of organic pollutants, microbes and heavy metals. The U.S. Environment Protection Agency (EPA) has approved CTS for the purification of drinking water [32]. Structurally, CTS is composed of β(1→4)linked *D*-glucosamine and *N*-acetyl-*D*-glucosamine repeating units [30]. Chemical structure of CTS, chitin and cellulose is exactly alike, the only difference is the presence of $–NH_2$, $–NHCOCH_3$ and –OH functional groups at C_2 position, respectively, as shown in Figure 1.1 [33]. The CTS average molecular

weight and degree of deacetylation vary from 3,800 to 500,000 g/mol and 60 to 98%, respectively. CTS is a non-toxic biopolymer with LD_{50} of 16 g/kg of the body weight in mice, similar to that of sugar and salt [34]. CTS is a bifunctional biopolymer containing cationic amino groups which can be easily react with inorganic materials and other polymers. CTS is the second most abundant biopolymer after cellulose, derived from chitin by alkaline *N*-deacetylation. Whereas, chitin, β(1→4)linked *N*-acetyl-*D*-glucosamine is a linear biopolymer of major importance, first identified in 1884 [35]. Chitin is the main component of the exoskeleton of arthropods, molluscs, crusts, carapaces and shells of crustaceans such as crabs, shrimps and lobsters, and also an ingredient of cell walls of yeast and fungi. The chitin annual estimated production ranges from 10^{10} to 10^{12} tons [34]. Chitin can be extracted from exoskeleton of crustaceans by various methods, however the common method of chitin and CTS extraction is described in Figure 1.2 [36].

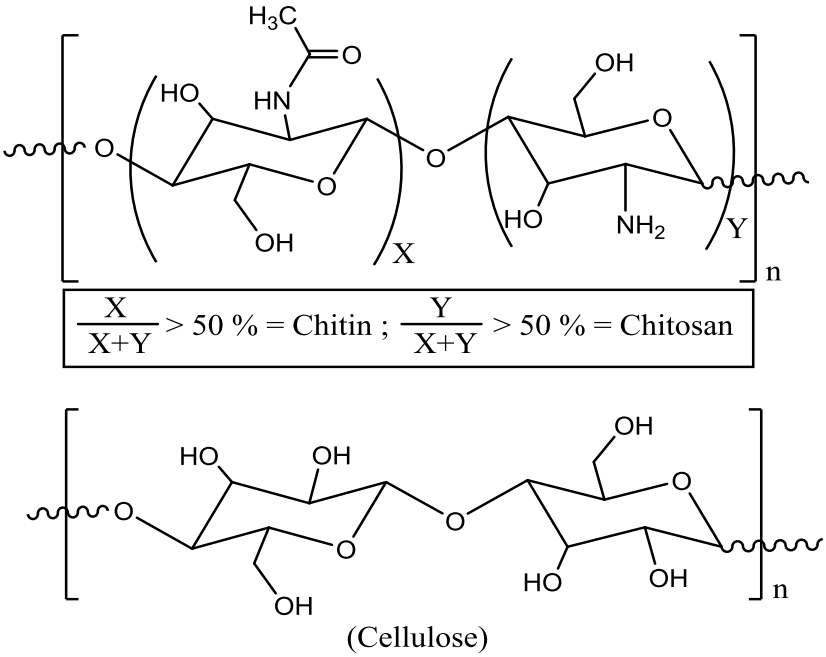

Figure 1.1: Chemical structures of CTS, chitin and cellulose.

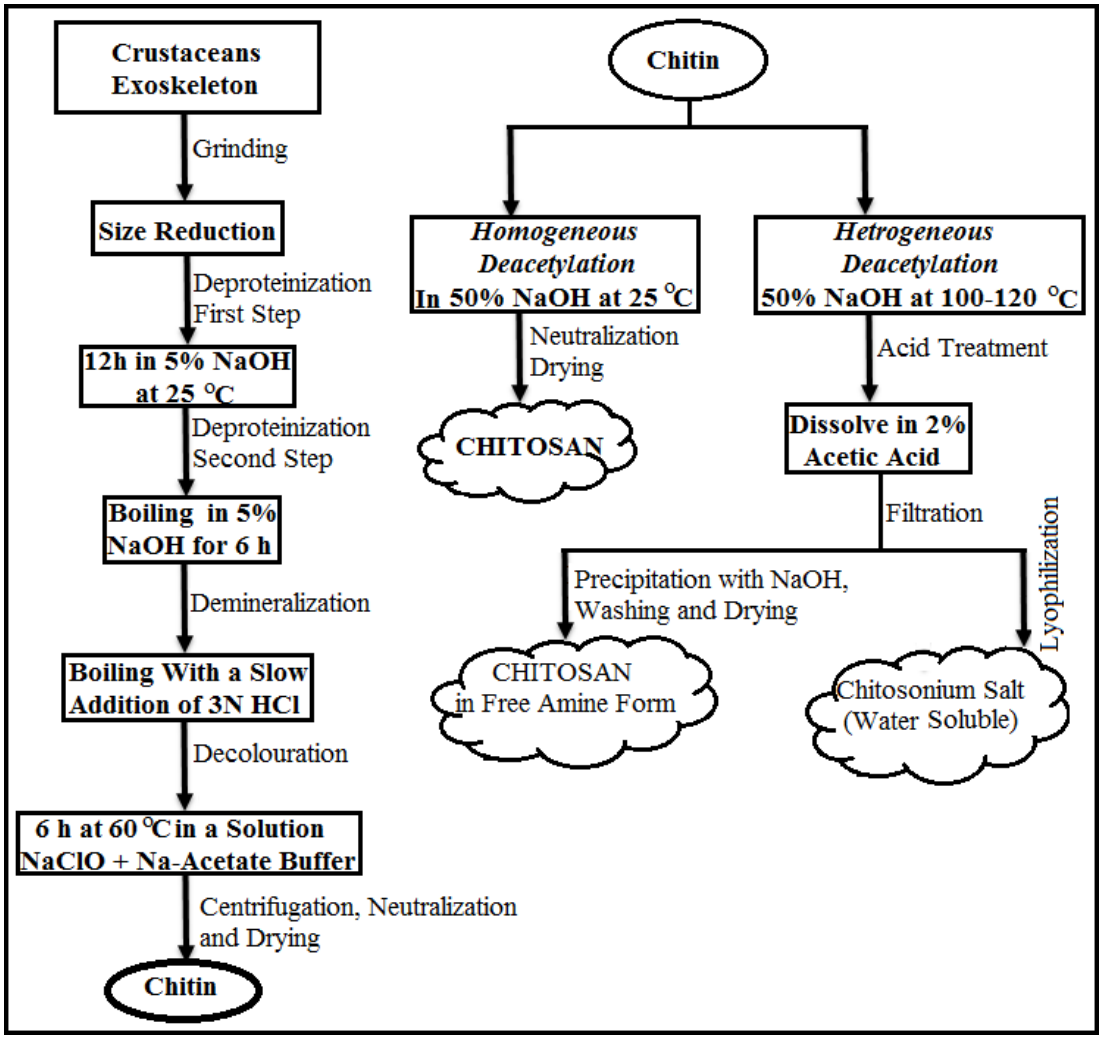

Figure 1.2: Extraction of chitin and CTS from crustacean exoskeletons [36].

1.2.1 Applications of CTS in Controlled Delivery

The previous studies showed that CTS matrix, beads, capsules, microspheres and nanoparticles have been used extensively for the controlled-release of not only drugs [37-44] but also for pesticides and fertilizers which are of interest in this research study. Some of the literature data are summarized in Table 1.1 for the controlled release of pesticides and fertilizers. Yi et al. [45] prepared photo-crosslinked carboxymethyl CTS. Photocrosslinkable carboxymethyl CTS was dissolved in distilled water and the solution was poured into a shallow silanized glass

dish. The solution was cross-linked and irradiated by UV-light. The sample was immersed in distilled water at room temperature for 48 h to remove unreacted photocrosslinkable carboxymethyl CTS, and dried under vacuum. The release behaviour of the diuron (pesticide) was studied. Kumar and Aminabhavi [46] prepared beads of poly(vinyl alcohol)-grafted acrylamide with sodium alginate by crosslinking with glutaraldehyde. The *in vitro* release studies of cypermethrin, a widely used pesticide, were performed under static conditions. Grillo et al. [47] prepared and characterized nanoparticles composed of CTS and sodium tripolyphosphate (TPP). The release behaviour of paraquat was evaluated and the release equilibrium time was obtained within 6 h. Wu and Liu [15] prepared poly(acrylic acid-co-acrylamide) coated granules of NPK fertilizer which possessed the three-layer structure. The core layer was water-soluble NPK fertilizer, the inner coating was CTS, and the outer coating was poly(acrylic acid-co-acrylamide) polymer. The nutrients slow release behaviours of the formulation was investigated in soil. Hussain et al. [48] prepared CTS microspheres via emulsification followed by cross-linking with genipin. The microspheres were used as a slow-release matrix for urea. The release rate was found to be dependent on the concentrations of urea, chitosan, cross-linking agent and temperature of the release medium. Higher concentration of loaded urea enhanced the release rate, whereas higher concentrations of CTS and cross-linking agent reduced their release rate. Higher temperature of the release medium improved the release rate. Gupta and Jabrail [49] prepared microspheres composed of tripolyphosphate-sodium and hexametaphosphate crosslinked chitosan by blowing through a nozzle as fine

droplets into a trough containing 250 mL of 5% methanol solution of NaOH (0.1M). The CTS microspheres were dried and the release of urea and rifampicin was studied in aqueous medium at a pH of 4.0. The literature survey indicated that all the controlled release formulations have been developed using either organic solvents or expensive chemicals which discouraged large scale production.

Table 1.1: List of CTS based formulations prepared by different methods for the controlled-release of pesticides and fertilizers

Controlled-release Application	Type of System	Method Used	Type of Compound	Reference
Pesticides	Hydrogel	Gelation of a photocrosslinkable carboxymethyl CTS	Diuron	[45]
	Beads	Polymerizing acrylamide in a 10% (w/w) PVA solution using ceric ammonium nitrate	Cypermethrin	[46]
	Nanoparticles	Ionic gelification	Paraquat	[47]
	Nanoparticles	Ionic gelification	Paraquat	[50]
	Nanocapsules	Interfacial deposition of preformed polymer, with modifications	Atrazine	[51]
Fertilizers	Granules	Spray drying	(NPK) fertilizer	[15]
	Microspheres	Emulsification followed by cross-linking	Urea	[48]
	Microspheres	Polyphosphate-anion-crosslinked CTS	Hydroxy urea and Rifampicin	[49]

1.2.2 Applications of CTS in the Removal of Metal Ions

Heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various adverse effects on animals and plants. The use of cost effective and eco-friendly materials has attracted much attention to replace costly

wastewater treatment techniques such as ion-exchange, electroflotation, membrane separation, electrodialysis, chemical precipitation, solvent extraction etc. Sorption, a physicochemical treatment is one of the effective techniques in removing metal ions from aqueous medium [29]. The literature strongly suggested that natural polymers are the excellent alternative sorbents for the removal of metal ions [52-54]. CTS, a natural polymer is the ideal sorbent for the removal of metal ions due to natural abundance, biodegradability, biocompatibility, easy accessibility, cost effectiveness, environmental friendliness, simple processing and high selectivity. Therefore, researchers have focused to develop polymeric hydrogel, composites, beads, microspheres and nano-particles for the removal of metal ions. CTS has higher sorption capacity towards metal ions due to the presence of reactive functional groups such as hydroxyl (−OH) and amino ($-NH_2$) [55]. The literature survey indicated that the sorption capacities of CTS have been increased by means of both physical and chemical modification for the removal of several metal ions, as shown in Table 1.2.

Laus and De Favere [56] prepared crosslinked CTS matrix using epichlorohydrin and triphosphate as crosslinking agents. The resulting adsorbent was tested for metal adsorption. The adsorbent was used in batch experiments to evaluate the adsorption of Cu(II) and Cd(II) ions in single and binary metal solutions. In single metal solutions the maximum adsorption capacities of Cu(II) and Cd(II) ions, obtained by Langmuir model, were 130.72 and 83.75 mg/g, respectively. Monier and Abdel-Latif [57] modified CTS with phenylthiourea via thioamide bond formation between the amino group in CTS and the active isothiocyanate group of

phenylthiourea. The reaction mixture was refluxed for 12 h. Then the product was isolated by filtration and thoroughly washed with methanol and distilled water. The resin was evaluated for the uptake of Cd(II) and the sorption capacity was 135 mg/g at pH 5.0. Yang et al. [58] synthesized Fe_3O_4 magnetic nanoparticles by chemical coprecipitation method. The magnetic CTS was modified with α-ketoglutaric acid. Typically, 0.25 g α-ketoglutaric acid was dissolved into 50 mL acetic acid buffer solution containing 100 mg magnetic CTS (pH 5.6). After stirring for 24 h, the obtained solid was separated by magnet, and washed 3–4 times with ethanol and diethyl ether, and freeze-dried. The sorption capacity towards Cd(II) of the modified CTS was 201.2 mg/g at pH 6.0.

Chen et al. [59] synthesized a series of CTS/montmorillonite–Fe_3O_4 magnetic microspheres. CTS is dissolved in 2% (v/v) acetic acid aqueous solution. Then Fe_3O_4 and montmorillonite were dispersed in the CTS solution under ultrasonic stirring for 2 h at 1500 rpm. Paraffin and emulsifier (Span-80) were poured into the as-prepared dispersion under mechanical stirring at 40 °C. After stirring for 1 h, glutaraldehyde (25%, v/v) was slowly dropped into the reaction system and stirred in a water bath at 60 °C for another 1 h. The resulting microspheres were centrifuged and washed with petroleum ether, ethanol and distilled water for three times, respectively. Finally, the product was dried in a vacuum oven at 60 °C. The sorption capacity of the microspheres was found 48.3 mg/g for Cr(VI) at a pH of 2.0. Kumar et al. [60] prepared n-butylacrylate modified CTS. 4.0 g of CTS was added to 8.0 mL of formic acid and n-butylacrylate (0.03 mol) was mixed, and irradiated in a microwave oven for 3 min. The n-butylacrylate grafted CTS was investigated for the

Table 1.2: Sorption capacities of CTS and modified CTS materials for various metal ions at different conditions of pH and initial concentration

Material used	Metal Ions	Initial Conc: (mg/L)	pH	Capacity (mg/g)	Reference
CTS epichlorohydrin	Cd(II)	50	7	83.7	[56]
CTS-phenylthiourea resin for	Cd(II)	100	5	135.0	[57]
α-ketoglutaric acid-modified magnetic CTS	Cd(II)	1000	6	201.2	[58]
Montmorillonite–Fe_3O_4	Cr(VI)	60	2	48.3	[59]
n-butylacrylate grafted CTS	Cr(VI)	20	3.5	17.1	[60]
CTS-single-walled carbon nanotubes	Cr(VI)	0.5-100	4	35.6	[61]
Iron-impregnated CTS	As(III)	1.007	8.0	6.5	[62]
CTS-coated sand	As(III, V)	0.5	7.0	17.0	[63]
Magnetic nanoparticles impregnated CTS beads	As(III, V)	2-10	6.8	35.3-35.7	[64]
Triethylene-tetramine grafted magnetic CTS	Pb(II)	200	6	370.6	[65]
Dithiocarbamate modified CTS beads	Pb(II)	0.02 M*	6	359.7	[66]
Imprinted CTS bead	Pb(II)	12	5.5	79.2	[67]
Polystyrene-supported CTS	Cu(II)	10-100	6.0	99.8	[68]
CTS–zeolite composites	Cu(II)	100	3-5	14-25	[69]
Cross-linked CTS beads	Cu(II)	0-14	6.0	45.9	[70]
CTS flake	Hg(II)	25-100	4.0	850.0	[71]
CTS cross-linked with genipin	Hg(II)	50	6.5-7	4.0	[72]
Xanthated CTS	Hg(II)	100-1000	4	425	[73]
Polyethylene oxide (PEO)/CTS nanofiber	Ni(II)	100	5	175.1	[74]
CTS–MAA nanoparticles	Ni(II)	50	5	0.87	[75]
Succinyl-grafted CTS	Zn(II)	100-200	6	290	[76]
CTS, itaconic acid and methacrylic acid	Zn(II)	4.6- 660	5.5	105.5	[77]
CTS/hydroxyapatite composite	Co(II)	10-500	7	190.8	[78]
Glycine modified CTS resin	Mn(II)	0.005 M	6	1.3	[79]
Imprinted O-carboxymethyl CTS beads	Ag(I)	160.5	5	156.32	[80]
CTS	Al(III)	5-40	4.0	50.27	[81]
Diethylenetriamine-functionalized CTS	U(VI)	209	4-6	160	[82]
CTS beads	V(III, IV, V)	0.500	6	99-100%	[83]
CTS nanoparticles modified with ethylenediamine	Pt(IV)	30–120	2.0	171	[84]
CTS nanoparticles modified with ethylenediamine	Pd(II)	30–120	2.0	138	[84]

* Molar

removal of Cr(VI) and the capacity was 17.1 mg/g at pH 3.5. The literature survey indicated that CTS has been modified/grafted with several organic and inorganic materials and their sorption capacities were evaluated. Some of the materials are carbon nanotubes [61], magnetic nanoparticles [64], triethylene-tetramine [65], dithiocarbamate [66], polystyrene [68], zeolite [69], genipin [72], xanthane [73], polyethylene [74], succinyl [76], hydroxyapatite [78], glycine [79], diethylenetriamine [82] and ethylenediamine [84], and their sorption capacities are 35.6, 35.3, 370.6, 359.7, 99.8, 14, 4.0, 425.0, 175.1, 290.0, 190.8, 1.3, 160.0 and 171.0 mg/g, respectively. The literature data showed that the use of organic solvents and expensive chemicals restricted the application of these materials on industrial scale.

1.3 Natural Rubber Latex

Natural rubber (NR) is a non-toxic, easily available [85] and naturally abundant biopolymer obtained from *Hevea brasiliensis* tree as a sticky latex of milky appearance [86]. *Hevea brasiliensis* (native plant of Brazil) fulfils 99% [87] of the World NR demand while small amount of NR can be obtained from other plants such as *Ficus elastica* (rubber plant), *Taraxacum kok-saghyz* (Kazakh dandelion), *Manihot esculenta* (cassava), *Parthenium argentatum* (guayule) and *Funtumia castilla* (Mexican rubber tree). As such, thousands of plant species which can produce NR latex have not been identified. The suitable climate for *Hevea brasiliensis* plantation, growth and development has been found in the tropical regions such as Malaysia, Indonesia and Thailand [88]. The chemical structure of NR, *cis*-1,4-polyisoprene is shown in Figure 1.3.

Chemically, NR latex is a colloidal dispersion of rubber hydrocarbon in an aqueous medium [89]. Chemical composition, NR latex contains 35% *cis*-1,4-polyisoprene [90] dispersed in 60% water along with other solid materials [91] with mean particle size of 0.15 to 3.0 mm. Besides *cis*-1,4-polyisoprene, NR latex contains 1.5% proteins, 1.5% carbohydrates, 1.4% lipids, 1.0% quebrachitol, 0.5% minerals, 0.4% organic acids, 0.4% phospholipids and 0.2% amino acid [92].

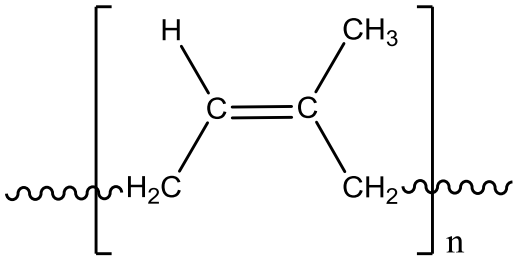

Figure 1.3: Chemical structure of *cis*-1,4-polyisoprene [88].

Due to its unique properties, such as dynamic mechanical properties and the ability to undergo large elastic deformation and to absorb energy, NR is widely used in various applications. NR products have been used in commodity applications, such as tires, shoes, rubber bands, tubes, chairs, outer covering of electric instruments, gloves, condoms, rubber utensils etc. Recently, the use of NR has been expanded into engineering purposes, for example, construction parts, automotive and machine parts [93].

The literature survey revealed that the use of NR has not been investigated for the controlled-release of pesticides and fertilizers which might be due to the problems associated to the biodegradation, storage and stability of NR latex at ambient conditions. Usually, NR latex air exposure leads to bacterial decomposition

which resulted in latex partial coagulation. The NR latex particles are surrounded by protein anions and are thus negatively charged which hinders further coagulation of the latex [88].

The stability of the dispersion is of great importance: a stable system is the one in which there is no phase separation or particles aggregation. The stability of a dispersion depends on the interaction (collision) among the particles. The interaction may be attractive or repulsive due to the Van der Waals forces. Mostly, dispersion stability depends upon the balance of attractive and repulsive forces. In case the of dominate attractive forces, particles form an aggregation and the dispersion is termed as "unstable dispersion" while on the other hand, if the particles have a mutual repulsion then the dispersion remains stable [94]. An initially formed aggregation, a floc may or may not phase out, if the floc phase out, the dispersion is said to undergo coagulation, some of these processes have been shown in Figure 1.4.

However, strong attractive forces have been observed among the particles of a dispersion. Therefore, it is necessary to produce strong repulsive forces among the particles in order to provide significant stability to the dispersion system. The dispersion can be stabilized by surrounding the dispersed particles either by charge/electrostatic stabilization (an electrical double layer), steric stabilization (chemically attached polymer molecules) or use of a surfactant.

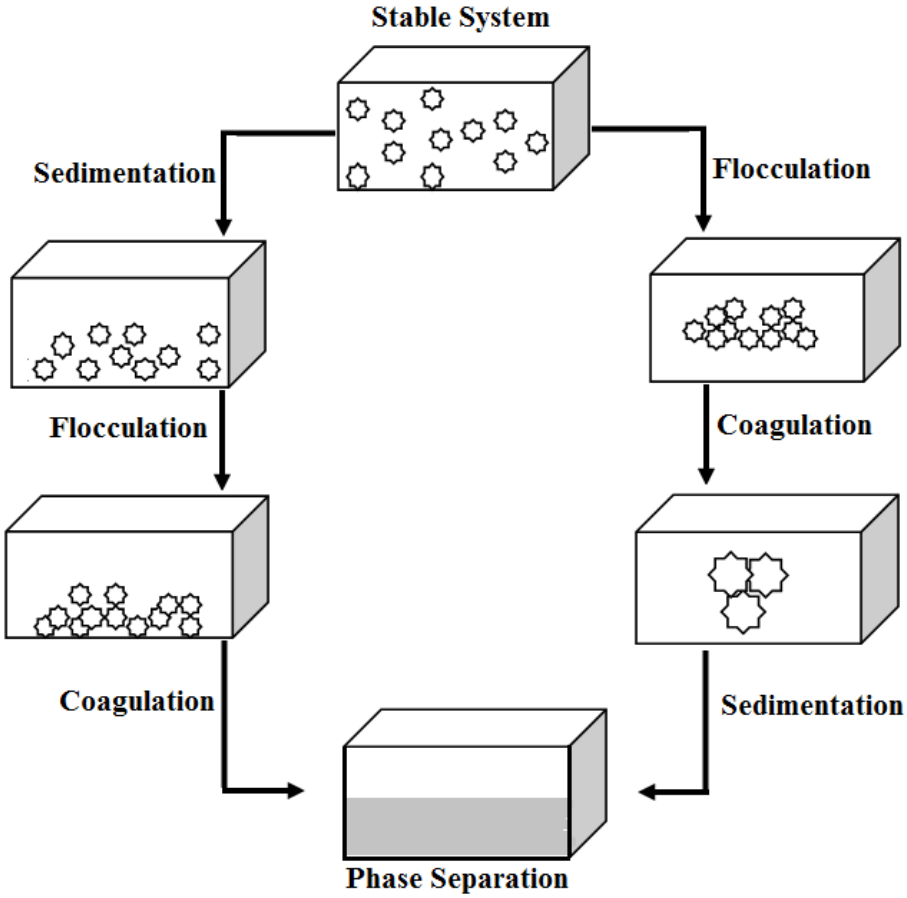

Figure 1.4: Aggregation/coagulation of particles in a dispersion [94].

Electrostatic stabilization is a process in which the attractive forces between the particles can be counterbalanced by the adsorption of ionic groups onto the surface of a colloidal particle to form a charge-neutral double layers. The colloidal particles can be surrounded by mutually balanced of opposite charged ions to maintain the electroneutrality. In electrostatic stabilization, mutual repulsion of double layers surrounding the particles provides high dispersion stability. Steric stabilization is a process where polymer of higher molecular weight can be attached to the surface of colloidal particles. This polymer forms an outer coating layer which separates the particles from one another and the dispersion can be stabilised.

However, the easiest way to increase the dispersion stability is by using surfactant. At low concentration, surfactant has the ability of adsorbing into the interface of a dispersion system and usually helps to reduce the interfacial free energy. Usually surfactant has a lyophobic and lyophilic groups, thus it is amphiphilic in nature. The lyophobic group may increase the free energy of the dispersion by distortion of the solvent structure. As the free energy of the system increases, the system tends to reduce the interaction between the solvent molecules and the lyophobic groups, resulting in a decrease of the solvent surface tension which increase the dispersion stability [94]. Few attempts have been carried out to prepare stable controlled release formulations using aqueous dispersions of the hydrophobic polymers. However, the attempts have been unsuccessful [95].

1.4 Banana Trunk Fibres

The use of natural fibres as reinforcement for polymeric composites has been developed around the world. Some of the advantages of natural fibres are low density, medium stiffness, thermal resistance, high disposability, low abrasion and cost effectiveness. Banana Trunk Fibres (BTF), a natural fibres can be described as lignocellulosics, i.e. resources comprised primarily of lignin, cellulose and hemicellulose. In general, lignocellulosics comprise of wood, agricultural residues, grasses, water plants and other plant substances. Structurally, cellulose is the −OH enrich linear polymer of β(1→4) linked *D*-glucose units (Figure 1.1) [96]. Plant fibres have the chemical composition and properties which make them suitable for composite, textile, pulp and paper manufacture. Furthermore, the plant fibres can be used to produce food, bio-fuel, chemicals and enzymes. Plant fibres are the largest

source of cellulose which is the most abundant natural polymer on the earth surface. According to an estimation, 2×10^{11} tons of lignocellulosics are produced every year, compared to 1.5×10^{8} tons of synthetic polymeric compounds [97].

The literature survey showed that plant fibres particularly BTF have been used as reinforcing material in polymer composites [98-100]. As such, the application of banana fibers for the removal of metal ions is also well known [101-103]. The literature study indicated that BTF has been used extensively for the removal of colours [104] and dyes from aqueous wastes [105]. Sathasivam and Mas Haris (2010) have reported the successful removal of oil from aqueous medium using fatty acid-modified BTF [106]. Therefore, it can be expected that the use of BTF in the composite materials should have to increase the mechanical properties and sorption efficiency of the biocomposites towards metal ions and organic pollutants.

1.5 Methods of Pesticides/Fertilizers Application

1.5.1 Conventional Method

One of the most common pesticide application methods is the use of mechanical/hydraulic sprayers. Hydraulic sprayers, containing mixture of water and agrochemical, converted the agrochemical formulation into large droplets as liquid suspension, applied by forcing the spray mixture through a spray nozzle under increased pressure. The droplets size can be controlled either through altering the pressure or by using varying size of nozzles [107]. Even though the technique is easily applicable, it is highly unsafe, non-eco-friendly, causing soil, water and air contamination [108]. Furthermore, 90% of the applied pesticide or combination of

pesticides are either lost or decomposed which not only increased the overall operational cost but also caused undesirable environmental problems. Agrochemical leaching and run-off are the main causes of surface and groundwater contamination [45, 109, 110]. The conventional agrochemical application method; the soil, water and air contamination routes are shown in Figure 1.5.

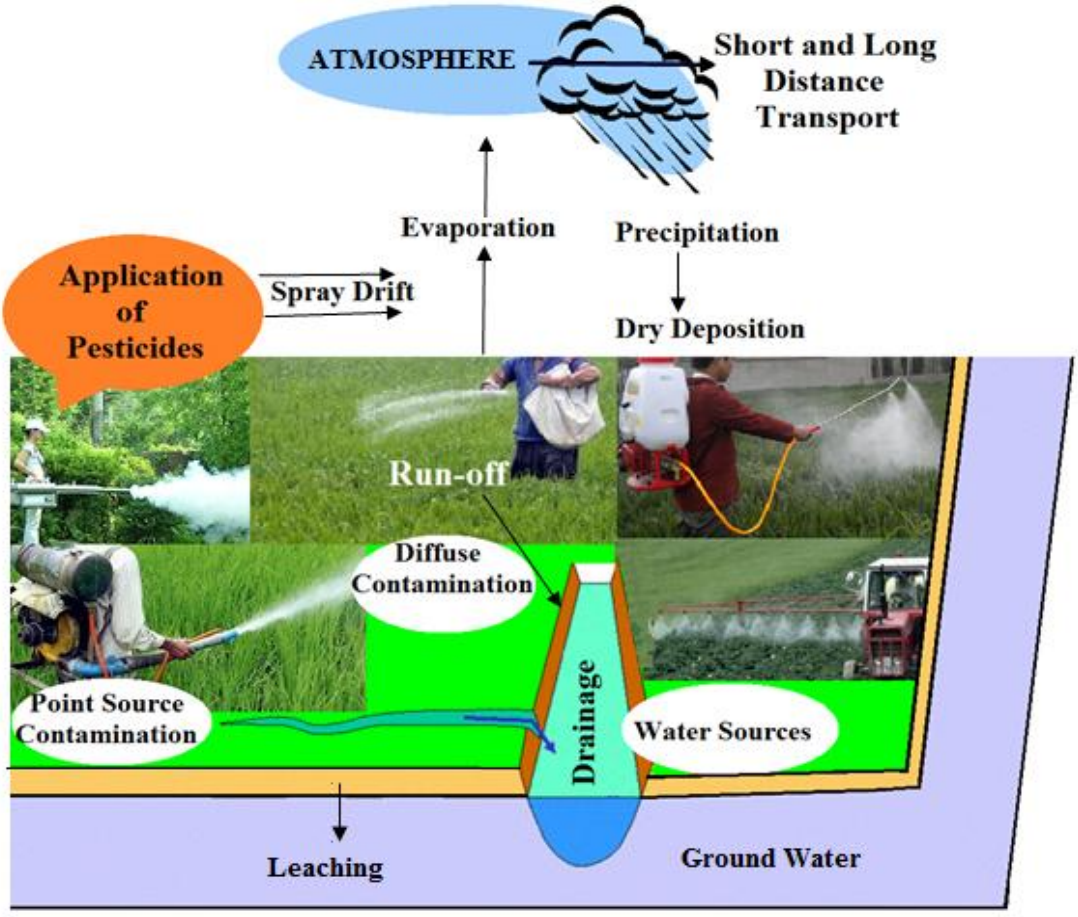

Figure 1.5: Conventional method of agrochemical application [111].

1.5.2 Controlled Release Technologies

Controlled-release technologies are widely used in biomedical, agricultural, cosmetics, dyes and food industries [112]. In 1964, Folkman and Long developed silicon rubber membrane device for the controlled-release formulation of anaesthetic

and cardiovascular drugs. The advantage of CRF was expended to agrochemicals, food and cosmetic industries in 1970-1980. CRF in the agricultural area are being used in order to overcome several problems such as ground water contamination, phyto-toxicity, degradation, runoff and excessive exposure of chemicals to the environment [113].

The mechanism of controlled release devices can be explained as diffusion-controlled or chemically-controlled. Diffusion-controlled release may occur from a matrix system (matrix diffusion, polymer swelling and/or polymer erosion) or membrane-reservoir systems (solution-diffusion). Chemically–controlled release may occur from a bio-erodible system and polymer-biochemical conjugation. Hence, the excessive release and frequent applications can be reduced using controlled release technologies [114]. Usually, biodegradable polymeric materials are used to develop various controlled release systems such as microcapsules, coated granules/capsules and blend-matrices [115].

1.5.2(a) Microcapsules

Microencapsulation is an important tool for controlled release of active ingredients [116], whereby the active ingredients are surrounded by an organic or inorganic membrane. As such, the membrane protects the active ingredients against adverse reactions, reduces volatilization, and control the rate of release into the environment [117]. Microcapsules can be prepared using several methods such as phase separation and emulsion solvent evaporation methods. Phase separation, a non-aqueous method, can be used for water soluble biochemicals, whereas solvent

evaporation technique can be used for water insoluble biological active ingredients [118]. In addition, the particles with the size distribution of 1 to 1000 µm are termed as microcapsule while particle size less than 1 µm can be called as nanoparticles. Particles with mean size distribution greater than 1000 µm can be termed either macrocapsules or microgranules [119]. However, to prepare the spheres of the desired size distribution and morphology is poorly controllable [120]. However, nano or micro-size particles can be achieved by careful selection of suitable materials and encapsulation conditions [121].

1.5.2(b) Coating

Coated material is biological active chemical surrounded either by single or double outer coating layers. The outer coating layer should be biodegradable and water insoluble or partially water soluble in order to prolong the release rate of active chemicals [113]. As such, conventional agrochemicals can be coated using various polymers and inorganic fillers [122]. However, super absorbent polymer coated water soluble agrochemicals would be an ideal controlled release formulation [123]. The release of active ingredients can be controlled by diffusion through the outer coating layer [124]. In view of this, various materials such as polymers [125-129], sulphur [130-132], pyrite [133] and polyethylene [134] have been used to formulate coated controlled release devices.

1.5.2(c) Dispersion/blending

Aqueous dispersion of polymers is the most promising way to formulate controlled-release matrices [135]. Various organic solvents can be used to produce

blended materials, but the use of organic solvents may lead to environmental problems and excessive costs of recovery [136]. Generally, most of the polymers are less soluble in neutral aqueous medium, and usually the solubility can be increased using organic solvent [95]. Aqueous polymeric coating through dispersion has attracted much attention because, the use of organic solvents may lead to environmental and human health problems [136, 137]. Several polymers along with other chemicals can be used to coat biological active compounds through dispersion, and the movement of the active chemicals can be controlled across the coating layer either by diffusion or osmosis [138]. In latex coating processes, the properties of coated film depend not only on the nature of polymer but also on the method of preparation and conditioning. The polymer latex should be mobile enough in order to inter-diffuse to form a homogenous coating layer. The coating layer forms in several steps, starting from the dispersion of cross-linking agent in the polymeric latex, followed by mixing and evaporation of the solvent. Which lead to the formation of a closely packed structure and formation of a homogeneous layer across the active chemicals [139].

1.6 Polymeric Biocomposites

Polymeric biocomposites, the most attractive materials, consist of biodegradable polymer as matrix and biofibres or inorganic material as reinforcing element [140]. However, the literature survey revealed that very little attention has been focused on the preparation and development of biocomposites in the past. The successful formulation development of biocomposites has been initiated in the year 1980 [141]. However, during the last two decades, the interest in biocomposites

preparation has grown due to the depletion of fossil resources and environmental concerns [142]. Several research and review articles have been published in the year 2000, devoted to the formulation, processing, and properties of polymeric biocomposites for a wide range of biomedical, agricultural and packaging applications [143]. The biocomposites derived from biopolymers are likely more environmental friendly, and such biocomposites are termed as "green composites" [144]. Other advantages of biopolymers over synthetic polymers are cost effectiveness, carbon dioxide sequestration, acceptable specific strength properties, non-toxicity, natural abundance and biodegradability. Biopolymer composites have been investigated as new material of the 21st century, to be a partial solution for human health and global environmental problems [145]. The degradation of biopolymer involves the cleavage of enzymatically and/or hydrolytically sensitive bonds, resulting in the polymer erosion [146], water and CO_2 production, as described in Figure 1.6.

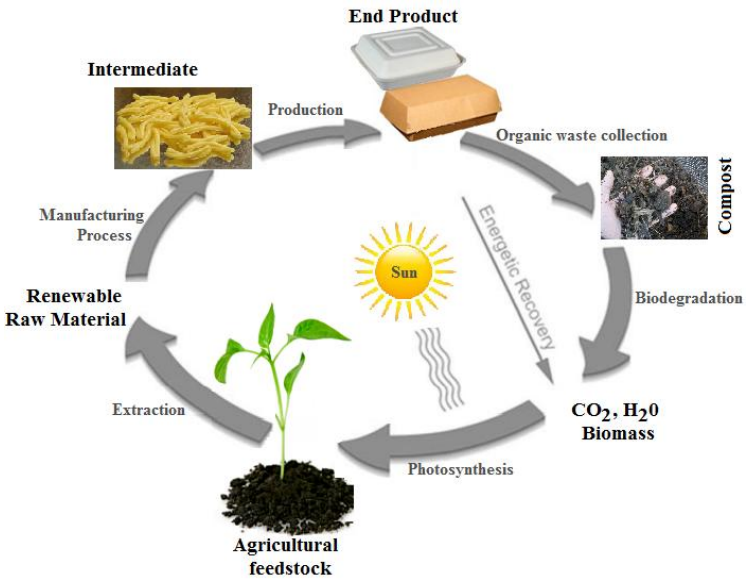

Figure 1.6: Life cycle of biodegradable polymers [147].

1.7 Literature Review of Biocomposites Composed of CTS and NR or Its Epoxidized Derivatives

1.7.1 CTS and Epoxidized Natural Rubber

Several reports are available in the literature pertaining the preparation and characterization of biocomposites consist of CTS and epoxidized natural rubber (ENR). ENR can be prepared by treating NR with formic acid in the presence of hydrogen per oxide, as shown in Figure 1.7 [148]. The epoxy content of ENR ranges from 5 to 75 mol% whereas, three levels of epoxidation are studied extensively i.e. 25, 50 and 75 mole% referring to ENR-25, ENR-50 and ENR-75, respectively [149-151]. However, modification of NR into ENR is an expensive, time consuming and energy intensive process.

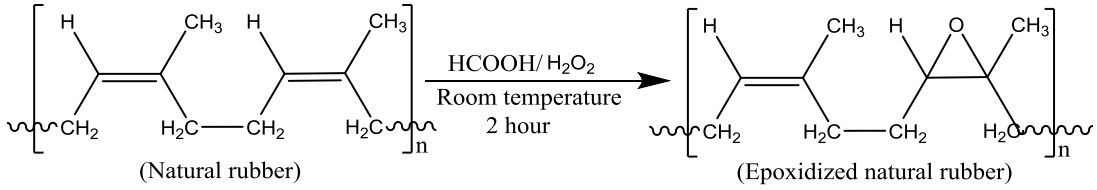

Figure 1.7: Modification of NR into ENR

Shaari et al. [152] have prepared CTS filled ENR blends in the presence of curing agents, using laboratory size two-roll mill. The effect of CTS loading on the curing characteristics, tensile properties and morphology of the blends have been investigated. The CTS loading has resulted in the increased tensile modulus, durometer hardness and the maximum torque but decreased the tensile strength and elongation at break. Zakaria et al. [153] have prepared poly(lactic acid)/CTS/ENR biocomposite through a solution casting technique and characterized using FT-IR

and SEM. The mechanical properties such as tensile strength and tensile modulus have been improved significantly up to CTS loading of 5-phr whereby Young's modulus increased up to 10-phr with a decreased of percent elongation at break. The improved mechanical properties have been attributed to a good dispersion of CTS at an optimum filler levels.

Riyajan and Sukhlaaied [154] have prepared CTS grafted ENR (CTS-g-ENR) latex using potassium persulphate as an initiator. The molecular weight of CTS has been reduced using $K_2S_2O_8$ at 70 °C for 15 min. The chemical structure of the CTS-g-ENR has been confirmed by ^{1}H-NMR and ATR-FT-IR techniques. Thermal stability of the CTS-g-ENR has been enhanced which might be due to good incorporation of CTS into ENR. The optimum conditions of CTS grafted ENR are 65 °C for 3 h reaction time with the ratio of CTS/ENR at 1:9. Taweepreda and Wichianchom [155] have prepared CTS/ENR membrane and studied its ionic conductivity and dielectric properties. The ionic conductivity and dielectric properties increased with CTS loading.

Guna et al. [156] have prepared a biocomposite of CTS and ENR, investigated the effects of CTS loading on mechanical properties and the uptake of water and toluene. The results have shown that CTS loading resulted in the increased tensile strength and cure torque. However, a decline was observed for the cure time and elongation at break. The CTS loading has also resulted in the increased water uptake but the decreased uptake of toluene. Mas Haris and Raju [157] have prepared CTS grafted ENR compound via acid induced reaction. An, appropriate amount of