

**MODIFICATION OF CHITOSAN WITH DEEP
EUTECTIC SOLVENT FOR THE ADSORPTION
OF MALACHITE GREEN**

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**MODIFICATION OF CHITOSAN WITH DEEP
EUTECTIC SOLVENT FOR THE ADSORPTION
OF MALACHITE GREEN**

by

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**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

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DECLARATION

I declare that the content which is presented in this thesis is my work which was done at Universiti Sains Malaysia unless informed otherwise. The thesis has not been previously submitted for any other degree.

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DEDICATION

I dedicate this thesis to Allahu (SWT) who provided everything for me. I dedicate this thesis with love and affection to my parents, family and all Muslim Umma around the globe.

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LIST OF ABBREVIATIONS

BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halenda
BOD	Biochemical Oxygen Demand
cal	Calculated
CEC	Cationic Exchange Capacity
CH	Chitosan
CH-DES A	Chitosan DES A based adsorbent
CH-DES B	Chitosan DES B based adsorbent
C.I.	Colour Index
DES	Deep Eutectic Solvent
DES A	Deep Eutectic Solvent consisting of Choline Chloride and Urea
DES B	Deep Eutectic Solvent consisting of Choline Chloride and glycerol
ECH	Epichlorohydrin
EDL	Electrical Double Layer
EDX	Energy Dispersion X-ray
exp	Experimental
FTIR	Fourier Transform Infrared Spectroscopy
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
MCH	Magnetic Nanosized Chitosan-based adsorbent
MG	Malachite Green
ND	Not Detected
PCDES	Protonated Chitosan-based DES adsorbent

pHpzc	pH of Point of Zero Charge (PZC)
R	Universal gas constant
r^2	Regression coefficient
SD	Standard Deviation
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TG/DTA	Thermo Gravimetric / Differential Thermal Analyses
TSS	Total Suspended Solids
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffraction

LIST OF SYMBOLS

\AA	Angstrom
C_o	Initial concentration (mg/L)
C_e	Equilibrium concentration (mg/L)
E_a	Activation energy (kJ/mol)
h	Hour or hours
K	Kelvin
K_L	Binding energy constant (L/mg)
k_1	Pseudo-first order rate constant (1/min)
k_2	Pseudo-second order rate constant (g/mg min)
k_i	Rate constant for intraparticle diffusion model (mg/g min ^{0.5})
m	Mass/weight of the material taken (g)
q_e	Amount adsorbed at equilibrium (mg/g)
q_{ref}	Amount adsorbed at t_{ref} (mg/g)
q_t	Amount adsorbed at time t (mg/g)
R_L	Separation factor
T	Temperature (K and/or °C)
t	Time (min)
t_{ref}	Reference time for Bangham model (min)
V	Volume of dye taken (mL)
$^{\circ}C$	Degree Celsius
ΔG°	Gibb's free energy change (kJ/mol)
ΔH°	Enthalpy change (kJ/mol)
ΔS°	Entropy change (J/mol K)

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**PENGUBAHSUAIAN KITOSAN DENGAN PELARUT EUTEKTIK
TERDALAM UNTUK PENJERAPAN HIJAU MALAKIT**

ABSTRAK

Kehadiran pewarna dalam air sisa alam sekitar menjadi perhatian serius kerana menimbulkan ancaman kepada ekosistem dan kebimbangan besar. Tesis ini memberikan maklumat latar belakang mengenai pelbagai teknik yang tersedia untuk penyingkiran pewarna malekit hijau (MG) dari medium akues. Terdapat pelbagai teknologi rawatan yang telah dikaji untuk penyingkiran pewarna, penjerapan dan membran separa telap menggunakan membran terangkum polimer (PIM) dianggap sebagai kaedah yang berkesan untuk penyahtoksikan pewarna daripada sisa air dalam kajian ini. Kitosan (CH) dianggap sebagai bahan penjerap yang berpotensi, mudah dan murah diperolehi daripada produk sampingan industri makanan laut. Sementara itu, CH telah difungsikan dan digunakan sebagai penjerap. Sementara itu, CH berfungsi digunakan sebagai penjerap disedia dengan menggunakan pelarut eutektik dalam (DES) bagi mensintesis manik, zarah magnetik bersaiz nano, pengekstrak dan pemplastik yang digunakan pada nisbah yang berbeza seperti bis-(2-etilheksil) fosfat (B2EHP), Aliquat 336, dan dioktil ftalat (DOP) masing-masing untuk penyediaan (PIM). Pelbagai teknik seperti pH_{pzc}, kelarutan, SEM, EDX, TEM, FTIR, XRD, VSM, dan BET dilakukan untuk menganalisis ciri-ciri fizikokimia bahan CH yang baharu disediakan. Analisis pencirian telah menunjukkan modifikasi permukaan, ion B2EHP, DOP, Aliquat 336, besi, dan klorida dimasukkan ke dalam molekul CH. Potensi penjerapan dan pengekstrakan penjerap dan membran diselidik menggunakan penjerapan berkelompok dan eksperimen sel berkelompok statik. Selain itu, kesan pH larutan, kepekatan awal, suhu, masa, kekuatan ion, dan dos dikaji. Sebagai tambahan,

data keseimbangan yang diperoleh dibandingkan dengan menggunakan model isoterm seperti Langmuir, Freundlich, Temkin, Halsey dan Dubinin-Radushkevich (D-R). Walau bagaimanapun, data keseimbangan dianalisis menggunakan urutan pseudo-pertama, urutan pseudo-kedua, pembauran intrazarah, kinetik penjerapan Elovich dan Bangham. Isoterm penjerapan Langmuir didapati lebih sesuai untuk data penjerapan bagi penjerap. Model isoterm lain seperti Freundlich, Temkin dan D-R juga diguna untuk menerangkan proses penjerapan monolayer dan homogen oleh penjerap. Sementara penentuan langkah pengendalian kadar dalam 60 minit menunjukkan bahawa urutan pseudo-detik adalah model kinetik penjerapan yang sesuai dengan data yang diperoleh dari proses penyerapan dalam kajian ini. Begitu juga, penyebaran intrapartikel dan Elovich turut melengkapkan penerangan sistem. Analisis data keseimbangan digunakan untuk menentukan kapasiti penjerapan bagi setiap penjerap. Di antara pelbagai sampel penjerap yang disediakan, penjerap magnetik bersaiz nano secara relatif menghasilkan kapasiti penyingkiran yang lebih baik hingga sekitar 87.72 (mg/g). CH tulen mempunyai kapasiti penyingkiran 13.61 mg/g, CH-DES A 26.04 mg/g, CH-DES B 30.30 mg/g, 78.13 mg/g pada suhu bilik. Sementara, dalam kecekapan pengekstrakan di antara membran separa telap, PIM yang disusun dengan Aliquat 336 sebagai pengekstrak menghasilkan peratusan penyingkiran yang lebih tinggi (98.35%) dalam 120 minit berbanding dengan PIM yang mengandungi B2EHP sebagai pengekstrak. Sementara itu, penjerap telah menunjukkan potensi nilai ekonomi melalui kebolegunaan semula yang konsisten selepas lima kitaran. Akhir sekali, penjerap digunakan untuk menghilangkan pewarna MG dari sampel sebenar yang bersumber dari, air paip, laut, dan sungai untuk menguji kegunaannya dalam jumlah yang lebih besar.

MODIFICATION OF CHITOSAN WITH DEEP EUTECTIC SOLVENT FOR ADSORPTION OF MALACHITE GREEN

ABSTRACT

The presence of dye in environmental wastewater is a serious concern as it poses a threat to the ecosystem. This thesis provides background information about different techniques to remove malachite green (MG) from an aqueous medium. Various treatment technologies have been studied to remove dye, adsorption and semi-permeable membrane extraction using polymer inclusion membrane (PIM). These methods are considered efficient methods for the decontamination of dyes from wastewater in this study. Chitosan (CH) is considered a promising, readily available, and inexpensive adsorption material obtained as a by-product from the seafood industry and other sources. Meanwhile, CH was functionalised and used as an adsorbent. CH was functionalised with using deep eutectic solvents (DES) to syntheses beads, magnetic nano-sized particles and was used as extractants and plasticisers at a different ratio. DES such as bis-(2-Ethylhexyl) phosphate (B2EHP), Aliquat 336, and dioctyl phthalate (DOP) were used to prepared PIMs. Various techniques such as pH point of zero charge (pHpzc), solubility, scanning electron microscopy (SEM), energy dispersion X-ray (EDX), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), thermo gravimetric/differential thermal analyses (TGA/DTA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Brunauer-Emett-Teller (BET) were carried out to analyse the physicochemical characteristics of the newly prepared CH materials. The characterisation analysis has shown surface modifications, incorporated B2EHP, DOP, Aliquat 336, iron, and chloride ions onto the CH molecules. The adsorption and

extraction potentials of the adsorbents and membranes were investigated by batch sorption and static batch cell experiments. Moreover, the effects of the solutions pH, initial concentrations, temperature, contact time, ionic strength, and adsorbent dosage were investigated. Incorporation of the DES into the CH has affected the surface chemistry of the adsorbents and shifted the adsorption to a higher pH for the equilibrium data obtained were compared using isotherm models such as Langmuir, Freundlich, Temkin, Halsey, and Dubinin–Radushkevich (D-R). The equilibrium data were analysed using pseudo-first-order, pseudo-second-order, intraparticle diffusion, Elovich, and Bangham adsorption kinetics models. The Langmuir adsorption isotherm fitted better for sorption data description for the adsorbents. Other isotherm models such as Freundlich, Temkin, and D-R were also fitted to describe the process showing monolayer and homogeneous adsorption sites by the adsorbents. The determination of the rate-controlling step in 60 min indicated that the pseudo-second-order was the adsorption kinetic model that fitted the data obtained from the sorption process in this study. Likewise, intraparticle diffusion and Elovich complemented the description of the system. The equilibrium data analysis was used to determine the adsorption capacity for each adsorbent. Among the various adsorbent samples prepared, the magnetic nano-sized adsorbent was comparatively produced better removal capacity up to about 87.72 (mg/g). The pristine CH has 13.61 mg/g, CH-DES A 26.04 mg/g, CH-DES B 30.30 mg/g, 78.13 mg/g removal capacities at room temperature. In terms of extraction efficiency of the prepared semi-permeable membranes, PIM constituted with Aliquat 336 as extractant depicted a higher removal percentage (98.35%) in 120 min compared to the PIM that contains B2EHP as extractant removed 96.25 %. Meanwhile, the adsorbents have shown economic viability through consistent significant reusability after five consecutive cycles. Finally, the adsorbents were

applied to remove MG dye from actual spiked samples sourced from tap water, sea, and rivers to test their applicability in larger volume.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Drinking water sources are mainly from rainwater, rivers, dams, lakes, sea, ground, canal, and streams. Industrialisation and other human activities resulted in significant challenges of contamination with tons of dyes, phenolic compounds, pharmaceuticals, pesticides, heavy metals, and other pollutants into the water sources. The point sources of these pollutants have no global regulations of limits especially in developing countries to monitor their discharge. Legislations for discharge of xenobiotics/pollutants into the public water sources to ensure adequate, diseases free, and suitable portable water provision was not in place until recent times (Lonfat et al., 2014).

Water pollution is a matter of great concern as it courses a significant proportion of havoc to human, terrestrial, and aquatic animals. Consequently, more than 780 million people are facing a tremendous challenge of good water supply for consumption and other uses (WHO and UNICEF 2008). Globally, water pollution according to report have risk some 2.1 billion or 3 in 10 people access to portable water readily available and 4.5 billion or 6 in 10 (WHO 2017). Among the pollutants, dyes are too intricate molecules with notorious characters because of resistance to oxidizing agents, toxicity and not easily remove efficiently by the traditional methods.

Therefore, researchers, governmental and non-governmental institutions focus on developing sustainable designs and establish remediation technologies to create alternative tracks in addressing wastewater decontamination from the traditional methods known for removal of the pollutants, such as dye, total dissolved solids

(TDS), total suspended solids, and different physical ways. The traditional methods do not have adequate efficiency and significance in larger wastewater volume. There are many techniques employed in large scale to remove pollutants from wastewater such as coagulation/flocculation, precipitation/flocculation, electrocoagulation, adsorption, and biodegradation. Among these, adsorption is found to be appropriate method for the removal of pollutants.

Dyes are usually organic substances which at some certain degree of performance impart colour when reacted, adsorbed, or deposited onto a substrate (Li et al. 2014). They are useful as attractive additives in textile, food, drug, and other products to entice users and consumers, but could be harmful to the users as many are carcinogenic at an absolute concentration. Nevertheless, dyes can be categorised in different manners, basically according to their chemical structures and method of application (Ghani et al. 2014; Girish and Murty 2016). Dyes usually undergo degradation at some point and harm the consumers when they exceeded a specific limit. Moreover, improper disposal of such dyes can cause severe disorder to an aquatic environment and creatures are affecting human life. A typical example is the release of azo dyes like malachite green (MG) to waterways that contain aromatic functional groups such as $-\text{NH}_2$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, OH , and amine. The dye molecular structure contains auxochromes and chromophores phases. Auxochromes are responsible for the dye physical properties (solubility, colour intensity) electron-withdrawing, and electrons' acceptance. Additionally, dyes contain other colour given molecules known as chromophores usually bear double bonds (delocalised electrons) in their structure these include, $-\text{NO}_2$, $-\text{C}=\text{N}^-$, $\text{N}=\text{N}^-$, $\text{C}=\text{O}$. When dye molecules are introduced into the aquatic environment by implication, they affects the aquatic community, their consumption causes restlessness, attention deficiency in children

(Zhang et al., 2008), and incessant headache in adults (Srinivasan & Viraraghavan, 2010). MG is among the most of organic dyes in industrial effluents that are damaging living aquatic organisms, therefore, it is very necessary to remove it from industrial effluents before it is discarded into the aquatic environment. However, the removal of dye from wastewater requires a simple, effective, and less cost technique such as adsorption and membrane separation technologies.

Adsorption is essentially a surface-based phenomenon classified as a physisorption process where surface adhesion of adsorbate is weakly attached through intermolecular interactions such as Van der Waal forces to the surface of the adsorbent. Contrarily, the adsorption process which involves surface chemical bonding is called chemisorption. The most common and useful adsorption type for treatment of polluted wastewater is with adsorbent that has less cost-effectiveness, free from creating secondary pollutants, environmentally friendly, physically simple, and reversible one. Hence, a biopolymer chitosan (CH) possesses such qualities since it occurs at low energy like cellulose. Whereas a related process is known as absorption, which the distinction of adsorption from absorption is that, absorption is an irreversible and not a surface-based phenomenon usually occurs by diffusion of the adsorbate molecules, so it involves high energy and not much suitable for remediation of wastewater (Benavente, 2008).

Membrane separation technologies are gaining attention as an alternative to the standard wastewater treatment process due to their simple processing conditions, small footprint, and low energy need in the application. This technology utilises a semipermeable membrane between a barrier of two phases via preferential transport of components for osmosis, chemical potential difference, temperature gradient, and pressure (Baker, 2012; Geise et al., 2010). Liquid separation with membrane-based

method could be classified into several types including hydrostatic pressure-based, osmosis-based, electrolytic, and vapour pressure gradient. Generally, membrane separation technique is designed for the removal of macromolecules, suspended solids, and/or multivalent ions such as dyes through semipermeable barrier (Uragami, 2017).

CH is a well-known adsorbent for the removal of both inorganic and organic contaminants from an aqueous solution. It was first discovered in 1859 by Touget from chitin when boiled with sodium hydroxide solution (Raafat et al., 2008). CH is the second most abundant biopolymer after cellulose that occurs naturally, it exists in the exoskeleton of sea creatures such as shrimps, krill, prawns, crabs, cartilages of molluscs, and insect cuticles (Khor and Lim, 2003; Olteanu, 2007). Moreover, it is the only known natural cationic polysaccharide (Abdul et al., 2016; Raza et al., 2020). Commercially, CH is synthesised from the above-mentioned animals through alkaline deacetylation of their body chitin, which is a hydrophilic amino polysaccharide containing linear acetylglucosamine and glucosamine poly- β -(1 \rightarrow 4)-2-amino-2-deoxy-d-glucose) units (Drahansky et al., 2016). CH is a hygroscopic pseudoplastic biopolymer in nature due to the presence of free hydroxyl and amine groups which enables to interact with other molecules through hydrogen bonding (Román-Hidalgo et al., 2019). It has been discovered that the CH functional groups, surface charge density, and molecules of its surface charge have a significant impact on the removal of contaminants from different environmental media. Moreover, the advantages of CH in dynamic characteristics have been utilised as a good alternative natural material for pollution control. CH are highly effective, low-cost, environmentally friendly, and available in abundant which makes it suitable as adsorbent.

CH has diverse applications with significant performances in every characteristic and desired usage in many systems. CH is usually modulated for the

desired use; However, it has some limitations such as soluble in acidic medium, low thermal resistance, less of mechanical and chemical strength. Nevertheless, some review had shown the surface chemistry and other features of CH were customised to suit particular applications (Terzopoulou et al., 2015; Li et al., 2014). Generally, the modifications of CH were included grafting, crosslinking, and membrane adapting to the physicochemical, and biological, characteristics of the CH for enhancement of dye sorption and other pollutants.

Generally, the dissolution of CH is required before functionalisation. The common solvents used for the dissolution are trichloroacetic acid (TCA) and dichloroacetic acid (DCA) in the absence or presence of alcohol. Other solvents reported to dissolve CH include; dimethylacetamide (DMA)/LiCl mixture, N-methyl-2-pyrrolidone, lithium thiocyanate, and ionic liquids (Roy et al., 2017). Even though these solvents have potentials to dissolve the CH, but many of them are toxic, corrosive, mutagenic or scarcely degradable. Therefore, the exploration of suitable solvent with harmless properties for functionalisation of CH is the primary subject for the study in the laboratory and industrial scale practices.

Deep eutectic solvents (DESs) are now extensively recognised as a novel alternative to conventional solvents like ionic liquid (IL) because they share many properties and characteristics. Interchangeably, the terms IL and DES are used in many kinds of literature though they are two different solvents. IL is solvent systems which primarily composed of one discrete type of anion and cation. While the DES are formed from a eutectic mixture of Brønsted or Lewis acids an anionic and/or cationic species varieties of bases. IL and DES have similar properties, but their applications suggest that they are significantly different in chemical properties. DES are environmentally friendly solvents that attracted the attention of researchers as

alternative media involving environmentally hazardous processes. Moreover, DES has the potential as good solvent that can be modified to a certain type of chemistry. They exhibit low vapour pressure, non-flammable character, and wide liquid-range. DES advantages over IL counterpart include ease of preparation, non-toxicity, easy availability, less chemically inert (Smith et al., 2014). DES was found to be a good solvent for several polymers that are difficult to be processed by other solvents (Jiang et al., 2018). It can be hypothesised that DES might potentially afford good compatibility and solubility with CH for the synthesis of beads. In addition, the low cost of DES production warrants it as the best choice solvent to be used for the functionalisation of CH.

1.2 Problem statements

Pollution of freshwater by textile and paper industrial effluents commonly contains azo dyes such as MG. MG is relatively available for industrial use, inexpensive, used for dyeing fabric materials, treatment of fungal and protozoan infections (Sathya, et al., 2015). However, consumption of MG-contaminated water poses a risk of reproductive system defects, immune system mutagenesis, chromosomal consequences, and respiratory toxicity. There's also a chance of severe health problems like teratogenicity, carcinogenesis, mutagenesis, and genotoxicity (Ling and Suah, 2017).

In addressing MG pollution in wastewater, this research focused on the development of beads, membrane, and nano size CH-based as adsorbents materials to remove MG contaminants. Considering the less cost-effective, environmentally friendly nature of pure CH, surface characteristics and modified materials were utilised to synthesis the said materials by loading with green deep eutectic solvent and ionic

liquids to increase CH utilisation. The pristine CH is mechanically deficient at low pH, as such it is crucial in this work to modify CH to enhance mechanical strength stability, swelling effect, permeability, solubility among others. Thus, a better alternative to the other traditional and scientific experimental processes simple approaches such as adsorption and separation processes to successfully remove MG from an aqueous solution were carried out in this work.

1.3 Significance of the study

CH has shown a great affinity for different pollutants due to its exceptional and distinct molecular structure. As new materials, modification of CH by dissolution into deep eutectic solvents, protonation, nano-sized, and modification of CH using IL into polymer inclusion membrane can provide an easy, environmentally friendly process for the removal of MG. Also, the innovative approaches may extend the usage, explore the potentials of the bio-renewable polymers and their chemical modifications, as contrasted with pristine CH. The prepared CH materials provide provides better and an improvement in dye adsorption efficiency and capacity.

1.4 Objectives of the study

This study is primarily reported on the utilisation of an inexpensive, efficient, simple, and environmentally friendly chitosan and chitosan-based adsorbents for the removal of malachite green dye from wastewater.

The specific objectives of the study are:

1. To synthesis of CH beads, nanoparticles, and membrane materials with modified with green hydrophobic deep eutectic solvent.

2. To characterise CH beads, nanoparticles, and modified membrane materials.
3. To optimise and compare the parameters from batch adsorption studies such as effects of pH, concentration, contact time, adsorbent dosage, and ionic strength.
4. To apply the material sample to test the applicability of the synthesised materials for the removal of MG using real water samples.

1.5 Scope of the study

This thesis validates the characterisations and applications of pristine and modified CH materials mainly as adsorbents and semipermeable membranes for the adsorption of MG in wastewater respectively. The objective for the functionalisation of CH surface is to discover its dynamic advantages and improve the performance efficiency. This was achieved by increasing the surface area, application potentials, mechanical and chemical stabilities. Subsequently, the material was applied to real samples on the laboratory scale for uptake of MG dye.

1.6 Outline of the study

This thesis is designed into six chapters separately. The introduction of the research, hypothesis, objectives, and the scope of the study are presented in Chapter 1. Chapter 2 presented a brief review on dye removal from wastewater utilizing different treatment technologies with emphasis on the chitosan-based adsorbents. The methodology of the syntheses, characterisations, optimisations of batch adsorption, and application of real samples are outlined in Chapter 3. Data presentation of the obtained characterisation results is outlined in Chapter 4 Part 1. The study on

optimisation of parameters such as pH, initial concentration, adsorbent dosage, ionic strength, and contact time for the adsorption equilibrium, kinetics and isotherms of the adsorbents using pristine CH, and comparative batch adsorption process using modified CH and membrane for the MG removal are up course designated in Chapter 4 Part 2. Chapter 5 drawn an overall conclusion from the study and some recommendations for the future utilisation of the CH materials.

CHAPTER 2

LITERATURE REVIEW

2.1 Chitosan

The chitosan CH (Figure 2.1) is a classical adsorbent that was reported for wastewater remediation. The extensive use of CH for decontamination is due to its surface characteristics that have good affinity to different pollutants. CH is produced from deacetylation of chitin found in the plant's body, oceanic invertebrates such as shrimps, crabs, and lobsters. Also, exist in the cell wall of some microorganisms and fungi (Wang and Chen, 2014). Chitin consists of an elongated chain of N-acetyl-D-glucosamine (2-acetamido-2-deoxy-D-glucopyranose) units linked through β -1,4-glycosidic linkages (Figure 2.2). Minerals, organic pigments and proteins are associated with chitin naturally (Kasaai, 2009). CH formed from partial or complete N-deacetylation of chitin. Importantly, CH can be distinguished from the chitin by the degree of N-acetylation when greater than 50 %, insolubility and deacetylation of the polymer of β -1,4-glycosidic linkages with 2-amino-2-deoxy-D-glucose. However, both are non-homopolysaccharides where acetylation of amino group can arise.

Degree of deacetylation (DD) of CH affects its biological, chemical and physical activities (Kyzas et al., 2010). DD is a term used to describe a distinction of acetyl content in chitin which is also used in naming the copolymers chitin and CH (Jiang et al., 2017). Moreover, the CH pK_a values varies between 6.46 to 7.32 had equally influence their activities but CH with higher DD shows better biological properties compare to lower DD. Chitin with DD of 75-95% is commercially supplied in whitish powder, beads, and flakes forms with nanoscale size (Kasaai, 2009). Chitin and CH also has high degree of crystallinity and strong intermolecular forces due to the molecular linearity, with OH group that lead to strong intermolecular and

intramolecular hydrogen bonding within their molecular chain resulting to hydrophilic and hydrophobic interactions (Kasaai, 2009).

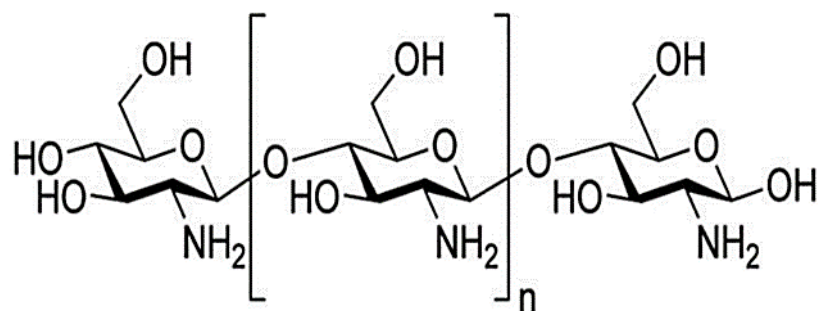


Figure 2.1 N-deacetylated chitosan chemical structure

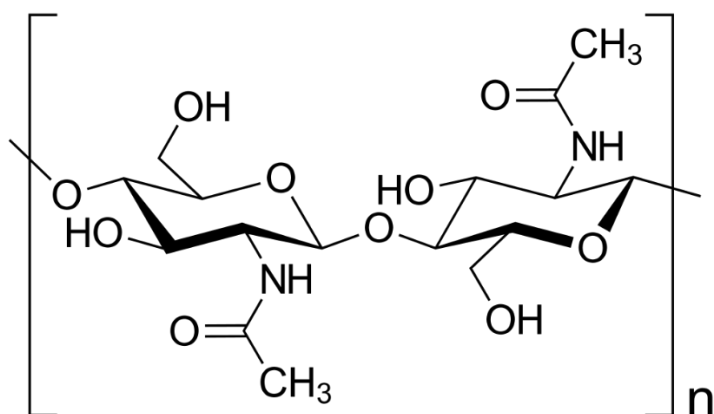


Figure 2.2 Chemical structure of N-acetylated chitin

2.1.1 Properties of chitosan

Primarily, the properties of CH are readily derivatised by utilisation of primary amino group, primary and secondary hydroxyl groups reactivity in diversified area. Molecular weight and degree of deacetylation (DD) parameters influence its rheological, physical and solubility properties (Yu et al., 2015; Li et al., 2020). CH has been a natural basic polysaccharide that has some unique properties such as solubility into various media, the formation of films, polyelectrolyte behaviour, chelation of metals, structural and optical characteristics. Other polysaccharides such as cellulose, agarose, pectin, carragenas, dextrin and alginic acid are acidic naturally, as such CH is considered to be more biocompatible and favourable biomaterial since it does not bear acidity, thus it is a weak base (Peter, 2000). Other physical and chemical properties of CH can be described as follows.

2.1.2 Solubility and N-acetylation degree (DD) of chitosan

Hydrolysis of chitin is usually achieved through free hydrophilic amino groups dispersed at random on its chain and acetyl groups are converted to free amine groups during deacetylation (Hou et al., 2012). The solubility of CH is usually possible in certain organic and inorganic acids such as acetic, tartaric, lactic, formic, citric, nitric and hydrochloric acids under prolonged stirring at a certain pH (Qin et al., 2006, Duarte et al., 2002). CH is insoluble in water, aqueous solution at $\text{pH} > 7$ and in many organic solvents such as sulphuric acid due to formation of a white crystalline CH-sulphate when reacted (Chung et al., 2005). However, the solubility of CH in the acidic medium depends on the concentration, DD, $\text{p}K_a$ and properties of the acid solution which has a significant influence on DD ratio for chitin and its derivative CH (Rinaudo, 2006).

There are strategies made to improve the solubility of CH. Firstly, CH can be resulted in a water-soluble by homogeneous phase reaction which involves deacetylation process control (Nghah et al., 2011), but the yield is less (Kurita et al., 2002). Secondly, the reduction of molecular weight which reduces high solubility of CH. In this approach, however, it is divided into acid hydrolysis, enzyme, and physical methods. Where acid hydrolysis involves deacetylation reaction to decompose CH into six units of N-acetylglucosamines with 10 % acetic acid and 5 % NaNO₃, such product at pH 7 is prone to dissolution (Aranaz et al., 2021). As such, CH loses chemical and/or biological activity where the molecular weight of the derivative is too low (No et al., 2002). The third process is by introducing a hydrophilic functional group (Chung et al., 2005) by chemical modification technique which the solubility ranges has been obtained up to 3-10 g/L (Travlou et al., 2013, Jiang et al., 2014).

2.1.3 Viscosity of chitosan

CH viscosity is an important parameter for determining the biological, chemical, and commercial values. The measure of resistance to deformation rate of CH is proportional to demineralisation time and molecular weight (Jiang et al. 2014, Kwan & Shin, 2000). However, other factors such as degree of deacetylation, ionic strength, temperature, pH, and concentration of the CH solution are also considered during the process of production. The degree of deacetylation of CH influences its viscosity and is more inherent to the CH than its ionic strength (Gachhi & Hungund, 2018). This is justified by the fact that when HCl is used to decrease the pH it causes lowering of viscosity. Thus, the decrease in pH increases the viscosity of CH and which means that type of acid used for lowering pH affects the viscosity. However, the use of acetone or 3% NaOH during the processing and production of CH affects

the final CH product for its viscosity (Gachhi & Hungund, 2018). They conclude that viscosity of CH is immensely affected by physical treatments such as crushing, heating, ultrasonication and autoclaving, likewise viscosity was shown to have decreased with temperature and time of treatment (El-Hefian et al., 2010)

2.1.4 Biological properties

CH and its derivatives have fascinating biological properties which lead them to large commercial production. Biodegradability, biocompatibility and low toxicity are so interesting qualities that made CH applicable in the fields of medicine, pharmacological and other industries (Kucharska et al., 2019; Cui et al., 2018; Franca et al., 2020; Iqbal et al., 2020).

2.1.5 Biodegradability

Valuable and essential biodegradability of CH and its derivatives made it applicable in several techniques such as suitability in substitution for bone defect through solvent casting method (Bakhtiari et al., 2019), combined with synthetic biopolymers to induce bioactivity and promote osteogenesis leading to an acceleration of new bone regeneration with the increase in vivo neovascularisation (Aguilar et al., 2019). Nonspecific enzymes like proteases, pepsin, papain, lysozymes, pectinase, lipases and cellulose found in the somatic cells of mammals can be degraded in vitro CH (Kumar, et al., 2007), *In vitro and in vivo* evaluation manifested haemolytic potentials of CH with great blood compatibility, excellent histocompatibility, biocompatibility and cytocompatibility in a thermo/pH controlled sol-gel as a drug carrier (Li et al., 2020), oligosaccharides incorporated into glycoproteins and glycosaminoglycans metabolic pathways (Francis and Matthew, 2000), for

invertebrates are degraded by CH mostly by the action of bacterial enzymes and lysozyme within their colon (Kean & Thanou, 2009).

2.1.6 Biocompatibility

CH is used in several biomedical applications due to its biocompatibility, promising and multifunctional capabilities. Research showed intrinsic properties of CH as antimicrobial, antioxidant, and antifungal bioactive applications (Prettol et al., 2002; Mesquita et al., 2020). The biocompatibility of CH made it as an ideal agent in the development of flexible, multifunctional stimuli-responsive biomaterials (Mesquita et al., 2020). However, living tissues have shown compatibility for anticancer agent delivery into cancer hepatocellular carcinoma without apparent side effect in induced affected cells, CH shows tolerance to the ocular membrane, nasal epithelium and skin (Bhatia, 2016). (Shigemasa & Minami, 1996) reported that, compatibility of CH is depending on its origin such as source, molecular weight, DD, and method of preparation.

2.1.7 Toxicity

CH has favourable less toxic property compares to other biopolymers. CH nanoparticle-based targeted therapy was used to deliver chemotherapy drug with systematic reduction in toxicity into their targeted sites without apparent effects on the healthy tissues (Harish et al., 2020). Furthermore, its low toxicity demonstrates excellent efficacy and protection in the burden reduction of nematode gastrointestinal tracks into an encapsulated bromelain and in vitro and in vivo of small mammals at doses up to 30 mg/kg for two weeks. Wasso et al., (2020) found that DD value is equally related to CH toxicity. It was reported that DD greater than 35% value of CH

exhibit low toxicity while less than 35% DD value depending on the dose showed toxic property (Kumar et al., 2007).

2.2 Modifications of chitosan surface for adsorption of dye from aqueous solution

CH surface modification is principally aimed for improvement of acidic medium resistance, thermal resistance, and mechanical strength. As such, to achieve various desired applications, crosslinking the functional $-NH_2$ - and $-OH$ groups using agents such as epichlorohydrin (Elwakeel *et al*, 2012), polyelectrolyte/organo-clay (Huang et al., 2019), glutaraldehyde (Kadam & Lee, 2015), and silica (Ryan et al., 2017) plays a vital role. Likewise grafting of other chemical components to the functional groups. However, crosslinking of the functional groups may reduce the adsorption capacity by rendering the functional groups unavailable (Guibal, 2004). Table 2.1 show some reported works for various modified CH derivatives used for absorption of dyes and maximum adsorption capacity (q_{max} (mg/g)) obtained from aqueous solution.

Table 2.1 Summary of modified chitosan-based materials for the adsorption of dye from aqueous solutions

Modification Component(S)	Dye	q_{max} mg/g	reference
Glutaraldehyde and HCl	Methyl orange	89.3	(Ruihua et al., 2017)
Ti ⁺⁴	Orange II	1120	(Gao et al., 2016)
Zr ⁺⁴	Orange II	926	(Zhang et al., 2015)

Cellulose	Methyl violet 2b	-	(Karim et al., 2014)
	Rhodamine 6G	-	
	Victoria blue 2b	-	
Ionic liquids	Malachite green	8.07	(Naseeruteen et al., 2018)
β -cyclodextrin	Methyl blue	2.78	(Fan et al., 2012)
TPP	Reactive red 120	910	(Momenzadeh et al., 2011)
		51	
Graphene oxide	Methyl violet	9.68	(Gul et al., 2016)
	Alizarin yellow	6.55	
Nano graphene	Brilliant green, methyl blue, Xylenol orange, crystal violet and Malachite green	1.8975 122.1	(Kaur et al., 2019)
Nano graphene	Methyl blue	179.6	(Fan et al., 2012)
Fly ash and Graphene oxide	Anionic acid red (arg)	38.87	(Sheng et al., 2016)
	Cationic red x-5gn	64.50	
Fe ₂ O ₃	Methyl orange	29.49	(Zhu et al., 2010)
Fe ₂ O ₃	Acid red 73	294.5	(Shen et al., 2011)
Fe ₂ O ₃ and Ethylenediamine	Acid orange 7	1215	(Zhou et al., 2011)
	Acid orange 10	1017	
Graphene oxide	Fuchsin acid	197.6	(Li et al., 2014)
Sulphuric acid	Humic acid	183.65	(Ngah et al., 2011)
Activated carbons	Methylene blue	270.27	(Marrakchi et al., 2017)
	Acid blue 29	199.2	
Clay	Methyl blue	143.53	(Auta and Hameed, 2014)

Table 2.1 Continued

Modification Component(S)	Dye	q_{max} mg/g	reference
Zeolite	Methyl blue	142.31	(Nešić et al., 2013)
Glutaraldehyde	Bezactive orange 16	305.8	(Elwakeel et al., 2012)
Activated oil palm ash zeolite	Brilliant blue R250	0.8	(Khanday et al., 2017).
Palygorskite	Reactive	71.38	(Peng et al. 2013)
Aminopropyl triethoxysilane		6.3	
Bentonite	Weak acid scarlet	102	(Guo et al., 2012)
Polypropylene Imine	Reactive black 5	6250	(Sadeghi et al., 2013)
	Reactive red 198	5882.35	
Diethylenetriamine	Acid orange	6.6914	(Yan et al., 2013)
	Acid red-green 25		
	Acid red 18		
	Acid green 25 AG25		
Sodium Dodecyl Sulfate	Congo red	271.74	(Chatterjee et al., 2011)
Polyethyleneimine	Reactive black 5	709.27	(Chatterjee, et al., Woo 2011)
Polymethyl Methacrylate	Reactive blue 19	1498	(Jiang et al., 2014)
Sponges	Rose Bengal	601.5	(Wang et al., 2017)
Scaffold	FD&C blue 2, FD&C red 40, FD&C yellow 5, FD&C yellow 6 and Food red 2	3316	(Esquerdo et al., 2014)
Crawfish	Methyl orange	60	(Esquerdo et al., 2014)
Scales of prawns and labeo rohita	Acid yellow 73	0.18	(Iqbal et al., 2011)
Fish shell	Methyl orange		(Angham, 2013)
Powder	Acid blue 9	3316	(Dotto and Pinto, 2011)
	Food yellow 3		
Film	Tartrazine	413.80	(Rêgo et al., 2013)
	Amaranth	278.30	

Table 2.1 Continued

Modification Component(S)	Dye	q_{max} mg/g	Source
Pristine	Direct red 23	155	(Mahmoodi et al., 2011)
	Acid green 25	178	
Siliceous mesoporous	Acid red	201.2	(Gao et al., 2014)
Flakes	Reactive red 3 (RR-3)	151.5 2	(Ignat et al., 2012)
	Direct brown 95	41.84	

2.2.1 Cross linkage of chitosan

Cross-linking agents are molecules with at least two reactive functional groups that enable bridges between polymer chains to be formed. Cross linkage is considered a covalent bond when the amino group and secondary hydroxyl group of the CH react in an intramolecular and intermolecular fashion with the aid of a crosslinking agent. Crosslinkers such as glutaraldehyde, formaldehyde, epichlorohydrin (ECH), and ethylene glycol diglycidyl ether (EGDE), isocyanates, and glyoxal are some commonly used crosslinkers. Epoxides, hexamethylene diisocyanate, and carboxylic acids are covalent crosslinkers for CH derivatives respectively. While an ionic cross-linkage involves a reaction of ionotropic gelation when the molecules of the crosslinking molecules contain opposite charges and blended with the hydrogel network of the CH molecules. Crosslinkers such as sodium tripolyphosphate (TPP), cyclodextrin (CD), and sodium sulphate are commonly used ionic cross-linkers (Chiou and Li, 2003, Abraham et al, 2018).

2.2.2 Chitosan-based membrane

Membrane adsorbents have emerged as desirable and effective tools for the removal of hazardous materials such as dyes, and heavy metals. CH solubility in low acidic solutions, insufficient mechanical resistance caused deteriorations in the

chitosan-based films to be stable in acidic medium. Therefore, CH solubility is a significant concern for its application in a solution below pH 6 as a biopolymer for wastewater environmental remediation. Several works of literature have been conducted to overcome these shortcomings (Seo et al., 2014; Olivera et al. 2016; Premakshi et al., 2015). Resistance to acidic environment and adsorption capacity enhancement was attained by a composite of CH preparation using bentonite, polyurethane, montmorillonite, activated clays, perlite PVA, PVC, use of cross linkers and kaolinite (Salehi et al., 2016). Nano biomaterials have been reported for embedding compatibility to achieve better physical strength for the membrane (Karim et al., 2014). Porosity is one of the most important features that greatly affect the separation performance of the polymeric membranes. Studies were made to control the membrane porosity to obtain a break-even threshold between the selectivity and permeability conferring to the separation mechanism involved (Bessbousse et al., 2010). The membranes prepared was treated using silica impregnation, the dissolution of silica in alkaline medium at high temperature (80 °C for 2h) did not apparently alter their mechanical properties, that is flexibility and resistance.

The methods of synthesis of CH-based membrane are designed for better stability. To do so, many inventive techniques were used to create porous and often dense films that were composited or assisted. Significantly, all the studied aims were to improve the adsorptive property of the membrane, as well as its permeability and physicochemical stability.

2.3 Surface functionalities on chitosan

CH physicochemical properties such as the functional groups, source, surface area, crystallinity, solubility, and porosity influence its adsorption performance.

Surface characteristics such as mechanical and chemical resistance impaired the surface of CH for the adsorption process. Hence, surface alteration of CH affects its efficiency and performance for different applications. It can be converted into beads, fibres, sponge/hydrogel, films, nanofibers, scaffold/bandage, composite, nanoparticles/ microparticles and membrane. Also with grafting/chemical addition to adding hydrophilic functional groups to improve its adsorption capacity, mechanical and chemical constraints are for better performance (Yu et al., 2018; Pang et al., 2020). Meanwhile, the functional group modification process for surface of CH includes crosslinking, grafting, N-alkylation, and O and/or N-acylation.

2.3.1 Grafting

The addition of polymer chains initiated and propagated onto the surface of CH through partial alkylation and/or acylation reaction is known as grafting. In other words, it is a process of introduction of side chains of new functional groups and designed to produce novel hybrid materials that tailored the properties of the composing molecular entities. Many promising CH derivatives could be obtained through grafting for variety of applications in environmental pollution control, pharmaceuticals, and medicine. It is currently considered and applied as carrier materials in drug delivery systems, haemostatic agent, wound healing, gene therapy, antibacterial, scaffold, enzymatic, and adsorption studies which are published in a large number of studies over few years (Wang et al., 2017; Yu et al. 2015; Ilyina et al., 2000). Grafting of new functional groups on CH make it as a versatile material to be processed into different forms, such as beads, membranes, sponges or hydrogels, nanoparticles/microparticles for the design of diverse medical and pharmaceutical devices (Yu et al., 2018). There are many grafted CH hybrid with improved properties

due to side-chain inclusion that changes the characteristics such as the molecular structure, crystallinity, hydrophilicity, length and other properties (Yu, et al, 2018; Kurita et al., 2002; Crini, 2005). Moreover, CH and CH grafted adsorbents were reported with high affinity for various classes of dyes such as anionic, vat, sulfur, naphthol, disperse, direct and reactive dyes were also have been reported to adsorbed dyes with the promising performance (Chao et al., 2004; Singh et al., 2009; Karthik and Meenakshi, 2014).

2.3.2 N-alkylation

Ketimines and aldimines known as Schiff base are produce when amino groups of CHs react with ketones and/or aldehydes respectively. Hydrogenation of the Schiff base with borohydride converts it to N-alkyl CH as presented in Figure 2.3.

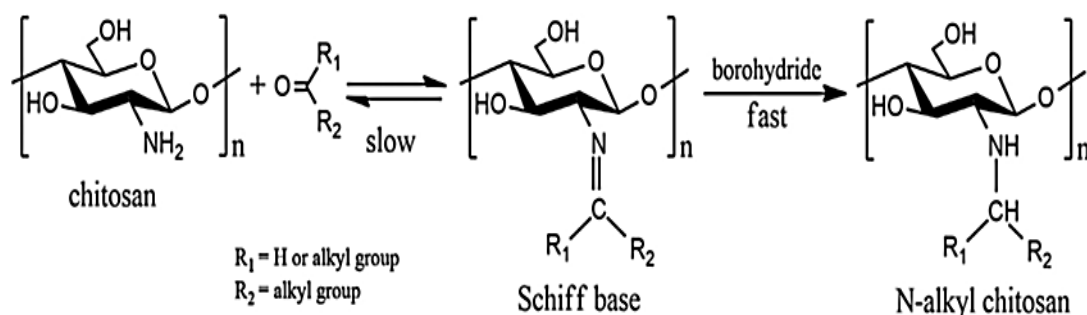


Figure 2.3 Reduction of N-alkylation of CH with aldehyde/ketone and borohydride

Amino groups have means to be protected and improve its activities by alkyl substitutions, it is decided by the ketones or aldehydes alkyl group through different grafting methods such as modification to various degrees of substitution to obtain N-alkyl CH using methanol solvent, here it produces 100 % ratio of alkylation (Sashiwa et al., 2003), reductive alkylation reaction to produce N-benzyl CH with significant fungicidal activity (Badawy, 2008). Therefore, CH alkylation is considered as an effective way to prepare a derivative with improved properties to CH molecules. N-

alkyl interaction through carboxyalkyl and hydroxyalkyl can be obtained equally by grafting through the CH skeleton to hydrogel crosslinked CH like alkyl reduction of starch (Baran et al., 2004).

2.3.3 Acylation of chitosan

Stability and solubility of CH could be improved in an organic solvent by the varied introduction of aromatic and fatty acyls of different molecular weight, due to the change in CH crystalline structure and breaking down of intermolecular hydrogen bonds (Kucharska et al., 2019; Franca et al., 2020). It is known that most acyl CH are soluble in water, organic solvents like dichloro-acetic acid and formic acid and benzyl alcohol. CH acylation is also used to improve the surface characteristics which is usually achieved through both amino and hydroxyl groups by reaction with mostly acyl anhydrides and chlorides to the O, N-acyl known as O-acyl and N-acyl CH respectively. Figure 2.4 and 2.5 illustrates route for N-heterocyclic chitosan derivatives and a synthetic scheme for the conversion of chitosan to O, O-decanoyl chitosan respectively.

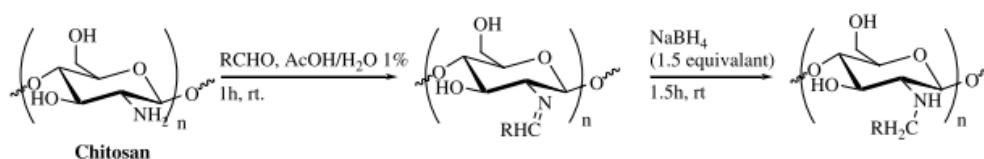


Figure 2.4 Synthetic route for N-heterocyclic chitosan derivatives

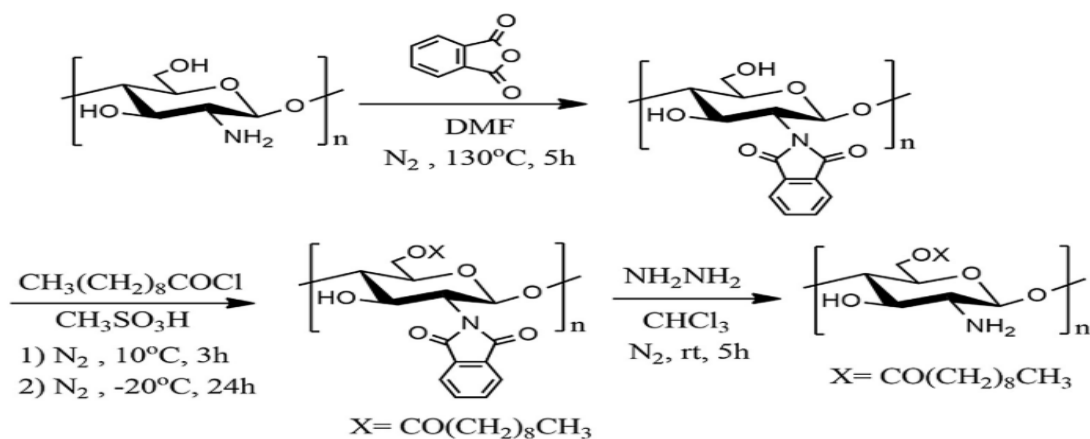


Figure 2.5 Synthetic scheme for the conversion of chitosan to O, O-decanoyl chitosan.

Hydrophobic CH derivatives were prepared through various methods by the hydrophobic combination of groups into it. The hydrophobic character of CH matrices increases the application potentials of CH for drug delivery after soaking in pyridine by reaction with fatty acid chloride (C₆–C₁₂) and the reaction with lauroyl, hexanoyl and decanoyl chlorides (Zong et al., 2000), triethylamine and acyl chloride produced for drug delivery systems (Rodrigues, 2005). However, by dissolving CH MeSO₃H, 4-dimethylamino pyridine (DMAP), N, N, dimethylacetoamide (DMAc), and fatty acyl anhydride to synthesis a novel N-fatty-O-dicinnamoyl, intermediate N-acyl products that protect the amino groups that use hydroxide group produce O-dicinnamoyl (Wu et al., 2005).

2.4 Solvent influence on modification of chitosan

CH like other typical polysaccharides is known to degrade before it is melted to form a solution. An appropriate solvent is necessarily required to dissolve CH and other polysaccharides like cellulose due to their unique intractable, high crystallinity and the limited number of solvent systems to dissolve them to impart functionality. Obviously, one of the reasons for the complexity of CH lies in the rigid crystalline structures (Roy et al., 2017), residues of acetamido or primary amino groups of (N-