EXTRACTION AND CHARACTERISATION OF CHITIN AND CHITOSAN FOR CHROMIUM (VI) ION REMOVAL FROM WASTEWATER

BY

Abdulwadud Yusuf ABDULKARIM, B. Eng. (A.B.U ZARIA) 2009

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DECLARATION

I **Abdulwadud Yusuf ABDULKARIM** declare that the work in this Thesis entitled "Extraction and Characterisation of Chitin and Chitosan for Chromium (VI) ion Removal from Wastewater**"** has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this work was previously presented for another degree or diploma at this or any other Institution.

- ---------- ----------

Signature Date

CERTIFICATION

This Project entitled "EXTRACTION AND CHARACTERISATION OF CHITIN AND CHITOSAN FOR CHROMIUM (VI) ION REMOVAL FROM WASTEWATER" by ABDULKARIM, ABDULWADUD YUSUF meets the regulations governing the award of the degree of Masters in Chemical Engineering of the Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Dr. M. T. Isa ---------- ----------

Chairman Supervisory Committee Signature Date

Dr. J. A. Muhammad ---------- ----------

Member Supervisory Committee Signature Date

Dr. A. O. Ameh ---------- ----------

Member Supervisory Committee Signature Date

Dr. I. A. Mohammed-Dabo ---------- ----------

Head of Department Signature Date

Prof A. A. Joshua ---------- ----------

Dean, School of Postgraduate Studies Signature Date

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ABSTRACT

This study was carried out to investigate the removal of chromium (VI) from chromate solution using deacetylated chitin extracted from mussel shell. Mussel shells were obtained from Gubi dam in Bauchi, Nigeria and chemical method was used to extract chitin and then chitosan from these shells. The mussel shell contained 15.14% chitosan as obtained from the proximate analysis. The extracted chitosan was characterised and used for removal of Cr^{6+} from dichromate – water solution of 0.62 mg of Cr^{6+} per litre of deionised water. The results obtained revealed that the Carbon-Nitrogen ratio of deacetylated chitin was 5.9, with a degree of deacetylation (DDA) of 60.69% and 60.66% as calculated from elemental analysis and FTIR spectra of chitosan respectively. The surface area of the chitosan was determined to be 2.7225 ± 0.0741 m^2/g using the BET machine. The optimum chitosan dosage for chromium removal was found to be 2.5 g at 28 ^oC with a Cr^{6+} removal of 82.3%, the time required for equilibrium to be attained was 80 minutes. The Langmuir isotherm was the best fitted isotherm with an R^2-value of 0.983 and the adsorption process follows the pseudo-second order kinetics with an R^2-value of 0.9997, the adsorption process was established to be reversible with an R_L-value of 0.314. The free sorption energy was (0.224 kJ/mol) which suggests the process was physical. The enthalpy of adsorption was -67.295 kJ/mol K and the Gibbs free energies were all negative, thus the process is spontaeneous and exothermic. The concentration of chromium (VI) ion was successfully reduced via adsorption from the chromium solution using the exctracted chitosan from mussel shell.

CHAPTER ONE

INTRODUCTION

1.1 Background

In the past century there has been a rapid change in industrialization, this has led to an increase in the complexity of toxic effluents discharged into the environment. Part of these toxic effluents is heavy metals. Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment therefore resulting in various diseases to man and wreaking havoc on the aquatic life (Quek, *et al.,* 1998; Sewvandi and Adikary, 2011). Wastes containing these heavy metals are generated by industries such as ternary, mining and petrochemicals.

Some of these heavy metals are extremely toxic elements and can seriously affect many living species especially human. Therefore the effluents being generated by these industries (which are rich in heavy metals) require treatment before being discharge into the water bodies (Sewvandi and Adikary, 2011). Efficient removal of toxic metal ions from wastewater is an important and widely studied research area where a number of technologies have been developed over the years (Bamgbose *et al.,* 2008). A wide range of physical and chemical processes for the removal of these metals from such waters are precipitation, ultrafilteration, adsorption, ion exchange, reverse osmosis, oxidation, ozonation etc. Among these, the adsorption method has been proven to be an excellent method to remove heavy metals from contaminated water due to its advantages over the other processes mentioned (Kaushik and Sharma, 2005). Adsorbent such as chitosan, activated carbon and zeolites have been used for the adsorption of heavy metals from waste water (Razali *et al*., 2010).

Chitosan is a natural polysaccharide comprising of copolymers of glucosamine and *N*-acetyl glucosamine, and can be obtained by the partial deacetylation of chitin, which is the main structural component of squid pens, cell walls of some fungi and also in shrimp and crab shells (Martino *et al.*, 2005 and Aranaz *et al.*, 2009). Chitin and chitosan are copolymers found together in nature, they are inherent to have specific properties of being environmentally friendly and easily degradable (Boonlertnirun *et al*, 2008). Chitin can be converted into chitosan by enzymatic means or alkali deacetylation, the latter being the most utilized method. During the course of deacetylation, part of polymer N-acetyl links is broken with the formation of D-glucosamine units, which contain a free amine group, increasing the polymer's solubility in aqueous solvents (Kalut, 2008). The sources of chitosan are abounded and not fully explored and they also, constitute environmental problems.

Chitosan being poly cationic in nature becomes very useful as flocculating and chelating agent. It can also be used as heavy metals trapper; in fact it competes effectively with synthetic resins in the capture of heavy metals from processing water (Dutta, 2004). Chitin can also be used to decontaminate plutonium containing wastewater and water containing methyl-mercury acetate (Chung and Wolfgang, 2003).

1.2 Problem Statement

Nigerian river banks are littered by the shells of crustaceans, and this constitutes environmental nuisance restricting tourism activities. Where they are consumed, the shells also constitute environmental problem due to improper disposal. In addition, most of the materials used for waste water treatment are non-biodegradable and poses environmental problem (e.g. the use sodium thiosulphate to neutralize residual chlorine when in excess can lead to sulphate formation, suppression of dissolved oxygen

content, and lowering of the pH of the effluent, thus changing the stability of the ecosystem). Furthermore, the kinetic parameters of chromium removal from water using chitosan have not been fully established.

Therefore, this present investigation was set out to explore and exploit the potentials in chitosan for the removal of heavy metal (Cr^{6+}) ion from chromium solution.

1.3 Justification

The extraction of chitin and chitosan from crustacean shells will cleanse the environment in regions where mussels are consumed and also cleanse the river banks off these pollutants, hence recreational and tourism activities will be improved thereby generating revenue to the Nigerian government. More importantly, the product can be used as a source of replacement for the non-biodegradable materials used for removal of heavy metals which is just a technology of conversion of waste to wealth. In addition, the work will contribute to already scanty kinetic data on heavy metals removal from wastewater using chitosan.

1.4 Aim and Objectives

This work is aimed at removal of chromium (VI) ion from chromium water solution using chitosan

The specific objectives of this research include:

a. To extract and characterise chitin and chitosan from mussel shell

b. To use the extracted chitosan for chromium (VI) ion removal from chromium water solution

c. To establish the isotherms and kinetics of chromium (VI) removal from chromium water solution.

d. To convert the shells (considered as waste which litter our environment) to waste water treatment adsorbent.

1.5 Scope

The research scope focused on the extraction and characterisation of chitin and chitosan from mussel shells, and to use the extracted chitosan in the removal of chromium (VI) from dichromate-water solution. Also, to use the chitosan in the removal of chromium (VI) ion from chromium solution using batch adsorption study.

CHAPTER TWO

LITERATURE SURVEY

2.1 Introduction

This chapter consists of a review of literature on the current trend in the following key areas: Historical background of chitin and chitosan, sources of chitin and chitosan, chemistry and properties of chitin and chitosan, application of chitin and chitosan, an outlook on wastewater and wastewater treatment options, chemicals used in wastewater treatment and also a review on kinetics and isotherm studies.

2.2 Historical Background of Chitin and Chitosan

Chitin, poly (b-(1-4)-N-acetyl-D-glucosamine), is a natural polysaccharide of major importance, first identified in 1884 (Rinaudo, 2006). Among the novel families of biological macromolecules, whose relevance is becoming increasingly evident, are chitin and its main derivative, chitosan. Potential and usual applications of chitin, chitosan and their derivatives are estimated to be more than 200 (Aranaz *et al*., 2009).

Chitin, the second-most abundant biopolymer, and its deacetylated product, chitosan, are high molecular-weight biopolymers and are recognized as versatile environmentally friendly raw materials in many applications (Honakar and Barikani, 2009). Chitin is the major component in the shell of the shrimps, and crabs, cartilage of the squid, and outer cover of insects, it also occur as ordered crystalline micro-fibrils forming structural components in the exoskeleton of arthropods or in the cell walls of fungi and yeast. It is also produced by a number of other living organisms in the lower plant and animal kingdoms, serving in many functions where reinforcement and strength are required (Rinaudo, 2006).

Chitin is a co-polymer of N-acetyl-glucosamine and N-glucosamine units randomly or block distributed throughout the biopolymer chain depending on the processing method used to derive the biopolymer (Khora and Limb, 2003). Also depending on the source, its degree of deacetylation may range from 30% to 95% (Martino *et al.*, 2005) and it is called chitosan. In its crystalline form, chitosan is normally insoluble in aqueous solutions above pH7; however, in dilute acids (pH6.0), the protonated free amino groups on glucosamine facilitate solubility of the molecule (Martino *et al.*, 2005).

2.3 Sources of Chitin and Chitosan

Chitin is widely distributed in marine invertebrates, insects, fungi, and yeast. However, chitin is not present in higher plants and higher animals. Generally, the shell of selected crustacean consist of 30-40% protein, 30-50% calcium carbonate and calcium phosphate, and 20-30% chitin (Fernandez-Kim, 2004). Chitin is widely available from a variety of source among which the principal source is shellfish waste such as shrimps, crabs, and crawfish, and it also exists naturally in a few species of fungi (Fernandez-Kim, 2004). Chitin in crustacean cuticles is tightly associated with inorganic salts such as calcium carbonate, and also associated with proteins and lipids, including pigments (Kim, 2010). It is likely that future sources of chitin and chitosan will come from biotechnology innovations, especially when medical applications are the focus (Khora and Limb, 2003).

2.3.1 Mussel and its use for extraction of chitosan

Mussel is the common name used for members of several families' of clams *bivalviamollusca*, from saltwater and freshwater habitats. These groups have in

common a shell as shown in Figure 2.1 whose outline is elongated and asymmetrical compared with other edible.

In most marine mussels, the shell is longer than its width, being wedge-shaped or asymmetrical. The external colour of the shell is often dark blue, blackish, or brown, while the interior is silvery and somewhat nacreous (Zeldes, 2010).



Figure 2.1: Mussel Shells

Freshwater Zebra mussels and their relatives in the family *Dreissenidae* are not related to previously mentioned groups, even though they resemble many *Mytilus* species in shape, and live attached to rocks and other hard surfaces in a similar manner, using a *byssus*. They are classified with the *Heterodonta*, the taxonomic group which includes most of the bivalves commonly referred to as "clams" (Zeldes, 2010).

The mussel's external shell is composed of two hinged halves or "valves". The valves are joined together on the outside by a ligament, and are closed when necessary by strong internal muscles. Mussel shells carry out a variety of functions, including support for soft tissues, protection from predators and protection against desiccation (Zeldes, 2010).

Presently, works on extraction of chitin and chitosan from mussel shell have not been reportded, but considering the similarity of other raw materials such as crab and shrimp shells to mussel, the mussel is seen to have a prospect.

2.3.2 Fungi

Chitosan was extracted from the mycelia of Rhizopus specie (Sp.) KNO. 1, Rhizopus Sp. KNO. 2), Mucor Sp. KNO. 3) and *Aspergilusniger*, with the highest amount of extractable chitosan obtained at the late exponential phase. The amount of chitosan produced varied widely amongst isolates. Mucor sp. produced the highest amount of extractable chitosan (Nadarajah *et al*., 2001).

Cheng *et al.* (2007) reported the production of chitin and chitosan from fungal cell wall. A fungus called *Ganodermatsugae* (*G. tsugae*) was used for this purpose. The main components of *G. tsugae* fruiting bodies are β-1,3-D-glucan and chitin which were found to be safe materials in enhancing wound healing in Wistar rats and accelerate proliferation and migration of fibroblasts and keratinocytes with no cytotoxicity (Cheng *et al.,* 2007).

George *et al*, 2011 carried out a study on chitosan from fungi. *Aspergillus flavus*, *Botrydiplodiatheo bromae*, *Cladosporium cladosporioides*, *Fusarium* Sp. and *Phoma* Sp. And these were all isolated from stem and leaf segments taken from medicinal plants (George *et al.,* 2011).

2.3.3 Shrimp shell

Chitosan was prepared from shrimp processing waste (shell) using conventional chemical process for the other crustacean species. The physicochemical properties,

molecular weight (165394g/mole), degree of deacetylation (75%), ash content as well as yield (15%) of prepared chitosan indicated that shrimp processing waste (shell) are a good source of chitosan. The water binding capacity (502%) and fat binding capacity (370%) of prepared chitosan are in good agreement with the commercial chitosan. FT-IR spectra gave characteristics bands of $-NH_2$ at 3443cm^{-1} and carbonyl at 1733cm^{-1}. X-ray diffraction (XRD) patterns also indicated two characteristics crystalline peaks approximately at 10° and 20° (2θ). The surface morphology was examined using scanning electron microscopy (SEM) (Tajik *et al.*, 2008 and Islam *et al.*, 2011).

Chitin was also synthesized from Nigerian brown shrimps by a chemical process involving demineralization, deproteinization and deacetylation. The degree of deacetylation of chitin was found to be 50.64% which was a low value compared to previous works and can be attributed to the low alkali concentration and heating time (Isa *et al*., 2012a). An investigation was carried out on some crustaceans by Isa *et al* 2012, it revealed that the shrimp had the highest yield of chitin of 8.15%, while crab, crawfish and periwinkle had yields of 7.8%, 2.88% and 0.44% respectively. The proximate analysis showed that chitin from shrimp had highest moisture and protein content of 8.70% and 4.16% respectively. Crawfish had the highest ash and fiber content of 7.20% and 6.98% respectively. Crab has the highest lipid content of 1.70% (Isa *et al.,* 2012b).

2.4 Chemistry and Properties of Chitin and Chitosan

This section describes the molecular structure of chitin and chitosan, it also describes some important properties such as the degree of deacetylation, viscosity, solubility bulk density, colour, water binding capacity and emulsification.

2.4.1 Chemistry of chitin and chitosan

Chitin and chitosan have similar chemical structure. Chitin is made up of a linear chain of acetyl glucosamine groups while chitosan is obtained by removing enough acetyl groups (CH_3-CO) from the molecule of chitin, rendering it soluble in most diluted acids. This process is called deacetylation. The actual difference between chitin and chitosan is the acetyl content of the polymer. Chitosan having a free amino group is the most useful derivative of chitin (Fernandez-Kim, 2004).

Chitin (Figure. 2.2) and chitosan (Figure. 2.3) are described as a family of linear polysaccharides consisting of varying amounts of β (1→4) linked residues of N-acetyl-2 amino-2-deoxy-D-glucose (denoted as A residues) and 2-amino-2-deoxy-D-glucose residues (denoted as D residues). Chitin samples have a low amount of D units and hence the polymer is insoluble in acidic aqueous media (Aranaz *et al*., 2009). On the other hand, the amount of D units in chitosan samples is high enough to allow the polymer to dissolve in acidic aqueous media. Chitosan can be prepared by cleavage of N-acetyl groups of the chitin A residues. This reaction is rarely conducted to full completion; hence chitosan polymeric chain is generally described as a copolymeric structure comprised of D-glucosamine (D residues) along with N-acetyl residues. Chitosan displays interesting properties such as biocompatibility, biodegradability and its degradation products are non-toxic, non-immunogenic and non-carcinogenic. Therefore, chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membranes and flocculation (Alves and Manoa, 2008).

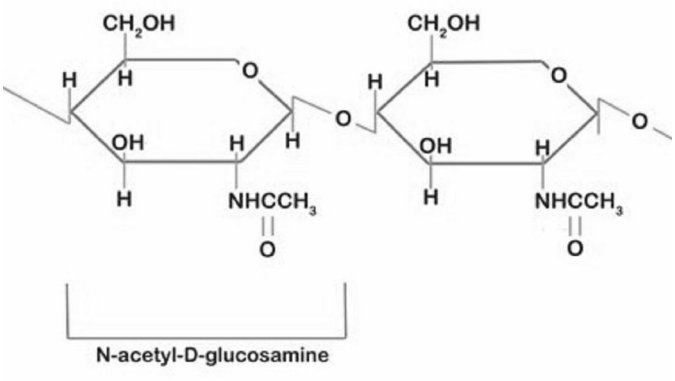


Figure 2.2: Chemical Structure of Chitin (Lertsutthiwong *et al*., 2002)

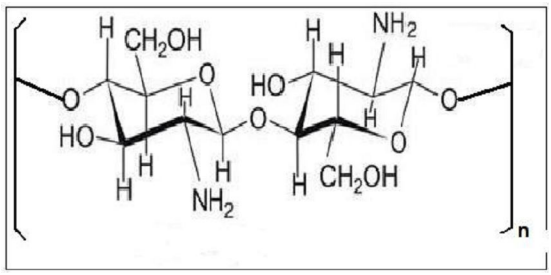


Figure 2.3: Structure of Chitosan (Lertsutthiwong *et al*., 2002)

2.4.2 Characteristics of chitosan

Chitosan is a non-toxic, biodegradable polymer of high molecular weight, and is very much similar to cellulose, a plant fibre. One difference between chitosan and cellulose is the amine (-NH_2) group instead of the (-OH) group found in cellulose (Rinaudo, 2006). However, unlike plant fiber, chitosan possesses positive ionic charges, which give it the ability to chemically bind with negatively charged fats, lipids and cholesterol, metal ions, proteins, and macromolecules. In this respect, chitin and chitosan have attained increasing commercial interest as suitable resource materials due to their excellent properties including biocompatibility, biodegradability, adsorption, and ability to form films, and to chelate metal ions (Fernandez-Kim, 2004). Chitosan can be moulded in to different forms. One form is chitosan nano-particles of size in the

range of 200-1000 nm. Many researchers concentrated in the area of chitosan nano-particle for different applications mainly in the medical field as drug carrier (Sonia and Sharma, 2011). Chitosan nano-particles can be prepared by different methods like freeze drying, multiple emulsion/solvent evaporation and ionic gelation method. From these methods ionic gelation is the best one for chitosan (Dustgania *et al.*, 2008).

2.4.2.1 Degree of deacetylation (DD)

Deacetylation simply means the removal of acetyl groups from the molecular chain of chitin, leaving behind a compound (chitosan) with a high degree chemical reactive amino group (NH_2). This makes the degree of deacetylation (DD) an important property in chitosan production as it affects the physiochemical properties, hence determines its appropriate applications. There is yet to be a difference between chitin and chitosan based on the degree of N-deacetylation. In any case, the degree of deacetylation can be employed to differentiate between chitin and chitosan because it determines the content of free amino groups in the polysaccharides. Evidences have been given suggesting that approximately one in every six to seven residues in the chitosan polymer chain has a proportion of free amino groups that manifests some histochemical properties (Kalut, 2008).

There are two advantages of chitosan over chitin. The first being that in order to dissolve chitin, highly toxic solvents such as lithium chloride and dimethylacetamide are used whereas chitosan is readily dissolved in diluted acetic acid. The second advantage is that chitosan possesses free amine groups which are an active site in many chemical reactions (Fernandez-Kim, 2004).

The IR spectroscopy method is commonly used for the estimation of chitosan DD values. This method has a number of advantages and disadvantages; it is relatively fast and unlike other spectroscopic methods, does not require purity of the sample to be tested nor require dissolution of the chitosan sample in an aqueous solvent. However, the IR method utilizing baseline for DD calculation, and as such there may be possible argument for employment of different baselines which would inevitably contribute to variation in the DD values.

Also, sample preparation, type of instrument used and conditions may influence the sample analysis. Since chitosan is hygroscopic in nature and samples with lower DD may adsorb more moisture than those with higher DD, it is essential that the samples under analysis be completely dry. The chemical composition of different types of chitosan is characterised by the molar fraction of acetylated units (*F*A value) or the degree of deacetylation [DD= 100(1- *F*A) %] (Fung, 2007).

2.4.2.2 Viscosity

Chitosan has the ability to form viscous solutions in various organic acids. These viscous solutions have been used to make functional films (Park *et al.,* 2002). Viscosity is a very important factor in the determination of molecular weight of chitosan and in determining its commercial applications in complex biological environments such as in the food system (Fernandez-Kim, 2004). Polymers dissolved in solution may have polymer-solvent interactions, and can result in an increase in viscosity. The viscosity of polymers is dependent on molecular weight (MW). The higher the MW of polymer, the more viscous the polymer solution will be (Fung, 2007) which may not be desirable for industrial handling. But a lower viscosity chitosan obtained from crawfish may facilitate easy handling. Some factors during processing such as the degree of

deacetylation, molecular weight, concentration of solution, ionic strength, pH, and temperature affect the production of chitosan and its properties. Viscosity of chitosan in acetic acid tends to increase with decreasing pH but decrease with decreasing pH in HCl, giving rise to the definition of 'Intrinsic Viscosity' of chitosan which is a function of the degree of ionization as well as ion strength. It was found that deprotienization with 3% NaOH and elimination of the demineralization process in the chitin preparation decreases the viscosity of the final chitosan products. It was also stated that it is not desirable to bleach the material (i.e., bleaching with acetone or sodium hypochlorite) at any stage since bleaching considerably reduces the viscosity of the final chitosan product. Similarly, it was demonstrated that chitosan viscosity is considerably affected by physical (grinding, heating, autoclaving, ultra sonication) and chemical (ozone) treatments, except for freezing, and decreases with an increase in treatment time and temperature. Chitosan solution stored at 4 ^{o}C was found to be relatively stable from a viscosity point of view. It was also reported that smaller particle size (1mm) results in chitosan products of both higher viscosity and molecular weight than those of either 2 or 6.4 mm particle size (Fernandez-Kim, 2004). It was also reported that when a polymer has a higher MW, it has a bigger hydrodynamic volume, that is, the volume of a polymer coil when it is in solution. The solvent molecules will be bound more strongly to the polymer with increasing hydrodynamic volume, leading to a decrease in the motion of the polymer in the solvent. Hence, the viscosity of a polymer solution is proportional to the MW of the polymer. Therefore, by measuring the viscosity of a polymer solution, the molecular weight of the polymer can be conveniently determined (Fung, 2007).

2.4.2.3 Solubility

Chitosan contains amino groups with a pKa value of 6.2-7, and it is considered strong base (Fernandez-Kim, 2004). While chitin is insoluble in most organic solvents, chitosan is readily soluble in dilute acidic solutions below pH 6.0. Organic acids such as acetic, formic, and lactic acids are used for dissolving chitosan. The most commonly used is 1% acetic acid solution at about pH 4.0 as a reference. Chitosan is also soluble in 1% hydrochloric acid but insoluble in hydrogen tetraoxosulphate (VI) acid and phosphoric acids. Solubility of chitosan in organic acid is quite limited. Concentrated acetic acid solutions at high temperature can cause depolymerisation of chitosan. Above pH 7.0 the stability of chitosan solubility is poor. At higher pH, precipitation or gelation tends to occur and the chitosan solution forms poly-ion complex with anionic hydrocolloid resulting in the formation (Kurita, 1998). The concentration ratio between chitosan and acid is of great importance to impart desired functionality. At concentrations as high as 50% organic solvent, chitosan still works as a viscosifier causing the solution to remain smooth. There are several critical factors affecting chitosan solubility including temperature and time of deacetylation, alkali concentration, and prior treatments applied to chitin isolation, ratio of chitin to alkali solution, and particle size.

The solubility, however, is controlled by the degree of deacetylation and it is estimated that deacetylation must be at least 85% complete in order to achieve the desired solubility. The acid-soluble chitosan with >95% solubility in 1% acetic acid at a 0.5% concentration could be obtained by treatment of the original chitin 45-50% NaOH for 10-30 min. Chitosan treatment with 45% NaOH for only 5min, and/or with 40% NaOH

for 30min, were not deacetylated sufficiently to be soluble in 1% acetic acid. Insoluble particles were found in both solutions, (Fernandez-Kim, 2004).

2.4.2.4 Bulk density

The bulk density of chitin from shrimp and crab is normally between 0.06 and 0.17 g/ml, respectively (Shahidi and Synowieck, 1991), indicating that shrimp chitin is more porous than crab chitin. Krill chitin was found to be 2.6 times more porous than crab chitin. Bulk density of ordinary chitosan is about 0.2-0.4 g/ml, but the bulk density of high density chitosan is about 0.4-0.8 g/ml. The bulk density of high density chitosan is much higher than ordinary chitosan, and the same type of capsule can contain more weight of chitosan.

2.4.2.5 Colour

The pigment in the crustacean shells forms complexes with chitin (4-keto and three 4, 4'-diketo-B-carotene derivatives). Chitosan powder is quite flabby in nature and its colour varies from pale yellow to white whereas starch and cellulose powder have smooth texture and white colour.

2.4.2.6 Water binding capacity (WBC) and fat binding capacity (FBC)

Basically, WBC for chitosan ranges between 581 to 1150% with an average of 702%. It was also noted that reversing the sequence of steps such as demineralization (DM) and deproteinization (DP) had a pronounced effect on WBC and FBC. DP of mineralized shell also gives higher WBC compared to the process when DM of the deproteinized shell is conducted. Besides, the process of decoloration (DC) also causes a decrease in WBC of chitosan than those of unbleached chitosan (Fernandez-Kim, 2004).

2.4.2.7 Emulsification

Even though chitosan alone does not produce emulsions, report has shown that emulsifying capacity of egg yolk increased with the addition of chitosan compared with the control. At 0.5% chitosan concentration, better emulsifying capacity was observed compared with at 0.1 or 0.3% chitosan. In general, chitosan emulsions tend to be very stable under temperature changes and ageing. With viscosity, the degree of deacetylation was reported to be a determining factor in the emulsification property of chitosan. The protein solution containing chitosan with intermediate DD produces less effective emulsion compared with that containing chitosan with higher DD. The optimum chitosan DD for sunflower emulsification is 89 as reported by (Fernandez-Kim, 2004)

2.4.2.8 Antimicrobial properties and film formation

Studies have shown that antimicrobial activities of chitosan have the ability to inhibit the growth of bacteria. The antimicrobial properties of chitosan depend on its molecular weight and the type of bacterium. For gram-positive bacteria, chitosan with 470 kDa (kilo Dalton) was the most effective, except for *Lactbacillus S*p., whereas for gram-negative bacteria, chitosan with 1,106 kDa was effective. Chitosan generally showed stronger bactericidal effects for gram-positive bacteria (*Lactobacillus plantarum, L. brevis, and L. bulgaris*) than for gram-negative bacteria (*E.coli, Pseudomonas fluorescens, Salmonella typhymurium, and Vibrio parahaemolyticus*) in the presence of 0.15 Chitosan (Moller *et al.*, 2004, Fernandez-Kim, 2004). Chitosan is antimicrobial against a wide range of target organisms. Activity varies considerably with the type of chitosan, the target organism and the environment in which it is applied. Consequently, literature reports vary somewhat and are, occasionally, contradictory (Moller *et al.,*

2004). But generally speaking, yeasts and moulds are the most sensitive group, followed by gram-positive bacteria and finally gram-negative bacteria (Rhoades and Rastall, 2003). Chitin and chitosan *in vitro* show antibacterial anti-yeast activities. One of chitosan derivatives; N-carboxybutyl chitosan, tested against 298 cultures of different pathogenic microorganisms showed bacteriostic and bactericida activities, and there were marked morphological alterations in treated microorganisms, when examined by electron microscopy. However, growth inhibition and inactivation of mould and yeasts seem to depend on chitosan concentration, pH, and temperature. The antimicrobial action of chitosan is influenced by intrinsic and extrinsic factors such as the type of chitosan (e.g.,plain or derivative), degree of chitosan polymerization, host nutrient constituency, substratre chemical and/or nutrient composition, and environmental conditions such as substrate water activity (Fernandez-Kim, 2004)

Chitosan has been approved as a food additive in Japan and Korea since 1983 and 1995, respectively. Higher antibacterial activity of chitosan at lower pH suggests that addition of chitosan to acidic foods will enhance its effectiveness as a natural preservative (Fernandez-Kim, 2004). Chitosan coating has been proved to significantly delay fruit spoilage or decaying of fruits and vegetables such as tomatoes and strawberries at different temperatures. Chitosan coated fruits were not only firmer and higher in titrable acidity, but were slow to decay and exhibited less pigmentation than control samples at the end of storage. The low molecular weight chitosan has greater inhibitory effects against phytopathogens than the high molecular weight chitosan (Fernandez-Kim, 2004). Highly deacetylated chitosans are more antimicrobial than those with a higher proportion of acetylated amino groups, due to increased solubility and higher charge density. Lower pH increases the antimicrobial activity of chitosan for

much the same reasons, in addition to the 'hurdle effect' of inflicting acid stress on the target organisms. Temperature also has an effect, as (although not ideal for many food applications) higher temperature (37°C) has been shown to enhance antimicrobial activity compared to refrigeration temperature (Rhoades and Rastall, 2003).

Chitosan has the ability to form film which makes it suitable for use as food preservation for control of psychotropic pathogen in fresh/processed meat and fish products packaged under modified atmosphere. The most potential application of chitosan is as a coating agent in the area of fruit preservation. The biodegradability of chitosan is one of the most advantageous features for concern of the environment damage occurring by improper disposal of petrochemical based plastics. N, O-carboxymethyl chitosan can form a strong film that is selectively permeable to such gases as oxygen and carbon dioxide. Apples coated with this material remain fresh for up to six months. The chitosan coating has been shown to delay ripening of banana for up to 30 days although chitosan film manifests a slightly yellow appearance, with the color darkening as thickness increased (Fernandez-Kim, 2004).

2.5 Application of Chitin and Chitosan

Chitosan exhibits a variety of physicochemical and biological properties, therefore it has found numerous applications in various fields such as waste and water treatment, agriculture, fabric and textiles, cosmetics, nutritional enhancement, and food processing. In addition to its lack of toxicity and allergenicity, its biocompatibility, biodegradability and bioactivity make it a very attractive substance for diverse applications as a biomaterial in pharmaceutical and medical fields (Senel and McClure, 2004).

Chitin, together with its variants, especially its deacetylated counterpart chitosan, have been a useful wound dressing material, drug delivery vehicle and increasingly a candidate for tissue engineering (Khora and Limb, 2003). Current tissue engineering strategies are focused on the restoration of pathologically altered tissue architecture by transplantation of cells in combination with supportive scaffolds and biomolecules. Considerable attention has been given to chitosan (CS)-based materials and their applications in the field of orthopedic tissue engineering. Due to its favourable gelling properties chitosan can deliver morphogenic factors and pharmaceutical agents in a controlled fashion. Its cationic nature allows it to complex DNA molecules making it an ideal candidate for gene delivery strategies. The ability to manipulate and reconstitute tissue structure and function using this material has tremendous clinical implications and is likely to play a key role in cell and gene therapies in coming years (Martino *et al.*, 2005).

Carbohydrate analysis of purified chitin deacetylase revealed that the enzyme is a high-mannose glycoprotein and that its carbohydrate content is 30% by weight. Chitin deacetylase is active on several chitinous substrates and chitin derivatives. The enzyme requires at least four N-acetylglucosamine residues (chitotetraose) for catalysis, and it is inhibited by carboxylic acids, particularly acetic acid (Kafetzopoulos *et al.,* 1993).

Chitosan can also be used as a seed fungicide and plant growth enhancer. A growth enhancement study was conducted with black-eyed peas exposed to the different chitosan treatments. A similar anti-fungal experiment with peanut seeds infested with Penicillium was conducted as well. Data on plant height stem diameter and leaf counts were recorded biweekly for four months and analyzed using PROC ANOVA and PROC General Linear Model Statistical Systems. These measurements suggested that

seeds pre-treated with the chitosan extracted with 0.5% HCl had the best overall growth and both chitosan (0.5% HCl) and Captan were the most effective in eliminating fungus from peanuts. This research presents plausible possibilities in which seafood waste can be utilized for agricultural purposes (Burrows *et al.*, 2007).

Chitosan is being used in waste water treatment. A study was also carried out on the removal of heavy metal from contaminated water by biopolymer crab shell chitosan, the heavy metals that were removed includes manganese, cadmium, zinc, cobalt, nickel and lead (Rana *et al*., 2009). Chitosan was also synthesised from locally available fish shell and was used in removal of copper ion from waste water, the amount of copper adsorbed was evaluated using atomic adsorption spectroscopy (Hadi, 2013).

2.5.1 Water treatment

At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health (Kortenkamp *et al.,* 1996). Chromium has both beneficial and detrimental properties. Two stable oxidation states of chromium persist in the environment, Cr (III) and Cr (VI), which have contrasting toxicities, mobilities and bio availabilities (Nomanbhay and Palanisamy, 2005). Whereas Cr (III) is essential in human nutrition (especially in glucose metabolism); most of the hexavalent compounds are toxic, several can even cause lung cancer. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Shim *et al.*, 2001). Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries (Nomanbhay and Palanisamy, 2005)

Razali *et al.,* (2010) studied the comparison of the adsorption capacity of chitosan, activated carbon, alum and zeolite. The waste water contains 230,000 mg L^{-1} of COD, 69,000 mg L^{-1} of suspended solids and 596 mg L^{-1} of residual oil. Summary of the result is presented as Table 2.1.

Table 2.1 Comparison of the adsorptive capacity of various adsorbents (Razali *et al.,* 2010)

Adsorbent	COD (%)	SS (%)	Residual Oil (%)
Chitosan	83	57	95
Activated Carbon	80	49	87
Alum	73	43	64
Zeolite	70	38	46

2.6 Adsorption

Adsorption operations exploit the ability of certain solids preferentially to concentrate specific substances from solution onto their surfaces. Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase.

Sorption, which is a general term introduced by McBain (Vasanth *et a.l,* 2004), includes selective transfer to the surface and from the bulk of the liquid. In a general sorption process, the sorbed solutes are referred to as sorbate and the sorbing agent is the sorbent. Early applications of adsorption involved only purification, for example:

adsorption with charred wood to improve the taste of water has been known for at least five centuries. Adsorption of gases by a solid charcoal was first described by Chele in 1773 (Kumar *et al.*, 2004). Commercial applications of bulk separation by gas adsorption began in early 1920s, but did not escalate until the 1960s, following the invention by Milton of synthetic molecular sieve zeolites, which provide high adsorptive selectivity.

2.6.1 Types of adsorption.

There are commonly two types of adsorption. Chemisorption and physiosorption.

2.6.1.1 Chemisorption

Chemisorption is a shorter way of writing chemical adsorption. It is also called specific adsorption and limited to monolayer coverage of the substrate. Here, a covalent bond is formed between the adsorbate and adsorbent (Itodo and Itodo, 2010). Therefore, the energy of chemisorption is considered like chemical reactions. It may be exothermic or endothermic processes ranging from very small to very large energy magnitudes. The elementary step in chemisorption often involves large activation energy (activated adsorption). This means that the true equilibrium may be achieved slowly (Al-Anber, 2012).

2.6.1.2 Physiosorption

This stands for physical adsorption. It is also called nonspecific adsorption which occurs as a result of long range weak Van der Waals forces between adsorbates and adsorbents. The energy released when a particle is physiosorbed is of the same magnitude as the enthalpy of condensation (Itodo and Itodo, 2010).

2.6.2 Adsorption isotherms

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption gives the capacity of the sorbent to adsorb sorbate. The relationships between sorbent and sorbate are described by adsorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium (Ho *et al.*, 2001).

2.6.2.1 The Freundlich isotherm

This empirical model has been applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (Ho *et al.*, 2001). This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution (Freundlich, 1906). It is often criticised for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations (Muhammad *et al.*, 2012). This isotherm is an empirical equation expressed as follows:

$$q_e = a_f C_e^{b_F} \tag{2.1}$$

$$q_e = \frac{v\,(C_o - C_e)}{m} \tag{2.2}$$

Where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g) calculated from Equation 2.2, a_f is the Freundlich isotherm constant; C_e solution phase oil concentration at equilibrium, mg dm^{-3}; C_o is the initial solution phase oil concentration, m is the mass of the adsorbent introduced into the solution, v is the volume of the solution in which the adsorbent is introduced and b_F is the heterogeneity parameter. Although, the smaller

the value of b_F, the greater the expected heterogeneity. Freundlich equation is strictly valid only for ion adsorption at low concentration

2.6.2.2 The Langmuir isotherm

In 1916 Langmuir developed a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas (Langmuir, 1916). The Langmuir model is probably the best known and most widely applied sorption isotherm, it has also produced good agreement with a wide variety of experimental data (Muhammad *et al*., 2012).

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. This equation can be derived theoretically based on evaporation and condensation rates. The Langmuir isotherm equation is stated as:

$$q_e = \frac{k_L b C_e}{1 + k_L C_e} \qquad (2.3)$$

Where, b is the Langmuir constant related to the energy of biosorption (L/mg), k_L is the maximum sorption capacity corresponding to complete monolayer coverage (mg/g), and C_e is the equilibrium solute concentration (mg/L). The Langmuir adsorption isotherm can be transformed to linear form thereby allowing the parameters to be estimated graphically or with linear regression. Various linear transformations resulted as follows:

The reciprocal Langmuir plot:

$$\frac{C_e}{q_e} = \frac{1}{k_L b} + \frac{1}{b} C_e \qquad (2.4)$$

The distribution coefficient or Scatchard plot:

$$\frac{C_e}{q_e} = bk_L - q_e k_L \qquad (2.5)$$

The Eadie-Hofstee plot:

$$q_e = b - \frac{q_e}{k_L C_e} \qquad (2.6)$$

The double reciprocal or Lineweaver-Burk plot:

$$\frac{1}{q_e} = \frac{1}{k_L b C_e} + \frac{1}{b} \qquad (2.7)$$

The favourable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, R_L which is defined by Equation (2.8)

$$R_L = \frac{1}{1 + bC_o} \qquad (2.8)$$

where, C_o is the highest initial solute concentration, b the Langmuir's adsorption constant (L/mg). q_e is expressed as given in Equation 2.9

$$q_e = \frac{V(C_i - C_e)}{m} \qquad (2.9)$$

Where, V is the biosorption volume (litres), C_i is the initial concentration of the sorbate (milligrams/litre), and m is the mass of biosorbent (gram). Use of Langmuir isotherm implies a finite number of uniform adsorption sites and absence of lateral interactions.

2.6.2.3 Dubinin–Radushkevich (D–R) isotherm

The D–R isotherm model is a semi-empirical equation where adsorption follows pore filling mechanism (Dubinin, 1960). It assumes that the adsorption has a multilayer character, involves van der Waals forces and is applicable for physical adsorption processes (Dubinin, 1965). The linear form of D–R isotherm model is expressed as:

$$lnq_e = lnq_D - \beta\varepsilon^2 \quad (2.10)$$

where, q_D is the D–R constant (mg/g), β is the constant related to free energy and ε is the Polanyi potential which is defined as:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (2.11)$$

The Polanyi potential ε will be determined from Equation (2.11) and lnq_e will be plotted against ε^2 from which the slope and the intercept values will reveal β and q_D respectively. The mean free energy (E) of biosorption gives an idea about biosorption mechanism, whether physical or chemical (Radushkevich, 1949). If the value of E lies between 8 to 16 kJmol^{-1}, the biosorption process takes place chemically and if the value of E is less than 8 kJmol^{-1} (Srividya and Mohanty, 2009), then the biosorption process takes place physically. E can be evaluated from Equation 2.12.

$$E = \frac{1}{\sqrt{2\beta}} \quad (2.12)$$

2.6.3 Kinetic models

Kinetic sorption models have been used to simulate conditions where sorption processes are believed to operate relatively slowly in relationship to solute residence time. Under these conditions, the degree of sorption continues to change with time, and frequently does not reach equilibrium, at least within the time constraints of the experiment (Muhammad *et al*., 2012). Sorption measurements must be carried out when equilibrium has been reached. It has been reported that times of 1 h or few hours to 1 day (Site, 2000) are often sufficient to reach equilibrium, but sometimes are necessary some days or several days, months, or years.

2.6.3.1 Pseudo-first-order kinetic model

Qui *et al*. (2009) opined that Lagergren pseudo-first-order rate equation describes the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It can be presented as follows:

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \qquad (2.13)$$

In 1898 Lagergren proposed kinetics equation has been used to describe the adsorption of an adsorbate from an aqueous solution. The integrated linear form of pseudo-first-order kinetic model can be seen as Equation 2.14) as proposed by Lagergren.

$$\ln(q_e - q_t) = \ln q_e - k_{p1}t \qquad (2.14)$$

Where, q_e is the amount of oil adsorbed at equilibrium (mg/g) obtained from Eq. 1, q_t is the amount of oil adsorbed at time *t* (mg/g), k_{p1} is the first order rate constant (min^{-1}) and *t* is the time (min). Hence, a linear trace is expected between the two parameters

$ln(q_e - q_t)$ and t, provided the biosorption follows first order kinetics. The value of k_{p1} can be determined from the slope of the plot.

2.6.3.2 Second-order kinetic model

The second-order kinetic model (Equation 2.17) is shown below, it is mostly used for chemical reactions in kinetics and chemical reaction engineering, but can also be applied for adsorption processes (Muhammad *et al.*, 2012)

$$\frac{1}{C_e} = k_2 t + \frac{1}{C_0} \quad (2.15)$$

Where, C_e is the ion concentration at equilibrium time (t) in (mg/l), k_2 is the second-order rate constant ($Lmg^{-1}min^{-1}$), t is the time in minute, and C_0 is the initial ion concentration (mg/l).

2.6.3.3 Pseudo-second-order kinetic model

In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat, in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. Therefore, the peat-metal reaction may be presented as shown in Equations 2.16(a) and 2.16(b), which can be dominant in the adsorption of Cu^{2+} ions onto peat:

$$2P^- + Cu^{2+} \leftrightarrow CuP_2 \quad (2.16\ a)$$

And,

$$2HP + Cu^{2+} \leftrightarrow CuP_2 + 2H^+ \quad (2.16\ b)$$

Where, P^- and HP are active sites on the peat surface. The main assumptions for the above two equations were that the adsorption may be second-order, and the rate limiting step may be chemical adsorption involving valence forces through sharing or the exchange of electrons between the peat and divalent metal ions. In addition, the adsorption follows the Langmuir equation. The rate of adsorption described by Equations (2.16a) and (2.16b) is dependent upon the amount of divalent metal ions on the surface of peat at time *t* and that adsorbed at equilibrium. Therefore the rate expression may be given as;

$$\frac{dP_t}{dt} = k_2[P_o - P_t]^2 \qquad (2.17)$$

where P_o denote the amount of equilibrium sites available on the peat, P_t denotes the amount of active sites occupied on the peat at time *t*, and k_2 (g/(mg·min)) is the pseudo-second-order rate constant of adsorption. The driving force, (q_e-q_t), is proportional to the available fraction of active sites. Then, it yields

$$\frac{dP_t}{dt} = k_2[q_e - q_t]^2 \qquad (2.18)$$

Integrating Equation (2.18) with the boundary conditions of qt=0 at t=0 and qt=qt at t=t, and re-arrangement yields;

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e}t \qquad (2.19)$$

Where, t is the time (minute), k_s is the pseudo-second-order kinetic model rate constant ($g.mg^{-1}.min^{-1}$), and q_e is the equilibrium ion concentration (mg ion/g adsorbent).

2.6.3.4 Elovich kinetic model

The Elovich model is mainly applicable for chemisorptions processes (Zeldowitsch, 1934). The equation is often valid for systems in which the adsorbing surface is heterogeneous. The model generally expressed (Hossain *et al*., 2012) as given by Equation (2.20).

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \qquad (2.20)$$

Where, 'α' is the initial biosorption rate (mg/g min) and b is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). A plot of q_t vs. *lnt* gives a straight line with a slope of $\frac{1}{b}$ and an intercept of $\frac{1}{b}\ln(ab)$ with good correlation coefficients.

CHAPTER THREE

MATERIALS AND METHODS

This chapter presents details of the materials and equipment used in the course of this work and also the detailed experimental procedure of the work. The chapter is divided into three sections; the materials and equipment (Section 3.1) and details of the experimental procedure of the work (Section 3.2 and 3.3)

3.1 Materials and Equipment

Tables 3.1 and 3.2 are respectively showing details of materials and equipment employed in this study.

Table 3.1: List of Materials

Material	Description	Manufacturers
Hydrochloric Acid	(35-38% wv, S.G.=1.18)	Solvay Chemicals International, Brussel
Sodium Hydroxide	(98% ww)	Poron Oil and Maritime Limited. Lagos
Acetic acid	(99.5% wv)	Tata Nigeria.
Powder pillows	1,5-Diphenylcarbohydrazide	Hach Company, Colarado U.S.A.
Mussel Shells	925 g	

Table 3.2: List of Equipment

Equipment	Description
Mettler Balance	Analytical weighing balance (digital), Model-A2005S, Made in Germany.
Oven	Hot air drying oven, Milano Italia, 50 ^{o}C-220 ^{o}C, 220 v
Heating Mantle	Made in India (BHA), 0 ^{o}C-100 ^{o}C
BET Machine	TriStar 3000 V, 6.05 A
pH Meter	Model No 3520, 9 V AC, Manufactured in U.K. by Bibby Scientific LTD.
Water Distiller	Made in Milano-Halia Sr.1, 220V, Type Vitadini.
Dr-2000 Spectrophotometer	Hach Company, Colarado U.S.A, 7-8 v, 700 mA
FTIR Machine	Perkin Elmer Spectrum 100FTIR spectrometer.

3.2 Experimental Procedure

This section consists of a detailed procedure and methods used in the research. The procedure of data collection and preparation of materials are presented.

3.2.1 Sample collection

The mussel shells used for the chitosan extraction were obtained from the Gubi dam bank of Bauchi, north eastern part of Nigeria. The extraction of chitosan was carried out in four steps; pre-treatment, demineralization, deproteinization and the deacetylation steps. Figure 3.1 presents a process flow diagram of the experimental procedure. There are several reported procedures of carrying out these processes, the one of Sewvandi and Adikary (2011) was adopted in this work.

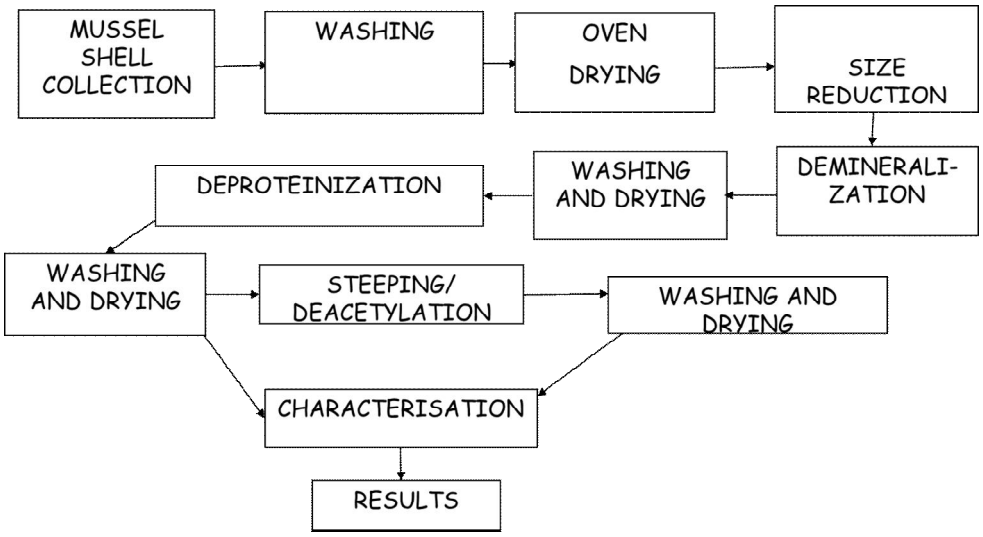


Figure 3.1: Process flow diagram for the production of chitosan

3.2.1.1 Pre-treatment stage

The shells obtained were washed thoroughly with water and dried in an oven to constant weight at a temperature of 35^{o}C. Then 100 g of the sample was taken out of the 925 g for the demineralization process.

3.2.1.2 Demineralisation

The dried shells were crushed and soaked in 0.68 M HCl (1:10 w/v) at ambient temperature (approximately 29^{o}C) for 6 hours after which it was washed in the acid until no bubbles were seen and no colour change was observed. The sample was then washed thoroughly with distilled water until a neutral pH was obtained (using a pH meter to measure the pH of the water used in rinsing the demineralised sample) and then the demineralized shell was dried to constant weight at 35^{o}C.

3.2.1.3 Deproteinization

The dried mussel shells was weighed and then soaked in 0.62 M NaOH solution (1:10w/w) at ambient temperature (approximately 28^{o}C) for 16 hours. The shells were then washed thoroughly with distilled water until a neutral pH was obtained. The chitin was then dried to constant weight, ground and screened with 150 μm sieve. The weight was then recorded.

3.2.1.4 Deacetylation

The chitin obtained from the demineralisation process was deacetylated in 25 M NaOH (1:10 w/w) for 20 hours at 75^{o}C using a heating mantle as presented in Plate 3.1. After deacetylation, the chitosan was then washed thoroughly with water followed by distilled water. The resulting chitosan was then dried to constant weight at 45 ^{o}C and prepared for characterisation.



Plate 3.1: Deacetylation set-up

3.2.2 Chitosan preliminary test

The solubility of the deacetylated chitin in acetic acid was tested, which is necessary, but not sufficient condition it must fulfil for the product to be chitosan. 1 g of the

deacetylated chitin was introduced into 1M acetic acid and stirred for 53 minutes vigorously after which the chitosan completely dissolved.

3.2.3 Characterisation of chitin and chitosan

The chitin and chitosan obtained were characterised to determine the carbon-nitrogen content and also to calculate the degree of deacetylation. These parameters are the distinguishing factors between the chitin and chitosan.

3.2.3.1 Proximate and elemental analysis

The proximate analysis on chitin and chitosan obtained was carried out to determine parameters such as: ash content, moisture content and protein content of the chitin and chitosan. The composition of the mussel shell and the elemental analysis of the chitin and chitosan were conducted using the standard method (AOAC, 1990). The analyses were done in food technology laboratory of the Institute for Agricultural Research (IAR) of Ahmadu Bello University, Zaria.

3.2.3.2 Functional group analysis

The functional group analysis was done by Fourier transformed infrared (FTIR) spectroscopy in the range of 400 to 4000 cm^{-1} using the Perkin Elmer Spectrum 100 FTIR spectrometer

3.2.3.3 Surface area determination

The surface area and the molecular cross sectional area were determined using BET equipment (TriStar 3000 V6.05 A) available at the Department of Chemical Engineering, Cape Peninsula University of Technology, Symphony way, Belleville, South Africa.

3.3 Adsorption Studies

This section involves the preparation of the chromate solution and the use of the adsorbent in the removal of the chromium ions, also the data obtained from these studies were used to fit various adsorption isotherms and kinetics to see which is the best fits and also used in calculating some thermodynamic quantities such as enthalpy, entropy and sorption energy.

3.3.1 Preparation of chromate solution

0.5 g of $K_2Cr_2O_7$ salt was weighed and added to 1000 ml of deionized water to simulate water for treatment using chitosan, with an initial concentration of 0.62 mg/L of Cr (VI) ion in solution as detected by the spectrophotometer.

3.3.2 Effect of stirring speed

Preliminary studies of the effect of variation of stirring speed did not show significant change in the adsorption process, therefore 350 rpm was chosen for the studies

3.3.3 Effect of chitosan dosage

100ml of solution was taken from the bulk solution prepared in section 3.3.1 and 0.5 g of chitosan sample was added to it and the mixture was stirred continuously for 5 minutes at room temperature. The mixture was allowed to settle to form two layers; the solution was then filtered to retrieve the clear solution after which a pillow of chromaVer 3 was added to the mixture and shaken thoroughly. The concentration of chromium (VI) was determined using the DR 2000 spectrophotometer. This procedure was repeated for chitosan dosage of 1.0 g, 1.5 g, 2.0 g, 2.5 g, 3.0 g, and 3.5 g, respectively. Optimum dosage of chitosan during the experiment was identified by

checking the mass of chitosan that gave the least residual concentration of Cr (VI) in the solution above which no appreciable change was observed.

3.3.4 Determination of contact time

Using the optimum dosage of chitosan (2.5 g) at room temperature (28^{o}C), contact time of the mixture was checked in succession of 20 minutes, from time t=20 min to determine the optimum time for adsorption. The time experiment was terminated at t=120 min when the adsorption process attained equilibrium.

3.3.5 Effect of temperature

The effect of temperature on the chromium uptake by the chitosan was studied. The temperature was varied from 28 ^{o}C to 45 ^{o}C keeping other parameters such as chitosan dosage (2.5 g) and contact time (80 min) constant.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterisation of Chitin and Chitosan

Mussel shell compositions, proximate analysis and carbon nitrogen content of chitin and chitosan are presented respectively.

4.1.1 Mussel shell composition

The composition of the mussel shell used as raw material for the extraction of chitin is presented in Table 4.1.

Table 4.1 Mussel shell composition

Component	Composition (%)
Protein	9.99
Mineral	51.62
Chitin	23.25
Chitosan	15.14

As presented in Table 4.1, the mussel cuticle was found to contain 23.25% of chitin which is close to 21.53% reported by Abdou *et al*, (2008) for shrimp shell. This may be due to variation in mineral content of different water bodies in which this crustaceans strive in and also, it may be due to the difference in raw material used.

The mineral content ($CaCO_3$) of the shell was found to be 51.62% which is slightly higher than the range in literature for crab as 40-50%, and higher than that of shrimp

which is 20-30% but lower than that of oyster cuticle which is 85-90% (Kurita, 2006). Thus it can be said that the mineral content of the cuticle varies in different members of the crustaceans and also varies with location.

The deacetylated chitin obtained was tested with acetic acid to see its dissolution in organic acids. 1 g of the chitosan dissolved in 1 M acetic acid after 53 minutes of vigorous stirring. Brugnerotto *et al,* 2001 stated that the solubility of chitosan is also controlled by the distribution of the acetyl groups remaining along the chain. Thus, the more deacetylated the chitin is, the better the solubility. This is a necessary condition to ascertain that chitosan has been obtained from chitin; it is not a sufficient condition, since other derivatives of chitin can give a similar behaviour. Thus the need to carry out other characterisation processes on the deacetylated chitin.

4.1.2 Proximate analysis of chitin and chitosan

This section presents the results on the composition of chitin and chitosan based on four most important factors; the moisture content, ash content, fat and protein content.

The moisture content of chitin was very much higher than that of the chitosan as indicated in Table 4.2. This was expected since the chitin was dried to constant weight before the deacetylation process. The ash content of chitin was lower than that of chitosan and this may be attributed the presence of the acetyl group in the chitin sample as also reported by Isa *et al.,* (2012). Protein content of the chitosan sample was considered high after deprotienization of the chitin and this could be attributed to the low degree of deacetylation of the chitin, though lower than that of chitin as expected.

Table 4.2 Proximate analysis of chitin and chitosan

S/N		Moisture Content (%)	Ash Content (%)	Fat (%)	Protein (%)
1	**Chitin**	12.90	26.45	0.63	4.93
2	**Chitosan**	1.40	36.87	0.05	2.29

4.1.3 Degree of deacetylation

Table 4.3, Figure 4.1 and 4.2 respectively present the results of the Carbon-Nitrogen analysis and the FTIR spectra of chitin and chitosan used in calculating the degree of deacetylation which is an important factor used for differentiating chitin from chitosan and also to establish functional groups present in the materials.

Table 4.3 Carbon-Nitrogen content of chitin and chitosan

S/N		Carbon (%)	Nitrogen (%)	DDA (%)	Carbon Nitrogen ratio
1	**Chitosan**	13.32	2.29	60.69	5.82
2	**Chitin**	26.23	4.02	19.37	6.52

From Table 4.3, the percentage degree of deacetylation can be calculated using the Kasaai Equation (Abdou *et al.*, 2008) presented as Equation 4.1

$$DDA\% = \frac{6.857 - (\frac{C}{N})}{1.7143} \times 100 \qquad (4.1)$$

$$DDA\% = 60.69\%$$

Using the carbon-nitrogen analysis, the chitosan obtain has a degree of deacetylation of 60.69% which is higher than that reported by Isa *et al.,* (2012), of 50.64% for shrimp shell lower than the reported degree of deacetylation of 98.38-98.79% achieved by Kalut (2008) using shrimp shell. This may be attributed to the nature of the raw material used, its immediate environment and also the methods applied during the processes. There is an indication that the chitosan has been extracted in this work, since the necessary condition as stated by some literature is that the degree of deacetylation should be above 50% and it should be soluble in acidic media (Honarkar and Barikani, 2009). The chitosan was found to dissolve completely in 1M acetic acid after 53 minutes with initial vigorous stirring and later allowed to stand.

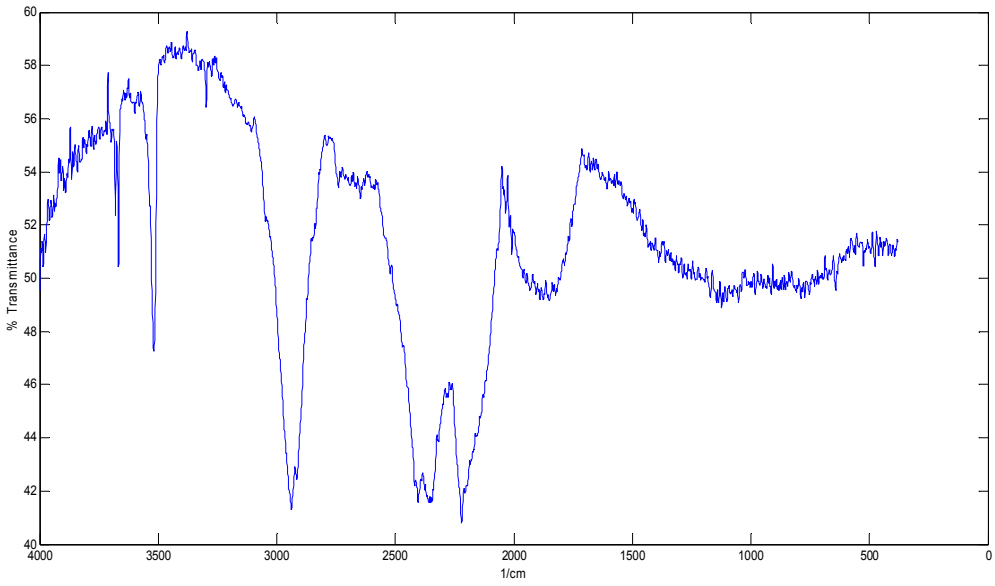


Figure 4.1: FTIR Spectrum of Chitin

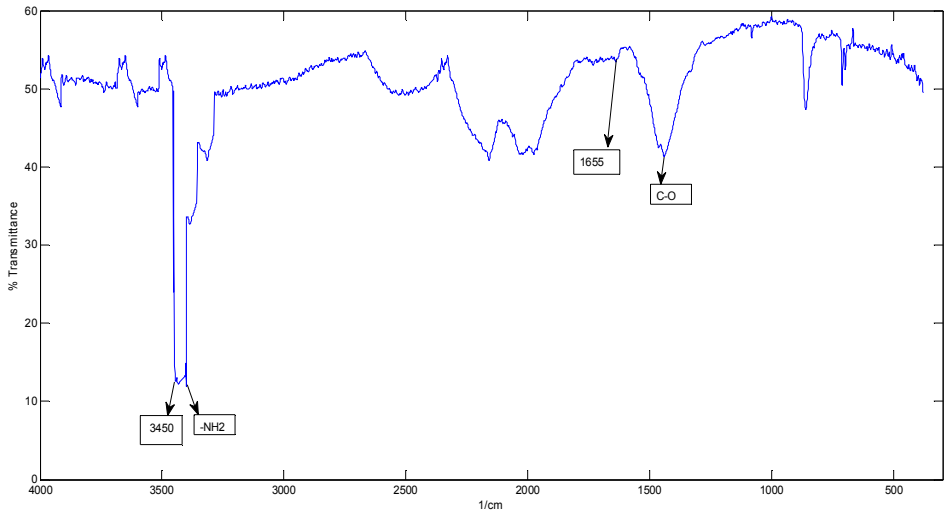


Figure 4.2: FTIR Spectrum of Chitosan

Figures 4.1 and 4.2 are the FTIR spectra for the chitin and chitosan respectively; the FTIR spectra gave characteristics bands of $-NH_2$ at 3447 cm^{-1} and carbonyl group band at 1477 cm^{-1}. It should be noted that the frequency ranges for the different classes of carbonyl compound overlap, and the carbonyl frequency alone is not sufficient to characterise the functional group (Coates, 2000), thus there is a need for the application of mathematical relationships to calculate some targetted features, in this case the degree of deacetylation.

The degree of deacetylation was calculated using the baseline equation (Equation 4.2) as used by Jiao *et al.,* (2010). The wavelengths 1655 and 3450 cm^{-1} was the baseline bands used in calculating the degree of deacetylation.

Using the FTIR spectra (Figure 4.2),

$$DDA = 100 - \frac{A_{1655}}{A_{3450}} \times 115 \qquad (4.2)$$

$$\text{But } A_{1655} = -\log(\frac{T_{1655}}{100}) \qquad (4.3a)$$

$$\text{Also } A_{3450} = -\log(\frac{T_{3450}}{100}) \quad (4.3b)$$

Where T= Transmittance

$$DDA = 60.66\%$$

It is interesting to know that both the degree of deacetylation calculated using the carbon-nitrogen ratio and that from the FTIR spectra are almost the same, this further confirms the fact that the mussel cuticle can be used as a raw material for chitin and chitosan extraction.

4.1.4 Surface area of chitosan

The surface area was determined as 2.7225 ± 0.0741 m²/g, and 0.1620 nm² as the molecular cross sectional area.

Chitosan beads was reported to have a BET surface area of 0.99 m^2/g and chitosan Ethylene glycol diglycidylether (EDGE) beads had 0.44 m^2/g (Kamari *et al.,* 2009).

The BET surface area of chitosan (Sigma C 3646) was also measured as 0.65 m^2/g with a Micrometrics Flow Sorb II 2300 (Uzun and Guzel, 2004). The variation in the values of the BET surface area may be associated with the different methods of extraction, the degree of the acetylation and the raw materials used for the extraction of the chitosan.

4.2 Analysis of Chromium (VI) Removal Using Extracted Chitosan

Figures 4.3, 4.4, and 4.5 illustrate the results obtained from chromium-water solution treatment with the synthesized chitosan from mussel shell. Figure 4.3 shows the variation of final concentration of chromium (VI) ion with the increase in chitosan dosage. At a room temperature of 28 ^{o}C and a contact time of 5 minutes, the equilibrium concentration was reached with chitosan dosage of 2.5 g after which the increase in dosage makes no reasonable difference, thus this dosage was selected as the optimum dosage, and the Cr^{6+} ion concentration (0.11 mg/l) was taken as the equilibrium concentration. The percentage uptake at this point was 82.3%.

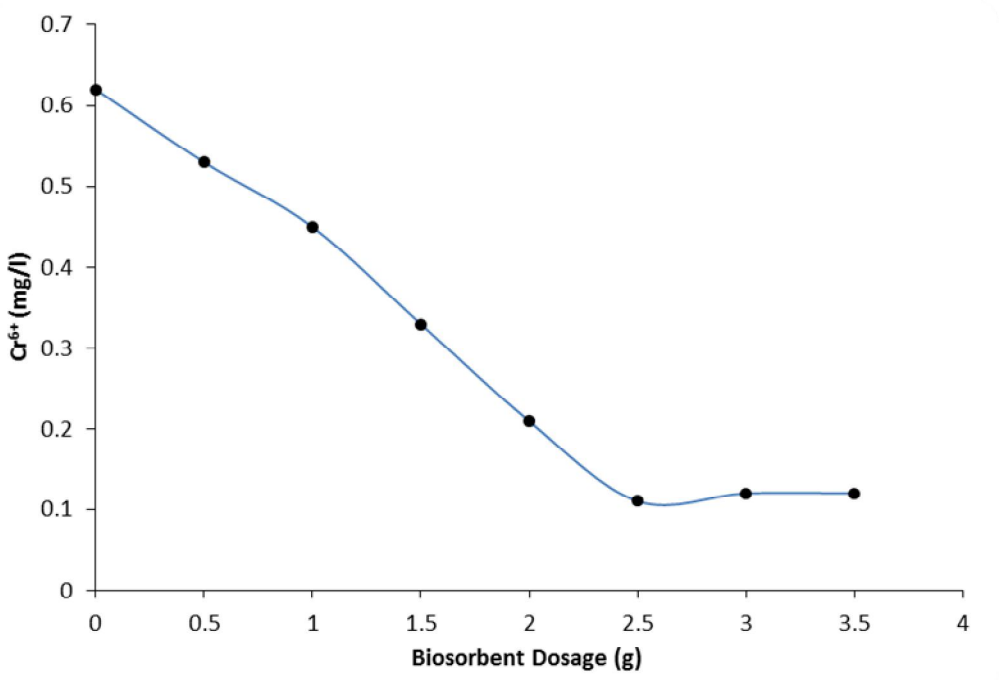


Figure 4.3: Effect of Chitosan Dosage on Cr^{6+} removal

Furthermore, the effect of contact time on the final concentration was investigated. At a fixed dosage of 2.5 g, and a temperature of 28 ^{o}C, the equilibrium time for the process was investigated. Figure 4.4 shows how the reductions in the ion concentration become almost constant from 80 minutes contact time.

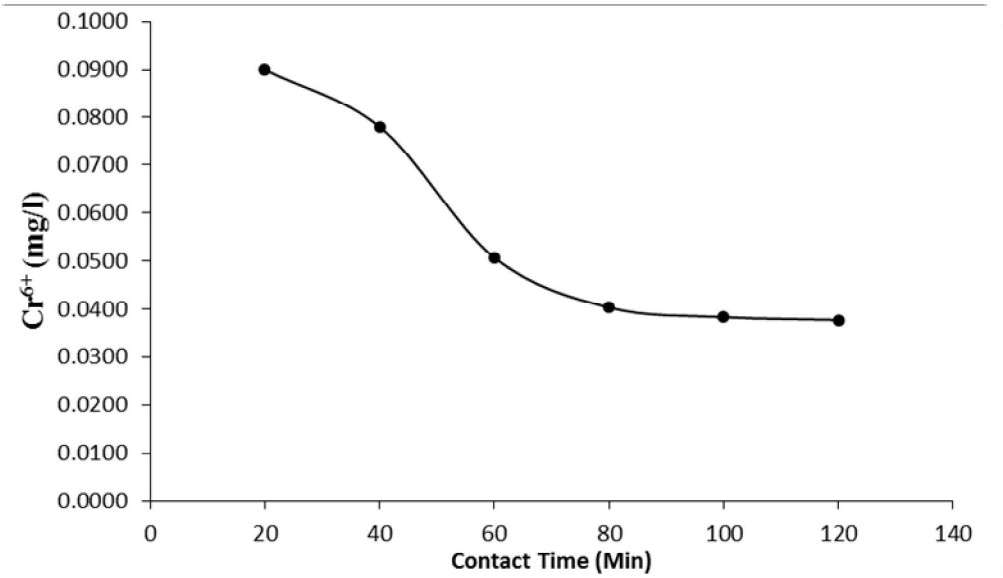


Figure 4.4: Effect of Contact Time on Cr^{6+} removal at 2.5 g Chitosan Dosage

Figure 4.5, presents the effect of solution temperature on the chromium ion uptake and it reveals that the best uptake was obtained at room temperature (28^{o}C), but at higher temperature, the uptake by chitosan reduces drastically. This behaviour can be attributed to the fact that the adsorption process in this case is not favoured by increase in temperature thereby reducing the adsorptive capacity of the adsorbent.

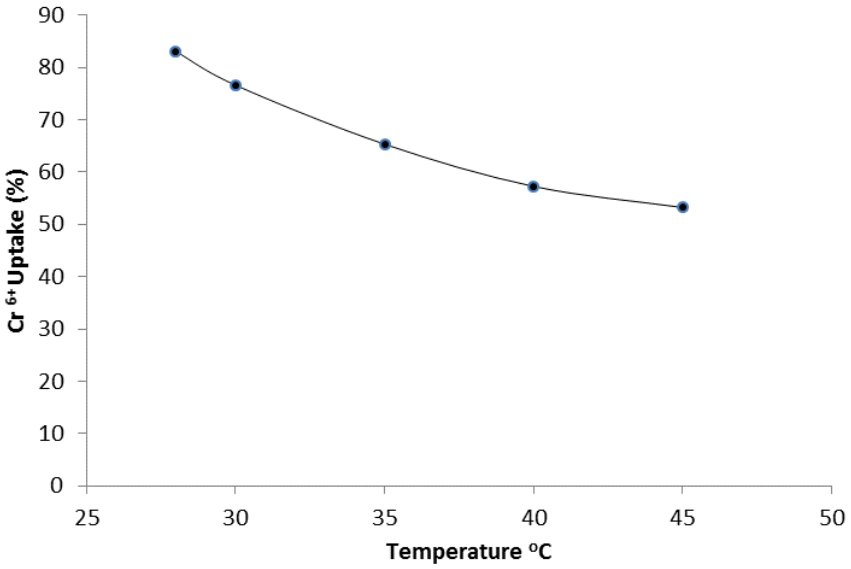


Figure 4.5: Effect of solution temperature on Chromium ion uptake (2.5 g dosage 80 min).

4.2.1 Adsorption isotherms for Cr (VI) removal using chitosan

The isotherm study in this work is illustrated in Figures 4.5 and 4.6 for Langmuir and Freundlich isotherms respectively. The Langmuir isotherm was built under the assumption that the adsorption takes place in a monolayer on a uniform surface with a finite number of adsorption sites. Once these adsorption sites are occupied, no further adsorption can take place. The Langmuir isotherm equation is shown as Equation 2.3

The Langmuir adsorption isotherm can be transformed to linear form thereby allowing the parameters to be estimated graphically or with linear regression. One of the linearized forms of the equation is shown as Equation 2.4.

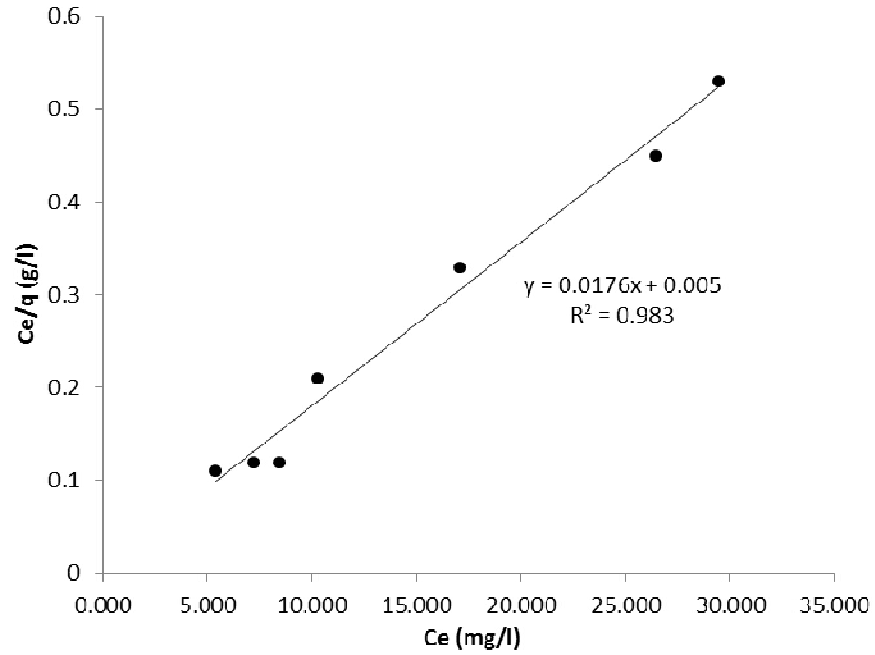


Figure 4.6: Langmuir plot for Cr^{6+} adsorption by Chitosan

Using Equation 2.4, Figure 4.6 was plotted (see Table A.4), such that $\frac{C_e}{q_e}$ is plotted against C_e from where the parameters shown in Table 4.4 were calculated. The details of the calculation is shown in Appendix B

The Langmuir adsorption isotherm equation is often used to describe the sorption of solute from solution. Table 4.4 shows the R-square value from the Langmuir plot and other constant. An important parameter determined also is the dimensionless separation factor (R_L). The value of R_L indicates the type of the isotherm to be either unfavourable (R_L>1), linear (R_L =1), favourable (0<R_L<1) or irreversible (R_L = 0). R_L is a positive number whose magnitude determines the feasibility of the adsorption process (Srividya and Mohanty, 2009). From Table 4.4, the R-square value for Langmuir adsorption isotherm is 0.983 signifynig a good fit, and an R_L value of 0.314 categorize the process ass being favourable and reversible

Table 4.4 Freundlich and Langmuir constants for the adsorption of Cr^{6+} by Chitosan.

Isotherm	R^2	Slope	Intercept	b_F	a_F	n	k_L	B	R_L
Langmuir	0.983	0.0176	0.005	-	-	-	56.82	3.52	0.314
Freundlich	0.0254	0.822	1.7997	0.822	6.048	1.217	-	-	-

The second isotherm considered was the Freundlich isotherm. It is an empirical equation and can be employed to describe heterogeneous systems. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution (Muhammad *et al.,* 2012). The linearized Freundlich equation is shown as Equation 4.4.

$$\ln q_e = \ln a_F + b_F \ln C_e \qquad (4.4)$$

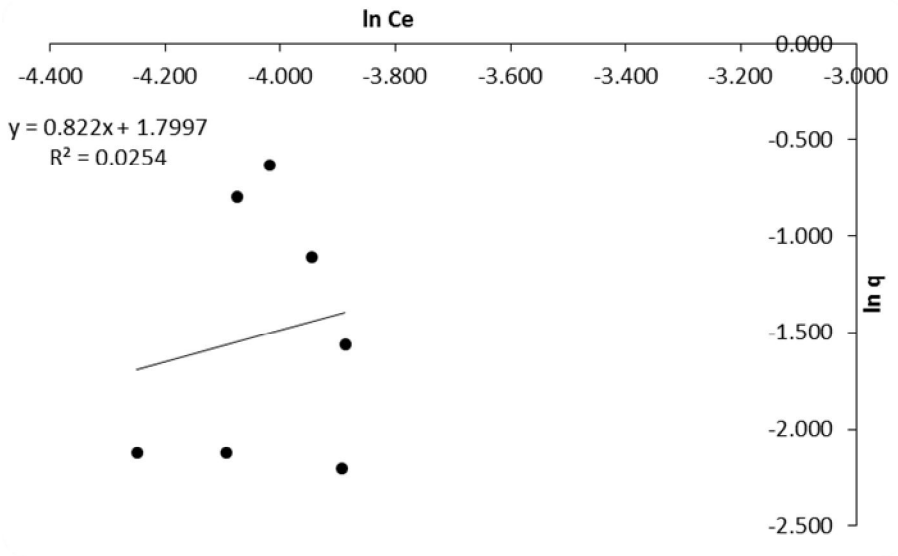


Figure 4.7: Freundlich plot for Cr^{6+} adsorption by Chitosan

Equation 4.4 was used to plot Figure 4.7 (See Table A.5). The R-square value in Table 4.4 is very low (0.0254), thus the data does not fit well with the Freundlich isotherm but important parameters like n and b_F were determined.

4.2.2 Kinetic modelling of chromium (VI) removal using chitosan

Four kinetic models were tested to know the best model describing the kinetics of Chromium (VI) removal from chromium solution using chitosan. The essence of kinetic investigation is to find out the stage which plays a decisive role to the adsorption reaction rate. Therefore, the use of kinetic models to fit the time dependent experimental data is one of important steps for the adsorption study (Muhammad *et al.*, 2012). Figure 4.8 shows the kinetic plot of chromium ion biosorption using chitosan as an adsorbent. In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in different fields, such as the adsorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fibre (Qiu *et al.*, 2009). The integrated linear form of pseudo-first order kinetic model as proposed by Lagergren was presented as Equation 2.14 in Chapter two.

Figure 4.8 is the pseudo-first order kinetic model and the R^2 value is 0.8003. The other constants in the equation are shown in Table 4.5.

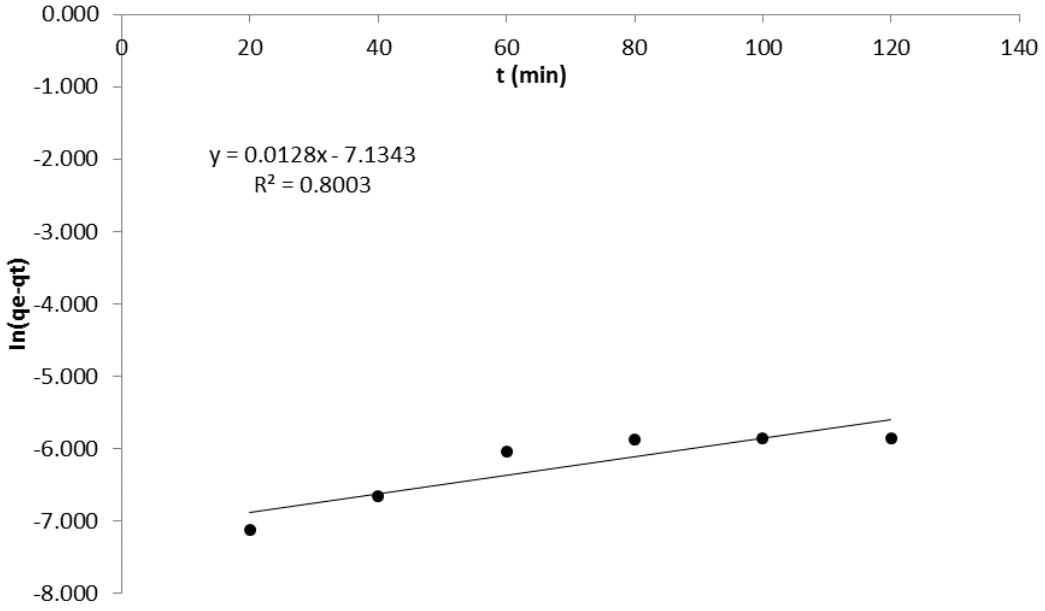


Figure 4.8: Pseudo First Order Kinetic model

The second order kinetic model was also tested to see its conformity with the generated experimental data. In earlier years, the second-order rate equations were reasonably applied to describe adsorption reactions occurring in soil and soil minerals. Recently, the equation has also been used to describe fluoride adsorption onto acid-treated spent bleaching earth and phosphamidon adsorption on an antimony (V) phosphate cation exchanger (Qiu *et al.*, 2009). The integrated form of the model (Equation 2.15) is presented in Chapter two.

Table 4.5 Evaluated constants obtained from kinetic models tested

Kinetic model	R^2	Slope	Intercept	Rate constant	Other constants
Pseudo-first order	0.8003	0.0128	7.1343	0.9881	q_e=-0.0204
Second order	0.885	0.1714	8.1198	0.1714	C_0=0.1232
Pseudo-second order	0.9997	41.776	130.43	403.7306	q_e=0.0077
Elovich	0.9318	0.0013	0.0172	b=769.231	a=724.4276

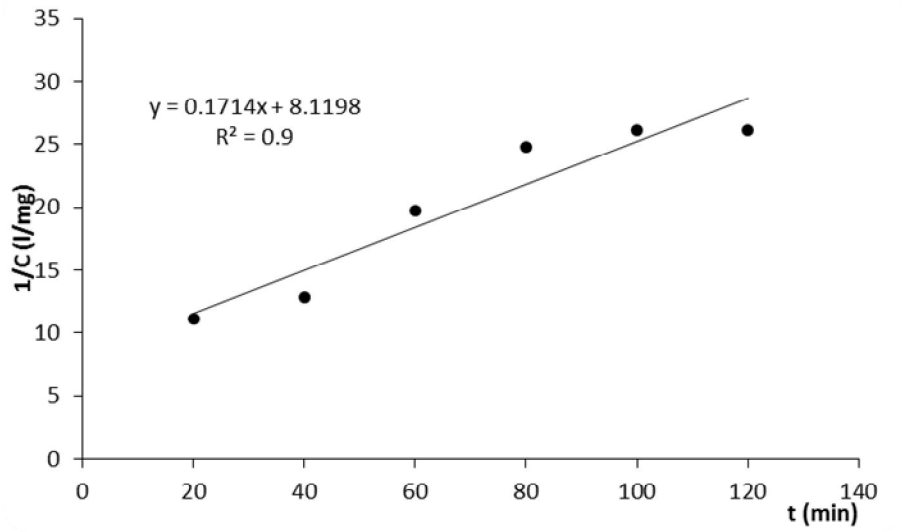


Figure 4.9: Second Order Kinetic Model

Equation 2.19 was used to plot Figure 4.10 which represents a plot for the pseudo second order model. A plot t/q_t against t should be linear if the adsorption follows pseudo-second order. q_e and k_2 can be calculated from the slopes and intercepts of the plots as shown in Table 4.5.

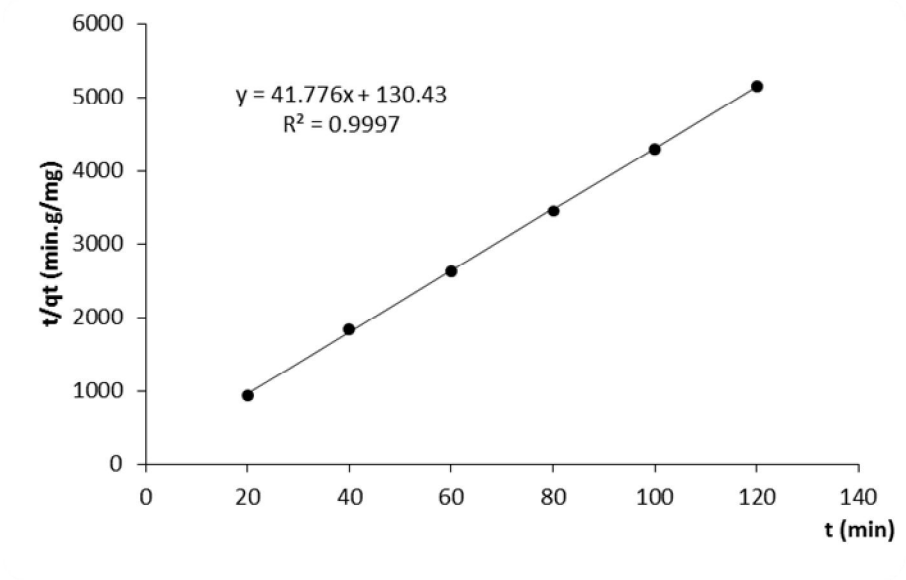


Figure 4.10 Pseudo Second Order Kinetic Model.

As shown in Figure. 4.10, the R^2 value is almost unity (R^2=0.9997) which indicates a perfect fit than that of the second order model (0.90). This shows that the data generated from the use of chitosan on the removal of chromium (vi) ion fitted best into the pseudo-second order kinetic model.

Furthermore, for the benefit of doubt, another model (Elovich) of frequent application was also tested. The Elovich model is generally expressed as shown in Equation 2.20. A plot of q_t vs. $\ln t$ gives a straight line with a slope of l/b and an intercept of $\frac{1}{b}\ln(ab)$ with good correlation coefficients.

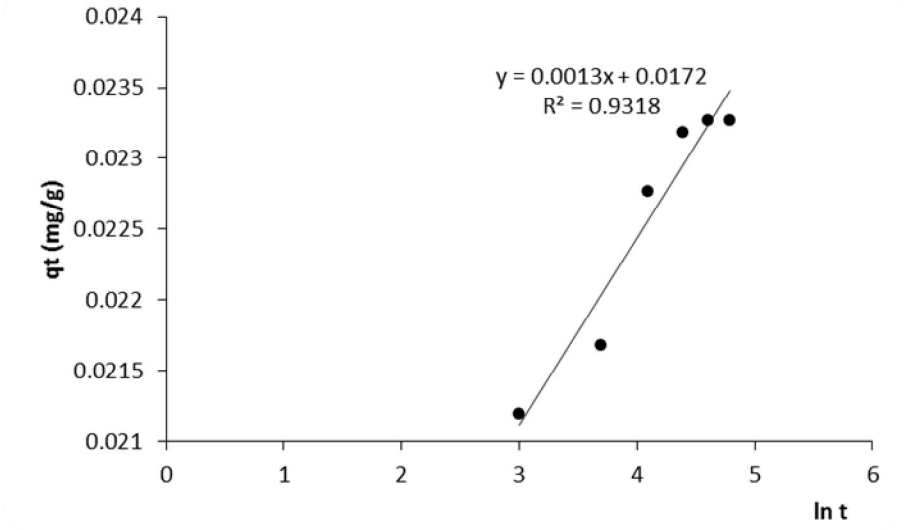


Figure 4.11: Elovich kinetic model

From the plot (Figure 4.11), it could be seen that the R^2 value is less than that of the pseudo-second order plot but better than the remaining models.

Table 4.5 shows the summary of the kinetic model and constants obtained from the test with the pseudo first order, second order, pseudo second order and the Elovich model. As discussed earlier, the data generated from the treatment fits best with the pseudo second order kinetics since it shows a highest R^2 Value of 0.9997.

4.2.3 Determination of some thermodynamic parameters for Cr (VI) removal using chitosan

In order to characterise the adsorption process for this work, some basic thermodynamic parameters are needed. These parameters are discussed in the following sections.

4.2.3.1 The free sorption energy (E_s)

This is a parameter which tells whether the adsorption process is either physiosorption or chemisorption. The sorption energy (E_s) can easily be calculated using the Dubinin-Radishkevich (D-R) isotherm presented as Equation 2.11.

Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent (Ho *et al*, 2001).

The D-R isotherm can be written in a linear form as

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + {}^{1}\!/\!_{C_e}) \qquad (4.5)$$

Where q_D is the D-R isotherm constant, B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution. The relationship between the free energy of sorption (E_s) and B_D is given by Equation 2.13

The mean free energy of sorption gives information about biosorption mechanism, physical or chemical. If E_s value is between 8 and 16 (kJ/mol), the sorption process follows chemisorption and if E_s<8 (kJ/mol), the sorption process is of a physiosorption (Kianfar *et al.,* 2012). As calculated in Appendix B, E_s= 0.224 kJ/mol, which implies the adsorption process is physical.

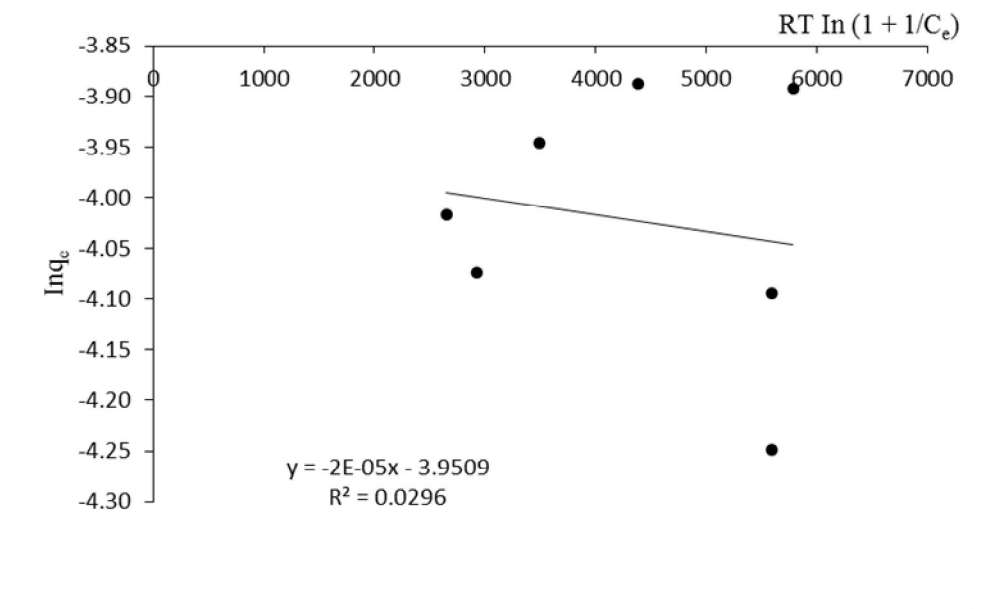


Figure 4.12: Dubinin-Radishkevich (D-R) isotherm

4.2.3.2 Calculation of enthalpy (ΔH_{ads}), Gibbs free energy (ΔG_{ads}) and entropy (ΔS_{ads}).

Thermodynamic parameters can be calculated using the relations used by Kumar and Gayathri (2009), Ren *et al.* (2012) and Kianfar *et al.* (2012).

$$K_c = \frac{C_o - C_e}{C_e} \qquad 4.6$$

$$\ln K_c = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \qquad 4.7$$

$$\Delta G_{ads} = -RT \ln K_c \qquad 4.8$$

Where K_c is the distribution coefficient, R= 8.314 mol/J/K and T is the absolute temperature.

Using Equation 4.7 and Table A.11, Figure 4.13 was plotted

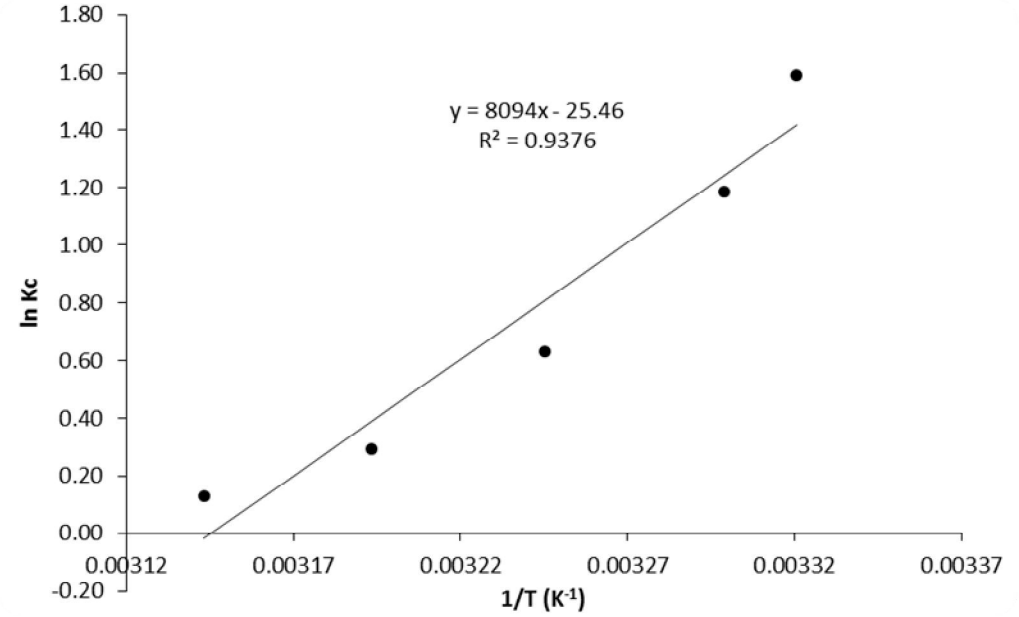


Figure 4.13: Plot for calculation of thermodynamic parameters.

The thermodynamic parameters as calculated in Appendix B gave an insight on the type of adsorption and the enthalpy of the adsorption process. The enthalpy of the process was determined to be -67 kJ/mol K, the negative sign in the value indicates that the adsorption is exothermic i.e, the adsorption takes place with the release of energy. On the other hand, the change in entropy value which is -0.212 kJ/molK indicates that there is decrease in the degree of disorderliness of the sorbates as they approach the adsorption layer.

Furthermore, the negative values of the Gibbs free energy as shown in Table A.11 show that the adsorption process is completely spontaneous.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents a summary of the main findings of the research as it relates to contribution to knowledge. Further areas of research are also suggested in this field of study.

5.1 Conclusion

From the work carried out on the extraction of chitin and then chitosan from mussel shell which is a member of the crustaceans in the mollusca family and the use of the extracted chitosan in removal of chromium (VI) ion from dichromate-water solution, the following conclusions can be drawn:

The mussel shell has a mineral content of 51.62%, a chitin composition of 23.25% and the chitosan composition of 15.14%. The chitosan extracted has a degree of deacetylation of 60.69% and 60.66% calculated from the elemental analysis and the FTIR spectra of chitosan respectively. The carbon-nitrogen ratio of the chitosan extracted is 5.9

From the adsorption studies data, the optimum chitosan dosage for the removal of 0.51mg/L of chromium (VI) which is 82.3% of the initial concentration (0.62mg/L) was determined to be 2.5g at 28^{o}C, also the time required for the adsorption process to attain equilibrium is 80 minutes.

The data obtained from chromium (VI) removal from water best fits the Langmuir isotherm with an R^2-value of 0.983 which is clearly higher than that of the Freundlich

of 0.0254, thus the adsorption process of chromium (VI) on chitosan follows the Langmuir isotherm.

The adsorption process was not favoured by increase in temperature as the adsorption decreased with increase in temperature within the temperature range of 28 ^{o}C to 45 ^{o}C. The negative values of enthalpy and Gibbs free energy obtained from the thermodynamic studies indicate clearly that the adsorption process was exothermic and spontaneous.

The R_L value is less than one and is positive, the adsorption process is favoured and reversible, and therefore the process is a physiosorption.

The value of the free sorption energy E_s (0.224 kJ/mol) determined using the Dubinin-Radishkevich model is also an evident that the adsorption is physical as the value is less than 8 kJ/mol which is a range for only physiosorption.

The BET surface area of the deacetylated chitin was determined to be 2.7225 ± 0.0741 m²/g using the BET machine.

The pseudo second order kinetic model with an R^2-value of 0.9997 was the best fitted kinetic model among the four models tested.

5.2 Recommendations

The following statements are recommendations for further studies in this area

The kinetics and mechanisms of chitosan extraction using mussel shell may be studied.

In this work, the batch adsorption study was used in obtaining the data used for the kinetic and isotherm study, a continuous adsorption studies may be applied and to be compared with the batch.

The chitosan should be used to treat industrial waste water where chromium (VI) and other metal ions are present to determine its competition with other ions for adsorption sites

References

Abdou, E., Nagy, K., & Elsabee, M. Z. (2008). Extraction and characterization of chitin and chitosan from local sources. *Bioresource Technology, IX*(99): 1359-1367.

Al-Anber, M.A. (2012). *Thermodynamics Approach in The Adsorption of Heavy Metals*, 1-29, Retrieved from http://cdn.intechopen.com/pdfs-wm/21870.pdf [20 August 2013].

Alves, N.M. and Manoa, J.F. (2008). Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications, *International Journal of Biological Macromolecules*: 401-414.

Anjaneya, O., Santoshkumar, M., Anand, S.N. and Karegoudar, T.B. (2009). Biosorption of acid violet dye from aqueous solutions using native biomass of a new isolate of Penicillium specie, *International Biodeterioration & Biodegradation*, 63: 782–787.

AOAC (1990). Official Methods of Analysis, *Association of Official Analytical Chemists: Washington DC*.

Aranaz, I., Mengíbar, M., Harris, R., Paños, I., Miralles, B., Acosta, N., Galed, G. and Heras, Á. (2009). Functional Characterisation of Chitin and Chitosan, *Current Chemical Biology*:203-230.

BangBose, J., S.Adewuyi, Bangbose, O., and Adetoye, A. (2008). Adsorpption Kinetics of Cadmium and Lead by Chitosan. *African Journal of Biotechnology, 9 (17)*: 2560-2565.

Boonlertnirun, S., Boonraung, C. and Suvanasara, R. (2008). Application of Chitosan in Rice Production, *Journal of Metals, Materials and Minerals*, 18(2): 47-52.

Brugnerotto, J., Lizardi, J., Goycoolea, F.M., ArguÈelles-Monal, W., DesbrieÁres, J. and Rinaudo, M. (2001). An infrared investigation in relation with chitin and chitosan characterisation, *Polymer 42 (2001)*, 42: 3569-3580.

Burrows, F., Louime, C., Abazinge, M. and Onokpise, O. (2007). Extraction and Evaluation of Chitosan from Crab Exoskeleton as a Seed Fungicide and Plant Growth Enhancer, *American-Eurasian Journal of Agricultural & Environmental Sciences*, 2: 103-111.

Cheng, C.C., Cheh, L.W., Yang, J.C., Tsai, C.M., Keh, E.S., Sheu, M.T., Su, C.H., Hong, H.H., Lin, C.T. and Lee, S.Y. (2007). Non-shellfish chitosan from the fruiting body residue of Ganoderma tsugae for long-lasting antibacterial guided-tissue regeneration barriers, *Journal of Dental Science*, 2: 19-29.

Chung, J. and Wolfgang, H. (2003). Chemical modification of chitosan and equilibrium study for mercury ion removal, *Journal of Water Reearch*, 37: 41-53

Coates, J. (2000). Interpretation of Infrared Spectra, A Practical Approach. In R. Meyers (Ed.), *Encyclopedia of Analytical Chemistry* John Wiley & Sons Ltd, Chichester: 10815–10837.

Dubinin, M.M. (1960). The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, *Chemical Revision*, 60: 235–266.

Dubinin, M.M. (1965). Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents, *Zhurnal Fizicheskoi Khimii*, 39: 1305–1317.

Dustgania, A., Farahani, E.V. and Imani, M. (2008). Preparation of Chitosan Nanoparticles Loaded by Dexamethasone Sodium Phosphate, *Iranian Journal of Pharmaceutical Sciences*, 4(2):111-114.

Dutta, P.K. (2004). Chitin and Chitosan: Chemistry, Properties and Applications', *Journal of Scientific and industrial Research*: 20-31.

Fernandez-Kim, S.O. (2004). Physicochemical and Functional Properties of Crawfish Chitosan as Affected by different Processing Protocols: 6-61.

Freundlich, H.M.F. (1906). Over the adsorption in solution, *Journal of Physical Chemistry*, 57:385–470.

Fung, A.L. (2007). A study on the characteristics of chitosan as an immobilization matrix for biosensors, Malaysia University Sains: 2-19.

George, T.S., Guru, K.S.S., Vasanthi, N.S. and Kannan, K.P. (2011). Extraction, Purification and Characterisation of Chitosan From Endophytic Fungi Isolated From Medicinal Plants, *World Journal of Science and Technology*, 1(4): 43-48.

Hadi, A.G. (2013). Synthesis of Chitosan and Its Use in Metal Removal, *Chemistry and Materials Research*, 3(3): 22-26.

Ho, Y.S. (2006). Review of second-order models for adsorption systems, *Journal of Hazardous Materials*, B136: 681–689.

Honarkar, H. and Barikani, M. (2009). Application of Biopolymers I: CHITOSAN, *Monnbatsh Chemistry*, 1(40): 1403-1420.

Ho, Y.S., Porter, J.F. and G.Mckay (2001). Equillibrium Isotherm Studies for the Sorption of Divalent Metal Ions into Peat:Copper Nickel and Lead Single Component Systems, *Water Air Soil pollution*, 1(2): 141-174.

Hossain, M.A., Ngo, H.H., Guo, W.S. and Nguyen, T.V. (2012). Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption, *Journal of Water Sustainability*, 2(1): 87–104.

Isa, M.T., Ameh, A.O., Gabriel, J.O. and Adama, K.K. (2012a). Extraction and Characterisation of Chitin from Nigerian Sources, *Leonardo Electronic Journal of Practices and Technologies*, 21: 73-81.

Isa, M.T., Ameh, A.O., Tijjani, M. and Adama, K.K. (2012b). Extraction and Characterisation of Chitin and chitosan from Nigerian Shrimps, *International Journal of Biological and chemical Sciences*, 6 (1): 446-453.

Islam, M. M., Masum, S. M., Rahman, M. M., Molla, M. A., Shaikh, A. A., and Roy, S. K. (2011). Preparation of Chitosan from Shrimp Shell and Investigation of Its Properties. *International Journal of Basic & Applied Sciences, 11*(1): 116-130.

Itodo, A.U. and Itodo, H.U. (2010). Sorption Energies Estimation Using Dubinin-Radushkevich and Temkin Adorption Isotherm, *Life Science Journal*, 7(4): 31-39.

Jiao, T. F., Zhou, J., Zhou, J., Gao, L., Xing, Y., and Li, X. (2011). Synthesis and Characterization of Chitosan-based Schiff Base Compounds with Aromatic Substituent Groups. *Iranian Polymer Journal, 20*(2): 123-136

Kafetzopoulos, D., Martinou, A. and Bouriotis, V. (1993). Bioconversion of chitin to chitosan: Purification and characterisation of chitin deacetylase from Mucor rouxii, *Applied Biological Sciences*, 90: 2564-2568.

Kalut, S.A. (2008). Enhancement of Degree of Deacetylation of Chitin in Chitosan Production, *Faculty of Chemical Engineering and Natural Resources Universiti Malaysia Pahang*.:5-31.

Kamari, A., Wan, S.W.N. and Ken, L.L. (2009). Chitosan and chemically modified chitosan beads for acid dyes sorption, *Journal of Environmental Sciences*, 21: 296–302.

Kaushik, N., & Sharma, J. K. (2005). Studies on the role of adsorbents in removal of direct dyes from textile effluent. *National Environmental Pollution Technology, 4*(2): 163-166.

Khora, E. and Limb, L.Y. (2003). Implantable applications of chitin and chitosan, *Biomaterials*: 2339-2349.

Kianfar, S., Moheb, A. and Ghaforian, H. (2012). Equilibrium, Kinetiic and Thermodynamic Studies on Solution Using a Spore Forming Bacillus Issolated from Waste Water of a Leather Factory, *World Academy of Science, Engineering and Technology*, 69: 481-485.

Kim, S.K. (2010). Chitin, Chitosan, Oligosaccharides and Their Derivatives., New York: CRC Press:3-11

Kortenkamp, A., Casadevall, M. and Faux, S.P. (1996). A role for molecular oxygen in the formation of DNA damage during the reduction of the carcinogen, *Archives of Biochemistry*, 329: 199-208.

Kumar, K.V., Subanandam, K., Ramamurthi, V. and Sivanesan, S. (2004). Solid Liquid Adsdorption for Waste Water Treatment, Principle Design and Operation, *Solid Waste Treatment*: 3-7.

Kumar, P.S. and Gayathri, R. (2009). Adsorption of Pb^{2+} ions from aqueous solutions onto Bael Tree leaf Powders: Isotherm, Kinetics and Thermodynamics study, *Journal of Engineering Science and Technology*, 4(4): 381-399.

Kurita, K. (2006). Chitin and Chitosan: Functional Biopolymers. *Marine Biotechnology.* Tokyo:13-27.

Langmuir, I. (1916). The adsorption of gases on plane surface of glass, mica and platinum, *Journal of American Chemical Society*, 40:1361–1368.

Lertsutthiwong, P., HOW, N.C., Chandrkrachang, S. and Stevens, W.F. (2002). Effect of Chemical Treatment on the Characteristics of Shrimp Chitosan', *Journal of Metals, Materials and Minerals*; 11-18.

Martino, A.D., Sittinger, M. and Risbud, M.V. (2005). Chitosan: A versatile biopolymer for orthopaedic tissue-engineering, *Biomaterials*: 5983-5990.

Moller, H., Grelier, S., Pardon, P. and Coma, V. (2004). Antimicrobial and physicochemical Properties of chitosan-HPMC-based films, *Journal of Agricultural and Food Chemistry*, 52(21): 6585-6591.

Muhammad, I.M., El-Nafaty, U.A., Abdulsalam, S. and Makarfi, Y.I. (2012). Oil removal from oil polluted water using eggshell', *civil and enviromental research*, 2(4): 52-63.

Nadarajah, K., Kader, J., Mazmira, M. and Paul, D.C. (2001). Production of Chitosan from Fungi, *Pakistani Journal of Biological Sciences*, 4(3): 263-265.

Nomanbhay, S.M. and Palanisamy, K. (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal', *Electronic Journal of Biotechnology*: 43-53.

Parimaladevi, P. and Venkateswaran, V. (2011). Kinetics, Thermodynamics and Isotherm Modeling of Adsorption of Triphenylmethane Dyes (Methyl Violet, Malachite Green and Magenta II) on to Fruit Waste, *Journal of Applied Technology in Environmental Sanitation*, 1(3): 273-283.

Park, S.Y., Marsh, K.S. and Rhim, J.W. (2002). Characteristics of different molecular weight chitosan films affected by the type of organic solvents, *food science*: 194-196.

Qiu, H., Lv, L., Pan, B.C., Zhang, Q.J., Zhang, W.M. and Zhang, Q.X. (2009). Critical review in adsorption kinetic models, *Journal of Zhejiang University Science*, 10(5): 716-724.

Quek, S.Y., Wase, D.A. and Forster, C.F. (1998). The use of sago waste for the sorption of lead and copper, *Water South Africa*, 24(3): 251-256.

Radushkevich, L.V. (1949). Potential theory of sorption and structure of carbons, *Zhurnal Fizicheskoi Khimii*, 23: 1410–1420.

Rana, M.S., Halim, M.A., Saifullahi, S., Mollah, M.m., Azam, M.S., Goni, M.A., Hossain, M.K. and Rana, M.M. (2009). Removal of Heavy Metal from Contaminated Water by Biopolymer Crab Shell Chitosan, *Journal of Applied Sciences*, 9(15): 2762-2769.

Razali, M. N., Yunus, R. M., Jemaat, Z., & Alias, S. (2010). Monoethanolamine Waste Water Treatment Via Adsorption Method; A study on comparison of Chitosan, Activated Carbon, Alum snd Zeolite. *Journal of Applied Science, 10*(21): 2544-2550.

Redlich, O.A. (1959). A useful adsorption isotherm', *Journal of Physical Chemistry*, 63:1024.

Rhoades, J. and Rastall, B. (2003). Chitosan as an antimicrobial agent, *Food Technology International*:32-32.

Ren, J., Mokgadi, F.B., Jacob, O.K. and Maurice, S.O. (2012). Sorption of Pb(II) and Cu(II) by Low-Cost Magnetic Eggshells-Fe_3O_4 Powder, *Chemical Industry & Chemical Engineering Quarterly*,18(2): 221-231.

Rinaudo, M. (2006). Chitin and chitosan: Properties and applications, *Progress in Polymer Science*: 603-632.

Senel, S. and McClure, S.J. (2004). Potential applications of chitosan in veterinary medicine, *Advanced Drug Delivery Reviews* , 56: 1467– 1480.

Sewvandi, G.A. and Adikary, S.U. (2011). Removal of Heavy Metals From Wastewater Using Chitosan. *Society for social management systems internet journals*:1-7.

Shahidi, F. and Synowieck, J. (1991). Isolation and charactrization of nutrients and value-added products from snow crab (Chinoecetes opilio) and shrimp (Pandalus borealis) processing discards.', *Journal of Agricultural Food Chemistry*, 39: 1527-1532.

Shim, J.W., Park, S.J. and Ryu, S.K. (2001). Effect of modification with HNO3 and NaOH by pitch-based activated carbon fibers, *Carbon*: 1635-1642.

Site, A.D. (2000). Factors Affecting Sorption of Organic Compounds in Natural Sorbent Water Systems and Sorption Coefficients for Selected Pollutants. A Review, *Journal of Physical Chemistry*, 30(1): 187-439.

Sonia, T.A. and Sharma, C.P. (2011). Chitosan and Its Derivatives for Drug Delivery Perspective', *Advanced Polymer Science*, 243: 23–54.

Srividya, K., & Mohanty, K. (2009). Biosorption Of Hexavalent Chromium From Aqueous Solutions By Catla Catla Scales: Equilibrium And Kinetics Studies. *Chemical Engineering Journal, 155*:666–673.

Tajik, H., Moradi, M., Rohani, S. M., Erfani, A. M., & Jalali, F. S. (2008). Product, Preparation of Chitosan from Brine Shrimp (Artemia urmiana) Cyst Shells and Effects of Different Chemical Processing Sequences on the Physicochemical and Functional Properties of the the Product. *Molecules, 13*:1263-1274.

Toth, J. (1962). Acta Chim, *Academic Science Hung*, 15: 415–430.

Uzun, I. and Guzel, F. (2004). External Mass Transfer Studies during the Adsorptions of Some Dyestuffs and p-Nitrophenol onto Chitosan from Aqueous Solution, *Turkey Journal of Chemistry*, 28: 731-740.

Vasanth K. K, Subanandam K., Ramamurthi V. and Sivanesan S. (2004). Solid Liquid Adsorption for Wastewater Treatment: Principle Design and Operation, Department of Chemical Engineering - A.C. College of Technology, Anna University, in Chennai, India. Retrieved from (20 August 2013) www.greenpages.com.

Zeldowitsch, J. (1934). Adsorption site energy distribution, *Acta Physicochim*, URSS 1:961–973.

Zeldes, L.A. (2010). Eat this! Mussels, mighty fine mollusks. Chicago's Restaurant and Entertainment Guide, Inc. Retrieved from (13 October 2012),www.DiningChicago.com,.

APPENDICES

This section shows the tables of the adsorption isotherms and kinetics (Appendix A) and the various calculations made in determination of isotherm constants and kinetic parameters (Appendix B)

APPENDIX A

Table A.1: Effect of biosorbent dosage on chromium (VI) adsorption by chitosan.

Biosorbent dosage (g)	Residual Cr^{6+} (mg/L)	Average Cr^{6+} (mg/L)	Amount removed (mg/l)	Uptake (%)
0	0.620, 0.620, 0.620	0.62	0	0
0.5	0.530, 0.530, 0.550	0.53	0.09	14.516
1.0	0.450, 0.440, 0.450	0.45	0.17	27.419
1.5	0.330, 0.320, 0.330	0.33	0.29	48.387
2.0	0.210, 0.210, 0.210	0.21	0.41	66.129
2.5	0.110, 0.110, 0.110	0.11	0.51	82.258
3.0	0.110, 0.140, 0.100	0.12	0.48	77.419
3.5	0.110, 0.100, 0.140	0.12	0.48	77.419

Reaction conditions: Agitation speed=350 rpm, Time=5 minutes.

Table A.2: Kinetics for Cr^{+6} at optimum biosorbent dosage of 2.5g at 350 rpm

Time (min)	Residual Cr^{6+} (mg/L)	Average (mg/L)	Amount removed (mg/l)	Uptake (%)
20	0.090, 0.090, 0.090	0.0900	0.529	85.323
40	0.078, 0.078, 0.078	0.0780	0.542	87.419
60	0.050, 0.052, 0.050	0.0507	0.569	91.774
80	0.040, 0.041, 0.040	0.0403	0.58	93.548
100	0.038, 0.038, 0.039	0.0383	0.582	93.871
120	0.038, 0.039, 0.038	0.0383	0.582	93.871

Table A.3: Effect of reaction temperature at optimum dosage of 2.5 g

Temp(^{0}C)	Residual Cr^{6+} (mg/l)	Amount removed (mg/l)	Uptake (%)
28	0.105	0.515	83.064
30	0.145	0.475	76.613
35	0.215	0.405	65.323
40	0.265	0.355	57.258
45	0.290	0.33	53.225

Table A.4: Values for Langmuir Isotherm

Biosorbent dosage (g)	C_e (mg/L)	q (mg/g)	C_e/q (g/l)
0.50	0.53	0.018	29.444
1.00	0.45	0.017	26.471
1.50	0.33	0.019	17.069
2.00	0.21	0.021	10.244
2.50	0.11	0.020	5.392
3.00	0.12	0.017	7.200
3.50	0.12	0.014	8.400

Table A.5: Values for Freundlich Isotherm

Biosorbent dosage (g)	C_e (mg/L)	q	C_e/q	lnq	lnC_e
0.50	0.53	0.018	29.444	-4.017	-0.635
1.00	0.45	0.017	26.471	-4.075	-0.799
1.50	0.33	0.019	17.069	-3.946	-1.109
2.00	0.21	0.021	10.244	-3.887	-1.561
2.50	0.11	0.020	5.392	-3.892	-2.207
3.00	0.12	0.017	7.200	-4.094	-2.120
3.50	0.12	0.014	8.400	-4.248	-2.120

Table A.6: Values for Pseudo First Order Plot

Time (min)	Cr^{6+} (mg/L)	Average (mg/L)	q_t(mg/g)	ln (q_e-q_t)
20	0.090, 0.090, 0.090	0.090	0.02120	-7.131
40	0.078, 0.078, 0.078	0.078	0.02168	-6.661
60	0.050, 0.052, 0.050	0.0507	0.02277	-6.044
80	0.040, 0.041, 0.040	0.0403	0.02319	-5.882
100	0.038, 0.038, 0.039	0.0383	0.02327	-5.854
120	0.038, 0.039, 0.038	0.0383	0.02327	-5.854

Table A.7: Values for Second Order Kinetic Plot

Time (min)	C (mg/L)	1/C (l/mg)
20	0.09	11.11111
40	0.078	12.82051
60	0.0507	19.72387
80	0.0403	24.8139
100	0.0383	26.10966
120	0.0383	26.10966

Table A.8: Values for Pseudo Second Order Kinetic Plot

Time (min)	Ct (mg/L)	Qt (mg/g)	t/qt (g min/mg)
20	0.0900	0.0212	943.396
40	0.0780	0.0217	1845.018
60	0.0507	0.0228	2634.815
80	0.0403	0.0232	3450.060
100	0.0383	0.0233	4297.748
120	0.0383	0.0233	5157.298

Table A.9: Values for Elovich Kinetic Model Plot

Time (min)	Average (mg/L)	q_t(mg/g)	Lnt
20	0.09	0.021200	2.9957
40	0.078	0.021680	3.6889
60	0.0507	0.022772	4.0943
80	0.0403	0.023188	4.3820
100	0.0383	0.023268	4.6052
120	0.0383	0.023268	4.7875

Table A.10: Values for Dubinin-Redushkevich Model Plot

q (mg/g)	Ce (mg/l)	RT In $(1 + 1/C_e)$	Inq_e
0.018	0.53	2654.4162	-4.0174
0.017	0.45	2929.6494	-4.0745
0.019	0.33	3489.9302	-3.9459
0.021	0.21	4384.8624	-3.8873
0.020	0.11	5787.9208	-3.8922
0.017	0.12	5592.5158	-4.0943
0.014	0.12	5592.5158	-4.2485

Table A.11: Values for Calculation of Thermodynamic Parameters

Temp(^{0}C)	Ce (mg/l)	kc=(Co-Ce)/Ce	In Kc	1/T (K^{-1})	ΔG
28	0.1050	4.9048	1.5902	0.00332	-3.98159
30	0.1450	3.2759	1.1866	0.00330	-2.99072
35	0.2150	1.8837	0.6332	0.00325	-1.62240
40	0.2650	1.3396	0.2924	0.00319	-0.76126
45	0.2900	1.1379	0.1292	0.00314	-0.34179

APPENDIX B

B.1 Calculation of Langmuir Constants

From Figure 4.6 of Langmuir plot,

$Slope = 0.0176$

$Intercept = 0.005$

$R^2 = 0.983$

Using Equation 4.5

$$\frac{C_e}{q_e} = \frac{1}{k_L b} + \frac{1}{k_L} C_e$$

$$Slope = \frac{1}{k_L} \Rightarrow k_L = \frac{1}{Slope} = \frac{1}{0.0176} = 56.82$$

$$Intercept = \frac{1}{k_L b} = 0.005$$

$$making\ b\ subject\ formular,\ b = \frac{1}{k_L \times 0.005} = 3.52$$

From Equation 4.6

$$R_L = \frac{1}{1 + bC_o}$$

C_o= Initial concentration of Cr^{6+} ion = 0.62.

$R_L = 0.314$

B.2 Calculation of Freundlich constants

From Equation 4.9

$$\ln q_e = \ln a_f + b_f \ln Ce$$
$$Intercept = \ln a_f$$
$$Slope = b_f$$
$$\ln a_f = 1.7997$$
$$a_f = e^{1.7997} = 6.048$$
$$b_f = 0.822$$

B.3 Calculation of D-R constant and Free Energy

From Equation 4.15,

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e)$$

Slope = $-2B_D = -2x10^{-5}$

Thus $B_D = 1x10^{-5}$

Also, the intercept = $\ln q_D$ = -3.9509

Thus, q_D = 0.0192

But E_s (free sorption energy) can be calculated from Equation 4.16

So that Es= 223.6068 J/mol = 0.224 kJ/mol

B.4 Calculation of Thermodynamic Parameters

The Change in Gibbs free energy for each run in the work was calculated using Equation 4.8 and can be seen in Table A 11.

From Figure 4.13,

$$\text{Slope} = \frac{-\Delta H_{ads}}{R} = 8094$$

$$\therefore \ \Delta H_{ads} = -8094 \times 8.3142$$
$$= -67.295\, kJ / mol\ K$$

Also,

$$\text{Intercept} = \frac{-\Delta S_{ads}}{R} = -25.46$$

$$\therefore \ \Delta S_{ads} = -25.46 \times 8.3142$$
$$\Delta S_{ads} = -0.212\ \text{k}J / mol\ K$$