SYNTHESIS OF CHITOSAN-ACTIVATED CARBON COMPOSITES USING HYDROPHILIC IMIDAZOLIUM-BASED IONIC LIQUIDS FOR ADSORPTION OF ACID BLUE 25 DYE, Cd(II) AND Pb(II) FROM AQUEOUS SOLUTIONS

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by

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DEDICATION

I would like to dedicate this thesis to my late father **Mallam Saheed Alade Olowookere,** and my late younger sister **Kafilat Saheed**. I so much appreciate your support and the confidence you have in me when you were alive. May Allah be pleased with both of you and grant you Aljanat Firdaus (Ameen).

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
AB25	Acid blue 25
AC	Activated charcoal/ or activated carbon
AmimBr	1-allyl-3-methylimidazolium bromide
AmimCl	1-allyl-3-methylimidazolium chloride
BET	Brunauer–Emmett–Teller
BmimAc	1-butyl-3-methylimidazolium acetate
C-amimBr	Chitosan/activated carbon composite powder prepared in 1-allyl-3-methylimidazolium bromide
C-amimCl	Chitosan/activated carbon composite powder prepared in 1-allyl-3-methylimidazolium chloride
CB-amimBr	Chitosan/activated carbon composite bead prepared in 1-allyl-3-methylimidazolium bromide
CB-amimCl	Chitosan/activated carbon composite bead prepared in 1-allyl-3-methylimidazolium chloride
CB-bmimAc	Chitosan/activated carbon composite bead prepared in 1-butyl-3-methylimidazolium acetate
CB-EmimAc	Chitosan/activated carbon composite bead prepared in 1-ethyl-3-methylimidazolium acetate
C-bmimAc	Chitosan/activated carbon composite powder prepared in 1-butyl-3-methylimidazolium acetate
C-EmimAc	Chitosan/activated carbon composite powder prepared in 1-ethyl-3-methylimidazolium acetate
Ch	Chitosan
Ch-AC	Chitosan/activated carbon composite prepared in acetic acid
Conc.	Concentration
CS-amimBr	Chitosan/activated carbon composite sponge prepared in 1-allyl-3-methylimidazolium bromide
CS-amimCl	Chitosan/activated carbon composite sponge prepared in 1-allyl-3-methylimidazolium chloride

CS-bmimAc	Chitosan/activated carbon composite sponge prepared in 1-butyl-3-methylimidazolium acetate
CS-EmimAc	Chitosan/activated carbon composite sponge prepared in 1-ethyl-3-methylimidazolium acetate
D-R	Dubinin-Radushkevich
EDX	Energy dispersive x-ray spectrometry
EmimAc	1-ethyl-3-methylimidazolium acetate
FTIR	Fourier transform infrared spectroscopy
ILs	Ionic liquids
PFO	Pseudo first order
PSO	Pseudo second order
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV	Ultraviolet-visible
XRD	X-ray diffraction

LIST OF SYMBOLS

A_T	represents the equilibrium binding constant
b_T	Temkin isotherm constant related to the heat of adsorption
C	Thickness of the boundary layer in intraparticle diffusion equation
c	Initial concentration of the adsorbate
c_e	Equilibrium concentration of the adsorbate
E	Adsorption mean free energy
k_1	Rate constant for pseudo first order
k_2	Rate constant for pseudo second order
K_F	Freundlich constant related to adsorption capacity
k_{id}	Intraparticle diffusion rate constant
K_L	Langmuir isotherm constant associated with free energy and the affinity of adsorption
n	Heterogeneity factor
pH_{pzc}	Point of zero charge
q_d	Dubinin-Radushkevich constant related to maximum adsorption capacity
q_e	Equilibrium amount of the adsorbate (AB25, Cd(II) or Pb(II)) adsorbed onto the adsorbent
q_{max}	Maximum adsorption capacity of the adsorbent
q_t	Equilibrium amounts of the adsorbate adsorbed onto the adsorbents at time, t
R^2	Correlation coefficient
R_L	Separation factor
β	Constant related to free energy
ε	Polanyi potential
ΔG^o	Gibb’s free energy change
ΔH^o	Enthalpy change
ΔS^o	Entropy change

SINTESIS KOMPOSIT KITOSAN-KARBON TERAKTIF MENGGUNAKAN CECAIR IONIK-IMIDAZOLIUM BERSIFAT HIDROFILIK BAGI PENJERAPAN PEWARNA ASID BIRU 25, Cd(II) DAN Pb(II) DARIPADA LARUTAN AKUES

ABSTRAK

Kitosan adalah penjerap yang menjanjikan untuk penyingkiran bahan cemar tetapi ketidakstabilannya dalam medium berasid mengehadkan potensinya, dan oleh itu pengubahsuaiannya adalah perlu. Pendekatan sintesis hijau yang menampilkan satu campuran pasu kitosan (Ch) dan arang teraktif (AC) dalam beberapa medium cecair ionik berasaskan imidazolium hidrofilik (ILs) terpilih telah digunakan untuk mengubah suai kitosan kepada serbuk komposit kitosan/karbon teraktif, manik dan span. Komposit yang disediakan telah digunakan untuk penjerapan ion biru asid 25 (AB25), Cd(II) dan Pb(II) daripada larutan akueus. Beberapa IL imidazolium hidrofilik terpilih termasuk 1-allyl-3-methylimidazolium bromide (AmimBr), 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium acetate (EmimAc) dan 1-butil-3-methylimidazolium acetate Medium (BmimAc) telah digunakan untuk pengubahsuaian. Kemungkinan variasi morfologi dan struktur berkenaan dengan watak penjerapan dan kestabilan komposit yang disediakan telah diperiksa menggunakan mikroskop elektron pengimbasan (SEM), spektrometer sinar-x penyebaran tenaga (EDX), analisis Brunauer-Emmett-Teller (BET), inframerah transformasi Fourier. (FTIR) spektrometer, analisis pembelauan sinar-x (XRD) dan analisis termogravimetrik (TGA). Jumlah pewarna AB25 yang terjerap pada komposit ini dipantau menggunakan spektrofotometer boleh dilihat UV, manakala Cd(II) dan Pb(II) yang terjerap dipantau menggunakan spektrofotometer serapan atom (AAS). Pencirian mendedahkan kejayaan interkalasi AC ke dalam Ch untuk membentuk penjerap amorfus yang didominasi permukaan mesopori. Pencirian juga mendedahkan ciri penjerapan yang lebih baik, dan kestabilan kimia dan haba yang lebih baik yang sesuai untuk penjerapan pewarna AB25, Cd(II) dan Pb(II) daripada larutan akueus. FTIR mendedahkan bahawa Ch dan AC disambungkan melalui kumpulan berfungsi O−H, N−H, C−O dan C═O pada kedua-dua prekursor. Pencirian juga mendedahkan bahawa penjerap melekat pada pelbagai komposit terutamanya melalui kumpulan berfungsi amino dan hidroksil, dan cadangan itu adalah selaras dengan mekanisme interaksi mereka. Analisis BET mendedahkan bahawa luas permukaan dan saiz liang bagi komposit Ch yang diubah suai berjulat dari 35.3 − 152.9 m^2/g dan 2.08 - 2.66 nm masing-masing, berbanding Ch iaitu 2.5 m^2/g dan 8.22 nm masing-masing. Komposit Ch/AC yang difabrikasi semuanya stabil dalam larutan berasid dan asas. Penjerapan AB25 pada komposit ubah suai berasaskan imidazolium adalah lebih cekap pada pH 2, manakala penjerapan Cd(II) dan Pb(II) masing-masing lebih cekap pada pH 6 dan 5. Penjanaan semula komposit yang menampilkan penyahjerapan AB25, Cd(II) dan Pb(II) boleh dilaksanakan. Secara amnya, susunan kecekapan penjerapan menunjukkan bahawa bentuk manik > bentuk serbuk > span terbentuk untuk pengambilan AB25, Cd(II) dan Pb(II), kerana ini juga disokong oleh susunan ciri penjerapan mereka yang lebih baik. Penjerapan AB25 pada pelbagai komposit paling baik dihuraikan oleh model Langmuir. Komposit yang disediakan dalam AmimBr dan AmimCl ILs secara konsisten dipasang ke dalam model isoterma Langmuir untuk pengambilan Pb(II) daripada larutan akueus tetapi hanya bentuk serbuk dan maniknya dipasang ke dalam model isoterma Langmuir untuk penjerapan Cd(II). Komposit diubah suai EmimAc dan BmimAc menunjukkan pematuhan yang ketara kepada model Langmuir untuk pengambilan Cd(II). Walaupun, bentuk serbuk dan span boleh diterangkan melalui model Freundlich. Bentuk manik komposit yang difabrikasi dalam AmimBr memberikan kapasiti penjerapan tertinggi untuk AB25 (4761.9 mg/g), manakala kapasiti penjerapan tertinggi untuk pengambilan Cd(II) dan Pb(II) diperolehi dalam manik komposit yang difabrikasi dalam EmimAc dengan nilai 84.75 mg/g dan 114.94 mg/g masing-masing. Kinetik penjerapan untuk pengambilan AB25, Cd(II) dan Pb(II) semuanya dipasang paling baik ke dalam model tertib pseudo-saat dan mekanisme penjerapan dikawal oleh penyebaran filem. Kajian termodinamik mengenai penjerapan AB25, Cd(II) dan Pb(II) ke atas pelbagai penjerap mendedahkan proses endotermik. Oleh itu, interaksi penjerap-penjerap antara komposit Ch/AC yang diubah suai dan Cd(II) dan Pb(II) berbeza daripada AB25 kerana larutan yang lebih berasid memihak kepada penjerapan AB25 (pH 2 untuk AB25, pH 6 untuk Cd(II) dan pH 5 untuk Pb(II)). Oleh itu, pelbagai bentuk komposit Ch/AC dengan kapasiti penjerapan yang baik dan kestabilan terhadap penjerapan AB25, Cd(II) dan Pb(II) telah berjaya difabrikasi dalam IL berasaskan imidazolium hidrofilik terpilih.

SYNTHESIS OF CHITOSAN-ACTIVATED CARBON COMPOSITES USING HYDROPHILIC IMIDAZOLIUM-BASED IONIC LIQUIDS FOR ADSORPTION OF ACID BLUE 25 DYE, Cd(II) AND Pb(II) FROM AQUEOUS SOLUTIONS

ABSTRACT

Chitosan is a promising adsorbent for the removal of contaminants but its instability in acidic medium limits its potentials, and therefore its modification is necessary. Green synthesis approach featuring one pot mixture of chitosan (Ch) and activated charcoal (AC) in some selected hydrophilic imidazolium based ionic liquids (ILs) medium was utilised to modify chitosan into chitosan/activated carbon composite powders, beads and sponges. The prepared composites was utilised for the adsorption of acid blue 25 dye (AB25), Cd(II) and Pb(II) ions from aqueous solutions. Some selected hydrophilic imidazolium ILs including 1-allyl-3-methylimidazolium bromide (AmimBr), 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium acetate (EmimAc) and 1-butyl-3-methylimidazolium acetate (BmimAc) medium were utilised for the modification. The possible morphological and structural variation with respect to adsorptive characters and stability of the prepared composites were examined using scanning electron microscope (SEM), energy dispersive x-ray spectrometer (EDX), Brunauer–Emmett–Teller (BET) analysis, Fourier transform infrared (FTIR) spectrometer, x-ray diffraction (XRD) analysis and thermogravimetric analysis (TGA). The amount of the AB25 dye adsorbed onto these composites was monitored using UV-visible spectrophotometer, while Cd(II) and Pb(II) adsorbed was monitored using atomic absorption spectrophotometer (AAS). Characterisation revealed a successful intercalation of AC into the Ch to form mesoporous surface dominated amorphous adsorbents. Characterisation also revealed an improved adsorptive feature, and improved chemical and thermal stability suitable for the adsorption of AB25 dye, Cd(II) and Pb(II) from aqueous solutions. The FTIR revealed that Ch and AC were connected through O−H, N−H, C−O and C═O functional group on both precursors. Characterisation also revealed that the adsorbates adhered to the various composites predominantly through the amino and hydroxyl functional groups, and the suggestion is concordant with their mechanism of interactions. The BET analysis revealed that the surface area and pore sizes of the modified Ch composites ranges from 35.3 − 152.9 m^2/g and 2.08 − 2.66 nm respectively, against that of Ch that was 2.5 m^2/g and 8.22 nm respectively. The fabricated Ch/AC composites were all stable in acidic and basic solutions. The adsorption of AB25 onto the imidazolium based modified composites was more efficient at pH 2, while that of Cd(II) and Pb(II) were more efficient at pH 6 and 5 respectively. Regeneration of the composites featuring desorption of AB25, Cd(II) and Pb(II) was feasible. In general, the order of adsorption efficiency shows that bead forms > powder forms > sponges form for AB25, Cd(II) and Pb(II) uptake, as this is also supported by the order of their improved adsorptive features. Adsorption of AB25 onto the various composites is best decribed by Langmuir model. Composites prepared in AmimBr and AmimCl ILs consistently fitted into Langmuir isotherm model for Pb(II) uptake from aqueous solution but only their powder and bead forms fitted into Langmuir isotherm model for adsorption of Cd(II). EmimAc and BmimAc modified composites show appreciable conformity to Langmuir model for Cd(II) uptake. Though, the powder and sponge forms could be described through Freundlich model. The bead form of the composite fabricated in AmimBr gave the highest adsorption capacity for AB25

(4761.9 mg/g), while the highest adsorption capacities for Cd(II) and Pb(II) uptake were obtained in the composite bead fabricated in EmimAc with the value of 84.75 mg/g and 114.94 mg/g respectively. The adsorption kinetics for AB25, Cd(II) and Pb(II) uptake all fitted best into pseudo-second-order model and the mechanism of adsorption is controlled by film diffusion. The thermodynamic studies of the adsorption of AB25, Cd(II) and Pb(II) onto the various adsorbents revealed an endothermic process. Thus, adsorbent-adsorbate interactions between the modified Ch/AC composites and Cd(II) and Pb(II) differs from that of AB25 as a more acidic solution favours the adsorption of AB25 (pH 2 for AB25, pH 6 for Cd(II) and pH 5 for Pb(II)). Hence, various form of Ch/AC composites with good adsorption capacity and stability towards the adsorption of AB25, Cd(II) and Pb(II) were successfully fabricated in the selected hydrophilic imidazolium-based ILs.

CHAPTER 1

INTRODUCTION

1.1 Overview

By nature, living things exist in both aquatic and terrestrial environments. The essential liquid that supports life in aquatic and terrestrial environment is water. Human consumes water for domestic and industrial activities and the wastewater emanating from these activities is often discharged into the environment (Wylson, 2019). The discharge of wastewater into the natural environment has influence on the composition of organic and inorganic matter in aquatic and terrestrial environments due to variation in the composition of chemical substances.

Organic dyes are coloured chemical substance that bond with material and impact colour onto the material in which it is attached. In the past few decades, increase in population and industrialisation has tremendously increased the demand and use of organic dyes. This has resulted into discharge of large amount of organic dyes from textile, printing, paper, plastics industries among others into the aquatic environment and therefore, causing environmental pollution (Kooh *et al.*, 2016). Acid dye, a typical class of organic dye is an anionic dye that is soluble in water and often applied to substrates/textiles at low pH. One of the most widely applied acid dyes is the anthraquinones (Kooh *et al.*, 2016). The anthraquinone type of colourants is quite rich in violet from blue to green colour (Yetilmezsoy *et al.*, 2020). Meanwhile, the AB25 is often used as a model compound for anthraquinone class of acid dye.

Heavy metals are chemical elements with relatively high densities that are obtained as natural components of the earth crust. They are harmful metals that are considered toxic even at low concentrations. Due to their non-degradable characteristics, they tend to bio-accumulate when they enter into human body through the food, water and air causing serious health disorder. Heavy metals find their ways into water system through some industrial and consumer waste discharge, or through leaching from rocks into rivers, streams and groundwater. Examples of these heavy metals include chromium (Cr), copper (Cu), zinc (Zn), silver (Ag), gold (Au), cadmium (Cd), mercury (Hg), lead (Pb), thallium (Tl). Meanwhile, Cd and Pb have been considered among the most harmful heavy metals which must be eliminated from the water system (Vakili *et al.*, 2019), and therefore Cd(II) and Pb(II) ions have been selected for this study.

In recent time, physical and chemical methods have been utilised in various ways for removing dyes and heavy metals pollutants from aqueous medium. These methods include precipitation, coagulation, photocatalytic degradation, electrochemical process, adsorption on solid surfaces such as clay, activated carbon and functionalised polymer materials, chemical oxidation, ion exchange, and ultrafiltration (Batool *et al.*, 2018; Salama *et al.*, 2018; Šíma & Hasal, 2013; Y. Wang *et al*., 2018). Among these methods, adsorption is said to be more popular for the removal of dyes and heavy metals from aqueous solutions due its simplicity of design, low cost and relative effectiveness (Morshedy *et al*., 2021; Yetilmezsoy *et al*., 2020).

Chitosan, a well-known polysaccharide and biopolymer that is biodegradable and non-toxic, commonly prepared via de-N-acetylation of chitin. Its distinct characteristics not limited to its active primary and secondary hydroxyl functional groups. In addition, the active amino functional group serves as binding sites for dyes and heavy metals. Thus, made it a potentially useful biopolymer for eliminating dyes and heavy metals from aqueous medium (Guibal, 2004; Wan Ngah *et al*., 2011; Jianlong Wang & Zhuang, 2017). Ch can be modified through chemical or physical process, or via combination of both processes to improve its adsorptive features for pollutants removal, and its chemical, thermal and mechanical stabilities.

Chemical modifications of Ch are carried out through grafting, crosslinking using crosslinkers such as glutaraldehyde and epichlorohydrin, and blending with solid support such as porous carbon, metals and clay (Demarchi *et al*., 2015; Jawad *et al*., 2021; Kausar *et al*., 2019; Vanamudan & Pamidimukkala, 2015; Yadaei *et al*., 2018). The crosslinking and blending are often utilised to improve the chemical, thermal and mechanical stability of the Ch (Malakootian *et al*., 2018). Furthermore, crosslinkers such as glutaraldehyde and epichlorohydrin which are used for Ch modification to improve its chemical and thermal stabilities have been reported to be toxic at certain level of concentrations (Szymańska & Katarzyna, 2015) and as well reduce adsorption capacity towards pollutants removal. Therefore, blending of Ch with carbonaceous materials (such as AC) and metals offers a good support to enhance the thermal and chemical stabilities of chitosan-based materials and as well enhance its adsorption capacity towards the pollutants (dyes and metals) removal (Arumugam *et al*., 2018; Chen & He, 2017; Wan Ngah *et al*., 2011). Physical modification of Ch into beads, sponge and membrane are often utilised to strengthen the stability of Ch and Ch-based materials for adsorption applications. This study provides information regarding good adsorptive features, and good thermal and chemical stability owing to the modification of Ch through blending with AC as support couple with the physical modification into bead and sponge forms.

Nowadays, there is a great attention towards the use of ionic liquids (ILs) as solvent, most especially due to its “green” property linked to its environmental friendly characteristics. ILs are organic salts with melting temperature considerably lower (usually below 100 ºC) for existing as liquid (Kim *et al*., 2009; Pham *et al*., 2010). Exceptional properties including non-flammability, negligible vapour pressure, good chemical and thermal stability and high solvent capacity have been attributed to ionic liquids (Silva *et al*., 2017). ILs are being widely applied as the substitute for most conventional organic solvents often utilised in various applications. Commonly, the modifications of Ch are often carried out in acetic acid as solvent medium which is less environment friendly compared with imidazolium-based ILs (Clarke *et al*., 2018; Hessel *et al*., 2022; Pacheco-Fernández & Pino, 2019; Welton, 2015). It has been reported that the commonly applied adsorbents such as AC and clay are relatively inefficient towards the adsorption of hydrophilic imidazolium based ILs (Mrozik *et al*., 2008; Palomar *et al*., 2009). Therefore, the hydrophilic imidazolium based ILs can serve as solvents medium for the modification of Ch. To the best of our knowledge, this work is reporting the first investigation on the use of environmental friendly hydrophilic imidazolium based ionic liquids medium for the modification of chitosan into chitosan-activated carbon composite. The influence of various hydrophilic imidazolium-based ILs solvent medium on the efficiency of the modified Ch composites for adsorption of AB25 dye, Cd(II) and Pb(II) was investigated. This was carried out by carefully selecting four highly water miscible ILs 1-allyl-3-methyl imidazolium chloride (AmimCl), 1-allyl-3-methyl imidazolium bromide (AmimBr), 1-ethyl-3-methyl imidazolium acetate (EmimAc) and 1-butyl-3-methyl imidazolium acetate (BmimAc) as the solvent medium.

1.2 Problem statements

The volume of wastewater being generated from industries around the world is enormous (Saheed *et al*., 2017; Wylson, 2019). Improper treatment of wastewaters containing anthraquinone dyes disturbs the natural water environment by not only impairing the environmental water quality, but also result into various health problems including skin irritation, dermatitis, cancer and reproductive system disorder in humans (Ghodbane & Hamdaoui, 2010; Jiang *et al*., 2020). Similarly, discharge of heavy metals into the environment has been a serious threat to the survival of human and other living organisms (Shan *et al*., 2015; Tangjuank & Insuk, 2009). In order to provide a healthy and safe environment for human and other living organisms, contaminated waters must be adequately treated before being discharged into the environment. Various methods such as flocculation, electrochemical treatments, oxidation, adsorption, biodegradation, photocatalytic degradation and Fenton's oxidation have been utilised to remove these harmful substances from wastewater (Jiang *et al*., 2020). However, due to the non-biodegradable and stable molecular structure of anthraquinone dyes in one hand and peculiar characters of heavy metals on the other hand, these contaminants are difficult to remove during wastewater treatment. Meanwhile, among these purification techniques, adsorption is often preferred due to its simplicity, low energy consumption, efficiency and rapid process (Jiang *et al*., 2020). This has intensified research interest into the search for an excellent adsorbent for the removal of these pollutants.

Despite the advantages offered by Ch and Ch-based materials on the elimination of dyes and heavy metals from aqueous medium, there are challenges on the use of Ch and Ch-based materials for the removal of anionic dyes and heavy metals (most especially Cd and Pb) that often show good sorption efficiency in acidic pH medium. As Ch and many Ch-based materials display good potential for the removal of anionic dye in acidic medium (Chiou *et al*., 2004; Sovan Lal, 2012), heavy metals like Cd(II) and Pb(II) are also sorbed in acidic medium to avert metallic ions precipitation in basic medium (Hasan *et al*., 2006). Meanwhile, chitosan has been reported to have low stability in highly acidic medium including its soluble character at low pH medium. This has made chitosan unfavourable for adsorption application in low pH medium (Lakkaboyana *et al*., 2021). Crosslinking using the commonly applied crosslinkers such as glutaraldehyde and epichlorohydrin is often used to modify Ch to improve its thermal stability as well as its chemical stability in acidic medium (Kyzas & Bikiaris, 2015; Wang & Zhuang, 2017). However, these frequently used crosslinkers like glutaraldehyde and epichlorohydrin are said to be toxic at certain concentrations (Szymańska & Katarzyna, 2015). In addition, crosslinking process has also been reported to reduce the adsorption efficiency of Ch and Ch-based materials for dyes uptake (Jóźwiak *et al*., 2017; Tahira *et al*., 2019) including the anionic dyes like AB25. In order to avoid the decrease in the adsorption efficiency of Ch and Ch-based material arising from crosslinking, Ch is blend with activated carbon as support. Introduction of toxic materials into adsorption medium via the use of crosslinkers is also avoided by blending chitosan with activated carbon as support to improve it adsorptive features, chemical and thermal stability for the removal of AB25, Cd(II) and Pb(II) from aqueous medium.

In most previous works done on the modification of Ch and Ch-based materials for the removal of pollutants from aqueous medium, Ch is often modified in aqueous solution of acetic acid. Meanwhile, acetic acid is one of the mostly utilised conventional organic solvents for laboratory and industrial applications. It often finds its way into the environment during usage due to its volatility or enters the environment after usage as a waste (Patil & Kulkarni, 2014; Witkowska-Dobrev *et al*., 2021). Acetic acid being a volatile organic compound and flammable liquid with a pungent odour reportedly has an odour threshold of 2 ppm (Ernstgård *et al*., 2006). Meanwhile, volatile organic compounds (VOCs) are emitted into the earth's atmosphere from a variety of natural and anthropogenic sources (Gouw & Warneke, 2007; Zhu et al., 2020). The anthropogenic emission sources of VOCs are primarily derived from industrial processes (43%), vehicle exhausts (28%), agriculture (14%), whereas the industrial production involve the use of solvents, paints, and other household chemicals which leads to the release of various VOCs (Gouw & Warneke, 2007; Zhu et al., 2020). One of the most abundant volatile carboxylic acids in the troposphere and fermented wastewater is acetic acid. It composed of about 2.5-10 g/L in fermented wastewater (Reyhanitash et al., 2017). The concentrations of acetic acid (in the troposphere) reported in the literature vary by season, location and time of day as its range from 0.05 to 16 ppbV gas-phase acetic acid. Usually, the concentrations are higher during the day, dry season, and in urban areas (Carlos-ceulllar et al., 2003). A high concentration of this solvent in the environment as a result of its frequent release is dangerous to human health (could cause irritation of eyes and respiratory tract, headaches, skin rashes, nausea and fatigue) and other living organisms (Pacheco *et al*., 2019).

In an attempt to find substitute for the modification of Ch in acetic acid medium, hydrophilic imidazolium-based ILs known as environmental friendly (Clarke *et al.*, 2018; Pacheco-Fernández & Pino, 2019; Welton, 2015) green solvents was employed. Imidazolium-based ILs with unique features such as negligible vapour pressure, low melting points, high thermal stability, large spectrum of room temperature, adjustable viscosity, high conductivity, and a wide widow of electrical stability were utilised as the modification medium. Therefore, 1-allyl-3-methylimidazolium bromide (AmimBr), 1-allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium acetate (EmimAc) and 1-butyl-3-methylimidazolium acetate (BmimAc) ILs were carefully selected for the study due to their stability and high level of miscibility with water.

In recent times, some of the commonly applied Ch-based adsorbents used for the removal of dyes and heavy metals from aqueous medium are being subjected to further modification into beads to improve its adsorptive properties and stability (Liu *et al*., 2012; Xu *et al*., 2017; Yu *et al*., 2013). This further modification could prevent leaching; improve its efficiency for pollutants uptake and as well consolidate its reusability (Li & Bai, 2005). In an attempt to further enhance the adsorptive features, chemical stability, and reusability of the Ch/AC composite, the modified Ch composite is subjected to further modification into beads and sponges.

1.3 Research objectives

In a bid to find solution to the aforementioned shortcomings, the main aim of this research work focus on the development of efficient, thermally and chemically stable Ch/AC composite materials modified in environmentally friendly hydrophilic imidazolium based ILs for the removal of contaminants (AB25 dye, Cd(II) and Pb(II)) from aqueous medium. In order to achieve the targeted goal, it is important to specifically understand the composition, surface characteristics and morphology of the modified Ch in one hand, and the interaction in relation to adsorption between the modified Ch and the contaminants (AB25 dye, Cd^{2+} and Pb^{2+}) on the other hand. Hence, the specific objectives of this research include:

i. To synthesise and characterise various Ch/AC composites' powder, bead and sponge in AmimCl, AmimBr, EmimAc and BmimAc solvent medium through gentle heating under airtight condition.
ii. To evaluate the adsorption features and chemical stability of the fabricated Ch/AC composites' powder, beads and sponges.
iii. To assess the affinity of Ch/AC composite for hydrophilic imidazolium-based ILs via the adsorption of 1-butyl-3-methylimidazolium bromide (utilised as a representative of hydrophilic imidazolium-based ILs).
iv. To determine the adsorption capacity of the fabricated Ch/AC composites' powders, beads and sponges with respect to AB25, Cd(II) and Pb(II) removal from aqueous solution.
v. To assess adsorption kinetics and thermodynamics of the composites-adsorbate interaction and the possibility of spent composite regeneration for the various fabricated Ch/AC composites.

In this research work, adsorption process was adopted due to its good efficiency, simplicity of design and low cost compared to other methods such as electrochemical method and photocatalytic degradation method. The ultraviolet-visible (UV-Vis) spectrophotometer was utilised to measure the concentration of the AB25 onto the modified chitosan because it is fast, simple and of low cost compare to chromatographic method like HPLC. The atomic absorption spectrophotometry (AAS) was utilised to measure the concentration of Cd(II) and Pb(II) onto the modified chitosan due to its simplicity of design and inexpensive compare to inductively coupled plasma optical emission spectroscopy (ICP-OES). Chitosan was selected as the primary material for modification not only because of the presence of good active sites like amino and hydroxyl functional groups in its structure but also because of its availability in abundant. Activated carbon was selected as a support for improving the stability of chitosan because of its history as a good adsorbent for pollutants uptake.

1.4 Thesis outline

This thesis is divided into five chapters. **Chapter 1** is the introduction part that describes the general overview of the research work, problem statements and the research objectives. **Chapter 2** is the literature review section that contains literatures that are relevant to this study. **Chapter 3** is the materials and methods section that succinctly highlight the chemical reagents and the experimental procedures utilised in this study. The chapter has nine subsections numbered 3.1−3.9 with details information and explanations on the following accordingly – chemicals, instrument and apparatus, preparation of solutions, preparation of samples, solubility test, sample characterisation, adsorption procedures, desorption procedures, and fitting of experimental data to isotherm, kinetics model and thermodynamics equations. **Chapter 4** is the results and discussion section that provides detailed information on the overall finding of the conducted experiments and analysis. This chapter is also divided into five subsections numbered as 4.1−4.5 encompasses results and detailed discussions on the subject of the subsections including solubility test on samples, sample characterisation, adsorption studies on BmimBr uptake, adsorption studies on AB25 dye uptake, and adsorption studies on Cd^{2+} and Pb^{2+} ions uptake. Section 4.3−4.5 of chapter 4 also highlights critical area of studies including optimisation, kinetic studies, thermodynamic studies, and material regeneration studies are all included in this section along with the relevant discussion. Lastly,

chapter 5 contains the general conclusion on the overall results and recommendations future research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

Adsorption is a process by which atoms, molecules or ions existing as solutes in gaseous or liquid phase adhere to the surface of solids, rarely liquids. The solute (i.e the molecules or ions) in the gaseous or liquid phase is called the adsorbate, while the solids onto which the adsorbate stick to its surface is called the adsorbent. The adsorption of molecules onto the solid surface is associated with the molecules or atoms on the solid surface having residual surface energy as a result of unbalanced forces. Therefore, attraction occurs due to unbalanced forces when some substances collide with the surface of the solid adsorbent and this makes the material to stick to the solid surface (Hu & Xu, 2020).

Adsorption is usually a surface phenomenon, in which only the adsorbent's surface is involved, and the adsorbate molecules do not penetrate into the structure of the adsorbent like in the case of absorption. Meanwhile, the reverse of adsorption process is desorption, in which the adsorbate molecules are detached from the surface of a solid surface (Artioli, 2008). Adsorption process could occur naturally in the environment and has tremendously found wide application in removal of contaminants from wastewater (Zhang *et al.*, 2016), and for other industrial applications.

Adsorption process can be categorised into two types based on the kinds of forces that exist between the adsorbent and the adsorbate. This includes; (i) physical adsorption (also called physisorption) and (ii) chemical adsorption (also called chemisorption). Physisorption occurs as a result of weak electrostatic interactions between the adsorbate molecules and adsorbent surface. The adsorbate-adsorbent interaction in physisorption usually involves the weak Van der Waals forces. Whenever the adsorbate molecules strike the surface of the adsorbent at low energy, it is dissipated as heat through the vibration of the lattice of solid, and therefore trapped onto the surface. However, if the molecules strike the surface with high energy, the energy wouldn’t be dissipated by the adsorbent, and the molecules separate from each other. The change in enthalpy that accompanies the physisorption is low, typically < 20 kJ/mol (Artioli, 2008). This implies that the adsorbate and the adsorbent do not undergo any changes in their chemical status (i.e no new bonds are formed and no change in the energetic state), and a phenomenon of a low heating of the adsorbent. The physical bound of the process is highly labile and could easily revert as a consequence of vibrational motion (Artioli, 2008). Physisorption commonly involved a low temperature, fast adsorption rate, low heat energy of adsorption, and non-selective process. As the effect of intermolecular attraction weakens, the structure of the adsorbate barely changes, the adsorption energy tend to smaller value, and the molecules of the adsorbed substance is easily separated (Hu & Xu, 2020).

Chemisorption is a kind of interaction between the adsorbate molecules and adsorbent’s surface that is due to the action of chemical bonds. Chemisorption process can involve the formation and destruction of chemical bonds to bring about adsorbate-adsorbent attraction (Artioli, 2008; Hu & Xu, 2020). The change in enthalpy of adsorption is higher, and it usually > 40 kJ/mol (Artioli, 2008).. An activated process may result from chemical adsorption such that the adsorbate possesses a minimum amount of energy in order to be adsorbed. This is associated with the presence of energetic barrier between the physisorbed and chemisorbed state. If the energy barrier is higher than the energy of the molecules in its free state, the adsorbate will engage in chemical bond with the adsorbent as its energy is higher than the energy barrier, otherwise it will desorb. More so, if the barrier has lower energy compare to the energy of the free molecules, the physisorbed molecules can rapidly form a bond with the surface of the adsorbent, thereby resulting into a rapid chemisorption process (Artioli, 2008). Desorption of a chemisorbed adsorbate-adsorbent interaction is usually an activated process. In order to detach the adsorbate from the surface of the adsorbent, energy is require to be supplied to the molecules to cleave the bonds. Chemisorption usually involves a monolayer (single layer) adsorbent-adsorbate interaction such that, when the surface of the adsorbent is completely occupied through a monolayer adsorbate coverage, there will be no more adsorption, or a dynamic equilibrium will be set up with desorption (Artioli, 2008; Webb, 2003). Physisorption and chemisorption are not isolated and often occur together. Several kinds of adsorption processes in wastewater treatment technology is due to the influence of adsorbates-adsorbent interactions, as either the physisorption or chemisorption might show a leading role (Hu & Xu, 2020).

Recently, several low-cost adsorbents including biosorbents, natural materials, and waste materials from agriculture and industries have been utilised for adsorption of pollutants from wastewater (Rafatullah *et al.*, 2010). Some of the reported sorbents include clay materials, zeolites, siliceous material (silica beads, perlite), agricultural wastes (maize cob, coconut shell and rice husk), waste products from industries (waste carbon slurries and metal hydroxide sludge) and biosorbents (cellulose, chitosan, biomass and peats) (Crini, 2006; Rafatullah *et al.*, 2010). These adsorbents interact with various adsorbates either by a dominant physisorption or chemisorption process (Arumugam *et al.*, 2018; Gomez-maldonado *et al.*, 2019;

Maleki *et al*., 2015). Meanwhile, commercial activated carbon is a popular sorbent for adsorption of contaminants from wastewater treatment, but its widespread use is relatively restricted due to its relatively higher cost (Dey *et al*., 2016; Rafatullah *et al*., 2010; Torabian *et al*., 2010). Alternative non-conventional adsorbents have been investigated featuring biosorbents such as chitosan, which could be prepared as inexpensive materials for adsorption of contaminats (Crini, 2006).

2.2 Chitosan

Chitosan is a polysaccharide obtained through de-N-acetylation of chitin. Chitin, the second most abundant naturally occurring biopolymer, is an amino polysaccharide material in the exoskeleton of insects, crustaceans (e.g shrimbs and crabs), etc that offers support to them. Chitosan consists of deacetylated unit, β-(1→4)-2-amino-2-deoxy-D-glucose and lower portion of the acetylated unit (usually < 20%), β-(1→4)-2-acetamido-D-glucose (Chokradjaroen *et al*., 2018; Ibrahim *et al*., 2011; Kumar *et al*., 2004; Kyzas & Bikiaris, 2015; Mourya & Inamdar, 2008) in its structure as shown in Figure 2.1. Chitosan is of commercial value owing to its higher amount of nitrogen content when compared to synthetically substituted cellulose (Kumar *et al*., 2004). The primary sources of chitosan and chitin includes: cuticle, ovipositors and beetle cocoon of insects; crab and shrimps shells; eye iridophores and epidermis of cephalopods and molluscan; centric diatoms such as *Thalassiosira fluviatilis* and algae; and fungi (Bakshia *et al*., 2019). Meanwhile, the main sources of chitosan for industrial production are crustaceans and fungal mycelia.

Most synthetic polymers usually possess low biocompatibility and biodegradability properties. In spite of that, chitosan is known to be a functionalised natural polymeric substance with a good biocompatibility and biodegradability features, non-toxic (Bakshia *et al*., 2019) among others. These features make chitosan to have diverse applications in many areas including medical, agricultural, food processing, nutritional enhancement, cosmetics, and wastewater treatment (Mourya & Inamdar, 2008). The amino functional groups in chitosan structure could be protonated to provide considerable solubility in dilute acid solutions. In biomedical applications for instance, its positive charge nature enables it to interact with the negative region of cells membrane to facilitate reorganisation and permeation of proteins (Bakshia *et al*., 2019). It is also used as an antimicrobial and wound healing biomaterials (Bakshia *et al*., 2019). In addition to that, chitosan also possesses chelating agent power as a result of its ability to bind with cholesterol, fats, proteins and metal ions (Bhardwaj & Kundu, 2010; Vakili *et al*., 2019).

Chitosan is advantageous for adsorption application (Vakili *et al*., 2019; Vilela *et al*., 2019; Yadaei *et al*., 2018; Yang *et al*., 2016), ranging from its usefulness in environmental remediation (Jawad *et al*., 2017; Li *et al*., 2016) due to its low cost and effectiveness, in addition to its simplicity in polymerisation and functionalisation processes (Aranaz *et al*., 2010; Salamatinia, 2015; Yang *et al*., 2019). It also finds application in the decontamination (Chen *et al*., 2011; Guibal, 2004) of wastewaters containing contaminants of various organic (Chen *et al*., 2017; Midya *et al*., 2019; Vanamudan *et al*., 2014) or inorganic species (Sharififard *et al*., 2018; Sharma *et al*., 2019; Wang *et al*., 2013).

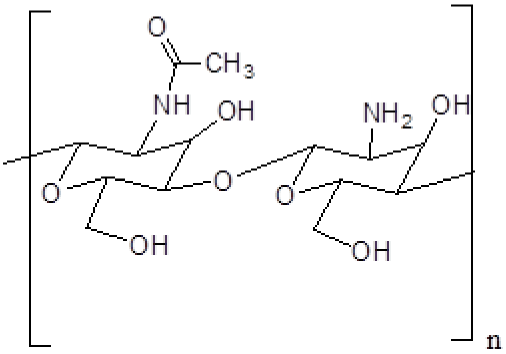

Figure 2.1 The chemical structure of chitosan.

2.2.1 History of chitosan

The discovery of chitin dated back to 1811 by a French researcher called Henri Braconnot while carrying out investigation on fungus, who named the fraction from isolates as fungine (Bakshia *et al.*, 2019). Around 1821, chitin was reported to be present in insects (Roberts, 1992). In 1823, there was a discovery of a material with similar properties fungine in the cuticle of beetles by Odier and was named as chitin (Bakshia *et al.*, 2019; Roberts, 1992). The word chitin was coined from the Greek word “chiton” meaning “coat of mail”. Subsequently, the structure of chitin was determined by Albert Hofmann in 1929 (Finney & Siegel, 2008).

Rouget in 1859 prepared “modified chitin” that was found soluble in organic acid by treating chitin with NaOH solution (Bakshia *et al.*, 2019). Subsequently, Hoppe-Seyler in 1894 prepared chitosan by treating chitin from various alkaline solution of KOH at 180°C (Bakshia *et al.*, 2019). In 1902, Frankel and Kelly ascertained the chemical composition of chitin and chitosan (Roberts, 1992). In 1950s, several researchers have assessed the chemical structures of chitin and chitosan through x-ray experimental determination as some have targeted chitosan as a potential source of bioactive substance in the last few decades (Kumar *et al.*, 2004).

In between 1930 – 1950, there are quite number of published articles on the use of chitin and chitosan before the invention of synthetic fibres overshadowed them later on (Roberts, 1992). Additionally, 1970s also witness a resurgence interest towards research findings on the use of chitin and chitosan (Bakshia *et al*., 2019), which has tremendously increased up to this present time.

2.2.2 Properties of chitosan

The physical and chemical properties of chitosan differ with its molecular weight, extent of the degree of deacetylation, degree of crystallinity, solubility, among others (Lizardi-mendoza *et al*., 2016). The amino/or acetamido and hydroxyl groups of the chitosan’s structural moieties are responsible for the inter/intramolecular hydrogen bonding in chitosan which in turns influence its solubility and reactions (Aranaz *et al*., 2010; Desbrieres, 2002). Mainly, chitosan is lower in structural crystallinity than its chitin counterpart. This lower crystallinity features of chitosan increases accessibility to most common reagents than chitin. However, its ability to decompose prior to melting is responsible for its inability to have a specific melting point range like chitin. Chitosan is soluble in most acidic solution, in which formic acid and ethanoic acid commonly utilised for its dissolution. The protonation of its $-NH_2$ functional group in its molecular structure by acids enhance its solubility in a solvent medium as the polarity of the medium is raised (Kasaai *et al*., 2013; Mourya & Inamdar, 2008). Research findings have also revealed that certain properties of chitosan such as toughness and water absorption could be altered through the modification of chitosan (Don *et al*., 2002; Mourya & Inamdar, 2008).

2.2.2.1 Physical properties

Molecular Weight: The molecular weight of chitosan affect its physicochemical properties such as viscosity, solubility, elasticity and mechanical strength (Bakshia *et al*., 2019; Lizardi-mendoza *et al*., 2016). The tensile strength and elongation effect in chitosan increases proportionally with molecular weight of chitosan. The size of crystals and morphological properties of chitosan's cast films are also affected by its molecular weight (Qinna *et al*., 2015). It has been reported that the crystallinity and permeability of membrane vary with the molecular weight of chitosan (Facchinatto *et al*., 2020; Krajewska, 2005). The extent of chitosan deacetylation could influence a change in molecular weight/average molecular weight within the range of 10 to 10000 kDa (Bakshia *et al*., 2019; Lizardi-mendoza *et al*., 2016). Depolymerisation of chitosan reduces its molecular weight which in turns result into improving its ease of solubilisation in aqueous solution (Aranaz *et al*., 2010; Kasaai *et al*., 2013).

Viscosity: There are various commercial product of chitosan produced widely in various degree of viscosity based on the degree of deacetylation (Szymańska & Katarzyna, 2015). The chitosan solution increases in viscosity as its solution becomes more concentrated and more deacetylated but decreases as the temperature is raised. Relatively high molecular weight and linear structure of chitosan make it useful as viscosity enhancement (Klossner *et al*., 2008). The unusual rheological characteristics of chitosan was linked to the intermolecular connections of its neighbouring hydrophobic substituents embedded into the molecular units via modification procedure (Desbrieres, 2002). The viscometric assessment of chitosan solutions examined using CH_3COOH/CH_3COONa and CH_3COOH /NaCl showed that, the viscosity and flow properties of chitosan solutions vary with the extent of deacetylation of chitosan molecules (Costa *et al*., 2015).

Solubility: Weak acid medium dissolve chitosan and in a general description, aqueous acidic solutions dissolve chitosan (Aranaz *et al*., 2010; Mourya & Inamdar, 2008). Large number of cationic sites produced on chitosan as a result of NH_2 protonation (via acid treatment) of the polymeric chain of chitosan which enhances its solubility, thereby assist in obtaining materials of higher polarity and as well enhance the degree of electrostatic repulsion (Guibal, 2004; Hajji *et al*., 2014). Diluted form of aqueous organic acids (such as formic acid and ethanoic acid) and mineral acids (such as hydrochloric, phosphoric, carbonic, nitric and perchloric acids) are good solvents for chitosan, most especially at pH below 6.5. Experimental findings has revealed that chitosan is soluble in dimethylsulfoxide, *p*-toulene sulfonic acid and 10-camphorsulfonic acid (Mourya & Inamdar, 2008). Meanwhile, sulfuric acid is not suitable for dissolving chitosan as it leads to the generation of insoluble chitosan sulphate substance (Lizardi-mendoza *et al*., 2016). Also, fatty acids medium have not been considered as suitable solvent medium for dissolving chitosan as well (Kurita, 2001). As depolymerisation of chitosan lower its molecular weight and viscosity, the solubility of chitosan in aqueous media are often enhanced (Aranaz *et al*., 2010). Deacetylation process as well as modification of chitosan through hydrophobic moieties affects the solubility of chitosan by altering its hydrogen bonds among other interactions (Knepper, 2015; Qinna *et al*., 2015).

2.2.2.2 Chemical properties

Chemical properties of chitosan depend largely on its functional properties. The polymeric units of chitosan possess the deacetylated and acetylated units that display dissimilar characters. Acetylated units tend to form hydrogen bonding and hydrophobic interactions that stabilize the molecule, which as well impact certain rigidity and therefore reinforce its structural properties. The amino functional group of the deacetylated units could be protonated ($pK_a \approx 6.5$) which transform chitosan into an uncommon cationic polyelectrolyte material (Lizardi-mendoza *et al.*, 2016). The $-NH_2$ and $-OH$ functional groups on the chitosan polymeric chain are susceptible to modification for an enhanced functional characteristics (Lizardi-mendoza *et al.*, 2016). The presence of NH_2 and OH functional groups on chitosan structure also allow good number possible chemical interactions with quite a number of inorganic and organic compounds.

Chemical characteristics of chitosan are also connected with some biological properties such as biocompatibility, biodegradability (Islam *et al.*, 2019), and it has also been linked to specific interactions with various living tissues (Zhang *et al.*, 2019). The interaction between chitosan and transition metals basically involves the coordination of metal with the amino group of chitosan, and it has been reported that the coordination of divalent heavy metals with amino group of chitosan are obtained in a mole ratio of 1:1 (Wu *et al.*, 2010).

Chitosan and chitin exhibit polymorphic behaviour due to their nature. Polymorphic phenomenon exhibited by chitosan result into the emergence of different forms of packing, and the occurrence of various degree polarities of the adjacent chains in the successive sheets. The primary forms of the chitosan's polymorphs are the hydrated form (also known as tendon chitosan) and the anhydrous form (also known as annealed polymorph) (Lizardi-mendoza *et al.*, 2016). The much uncommon functional features of chitosan are associated with the chain conformation structure as well as the structural contacts surrounding the domains of amino functional groups.

X-ray diffraction (XRD) analysis, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) analysis, thermo-physical analysis, scanning electron microscopy and Brunauer–Emmett–Teller (BET) surface area and porosity analysis are among the analytical methods that had been utilised to determine the structural data of chitosan (Grzabka-Zasadzinska *et al.*, 2019; Ibrahim *et al.*, 2011; Kumirska *et al.*, 2010). The BET surface area of chitosan is low (within 2−5 m^2/g), and it is also microporous (Yang et al., 2019). Various modification processes including crosslinking and blending have been employed to improve the surface area and porosity of chitosan for better adsorption performance (Wu et al., 2019; Yang et al., 2019; Zhang et al., 2019). The polar groups of the chitosan moieties offer good region for intra/intermolecular hydrogen bonding, which in turn give rise to linear aggregates material with rigid crystalline domains. Findings revealed that the XRD pattern for hydrated chitosan have orthorhombic unit cell (Ioelovich, 2014; Kumirska *et al.*, 2010). In addition, there are three possible positions of water molecules in the asymmetric unit suggested through modelling. However, the density and thermogravimetric analysis data obtained for the chitosan's polymorph suggested the existence of two water molecules per chitosan identity period. The water molecules found in the hydrated polymorph's structure of chitosan stabilize as its lead to the formation of column-like joints between the crystal layers (Okuyama *et al.*, 1997). Chitosan could exhibit various XRD patterns which give different crystal structures, usually orthorhombic and monoclinic unit cells subject to its polymorphic modifications with acids such as formic, acetic, and propionic acids (Baklagina *et al.*, 2018). Meanwhile, the hydrated and anhydrous chitosan sometimes possess similar crystal structure, but the transformation from hydrated to anhydrous forms are often irreversible and frequently result into loss of chitosan solubility and alteration of its biological properties (Baklagina *et al*., 2018).

In an attempt to further understand the structure of chitosan, FTIR and NMR have also been utilised to give more explanation on the structure of chitosan. Different FTIR absorption bands have been ascribed to various stretching and bending vibrations of chitosan. The stretching vibration signal often observed around 3450−3400 cm^{-1} is assigned to N−H and O−H stretch. The methyl group in $NHCOCH_3$, methylene group in CH_2OH and methyne group in the pyranose ring are ascribed to stretching vibrations signals within the region of 2940−2850 cm^{-1} (Kasaai, 2007). The signals around 1680−1620 cm^{-1} and 1550−1300 cm^{-1} are assigned to C=O of the $NHCOCH_3$ group (Amide I band) and C−N in Amide II, respectively. The region between 1180 and 1000 cm^{-1} in the FTIR spectra of chitosan is always saturated due to the presence of three distinct vibrational signals for C−O−C, C−O−H and C−C ring vibrations (Kolhe & Kannan, 2003; Zvezdova, 2010).

2.2.3 Preparation of chitosan

Recently, chitosan has been isolated from the cell walls of fungi and other living organisms by microwave assisted method, autoclave and liquid cultivation methods among others (Pochanavanich & Suntornsuk, 2002; Sebastian *et al*., 2019; Streit *et al*., 2009). It can also be obtained through enzymatic action of chitin deacetylase on the substrate chitin. Chitosan prepared through microwave assisted extraction method is better deacetylated to higher yield when compare with conventional autoclave method. However, findings have revealed that both methods leads to the production of chitosan having comparable molecular weight and crystallinity (Sebastian *et al*., 2019). Furthermore, the isolation of chitosan from fungi involves a lesser quantity of chemical reagents as only mild conditions are utilised for extraction. Preparation stages involved in this method is minimal, without demineralisation and depigmentation steps, hence less toxic waste substances are generated and therefore being considered as a greener process. An autoclave method that involves the suspension of finely ground mycelia in a solution of 1 M NaOH, with subsequent autoclaving at 121 °C for 15 min have also been reported (Sebastian *et al*., 2019). Alkali insoluble material obtained after the autoclaving was extracted into 2% acetic acid, centrifuged and then the pH of the supernatant was adjusted to pH 10 and re-centrifuged to produce the chitosan's precipitate (Pochanavanich & Suntornsuk, 2002; Sebastian *et al*., 2019).

The various processing steps for the preparation of chitosan from skeletal components of crustaceans includes: Demineralisation (using dilute acid such as dilute HCl), deproteinisation in alkaline solution using sodium hydroxide at about 100ºC to give chitin, and further deactylation of chitin in sodium hydroxide to give chitosan (see Figure 2.2). The preparation of chitosan is often made by deacetylation of chitin through reaction with aqueous alkali solution few hours at 100°C -160 °C or slightly higher temperature for the removal of the acetyl groups from chitin the polymer. Usually, hydrolysis of polysaccharides occurs through acidic attack, therefore alkaline solutions are used for N-deacetylation of chitosan. Crustaceans such as crabs and prawns have been known as the main source of chitin for the preparation of chitosan, meanwhile 40−60% alkaline solutions of sodium hydroxide or potassium hydroxide are often utilised to prepare about 65-97% deacetylated chitosan. The commercial product of chitosan is available in the market in different