THE STUDIES OF ADSORPTION ISOTHERMS AND KINETICS OF CHROMIUM REMOVAL FROM TANNERY EFFLUENTS USING CROSS-LINKED CHITOSAN OBTAINED FROM SNAIL SHELL

BY

UGAH JACOB

MSC/SCI/08355/2009-2010

A Thesis submitted to the School of Post Graduate Studies Ahmadu Bello Zaria
In partial fulfillment of the Requirements for the award of Master Degree in Colour Chemistry and Technology
Department of Textile Science and Technology, Faculty of Science,
Ahmadu Bello University, Zaria, Nigeria

MARCH 2013

Declaration

I hereby declare that the work in this Thesis titled "The Studies of Adsorption Isotherms and Kinetics of Chromium Removal from Tannery Effluents Using Cross-linked Chitosan Obtained from Snail Shell" was performed by me in the Department of Textile Science and Technology, Ahmadu Bello University, Zaria Nigeria under the supervision of Dr. Abdulraheem Giwa and Prof. M. K. Yakubu.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part f this work has been presented for another degree or diploma at any institution.

Ugah Jacob …… ……

Signature date

Certification

This Thesis titled "The Studies of Adsorption Isotherms and Kinetics of Chromium Removal from Tannery Effluents Using Cross-linked Chitosan Obtained from Snail Shell" by Ugah Jacob meets the regulations governing the award of M.Sc. Colour Chemistry and Technology, of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

…… ……

Dr. A. Giwa Date

Chairman Supervisory Committee

……. …….

Prof. M.K. Yakubu Date

Member Supervisory Committee

…… …….

Dr. A. Danladi Date

Head of Department

…….. …….

Prof. Adebayo A. Joshua Date

Dean, School of Post Graduate Studies

ACKNOWLEDGEMENTS

I would like to thank Dr. Giwa, the major supervisor of this project, for his cooperation and constant support even when things did not go as expected. One attribute that I am most grateful for, were his advice, when I had any doubt concerning my experiments or result. Thanks to my able professor, in person of Mohammed K. Yakubu, a co-supervisor, for his expertise and help in the whole experiments. Their constant backing made it possible to finish this project. I am gratified to have had such excellent mentors. In addition, I will like to thank Mr. Samuel Okeji for support with some laboratory equipments. Special thanks to Mr. Nuhu Lawal, lab Coordinator of the research laboratory for his assistance in setting up of some laboratory equipments. I will also like to thank all the staff of Textile Science and Technology Ahmadu Bello University Zaria. Finally I would like to thank my parents, relatives and friends especially Ibrahim Adze Ugah who directed my study life from childhood.

ABSTRACT

Chitosan is a natural polymer that has been employed in dye adsorption. In this work, adsorption and thermodynamic data for the interaction of Chromium in tannery effluent with chitosan in aqueous solutions were investigated. The equilibrium adsorption isotherms were determined, from 298 to 345 K. Adsorption data were adjusted to Langmuir, Freundlich, as well as Pseudo second order Kinetic model and van't Hoff model of analysis of adsorption parameters. The analysis showed that the Langmuir isotherm model was the most appropriate for fitting the experimental data, with a maximum monolayer adsorption of 33.3mg/kg at 298 K this value decreased with increase in temperature. The enthalpy of adsorption; ΔH, and the entropy; ΔS were – 13.54 kJ mol^{-1} and -0.1005kJ mol^{-1} K^{-1} respectively. The values demonstrated that the adsorption process was exothermic, favorable, and that randomness of the system decreased during the adsorption process. The Freundlich adsorption model, gave favorable constants; Kf and n consistent with good adsorption process. The pseudo-second reaction model gave straight line plot with rate constant of 1.1673x 10^{-3} kg mg^{-1} min^{-1} and the q_e was 29.85 mg/kg, this showed that the adsorption of Chromium ion by the chitosan followed the pseudo-second order kinetic model.

Table of Contents

Declaration ii

Certification iii

ACKNOWLEDGEMENTS iv

ABSTRACT v

Table of Contents vi

List of figures viii

List of Tables ix

CHAPTER ONE 1

1.0 INTRODUCTION 1

1.1 PURPOSE OF THE STUDY 2

CHAPTER TWO 4

2.0 LITERATURE REVIEW 4

2.1 METAL CONTAMINATION 4

2.2 CHROMIUM CONTAMINATION 6

2.3 NEED FOR NEW METHODS OF REMOVAL 7

2.4 BIOSORPTION OF HEAVY METALS 8

2.5 ISOTHERM MODEL FOR ADSORPTION 10

2.6 EFFECTS OF WASTE WATER COMPOSITION ON BISORPTION 12

2.7 CHITOSAN AS A BIOSORBENT 13

2.8 PARAMETERS AFFECTING METAL ADSORPTION BY CHITOSAN 14

2.9 BINDING OF METAL ANIONS 15

2.10 EFFECTS OF IONIC STRENGTH ON BINDING OF ANIONS 16

2.11 BINDING OF CATIONS 16

2.12 MODIFICATION OF CHITOSAN 17

2.13 RECYCLING OF CHITOSAN AND ADSORPTION OF METAL 18

2.14 RHEOLOGICAL STUDIES 20
2.15 RHEOLOGICAL PROPERTIES OF CHITOSAN 21
CHAPTER THREE 22
3.0 MATERIALS AND METHODS 22
3.1 Sample Preparation 22
3.1.1 Deproteination 22
3.1.2 Demineralization 22
3.1.3 Deacetylation (Formation of Chitosan) 22
3.1.4 Formation of Fine Particles 23
3.1.5 Cross-Linking of Chitosan 23
3.2. CHARACTERIZATION 23
3.2.1 Infrared Spectroscopy 23
3.2.2 Determination of Degree of Deacetylation 23
3.3 ADSORPTION ISOTHERM ON CHROMIUM ADSORPTION 24
3.5 KINETIC STUDY OF CHROMIUM ADSORPTION 24
CHAPTER FOUR 26
4.0 RESULTS AND DISCUSSIONS 26
4.2 Adsorption kinetics 28
4 .3 Adsorption isotherm 29
4.4 FTIR CHARACTERIZATION 33
CHAPTER FIVE 35
5.0 CONCLUSION & RECOMMENDATIONS 35
5.1 CONCLUSIONS 35
5.2 RECOMMENDATIONS 35
REFERENCES 37

List of figures

Figure 3.0 The van't Hoff plot, of lnk v. 1/T

Figure 4.0 Figure 4.0 Graph of ΔG versus T

Figure 4.1 Graph of pseudo second order kinetic model

Figure 4.2 Graph of Freundlich Adsorption Isotherm at 25^0 C

Figure 4.4 Graph of Freundlich Adsorption Isotherm at 55^0 C

Figure 4.5 Graph of Freundlich Adsorption Isotherm at 64^0 C

Figure 4.6 Graph of Freundlich Adsorption Isotherm at 72^0 C

Figure 4.7 Langmuir Isotherms at 25^0 C

Figure 4.8 Langmuir Isotherms at 44^0 C

Figure 4.9 Langmuir Isotherms at 55^0 C

Figure 4.10 Langmuir Isotherms at 64^0 C

Figure 4.11 Langmuir Isotherms at 72^0 C

List of Tables

Table 4.01 Chemical Structure of Chitosan

Table 4.1 Determination of degree of Deacetylation by Acid Base Titration

Table 4.2 Freunlich Adsorption Isotherm Parameters

Table 4.3 Langmuir Adsorption Isotherm Parameters

CHAPTER ONE

1.0 INTRODUCTION

Many Industries such as textile, paper, plastics and dyestuffs, consume substantial volume of water and also use chemicals during manufacturing and dyeing to color their products. As a result, they generate considerable amount of polluted water depending on the type of process. Their toxic effluents are major source of aquatic pollution and cause considerable damage to the receiving water if discharged untreated.

During the past three decades, several waste water treatment methods have been reported and attempted for the removal of pollutants from tannery, textile, pulp and paper mill effluents. It is now recognized that adsorption using low-cost adsorbent is an economic method for water decontamination. A large variety of non-conventional adsorbent materials have been proposed and studied for their ability to remove toxic metals from waste water. However, low-cost adsorbents with high adsorption capacity are still under development to reduce the adsorbent dose and minimize disposal problems. Much attention has recently been focused on various biosorbent materials such as fungal or bacterial biomass and biopolymers that can be obtained in large quantities and that are harmless to nature. Special attention is given to polysaccharides such as chitosan, a natural amino-polymer. It is clear from the literature that biosorption of toxins using chitosan is one of the more frequently reported emerging methods for the removal of pollutants.

In the past century, a rapid expansion in the chemical industries leads to increase in complexity of toxic effluents. Several industrial processes generate metal containing wastes. Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment (Forstner, 1983). Chromium is one such toxic metal which is being widely

used. Chromium is generated by electroplating, tanning and textile industry and is potentially toxic to humans (Palanisamy & Nomanbhay, 2005) therefore the effluents being generated by these industries are rich in chromium.

The current physio-chemical processes for chromium removal like precipitation, reduction, ion-exchange, e.t.c. are expensive and inefficient in treating large quantities. They also cause metal bearing sludge which is difficult to dispose off. The harmful effects of our tannery effluents have necessitated the research.

Biosorption which involves active and non-active uptake by biomass is a good alternative to traditional processes. Widely available biopolymers being used for sorption, they are from cheap resource (Niu & Volesky, 2003).

Chitosan is obtained from the deacetylation of chitin. Chitin is one of the most abundantly available polymers after cellulose. Chitosan is a copolymer of glucosamine and N-acetylglucosamine and it has an amine functional group which is strongly reactive with metal ions. Considerable research has been done on the uptake of metal cation by chitosan (Rhazi, et al., 2002). However, there are some metals which exist in aqueous solutions as anions, for example chromium. The amino groups on chitosan bind metal cation at pH close to neutral. At low pH, chitosan is more protonated and therefore it is able to bind anion by electrostatic attraction (Chassary, et al., 2004). Chitosan is chosen as biosorbent because it is cheaply available polymer, a characteristic ideal for the binding of metal anions such as chromate.

1.1 PURPOSE OF THE STUDY

The aim of the study is to synthesize chitosan from snail shell and also to demonstrate the use of chitosan as adsorbent for uptake of metal ions. The chitosan will be dispersed in the tannery

effluent and the filtrate can be analyzed for the presence of metals. The concentration of residual chromium will elucidate the binding ability of chitosan. Some of the other objectives of this research are:

- To characterize optimum metal uptake conditions of temperature and time
- To determine kinetics of chromium adsorption.
- To determine equilibrium isotherm for the adsorption of chromium.

CHAPTER TWO

2.0 LITERATURE REVIEW

There are many studies on techniques for removal of metals from water. Adsorption using low-cost adsorbent is one of the economically most viable methods with high efficiency for water decontamination. A large variety of conventional and non-conventional adsorbent materials have been proposed and studied for their ability to remove toxic metals. The use of biopolymers is attracting attention recently. Chitin is one of the most abundant natural polymers and can be extracted from different sources such as crustaceous cells. It is highly hydrophobic and insoluble in water as well as organic solvents. Chitosan which can be obtained by deacetylation of chitin is a linear polysaccharide based on glucosamine unit.

there has been a rapid expansion in the chemical industry. As the use of chemicals increases, there is increase in the complexity of toxic effluents. Traditional methods of effluents treatment have to be supplemented with modern and more effective means of treatment. Bioremediation provides a technique for cleaning up pollutants by means of biological tools.

2.1 METAL CONTAMINATION

Heavy metals are natural constituents of the earth's crust. Human activities have drastically altered the biochemical, geochemical cycles and balance of some of the heavy metals. Heavy metals are stable and tend to persist and accumulate in the environment. They cannot be degraded or destroyed. Aquatic system is particularly sensitive to pollution possibly due to the structure of their food chains. In many cases, harmful substances enter the food chain and are concentrated in fish and other edible organisms (Forstner, 1983). As they move from one ecological trophic level to another, metallic species start damaging the ecosystem. They also become difficult to trait as they move up tropic levels. They accumulate in the living tissue

throughout the food chain. Due to biomagnifications, humans receive the maximum impact, since they are at the top of the food chain (Velosky, 2003).

Many metallic elements play an essential role in the functioning of living organisms, they constitute our nutritional requirement. However, over abundance of the essential trace elements can cause toxicity symptoms or death (Volesky, 1990) . There are many sources through which metal pollution of the environment occurs which include geological weathering, industrial processing of ores and metals, leaching of metals from garbage and solid waste dumps (Forstner, 1983). There is a tremendous need to control heavy metal emission into the environment. The use of biological materials including living and non living micro-organisms in the removal and possibly recovery of toxic substances from industrial wastes has gained important credibility during recent years because of the good performance and low cost of these materials. The natural affinity of biological compounds for metallic elements could contribute to the purification of metal loaded waste water (Sahin & Ozturk, 2005). There are several metals which are studied mainly due to their toxicity and pollution concerns. Mercury as a pollutant has received extensive exposure because of its toxicity to humans. In 1953, people died in the fishing village along Manimata bay in Japan due to mercury poisoning. High levels of mercury were discharged by the nearby plastics factory and were accumulated in the shellfish eaten by the villagers. Lead pollution from mining activities and smelting operation is of concern because inorganic and organic lead is considered extremely toxic. Over two hundred people died in Zamfara state of Nigeria because of lead deposits from gold mine. Cadmium is the third of the "big three" of heavy metals with greatest potential hazards in addition to lead and mercury. A disease known as "Itai Itai" in Japan is associated with cadmium poisoning which results in

multiple fractures in the body. Chromium, cobalt, molybdenum, arsenic are other metals whose growing levels in the environment have caused major concern (Volesky, 1990).

2.2 CHROMIUM CONTAMINATION

Textile leather, tanning and metallurgical industries extensively use chromium and therefore the wastes generated by these industries are rich in hexavalent or trivalent forms of chromium. Leakage, poor storage and improper disposal at the manufacturing and ore processing facilities have lead to release of chromium into the environment. This has lead to contamination both ground and surface water (Dantas, et al., 2001).

The processes that are generally used for the removal of chromium are physical and chemical process such as adsorption by activated carbon, reverse osmosis, reduction of hexavalent chromium into trivalent form and precipitation as chromium hydroxide. These treatments are expensive and not completely effective (Sage & Aktay, 2001).

Chromium exists in oxidation states ranging from 0 to +6. It occurs mainly in three forms- metallic chromium (Cr [0]) is a steel gray solid used to make steel and other alloys. This form does not occur naturally but is produced from chrome ore. In nature, it exists in two oxidations states Cr (III) and Cr (IV). Cr (III) occurs naturally in rocks, soils, plants and animals. Hexavalent chromium Cr (VI) is produced industrially when Cr (III) is heated in the presence of atmospheric oxygen. Cr (VI) is more toxic than Cr (iii) and has therefore led to greater environmental concern. ((Armienta-Hernandez & Rodriguez-Castillo, 1995); (Booker & Pellerin, 2000)). Chromium (VI) exists in aqueous solution $Cr_2 O_7^{-2}$, $HCrO_4^{-2}$, CrO_4^{-2} and $HCr0^{-7}$ (Lee, et al., 2005). The fraction of any particular species depends upon chromium concentration and pH. (Sage & Aktay, 2001; Udaybhaskar, et al., 1990). At neutral pH Cr (VI)

exist at $Hcro_4^-$, CrO_4^{-2} and HCr_40^0. Under acidic concentration above 1mg/L (Palmer & Wittbrodt, 1991).

Cr (III) is an essential trace element in human nutrition. It is evolved in glucose metabolism. The required dietary amount has been reported from 50 to 200 µg per day (Katz, 1991; Shupack, 1991).

Chromium (VI) can enter the body on breathing air, consuming food or water contaminated with it. Short term exposure due to inhalation at high levels can cause nose bleeds, ulcers, irritation of the nasal mucosa and holes in the nasal septum. Dermal exposure can also cause skin irritation and allergies (Booker & Pellerin, 2000). Chromium is potentially toxic to humans as it is considered a carcinogen. It is also known to cause kidney failure, metabolic acidosis and oral ulcers.

2.3 NEED FOR NEW METHODS OF REMOVAL

The toxic effects of heavy metals and their impact on human health care have been understood but current technologies used for metal effluents treatment are inadequate due to the quantity of these wastes. It leads to problems such as metal bearing sludge which are difficult to dispose off. Some of these traditional methods are extremely expensive thereby proving uneconomical, especially for developing countries where large small volumes of these waste are generated (Volesky, 2001). Therefore there is requirement for newer and effective methods which are also because it is both efficient and cheap. Compared with conventional methods for removing toxic metals from effluents, the biosorption process has the advantage of low operating cost, minimization of volume of chemicals and biological sludge to be disposed off and high efficiency in detoxifying very dilute effluents.

2.4 BIOSORPTION OF HEAVY METALS

The term biosorption refers to many modes of non active metal uptake by biomass. There are many different types of biosorbents like:

- Active biomass belonging to algae, bacteria or fungi.
- Non active kind of biosorbent which is essentially a waste product or a byproduct of fermentation process.
- Abundant natural materials or polymers (Volesky & Holan, 1995).

The advantage of biosorption is that the biomass used could be a raw material which is either abundant, a waste from another industrial operation or could be cheaply available. There are certain broad range biosorbents which can collect all heavy metals from the solution with small degree of selectivity. Metal sequestration can occur by complexation, chelation, ion exchange or coordination. Other mechanisms are physical such as adsorption or precipitation. Any of these mechanisms may be important in immobilizing the metal on the biosorbent. Since the biomaterials that are used for sorption are complex, a number of these mechanisms could be occurring simultaneously (Volesky, 2001). There are several chemical groups in biomass that could potentially attract and sequester metal ions: acetamido groups in chitin, amino and phosphate groups in nucleic acids, amino, amido, sulfhydryl and carboxyl groups in proteins and hydroxyl in polysaccharides (Volesky & Holan, 1995).

The biosorption of metal uptake can be quantified by experimental biosorption equilibrium isotherms. Uptake of species by sorbent involves several steps that transfer the solute from the bulk of the liquid phase to certain sites on the sorbent (Guibal, 2004). On contact between the sorbent material and the adsorbed species, equilibrium is established at a given temperature

where certain amount of the metal species controlled by the adsorbent is in equilibrium with the residue left free in the solution. The affinity of the adsorbent material for the sorbate determines its distribution between solid and liquid phases. The quality of the adsorbent is judged by how much sorbate it can attract and retained in immobilized form. The isotherm graphical expression is a plot of the metal uptake (q) by the biosorbent (weight/weigh or mole/weight units) against the residual concentration of the sorbate (metal) (Kratochvil & Voleskey, 1998).

Uptake of the metal (Q) in milligrams of metal per gram of biomass is calculated by the formula:

$$Q = \frac{V(C_1 - C_2)}{M} \qquad \text{Equation 2:1}$$

Where V = Volume of metal bearing solution.

C_1 = Initial metal concentration

C_2 = Find metal concentration

M= Amount of biomass.

The amount of uptake value gives an estimate of the performance of the biosorbent at high residual concentration of metal. The isotherm mainly represents an equilibrium process where the metal bound to the adsorbent is in equilibrium with the metal that is free. Therefore, sufficient contact time needs to be provided for the system to reach equilibrium. An isotherm which is steep at low residual metal concentration is highly desirable because it indicates high affinity of the metal for the given metal species.

It indicates high affinity of the metal for the given metal species. Such a metal will perform well at low concentration of the metal. The initial concentration of the metal does not play a

significant role in the equilibrium characterization of the metal because the final equilibrium concentration is of importance. Equilibrium adsorption studies with simple one metal adsorption systems are usually completed first and then extended into examination of multimetal biosorbent behavior along with the selected biosorbent.

Kinetics studies are also important in addition to equilibrium data because it helps one determine the time course of metal uptake. A rapid uptake would mean shorter contact times required between biosorbent and metal and therefore smaller equipment and reduced cost. Both equilibrium and kinetics data are important for process design (Volesky, 1990).

2.5 ISOTHERM MODEL FOR ADSORPTION

There are two widely accepted and easily linearized adsorption isotherm models proposed by Langmuir and Fruendlich respectively. The assumptions of Langmuir model are:

1. The surface consists of adsorption sites.

2. All adsorbed species interact only with sites and not with each other.

3. Adsorption is limited to a monolayer.

4. Adsorption energy of all sites is identical and independent of the presence of adsorbed specie on the other sites.

A general form of Langmuir model equation is:

$$Q = \frac{q_{\max} b C_{eq}}{1 + b C_{eq}} \qquad \text{Equation 2:2}$$

Where q = uptake of species (mg/g), qmax = maximum uptake, Ceq = equilibrium (final concentration in solution (mg/L) and b= constant related to energy of adsorption. b is the

equilibrium or association constant (L/mg) and is related to the affinity between adsorbent and sorbate (metal). It is also represented as K_A. Dissociation constant of K_D is another constant which represents the metal concentration corresponding to half saturation of sorbent. Low values of b are reflected in the steep initial slope of an adsorption isotherm indicating a desirable high affinity. Thus, for "good" adsorbents a high qmax and a steep initial isotherm slope are desired.

The values of qmax and K_A can be found using the linear reciprocal plot of the equilibrium isotherm.

$$1/q = 1/q_{max}\, K_A\, C + 1/q_{max} \qquad \text{Equation 2.3}$$

This is a plot of 1/q vs 1/C, where qmax and K_A can be found from the slope and intercept (Tomida & Ikawa, 1993; Mark, et al., 2006; Kratochvil & Voleskey, 1998).

The form of Fruendlich adsorption model is:

$$Q=K_f\, C^{1/n} \qquad \text{Equation 2:4}$$

Where Q= solid phase metal concentration (mg/g),

K_f= related to adsorption capacity,

1/n = 'heterogeneity factor' ranging from 0 to 1 and

C= bulk liquid phase metal concentration.

This can be linearized by taking the natural logarithm of both sides of the equation to give

$$InQ = lnK + 1/n\ InC \qquad \text{Equation 2.5}$$

The intercept lnK gives the measure of the adsorbent capacity and the slope 1/n gives the intensity of adsorption.

Both of these models are able to describe many data effectively. Since the parameters of these models do not have a physical interpretation to them, their use is limited. Fitting the model to the process behavior does not necessarily imply that a pure adsorption phenomenon has taken place (Mark, et al., 2006; Volesky, 1990).

Another aspect of biosorption is to determine the strategy for releasing the sequestered metal from the biosorbent. The kinetics of the adsorption cycle can be established as well as the regeneration of the biosorbent. The desorption process should yield the metal in a concentrated form and also restore the biosorbent as close to the original condition as possible so that its metal uptake capacity is undiminished and there is no physical change or damage to the biosorbent. (Volesky, 2001; Volesky, 1990).

2.6 EFFECTS OF WASTE WATER COMPOSITION ON BISORPTION

The efficiency of a biosorption process depends not only on the binding properties of the biosorbents but also on the composition of the waste water that it will be used for treating. There are certain limits that might be imposed on the biosorption process by the composition of waste water. Majority of industrial effluents contain more than one toxic metal. For example, effluents produced at a copper mine would contain a high level of Cu^{2+} and traces of Cd^{2+}, $Ni^{2+}$and Mn^{2+}. If the biosorption involves ion exchange, it will lead to competition among the metal species for a limited number of binding sites on the biosorbents. Conversely, the industrial effluent might also contain certain non toxic species that might have a greater affinity for the binding sites on the biosorbent than the toxic target metal. For example, a variety of ionic specie of iron is a matter of concern for bisorption processes treating mining effluents like acid-mine

drainage. In this case, it is important to establish the selectivity of the biosorbent for toxic metals over iron (Kratochvil & Voleskey, 1998).

2.7 CHITOSAN AS A BIOSORBENT

Chitin is an abundant organic material found mostly in crustaceans, mollusks and insects where it forms the constituent of the exoskeleton. It is also represented in fungal cell walls (Guibal, 2004). Chitin can be obtained from fungi, insect, lobster, shrimp and krill. Crabs obtained from seafood processing waste are an important commercial source (Niu & Volesky, 2003). According to some reports, 5000-8000 tons of crab shell material is disposed off by the sea food industry annually. Chitosan is derived from chitin, by a deacetylation reaction using an alkali. Chitosan is therefore a copolymer of glucosamine and N-acetyl glucosamine (Rojas, et al., 2005). It is composed of B-(1,4) -2-acetamido-2-deoxy-D-glucopyranose (acetylglucosamine unit) (Hamdine, et al., 2005). The term chitosan refers to as chitin that has been deacetylated to greater than 60%. Chitosan has many properties that have generated interest in its use such as biodegradability, biocompatibility and its non toxic nature (Varma, et al., 2004).

The deacetylated product, chitosan has an amime functional group which is strongly reactive with metal ions. This has initiated research into the use of chitosan in metal uptake. The deacetylation degree will control the content of glucose amine and therefore the fraction of free amine groups available for metal binding. These groups are more reactive than the acetamide groups present in chitin. Also, the solubility in acidic solution differs, chitosan soluble. The physic-chemical properties of chitosan depend on various parameters such as degree of deacetylation, polymer weight, e.t.c. (Guibal, 2004).

These reactive amine groups interact with the metal ions in different ways such as by chelation or electrostatic attraction, depending on the parameters such as pH and the total composition of

the solution. At pH values close to neutral or in the non protonated form, the free electron doublet on nitrogen may be used to form donor bonds with coordination transition metals such as Cu, Ni, Zn, e.t.c at low pH where protonation of the amino group takes place, the polymer attains cationic groups which can bind anions through electrostatic interactions (Juang & Shiau, 2000; Guibal, 2004).

There are many theories as far as the structure of chitosan metal ion complex is concerned. One theory is that, two or more amino groups bind to the same metal ion, the bridge model. According to the bridge model intra or intermolecular complexation may occur between the metal ion and amine groups from the same or different chains. Some other experiments suggest that only one amino group is involved in the binding and the metal ion is bound to the amino group like a pendant, called the pendant model (Vold, et al., 2003; Piron & Domard, 1998).

2.8 PARAMETERS AFFECTING METAL ADSORPTION BY CHITOSAN

There are several parameters affecting the complex formation of metal ion to chitosan. One of them is the fraction of acetylated units. This determines the number of free amine groups available for binding. To be good adsorbent the polymer needs to have a high degree of deacetylation, conversely a low fraction of acetylated units. (Guibal, 2004; Vold, et al., 2003). A study conducted showed that chitin which was obtained by N-acetylation of chitosan did not form complex with metallic ions such as Cu (ii) Co (ii) or Ni (ii) (Desbrieres, 2002).

In addition to the number of groups accessible to the metal ions, some of the amine sites are sometimes involved in some kind of inter and intra molecular bonds. The crystalline nature of the polymer may make some groups inaccessible to the metal ions (Guibal, 2004). Another important parameter is the chain length or the degree of polymerization. Also the degree of mixing of the metal-chitosan complex and the physical state of the chitosan affected the capacity

of chitosan (Desbrieres, 2002). Chitosan solubility has been widely investigated. It is an important property which can be controlled by polymer weight, type and concentration of the acid used for dissolving the polymer and the presence of metal ions in the solution. Metals present in the solution can bind to the polymer and affect its solubility (Guibal, 2004) chitosan was found to be soluble in formic, acetic acid, citric acid pyruvic and lactic acids. It does not dissolve in other organic acids (Hamdine, et al., 2005).

2.9 BINDING OF METAL ANIONS

Several studies have been done on the electrostatic attraction between chitosan and anions and anionic dyes. These mostly occur at low pH. At neutral pH about 50% of the total amine groups are protonated and therefore are theoretically available for the binding of anions. The optimum pH is therefore 2-4, pH lower than this does not give a better uptake because a competitor effect comes into play. At extremely low pH there is a large excess of competitor anions from the dissociated acid (Guibal, 2004). Uptake by anions such as selenite (SeO_4^{-2}) Vanadate (VO_4^{3-}) and Molybdate (MO_4^{2-}) has been studied. In the case of molybdate, a marked preference of chitosan for complex polynuclear and poly anionic specie was seen. The poly nuclear species such as heptomolybdate was found to be highly absorbable on protonated chitosan (Chassary, et al., 2004).

In the case of chromium, the Cr (VI) ions are present in solution in the form of chromate ions which are negatively charged (Sag & Aktay, 2000). These can easily bind the cationic amine group of chitosan at acidic pH. The pKa value of these amine group is 6.3, therefore, at pH value lower than that, most of the chitosan will be protonated and cationic. Therefore at acidic pH, anion removal would mostly be by electrostatic attraction and cation removal would be by chelation or covalent binding. (Rojas, et al., 2005; Guibal, 2004). Above the pKa, the adsorbent

undergoes deprotonation, is negatively charged and therefore the adsorption capacity decreases and so chromium removal gets reduced. There is increased adsorption of chromium at lower pH (Udaybhaskar, et al., 1990; Boddu, et al., 2003). Also, at higher pH, there are fewer protonated positively charged groups in chitosan and therefore there are fewer repulsion forces between the molecules leading to aggregation of the polymer (Juang & Shiau, 2000).

2.10 EFFECTS OF IONIC STRENGTH ON BINDING OF ANIONS

Uptake of metal ion is reduced by increase in ionic strength. Changing ionic strength affects adsorption by affecting the activity of electrolyte ions and causing competition between the electrolyte ion and the adsorbing anions for the available adsorption sites. The adsorption of selenite and chromate is greatly affected by at high ionic strengths thereby fortifying the idea that adsorption of these anions occurs through electrostatic attraction (Velosky, 2003). The removal of arsenate was almost complete when arsenic solution in deionized water was used, but the removal deteriorated in the presence of other anions such as sulphate, chloride and Nitrate (Volchek & Geckeler, 1996). It is also seen that chlorides at low concentration allows the formation of chloro-anionic species for platinum and palladium and improves its adsorption capacities. However at high concentration it greatly reduced metal recovery on cross-linked chitosan. The polynuclear species interacts with different monomer units of chitosan either on the same chain or adjacent chains (Chassary, et al., 2004).

2.11 BINDING OF CATIONS

The binding of metal cations to chitosan occurs through a different mechanism. The binding site in this case is also the amine group which initiates a coordinate bond with the metallic ions. The bond formed is between the free electron pair of the nitrogen in the amine group and the void orbitals of the metal. The affinity of chitosan for copper has been studied and found that the optimal pH for copper binding is in the range 5-7 (Desbrieres, 2002). Since low pH favors the

protonation of the amine groups, the charge reversal would affect the ability to chelate metal cations. This suggests that binding of cations would take at a more neutral pH. At lower pH, chelation also gets reduced by the competitor effect of protons. (Chassary, et al., 2004). It is known that chitosan forms chelates with metal by releasing hydrogen ions. Hence, adsorption of metal cations with chitosan leads to a decrease in pH (Schmuhl, et al., 2001). A high equilibrium adsorption capacity for cadmium was also seen. It is seen that uptake process generally involves pore diffusion through the solid matrix followed by adsorption (Evans, et al., 2002). Cadmium uptake was also studied in conjunction with ultra-filtration. Chitosan was found a good candidate for binding cadmium at neutral pH. When the pH was reduced to 4, Cd^{2+} was released and chitosan was regenerated (Llorens, et al., 2004). According to a study in the case of copper, a unique complex is formed with chitosan, copper bind to three oxygen atoms and one nitrogen atom, with square planar and tetrahedral geometry. (Guibal, 2004). Zinc uptake was studied at different pH. Optimum binding by chitosan derivatives occurred at pH 6.0, since higher pH allowed adsorption of Zn (II) to non protonated amine groups. Uptake was reduced at pH 7.0 since precipitation of Zn (II) occurred at that pH (Ding, et al., 2006).

2.12 MODIFICATION OF CHITOSAN

The versatility of chitosan allows it to be easily modified in order to change its properties, depending on the field it needs to be applied to. It can be physically modified into gels, beads and membranes. Chemical modification is more common which involves either grafting a specific group onto the chitosan backbone or cross-linking. This is done to increase metal adsorption capacities or improve selectivity of the polymer for certain species. Modification is also done to prevent dissolving of the polymer where soluble chitosan is not required and the sorbation is performed at acidic solutions. Cross-linking can be done using cross-linking agents such as glutaraldyhyde, cyclodextrin and epichlorohydrin. However, cross-linking step might

reduce the uptake efficiency of chitosan especially in the case of glutaraldehyde. Reaction of the chitosan amine groups with glutaraldehyde leads to the formation of imine functional groups thereby reducing the number of amine groups. Epichlorohydrin and ethylene glycol can also be used since they react with –OH groups of chitosan, therefore they would not affect the residual amine functional groups for binding. (Tienwei, et al., 2001) the adsorption capacity depends on the extent of cross linking and generally decreases with increase in the extent of cross linking. According to the study by Rojas et al, adsorption of Cr (VI) onto cross-linked chitosan was found to be 215 mg/g (Rojas, et al., 2005)).

A novel diethylene triamine derivative of chitosan was studied with regards to its binding properties with palladium, silver, copper and cadmium ions. This introduction of diethylene triamine into the chitosan backbone prevents the loss of amine groups due to cross-linking reaction with aldehydes. This modification enhanced the adsorption ability and selectivity of chitosan for silver ions. (Yi, et al., 2006). New functional groups are also grafted to increase the density of the sorption sites, to broaden the optimum pH range and to increase the selectivity of the target metal. According to a study by (Chassary, et al., 2004), polythyleneimine (PEI) was grafted onto chitosan and tested for platinum and palladium uptake. Grafting of PEI gives chitosan supplementary amine functions, primary, secondary and tertiary amines. It was found that this grafting improves sorption capacity but had limited effect of sorption selectivity. The grafting of carboxylic functions is also done mainly to design chelating derivatives for sorption of metal cations (Guibal, 2004).

2.13 RECYCLING OF CHITOSAN AND ADSORPTION OF METAL

The studies of metal desorption and polymer recycling is important to improve the cost-effectiveness of the sorption process. The cost of polymer can be a limiting factor except in the

case of precious metal sorption. The recovery of metal also determines the efficiency of the process. In desorbing processes, regeneration of the biosorbent may be accomplished by washing the metal laden biosorbent with an appropriate solution, the type and strength of which would be determined by how the metal is bound to the bisorbent. The sorption mechanism can help design a desorption strategy (Volesky, 2001). Since pH is an important parameter in binding a sample, change in pH can allow the metal to desorb. Chelating agents such as EDTA can also be used especially for desorption of metal cations. When law pH is used for desorption of metal anions, increasing the PH might allow the reverse reaction since binding occurs at low pH of anions. Molybdate and Vanadate have been recovered using sodium hydroxide to increase pH (Guibal, 2004). Successful desorption of chromate from chitosan was carried out using 10-100mM EDTA. The sorbent were regenerated and could be used again to adsorb heavy metal ions (Baral, et al., 2006). However, continued recycling of chitosan may not be possible due to its biodegradability. Recycling is less important in the case of precious metal sorption because the cost of the target metal would allow use of the polymer. Also, since chitosan is essentially derived from a waste product of the food industry, its production cost is not too high. Also metal loaded chitosan can also be used for other sorption processes, taking advantage of the affinity of the metal loaded on chitosan for other solutes. For example, the chelating affinity of molybdate for arsenic has been used. Molybdate loaded chitosan beads have been used for uptake of As (V) and As (III) from dilute solutions. This makes use of the knowledge that chitosan has a strong affinity for molybdate and molybdate is known to form strong complexes with arsenate ions (Dambies, et al., 2002).

An important aspect to be studied here is during a desorbing process, the desorbed sorbate (metal) stamp in the solution and a new equilibrium is established between that and the metal

still bound to the biosorbent. This leads to the concept of a desorption isotherm where the equilibrium is strongly shifted towards the sorbate dissolved in solution. Recovery of the metal from these concentrated desorption solutions can be carried out by using electroplating procedures (Volesky, 2001).

2.14 RHEOLOGICAL STUDIES

The study of rheology is the study of deformation of matter resulting from the application of a force. The type of deformation depends on the type of matter. Gases and liquid will flow when a force is applied while solids will be deformed by a fixed amount. The stress is defined as the force divide by the area over which it is applied to a material. When a fluid system is studied by the application of stress, motion is produced until the stress is removed. Consider two surfaces separated by a small gab containing a liquid. A constant shear stress must be applied on the upper surface for it to move a constant velocity 'U': the rate of strain or shear rate is given by velocity/displacement i.e. u/x when a plot of shear stress versus shear rate is linear, the liquid behavior is simple and the liquid is Newtonian, the constant slope of the straight line being the viscosity of the fluid. Fluid such as water and ethanol are Newtonian. Any fluid that does not obey the Newtonian relationship between the shear stress and shear rate is called non-Newtonian. High molecular weight liquids are usually non-Newtonian. When the viscosity decreases with increase in shear rate, the fluid is called a shear thinning whereas if the viscosity increases with increase in shear rate, the fluid is called shear thickening. The backbones of most polymers are made up of carbon chains. The bonds are usually single but there may be a significant number of double bonds. The side group or side chain are important because these control the rotation around the bonds. This bond rotation gives the polymer its flexibility. (Goodwin & Hughes, 2000).

2.15 RHEOLOGICAL PROPERTIES OF CHITOSAN

Polymers exist as an intermolecular entangled state in concentrated domain in which accurate rheological characterization helps in determining the processibility and activity of the polymer. The physiochemical properties of dilute solutions of the chitosan are governed by pH, ionic strength, degree of deacetylation, concentration of molecular weight. The effect of concentration of chitosan has been studied and it was found that viscosity increases with increase in concentration of chitosan (Nystron, et al., 1999). For a low concentration, the chitosan solution exhibits a Newtonian behavior, but increasing polymer concentration leads to the appearance of non-Newtonian behavior. Also at low concentration, Newtonian behavior can be maintained but not at high shear rates. At low shear rate, a constant zero shear viscosity can be maintained, the rate of intermolecular disentanglements brought about by shear force exerted is nearly the same as that of newly formed entanglements. Conversely, the viscosity decreases with increasing shear rates, because the rate of entanglements is higher than that of entanglements (Hwang & Shin, 2000; Desbrieres, 2002). The polymer starts to show shear thinning with increase in concentration. As the polymer concentration is increased, the freedom of movement of the individual chains becomes restricted due to the increased number of enlargements to replace does disrupted by deformation. Thus, the shear rate at which Newtonian behavior is lost progressively moves to lower values (Hwang & Shin, 2000).

Hydrophobic chitosan were prepared by modification of raw chitosan and its rheological properties were studied. The hydrophobic chitosan shows unusual rheological characteristics which arise due to intermolecular associations of neighboring hydrophobic substituent. It was shown that intermolecular association phenomenon was promoted by increasing hydrophobicity. (Nystron, et al., 1999).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample Preparation

Snail shell was obtained from waste disposal in Abuja. The snail exoskeleton was crushed into pieces using pounder (pestle) and the particles were filtered to fine sizes using sieve.

3.1.1 Deproteination

The chitin and chitosan sequence involve the crushing and washing of discarded exoskeletons. The snail's powdered exoskeleton (100g) as placed in 250ml beakers and treated in boiling sodium hydroxide (4% w/v) for two hours to dissolve the proteinous matters and sugars. The crude chitin particles were allowed to settle down and the sediment was isolated after washing with distil water. The crude material was allowed to cool at room temperature. (Yield, 95.2 %).

3.1.2 Demineralization

The deproteinated material above weighing approximately 30g was demineralized with 100ml of 5% HCl. The samples were allowed to soak for 24 hours to remove the minerals (mainly calcium carbonate). The demineralized sample was also treated with 2% NaOH (50ml) solution to decompose the albumen into water soluble amino acids. The remaining chitin was washed with distil water and dried. (Yield, 35%)

3.1.3 Deacetylation (Formation of Chitosan)

This process was carried out by adding 100ml of 40% NaOH to each sample and then boiled at 100^0C for 10 hours on a hot plate. The samples were cooled at room temperature and further washed with distil water and the solid matter, chitosan was retained. After the final distil water wash, the chitosan was further washed with methanol and lastly with acetone. The samples were left uncovered in 250ml beakers to dry at room temperature for 24h.

3.1.4 Formation of Fine Particles

Chitosan solution was prepared by dissolving 3g chitosan flakes into 100ml of 5% acetic acid solution for 10h. The solution was dropped into 2.0M NaOH which neutralized the acetic acid within the chitosan, forming pure white fine particles. The fine particles were washed with distilled water. The distilled water was poured into 500ml beaker containing the fine particles and the particles were allowed to settle down after which decantation followed to remove the water. The washing was done repeatedly and the solution was finally filtered using filter paper.

3.1.5 Cross-Linking of Chitosan

15g of wet sample of chitosan (fine particles) was dissolved in the solution comprises of 200ml ethanol, and 10ml of glutaraldehyde. The solution was stirred for 24h using magnetic stirrer and the cross-linked chitosan was washed with distiled water, decanted and dried.

3.2. CHARACTERIZATION

3.2.1 Infrared Spectroscopy

The IR of the cross linked chitosan was run to determine the functional groups present.

3.2.2 Determination of Degree of Deacetylation

Chitosan (0.3g) was dissolved in 30ml, 0.5M HCl at room temperature with stirring in a beaker, two drops of methyl orange indicator was added and titrated against 0.1M, NaOH. The readings were tabulated. The percentage of free NH_2 groups in chitosan was calculated as follows:

$NH_2\ \% = [(C_1 V_1 - C_2 V_2) \times 0.016] / [G\ (100-W)] \times 100$ Equation 2.6

Free $NH_2\ \% = [NH_2 / 9.94\%] \times 100$ Equation 2.7

Chitosan theoretical NH_2 content % = (16/161) x 100% =9.94% Equation 2.8

The Degree of deacetylation = $[NH_2\ \% / 9.94\ \%]\ 100\%$ Equation 2.9

C_1: Concentration of HCl (M); C_2: Concentration of NaOH (M); V_1: the volume of NaOH added by titration (ml); G: Sample weight (g); W: sample water content (%).

3.3 ADSORPTION ISOTHERM ON CHROMIUM ADSORPTION

Ten test tubes each containing 0.1g chitosan samples were used for the experiment. Different volumes of tannery effluents were added to the 0.1g sample of the test such that each test tube had different volume of the effluent. The volumes of the effluents ranged from 1, 1.5, 2, 2.5 …….5.5ml and different volumes of distilled water at range of 5, 4.5, 4……0.5 respectively so that each test tube contained 6ml of solution. The solution was treated for six hours to obtain equilibrium adsorption of chromium by the chitosan. At the end, the solution in each of the test tubes was filtered using filter paper. The concentration of chromium in various filtrates was determined using atomic adsorption spectrometer. The experiment was repeated at 45, 55, 64 and 72^{o}C without stirring. The amount of chromium (VI) concentration retained in the adsorbent phase (Q_e) was calculated according to the equation.

$$Q_e = \frac{(C_0 - C_e)\,V}{W} \qquad \text{Equation 3 :0}$$

Where C_0 and C_e are the initial and final concentrations (mg/L) of Chromium (VI) solution respectively

3.5 KINETIC STUDY OF CHROMIUM ADSORPTION

The kinetic adsorption study was conducted in seven test tubes each containing 0.1g of cross-linked chitosan in 7ml of tannery effluent. The chitosan was placed in the test tubes at the same time and each sample was allowed to adsorb at predetermined time. The time given to the

samples in the test tube one after the other was 60, 100, 210, 250, 430,580 and 670 minutes respectively. The samples were filtered at the given time and the concentration of the filtrate was determined by atomic adsorption spectrometry. The experiment was carried out at room temperature (25^0 C)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Table for Determination of Degree of Deacetylation by Acid Base Titration

Titre	1st Volume (ml)	2nd Volume (ml)
Final	26.50	26.50
Initial	0.00	0.00
Average	26.50	26.50

Data:

V_1 = 26.50ml

V_2=10ml

C_1 = 0.5M (concentration of HCl)

C_2=0.1M (concentration of NaOH)

G=0.3g (weight of chitosan) = 0.03 in $1000cm^3$

W = 8.9%

NH_2 % = $[(C_1 V_1-C_2V_2) \times 0.016]/ [G (100-W)] X100$

Free NH_2 % =$[NH_2 / 9.94\%] \times 100$

Chitosan theoretical NH_2 content % = $(16/161) \times 100\%$ =9.94%

The Degree of deacetylation = $[NH_2 \%/9.94 \%] 100\%$

NH_2 % =(25.5X0.5-0.1X10) X0.016X100/0.03(100-8.9)

=(13.25-1)X1.6/0.03(91.1)

=19.6/2.733

=7.172

The Degree of deacetylation = [NH_2 %/9.94 %] 100%

= (7.172/9.94) X 100%

72.15%

The deacetylation process was carried out using 40% NaOH for over ten (10) hours. The result of determination of degree of dacetylation by Acid-base titration shows that 72.15% of the chitin was deacylated and that qualified the chitosan and made it good adsorbent as required by theory (Guibal, 2004). Solubility of chitosan in acidic solution depends on it degree of deacetylation. The term chitosan refers to chitin that has been deacetylated to greater than 60% (Varma, et al., 2004).

The deacetylation degree controls the content of glucose-amine and therefore the fraction of free amine groups available for metal binding. These groups are more reactive than acetamide group present in chitin.

4.2 Adsorption kinetics

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo second order equation was applied to model the kinetics of chromium adsorption on to chitosan.

The pseudo second order equation is expressed as:

$t/q_t = 1/h + 1/q_e$ (t) equation 3.1 (Kumar & Kirthika, 2009)

Where $h = kq_e^2$ ($mgg^{-1}min^{-1}$) can be regarded as the initial adsorption rate as t—0 and k is the rate constant of pseudo second order adsorption (g $mg^{-1}min^{-}$

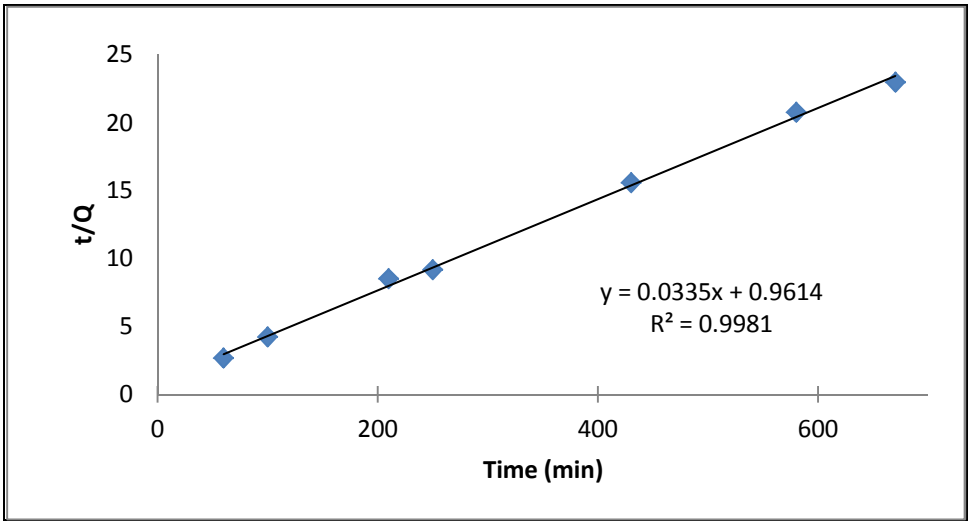


Figure 4.1 Graph of pseudo second order kinetic model

Adsorption kinetics is an important parameter to evaluate the basic qualities of a good adsorbent. It helps us to determine whether or not the adsorbent adsorbed metals and to what extent. These

indicate that fairly good binding of chromium occurs in the presence of chitosan. These also give indication that there is a time required by the metal polymer reaction to reach equilibrium.

C_0 and C_e are initial concentration and equilibrium concentration at specific time t, respectively. Pseudo-second order kinetic model yielded correlation ratio (0.998). Removal of copper (II) and lead (II) from wastewater by sorption on bottom ash has been reported in many literatures. A plot of t/*Qt* against time for sorption of copper (II) and lead (II) for the Pseudo-second order model gave values of the correlation coefficients 0.990 . The pseudo-second order rate constant (k) for chromium adsorption in this work was 1.1673x 10^{-3} kg mg^{-1} min^{-1} and the q_e was 29.85 mg/kg. Figure 4.1 illustrates the plot using pseudo-second order kinetic model. The result suggested that the adsorption of chromium ions by the chitosan follows the pseudo second order model, which relies on the assumption that chemisorptions may be the rate limiting step.

4 .3 Adsorption isotherm

Table 4.2 Freundlich Adsorption Isotherm parameters

Temperature (^{0}C)	R^2	K_f	n
25	1.000	10.0041	1.002
55	1.000	10.0041	1.001
64	0.998	9.8947	0.9901
72	0.988	10.5066	1.0504

From Equation 2.4, k_f and n are the Freunlich constants; the characteristics of the system. k_f and n are the indicators of the adsorption capacity and adsorption intensity respectively. The ability of

Freunlich Model to fit the experimental data was examined. For this case, the plot of log C_e vs $\log Q_e$ was employed to generate the intercept values k_f and the slope of n.

Freundlich equilibrium constants were determined from the plot, on the basis of the linear form of Freundlich equation. The "n" value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process. (Desta, 2013) If 1/n = 0, hence extent of adsorption becomes independent of pressure the "n" value in Freundlich equation was found to be 0.9901-1.0504 (Table 4.2). The values of "n" Within the range of 1–10 represent good adsorption. In the present study, since "n" lies between 0.9901 and 1.0504 it indicates both physical and chemical adsorption of metal ions onto Chitosan. (Desta, 2013)

The magnitude of k_f and n show easy separation of chromium ion from the aqueous solution and indicate favourable adsorption. The intercept k_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table 4.2, n values were found high enough for separation. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with correlation coefficient of 0.998.

It is important to note that the Freundlich equation has some limitations. The main flaw of the equation can be seen as the system approaches saturation. In accordance with the mathematics of Equation 2.5**,** the ratio of x:m will continue to increase with increasing solute equilibrium concentration. This, however, is not the case at saturation. At saturation, the ratio of x: m=Q_e (x = the amount of solute adsorbed m = the weight of adsorbent) is a constant, independent of

changes in the solute equilibrium concentration. At this point, the Freundlich equation will not accurately describe the system at hand. There is also no guarantee that the equations will accurately describe systems with concentrations less than the saturation concentration because of the empirical nature of the equation.

Table 4.3 Langmuir Adsorption Isotherm Parameters

S/N	T (k)	1/T (k^{-1})	K_d mg/ml	q_{max} (mg/g)	lnk_d	Dμ ($kJmol^{-1}$)
1	298	0.002356	0.000300	33333.33	-8.1117	20.09732
2	317	0.003155	0.000500	20 000.00	-7.6009	20.03245
3	328	0.003049	0.000909	11111.1	-7.0131	19.12467
4	337	0.002967	0.000802	12500.00	-7.1309	19.97948
5	345	0.002886	0.000707	14285.71	-7.2644	20.83670

$1/q=1/q_{max}k\,C_e + 1/q_{max}$ ----- Equation 3.3

In the Langmuir adsorption Isotherm model, the maximum adsorptions ($q_{max)}$ for chromium at all temperatures were calculated from linear regression analysis of the experimental data. The maximum adsorption at 25^0C was 33.3g/g and was the highest. The result indicated that, this value decreased with increase in temperature within the limits of experimental errors. The Langmuir constants ($K_{d)}$ increased with increase in temperature as shown in Table 4.3.

It has been reported that up to -20kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption) while Δμ values more negative than -

40kJ/mol involves charge sharing or transfer from the biomass surface to the metal ion to form coordinate bonding ie chemisorptions (Kumar & Kirthika, 2009)

Thermodynamic considerations dictate that the Δμ value is the fundamental criterion for determination of adsorption process characteristics. In this study Δμ values decreased with increase in temperature as seen in Table. 4.3, the decrease in value of Δμ with increasing temperature indicates the spontaneity (Alok, M; Jyoti, M; Lisha, K, 2007)of the adsorption process at higher temperature. A negative ΔH value of -13.54 kJ mol^{-1} was obtained from the slope in Figure.3 (graph of lnk v. 1/T) which confirms the exothermic nature of the adsorption process. In the graph ΔS was calculated from the intercept to be -0.1005kJ mol^{-1} K^{-1} which indicates that the degree of disorderliness or randomness of the solid-solution interface during the adsorption of chromium ion by chitosan was low. The negative ΔH and ΔS values suggest that enthalpy contributes more than the entropy in the adsorption process the degree of randomness is low. This result is in conformity with thermodynamic parameters that were obtained for chitosan adsorption of chromium ion (Sakkayawong, et al., 2005), Reactive Red n° 189 ((Chiou, et al., 2001); (Dos Anjo, et al., 2003).

Figure 3 shows the van't Hoff plot, of lnk v. 1/T and a straight line graph was obtained, the slope of which yields ΔH and ΔS values.

$\ln K_D = .\Delta H/RT + \Delta S/R$ Equation 3.4

$\Delta U = -RT \ln Kd$ Equation 3.5

$\Delta U = \Delta H - T\Delta S$ Equation 3.6

Where R is the universal gas constant (8.314 J mol$^{"1}$ K$^{"1}$) and T is the temperature (K), ΔH is enthalpy change, ΔS is entropy change and Δμ is Gibbs free energy of adsorption. The van't Hoff plot was considered satisfactory due to the coefficient of correlation value, 0.991

In the system, the adsorption resulted in the removal of metal from the tannery effluents as it gets adsorbed onto binding sites on the adsorbent. These leads to a decrease in free chromium in solution and increase in chromium adsorbed on the adsorbent, until the equilibrium is reached between uptake of chromium by chitosan and the equilibrium concentration of chromium in solution. At this equilibrium, there is a defined distribution of metal between the solid and the liquid phase.

4.4 CHARACTERIZATION

The IR result from the graph below gives the following readings:

3447cm^{-1} this is due to O-H and N-H stretching Vibration

At 1622 cm^{-1} due to NH_2 Characteristic adsorption

At 2917.66 and 2881.54 cm $^{-1}$ due to C-H stretching vibration of methyl and methylene

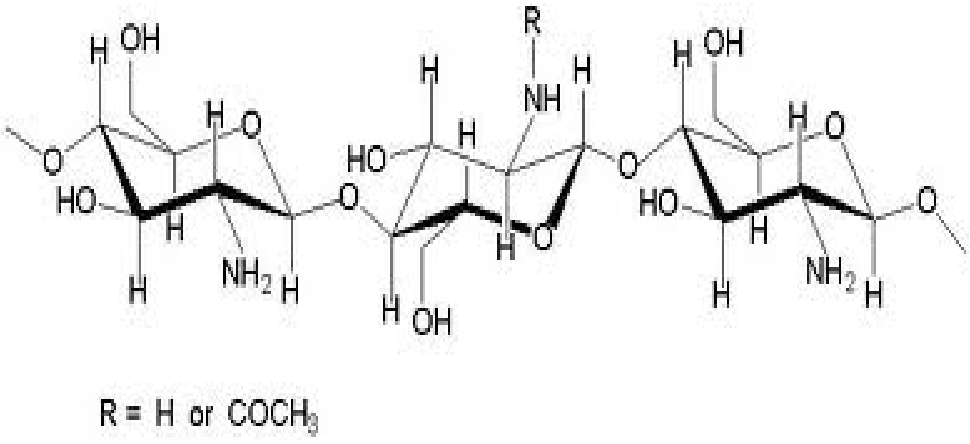


Figure 4.10 Chemical structure of chitosan

(www.google.com.ng/search?q=chemical structure of chitosan)

CHAPTER FIVE

5.0 CONCLUSION & RECOMMENDATIONS

5.1 CONCLUSIONS

In the present work, it was found that chitosan is an effective adsorbent for the removal of Chromium ion from solution. The equilibrium adsorption isotherms were carried out at 298 to 345 K. Maximum adsorption was observed at the temperature of 298 K, corresponding to 33.3 g/g. two isotherm models were studied and the Langmuir model was the most appropriate for fit of the equilibrium experimental. The kinetics of chromium adsorption on the cross-linked chotosan was found to follow second order rate mechanism. Cross-linked chitosan was shown to be an effective adsorbent for the removal of chromium from tannery water. Thermodynamic parameters indicate that the adsorption process is favorable and exothermic in nature.

5.2 RECOMMENDATIONS

- More research is needed to be done on chitosan extracted from snail shell to make it good enough for industrial use in treatment of waste water.
- The use of chitosan for treatment of waste water does not need heat because it is exothermic process. Therefore its usage could fulfill the dream of the industrial sector in that it minimizes energy consumption in water treament.
- Other cross linking agents such as thiourea, epichlohydrine, formaldehyde etc can be used to optimize the process.
- The demineralization of the snail shell releases carbon dioxide into the atmosphere and therefore needs to be carried out in a system that has carbon capture apparatus.

- Studies show that chitosan has unique ability to bind and dissolve and bind to fat and cholesterol in human stomach and prevent the lipid from being absorbed in digestive tract. This can ultimately promote safe weight loss reduction in cholesterol level
- A system need to be put in place in Nigeria to produce chitosan from insect pests like locus. This will serve as effective biological pest control

REFERENCES

Alok, M; Jyoti, M; Lisha, K, 2007. Utillization of Hen Feathers for the Adsorption of Indigo Carmine from Simulated Effluent. *Journal of Eviromental Protection Science,* Volume 1, pp. 92-100.

Anon., n.d.

Anon., n.d.

Armienta-Hernandez, M. & Rodriguez-Castillo, R., 1995. Environmental exposure to chromium compound in the valley of Leon, Mexico. *Environmental Health Perspective,* Volume 103, pp. 1-8.

Baral, S., Das, S. & Rath, P., 2006. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochemical Engineering Journal,* 31(3), pp. 216-222.

Boddu, V., Abburi, K., Talbott, J. & Smith, E., 2003. Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. *Environmental Science and Technology,* Volume 37, pp. 4449-4556.

Booker, S. & Pellerin, C., 2000. Reflections on hexavalent chromium. *Environmental Health Pespectives,* Volume 108, pp. 402-407.

Chassary, P., Vincent, T. & Guibal, E., 2004. Metal anion sorption on chitosan and derivative materials; a strategy for polymer modification and optimum use. *Reactive and Functional Polymers,* 60(74), pp. 137-149.

Chiou, M., Ho, P. & Li, H., 2001. *Dyes and Pigments,* Volume 60, p. 69.

Dambies, L., Vincent, T. & Guibal, E., 2002. Treatment of arsenic- containing solutions using chitosan derivatives: uptake mechanism and sorption performances. *Water Research,* Volume 36, pp. 3699-3710.

Dantas, T. et al., 2001. Chromium adsorption by chitosan impregnated with microemulsion. *Langmuir,* Volume 17, pp. 4256-4260.

Desbrieres, J., 2002. Viscosity of semi flexible chitosan solutions: influence of concentration, temperature and role of intermolecular interractions. *Biomacromolecules,* Volume 3, pp. 342-349.

Desta, M. B., 2013. Langmuir and Freundlich Isotherm studies for the adsorption of textile metal ions on teff straw (eragrosti tef) agricultural waste. *Journal of thermodynamics,* Volume 2013 (2013).

Ding, P., Huang, K., Li, Y. & Zeng, W., 2006. Kinetics of adsorption of Zn(II) ions on chitosan derivatives. *International Journal of Biological Macromolecules.*

Dos Anjo, F., Viera, E. & Cestari, A., 2003. An alternative avrami equation to evaluate kinetic parameters of the interraction of Hg(II) within chitosan membranes. *Journal Colloid Interface Science,* Volume 263, pp. 542-547.

Evans, J., Davids, W., MacRae, J. & Amirbahan, A., 2002. Kinetics of cadmium uptake by chitosan-based crab shells. *Water Research,* Volume 36, pp. 3219-3226.

Forstner, U., 1983. *Metal pollution in the aquatic environment.* Second ed. New York: Springer-Verlag.

Goodwin, J. & Hughes, R., 2000. *Rheology for chemists.* UK: Royal Society of Chemistry.

Guibal, E., 2004. Interractions of metal ions with chitosan-based sorbents: a review. *Separation and Purification Technology,* Volume 38, pp. 43-75.

Hamdine, M., Heuzey, M. & Begin, A., 2005. Effect of organic and inorganic acids on concentrated chitosan solutions and gels. *International Journal of Biological Macromolecules,* Volume 37, pp. 134-142.

Hwang, J. & Shin, H., 2000. Rheological properties of chitosan solutions. *Korea-Australia Rheology Journal,* Volume 12, pp. 175-179.

Juang, R. & Shiau, R., 2000. Metal removal from aqueous solutions using chitosan enhanced membrane ultrafilteration. *Journal of Membrane Science,* Volume 165, pp. 159-167.

Katz, S., 1991. The Analytical biochemistry of chromium. *Environmental Health Perspectives,* Volume 92, pp. 13-16.

Kratochvil, D. & Voleskey, B., 1998. Advances in the biosorption of heavy metals. *Tibtech,* Volume 16, pp. 291-300.

Kumar, P. & Kirthika, K., 2009. Equilibrium and kinetic study of adsoption of nickel from aqueous solution of bael tree leaf powder. *Journal of Engineering Science and Technology,* 4(4), pp. 351-363.

Kumar, P., n.d. Equilibrium and kinetic study of adsorption of nickel from aqueous onto bael tree leaf powder.

Lee, M., Hong, K., Shin-Ya, Y. & Kajiuchi, T., 2005. Adsoprtion of hexavalent chromium by chitosan-based polymeric surfactants. *Journal of Applied Polymer Science,* Volume 96, pp. 44-50.

Llorens, J., Pujola, M. & Sabate, J., 2004. Separation of cadmium from aqueous streams by polymer enhanced ultrafilteration: a two - phase model for complexation binding. *Journal of Membrane Science,* Volume 239, pp. 173-181.

Mark, S., Crusberg, T., DaCunha, C. & Di Lorio, A., 2006. A heavy metal biotrap for wastewater remediation using poly-gamma-glutamic acid. *Biotechnological Progress,* Volume 22, pp. 523-531.

Niu, H. & Volesky, B., 2003. Charasteristics of anionic metal species biosorption with waste shells. *Hydrometallurgy,* Volume 71, pp. 209-215.

Nystron, B., Kjoniksen, A. & Iversen, C., 1999. Characterization of association phenomena in aqueous systems of chitosan of different hydrophobicity. *Advances in Colloid and Interface Science,* Volume 79, pp. 81-103.

Palanisamy, K. & Nomanbhay, S., 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology,* p. 8.

Palmer, C. & Wittbrodt, P., 1991. Processes affecting the remediation of chromium contaminated sites. *Environmental Health Perspectives,* Volume 92, pp. 25-40.

Piron, E. & Domard, A., 1998. Formation of a ternary complex between chitosan and ion pairs of strontium carbonate. *International Journal of Biological Macromolecules,* Volume 23, pp. 113-120.

Rhazi, M. et al., 2002. Contribution to the study of the complexation of copeer by chitosan ond oligomers. *Polymer,* Volume 43, pp. 1267-1276.

Rojas, G. et al., 2005. Adsorption of chromium onto cross-linked chitosan. *Separation and Purification Technology,* Volume 44, pp. 31-36.

S.S, B., S.N, D. & P, R., 2006. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. *Biochemical Engineering Journal,* 31(3), pp. 216-222.

Sag, A. & Aktay, Y., 2000. Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin. *Process Biochemistry,* Volume 36, pp. 157-173.

Sage, Y. & Aktay, Y., 2001. Application of equilibrium and mass transfer models to dynamic ions by chitin in packed column reactor. *Process bio,* 36(12).

Sahin, Y. & Ozturk, A., 2005. Biosorption of chromium(VI) ions from aqueous solution by the bacterium Bacillus thuringiensis. *Process Biochemistry,* Volume 40, pp. 1895-1901.

Sakkayawong, N., Thiravetyan, P. & Nakbanpote, W., 2005. Adsorption Mechanism of Synthetic reactive dye waste water by chitosan. *Journal of Colloid and Interface science,* Volume 286(1), pp. 36-62.

Schmuhl, R., Krieg, H. & Keizer, K., 2001. Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies. *Water SA,* Volume 27, pp. 1-7.

Shupack, S., 1991. The chemistry of chromium and some relating analytical problems. *Environmental Health Perspectives,* Volume 92, pp. 7-11.

Tienwei, T., Xianjing, H. & Weixia, D., 2001. Adsorption behavior of metal ions on imprinted chitosan resin. *Journal of Chemical Technology and Biotechnology,* Volume 76, pp. 191-195.

Tomida, T. & Ikawa, T., 1993. Recovery of metal ions from dilute solutions using a water-soluble chelating polymer and dialysis membrane. *Journal of Chemical Technology and Biotechnology,* Volume 26, pp. 575-577.

Udaybhaskar, P., Iyengar, L. & Prabhaskar Rao, A., 1990. Hexavalent chromiium interraction with chitosan. *Journal of Applied Polymer Science,* Volume 39, pp. 739-747.

Varma, A., Deshpande, S. & Kennedy, J., 2004. Metal complexation by chitosan and its derivatives: a review. *Carbohydrate Polymer,* 55(78), pp. 77-93.

Velosky, B., 2003. Sorption and biosorption,BV. *BV,* pp. 103-116 (www.biosorption.com).

Volchek, K. & Geckeler, K., 1996. Removal of harzadous substances from water using ultrafilteration in conjunction with soluble polymers. *Environmental Science and Technology,* Volume 30, pp. 725-734.

Vold, I., Varum, K., Guibal, E. & Smidrod, O., 2003. Binding of ions to chitosan selectivity studies. *Carbohydrate Polymers,* Volume 54, pp. 471-477.

Volesky, B., 1990. *Biosorption of heavy metals.* Florida: CRC Press.

Volesky, B., 2001. Detoxification of metal bearing effluents: biosorption for the next century. *Hydrometallurgy,* Volume 59, pp. 203-216.

Volesky, B. & Holan, Z., 1995. Biosorption of heavy metals. *Biotechnological Progress,* Volume 11, pp. 235-250.

Yi, Y., Wang, Y. & Ye, F., 2006. Synthesis and properties of diethylene triamine derivative of chitosan, colloids and surfaces. *Physicochemical Engineering Aspects,* pp. 203-216.

Appendix

Table 4.4 Pseudo First order Kinetic data for removing chromium by cross-linked Chitosan.

Weight of chitosan (g)	Time of adsorption (minutes)	($C_{filtrate}$ (ppm)	C_e (mg/L)	Q_e (mg/kg)	t/Q	C_e/C_0
0.1	60	1.1991	2.2355	22.36	2.6833	0.6509
0.1	100	1.0670	2.3676	23.68	4.2230	0.6893
0.1	210	0.9654	2.4692	24.70	8.5020	0.7190
0.1	250	0.7113	2.7233	27.23	9.1810	0.7923
0.1	430	0.6707	2.7639	27.64	15.5572	0.8047
0,1	580	0.6402	2.7944	27.94	20.7588	0.8136
0.1	670	0.5182	2.9164	29.16	22.9767	0.8491

Table 1 adsorption Isotherm					
C_e (mg/kg At 25^0C	Q_e (mg/kg At 25^0C	C_e(mg/kg) At 45^0C	Q_e (mg/kg) At 45^0C	C_e (kg/kg) At 55^0C	Q_e(mg/kg) At 55^0C
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2.7131	27.13	2.5607	25.61	2.6115	26.12
2.7741	27.74	2.7436	27.44	2.8147	28.15
2.8147	28.15	2.7741	27.74	2.8351	28.35
3.0180	30.18	2.9976	29.97	2.9570	29.57
3.0485	30.49	3.0078	30.08	3.0789	30.79
3.0789	30.79	3.0281	30.28	3.0993	30.99
3.1704	31.70	3.0281	30.28		
3.2212	32.21	3.2314	32.31	3.1602	31.60

Table 1 Adsorption Isotherm			
C_e (mg/L) At 64^0C	Q_e (mg/kg) At 64^0C	C_e. (mg/L) \At 72^0C	Q_e (mg/Kg) 72^0C
0.OO00	0.0000	0.0000	0.0000
2.7639	27.64	2.7833	27.83
2.7741	27.74	2.8351	28.35
2.8960	28.96	2.9570	29.57
3.0078	30.08		
3.0100	30.10	3.1298	31.30
3.0789	30.79	3.1602	31.60
3.0891	30.89	3.2110	32.11
3.2517	32,53	3.2619	32.62

Table 4.5. The kinetic data of chromium adsorption (At 25^0 C)

Weight of chitosan (g)	Time of adsorption (minutes)	($C_{filtrate}$ (mg/L)	C_e (mg/L)	Q_e (mg/kg)	t/Q (mg/kgs
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	60	1.1991	2.2355	22.36	2.6833
0.1	100	1.0670	2.3676	23.68	4.2230
0.1	210	0.9654	2.4692	24.70	8.5020
0.1	250	0.7113	2.7233	27.23	9.1810
0.1	430	0.6707	2.7639	27.64	15.5572
0,1	580	0.6402	2.7944	27.94	20.7588
0.1	670	0.5182	2.9164	29.16	22.9767

Figure 3.0: The van't Hoff plot, of lnk versus 1/T

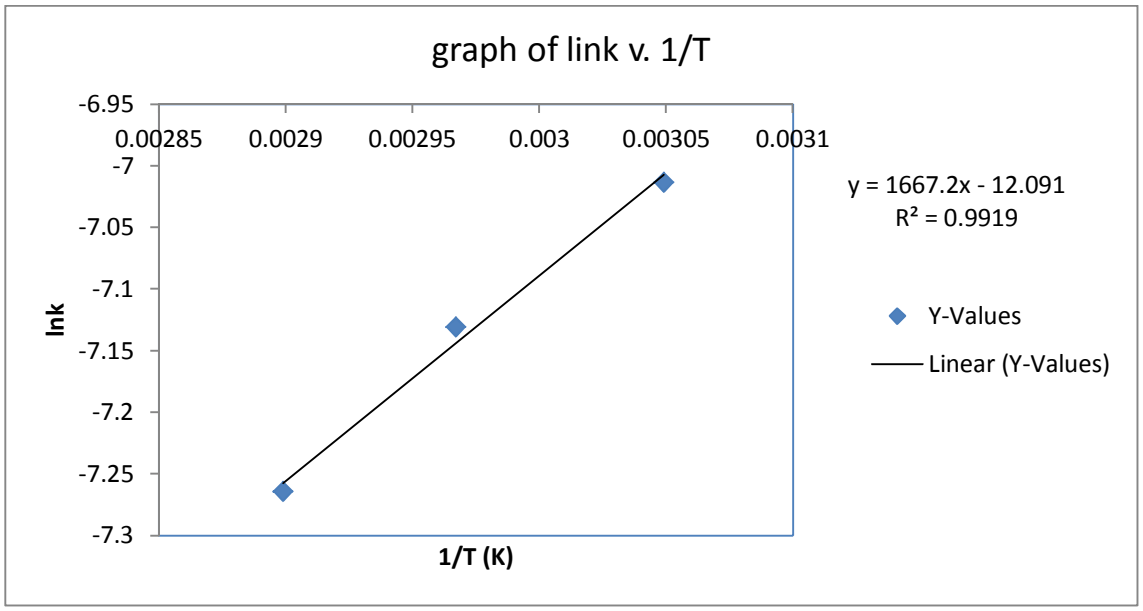


Figure 4.0 Graph of ΔG versus T

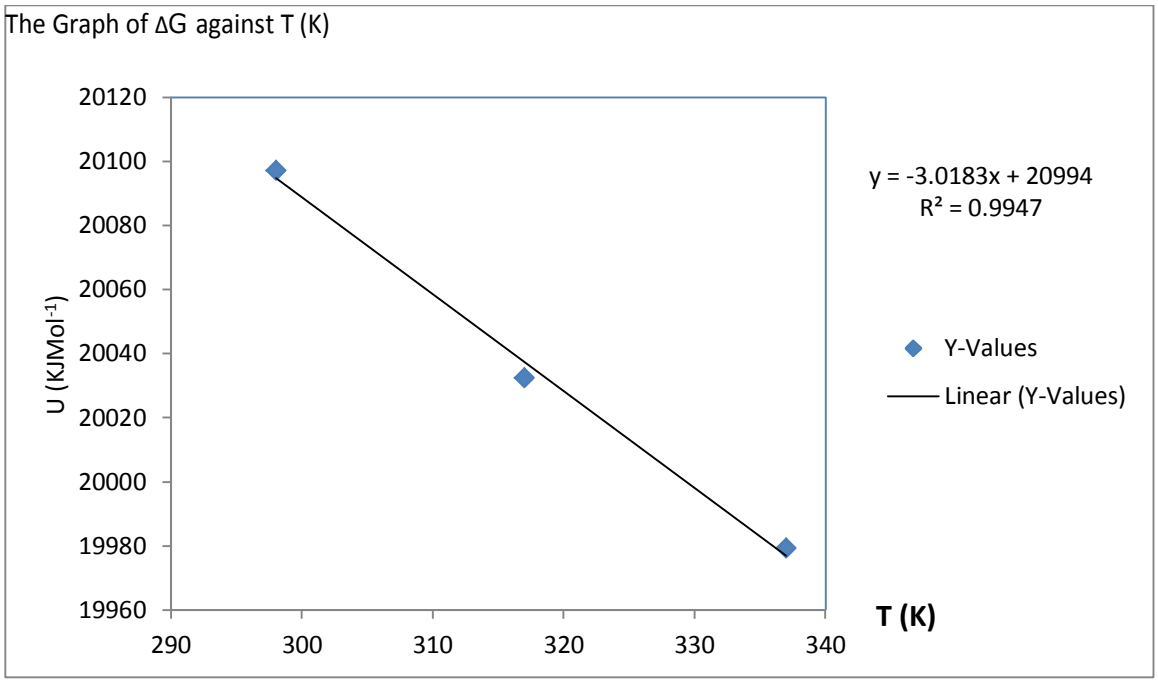


Figure 4.2, Graph of freundlich adsorption isotherm at 25^0C

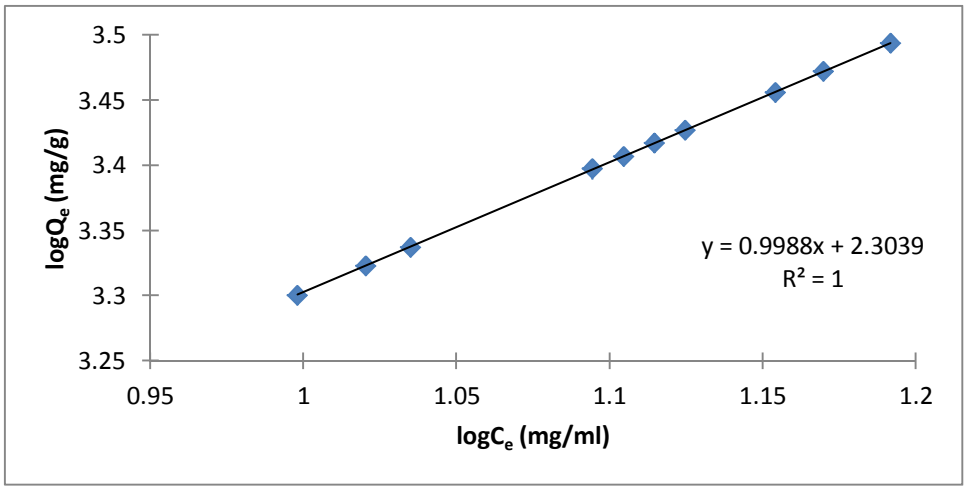


Figure 4.4 Graph of freundlich adsorption isotherm at 55^0C

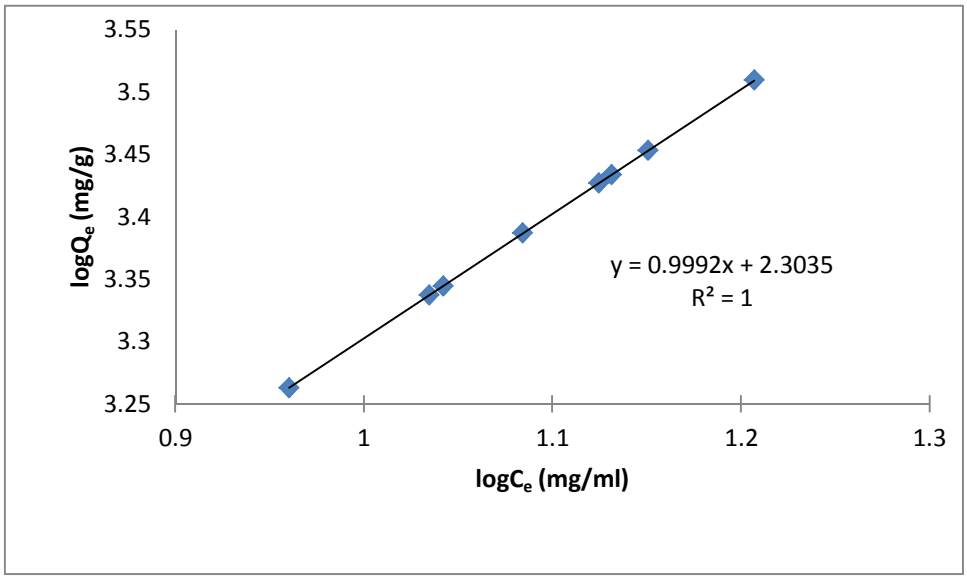


Figure 4.5 Graph of freundlich adsorption isotherm at 64^0C

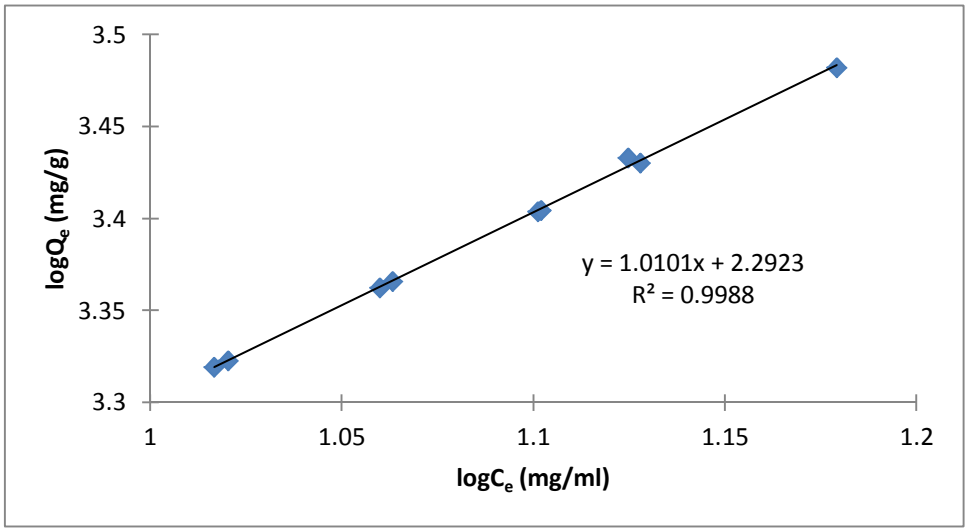


Figure 4.6 Graph of freundlich adsorption isotherm at 72^0C

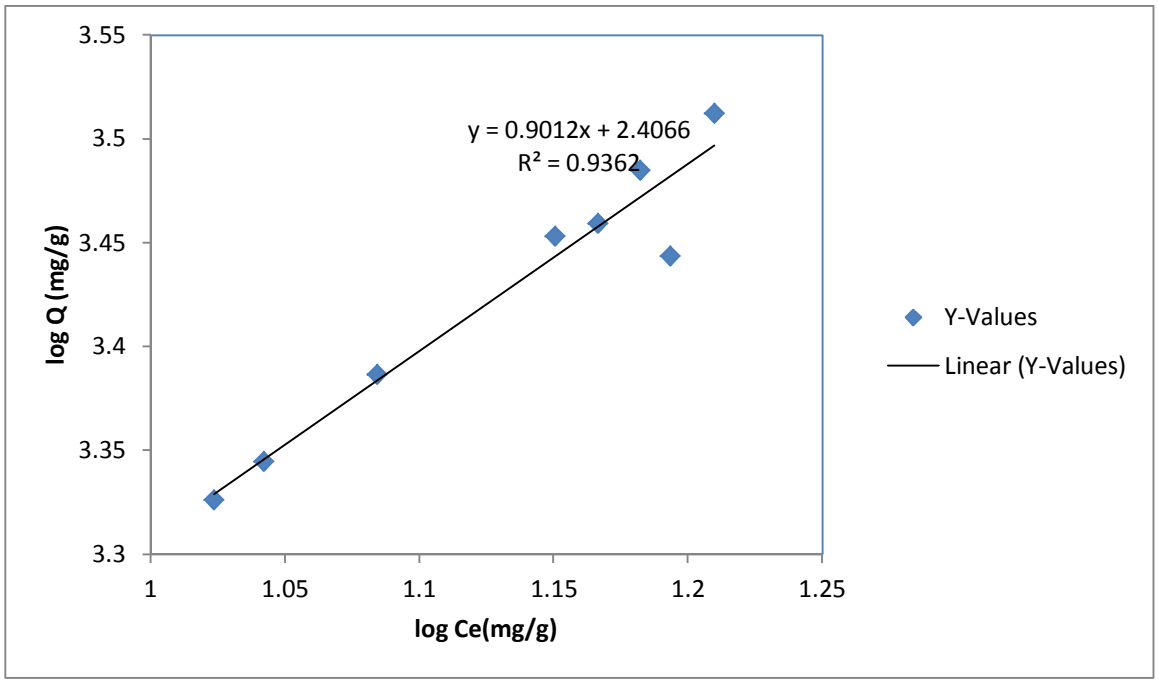


Figure 4.7 Langmuir Isotherm at 25^0 C

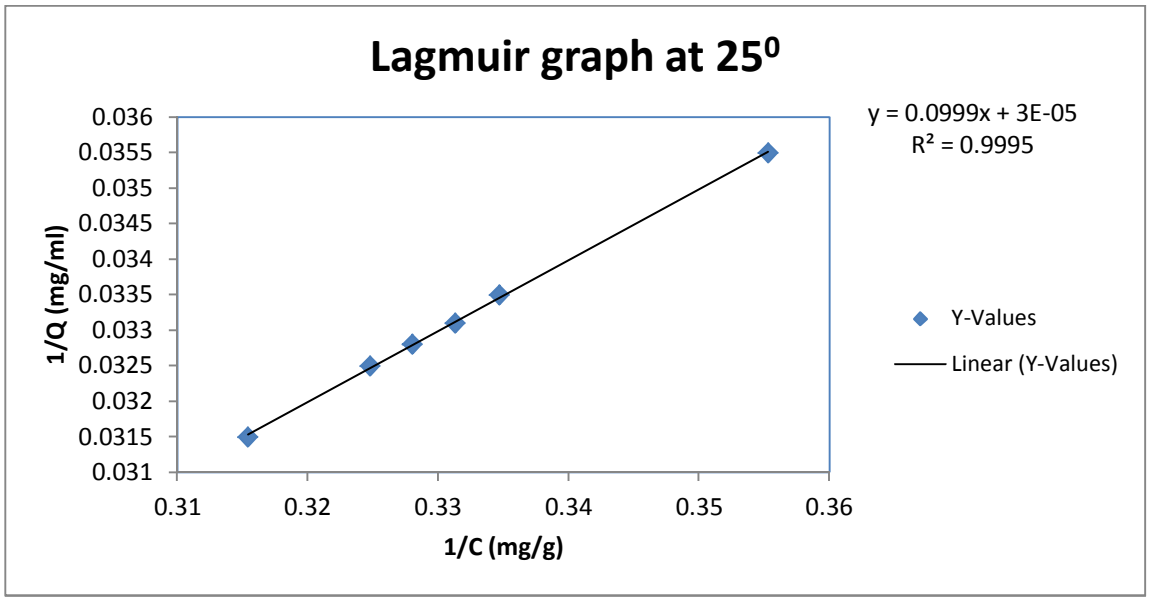


Figure 4.8 Langmuir Isotherm at 44^0 C

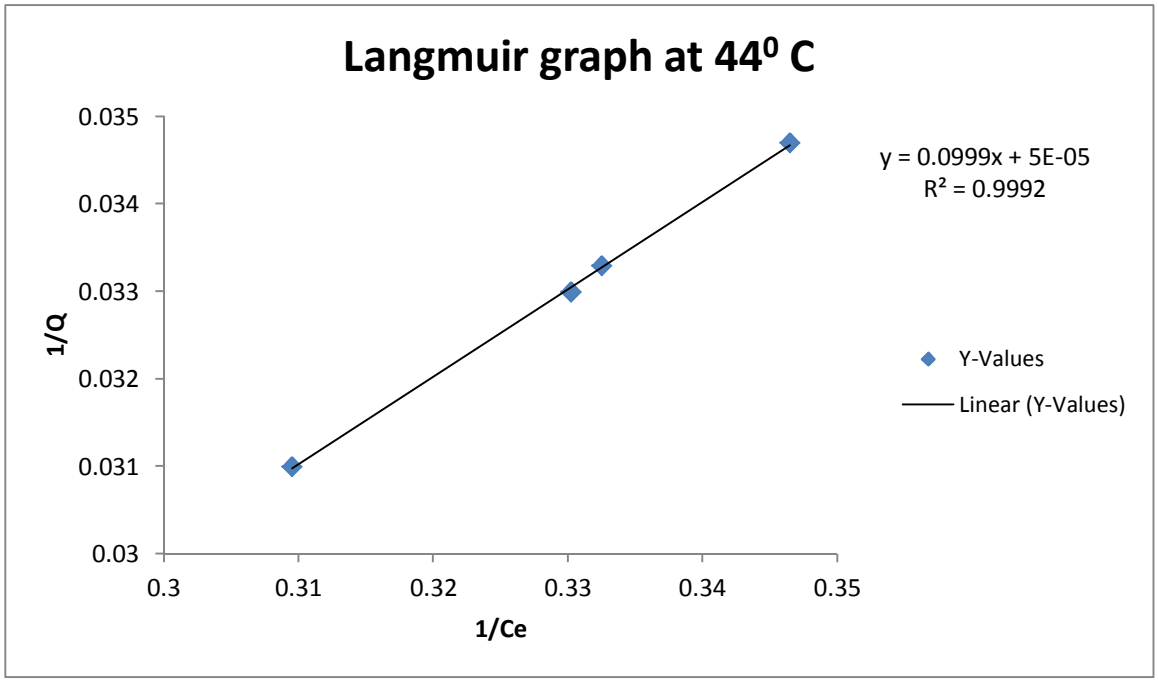


Figure 4.9 Langmuir Isotherm at 55^0 C

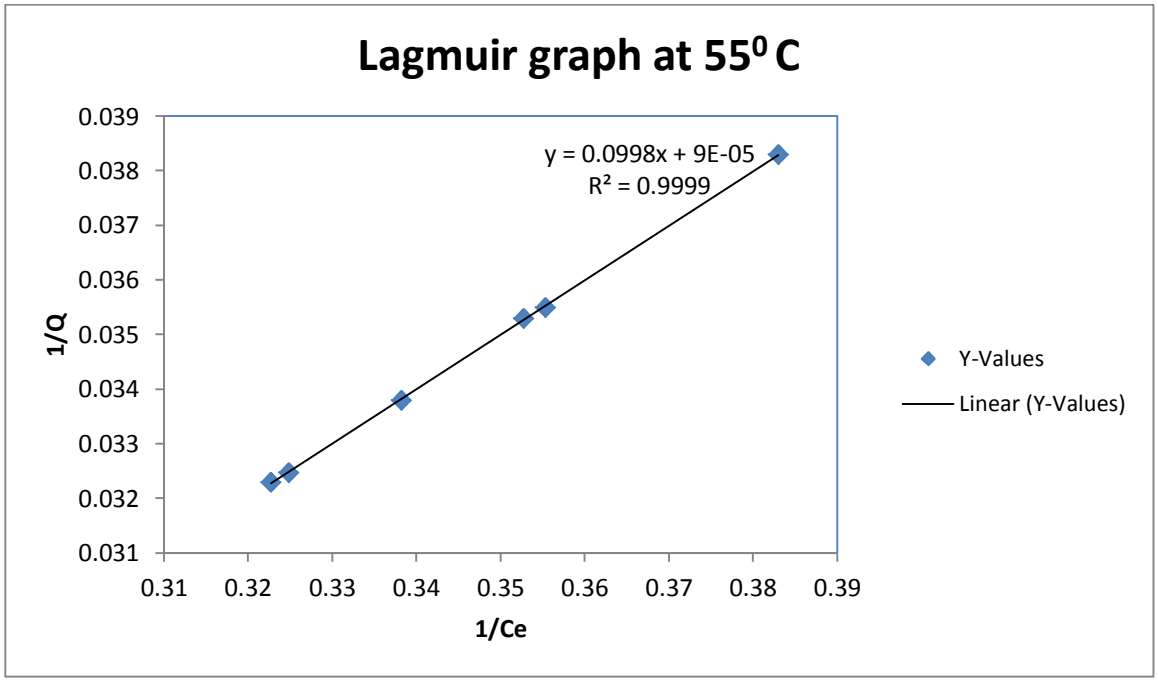


Figure 4.10 Langmuir Isotherm at 64^0 C

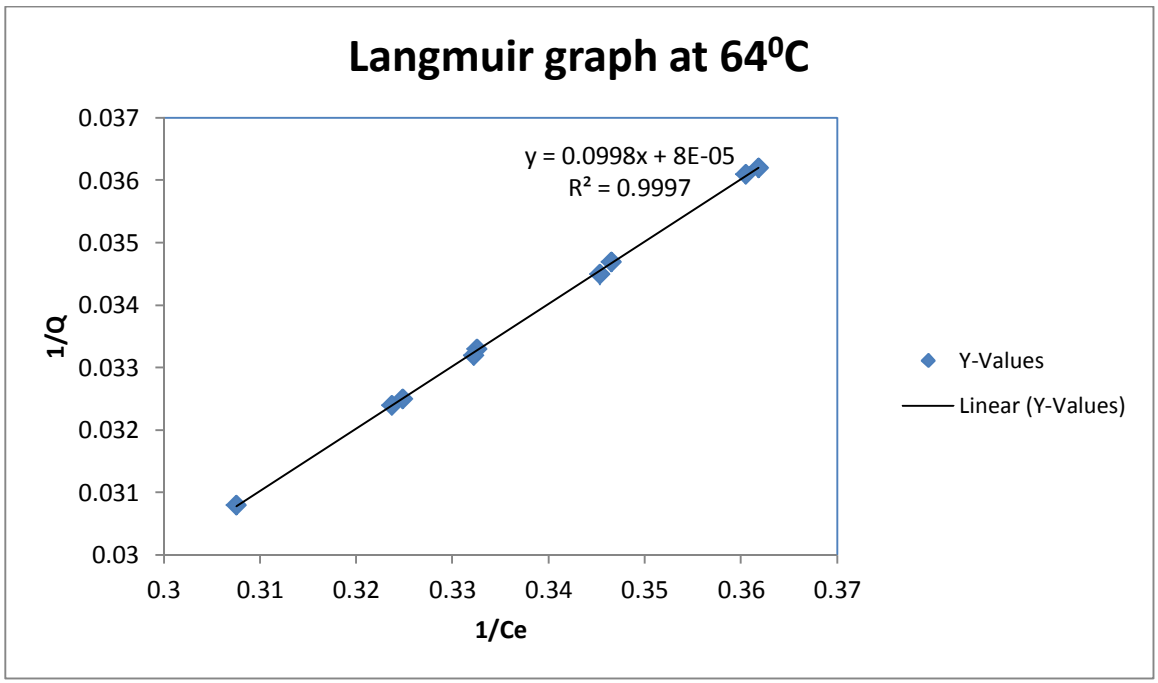
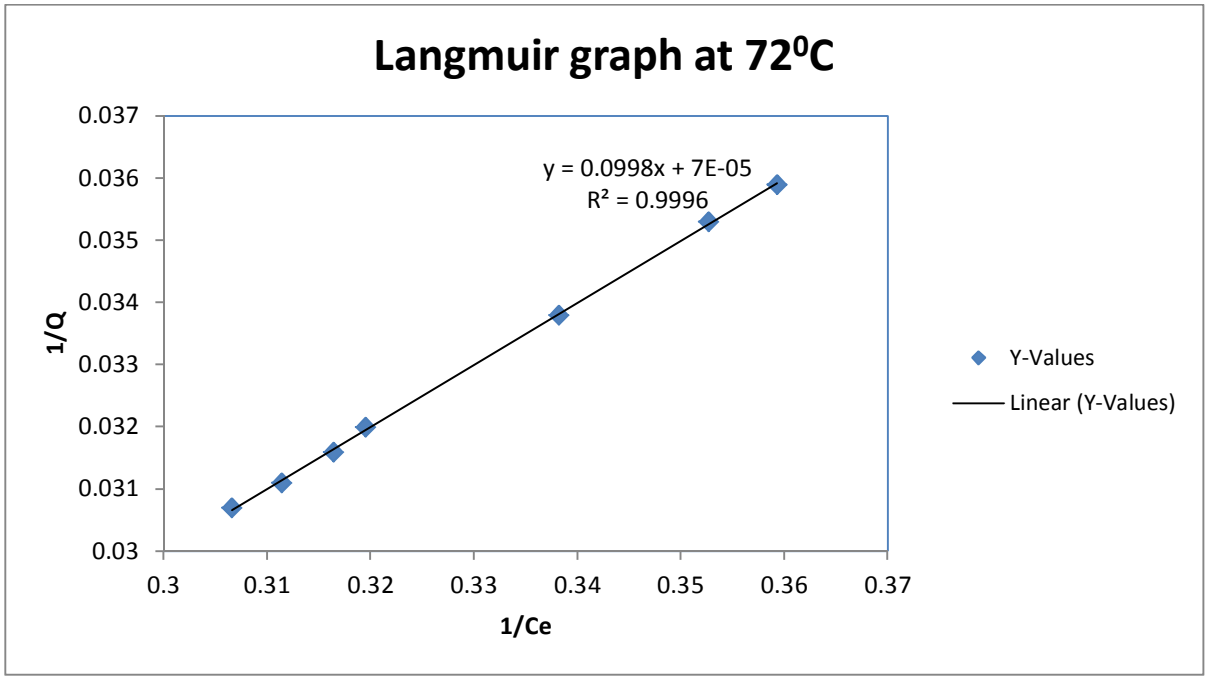
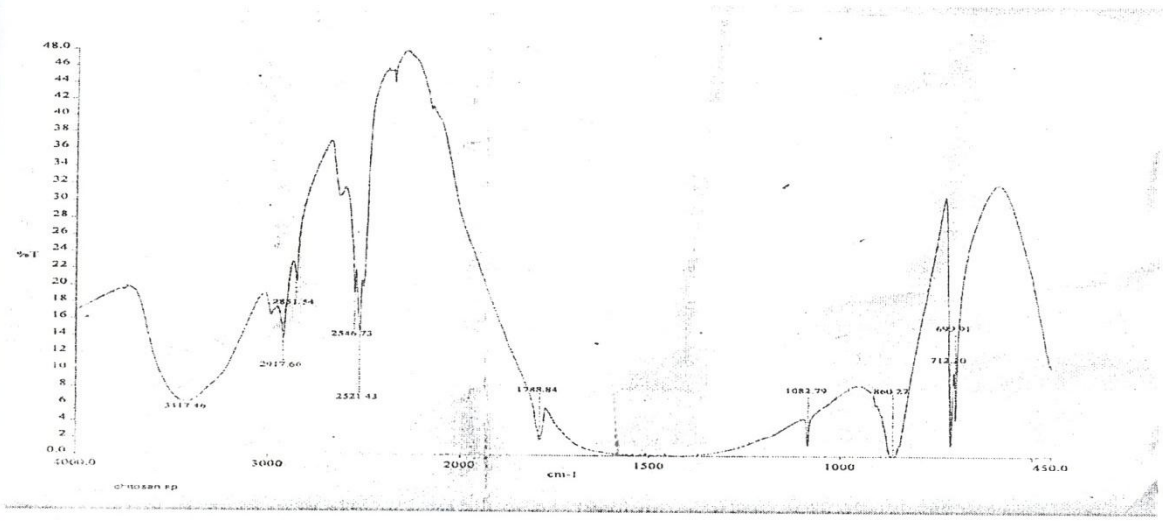


Figure 4.11 Langmuir Isotherm at 72^0 C



IR GRAPHS



CHITOSAN

28