UNIVERSITY OF NAIROBI

School of Physical Sciences

Department of Chemistry

DETERMINATION OF EFFECTIVENESS OF *LUFFA CYLINDRICA* AS AN ADSORBENT IN REMOVAL OF HEAVY METALS FROM WASTEWATER

BY

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i

DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, the award of a degree or publication. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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ABSTRACT

This piece of work reports the sorption properties of *Luffa Cylindrica* that have not been exploited and carbon from luffa to remove copper and chromium ions from aqueous solution. The effect of contact time, adsorbate concentration, particle size, pH, biomaterial dosage and Temperature was investigated. Particle size A (<425) gave the best adsorption values. Increase in concentration of metal ions resulted in decrease in % adsorption of the adsorbate, while increased pH values led to increase in % adsorption for both copper and chromium ions. Increased biomaterial loading also led to increased adsorption for both copper and chromium ions. Desorption studies were done with 0.1M concentrations of H_2SO_4, HCl and EDTA. It was noted that for copper, H_2SO_4 was the best followed by HCl and finally EDTA. Chromium on the other hand was best desorbed by EDTA but H_2SO_4 was still better than HCl. Luffa-metal ion bond and EDTA-metal ion bond played a significant role in the desorption capability of EDTA. The regenerated biomaterial was then subjected to another set of adsorption experiments to study the effect of concentration of the metal ion on adsorption and for both copper and Chromium, EDTA treated biomaterial gave higher adsorption percentages.   Luffa sponge was also carbonized and 0.5g, 0.75g and 1g portions of carbonized biomaterial was used to determine the effect of concentration of both Copper and Chromium ions on their adsorption onto the carbonized biomaterial. Carbonized biomaterial gave higher adsorption percentages than fresh Luffa.30ml portions of real effluent samples from KIRDI'S leather division was treated with 0.5g and 2g portions of fresh Luffa to determine its efficacy in removal of Chromium. 2g portions were able to remove over 92% of Chromium from the effluent.   Two adsorption isotherms were tested and Langmuir gave the best fit for chromium and copper, copper giving R^2 value of 0.9570 and Chromium R^2 value of 0.9728. q_{max} value, the monolayer adsorption capacity for copper using fresh luffa was found to be 2.9753mg/g, and b the Langmuir constant was found to be 0.1933l/mg.qmax for Chromium was found to be 1.3466mg/g and b Langmuir constant was found to be 0.6639l/mg.This means Luffa Cylindrica has a higher affinity for copper than   chromium. The experimental data from carbonized biomaterial was also fitted to Langmuir isotherm. The R^2 value for copper was found to be 0.9826 and q_{max} value of 5.4288mg/g, 1.8 times that of fresh luffa. R^2 value for chromium with carbonized Luffa was found to be 0.9144 with q_{max} value of 2.3479mg/g which again is almost twice as much as that of fresh Luffa. Freundlich Isotherm gave R^2 value 0.8194 for copper which was not close to unity so the data didn't adhere to the isotherm. Chromium however gave gave R^2 value of 0.9501with K_F value of 0.5768 and n value of 3.367 indicating good adsorption. This study demonstrates that *Luffa Cylindrica* could provide a cheaper alternative for removing heavy metals from waste water.

DEDICATION

I can do all things through Christ Jesus who strengthens me, I therefore dedicate this work to him.

I also dedicate this work to my loving husband Mr. Jared Obong'o and my children Tina Effie, DonnaFedha, Shalom Obong'o, Israel Shawn and Angel Obong'o.

ACKNOWLEDGEMENT

TABLE OF CONTENTS

vii

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

NEMA   National Environmental Management Authority

EDTA   Ethylene Diamine Tetraacetic Acid

KIRDI   Kenya Industrial Research and Development Institute

LDC   Leather Development Centre

AAS   Atomic Absorption Spectrophotometer

POU   Point Of Use

Cu^{2+} Copper ions

Cr^{3+} Chromium ions

C_e Concentration at equilibrium (mg/l)

q_e Adsorption capacity at equilibrium (mg/g)

K_F Freundlich adsorption capacity constant (mg/g)

R^2 Correlation Coefficient

q_{max} The amount of metal ion for complete monolayer coverage

rpm   Revolution per minute

ppm   parts per million

mg/g   milligram per gram

mg/l   milligram per liter

ml   milliliter

n   Adsorption intensity

C_1 Initial concentration of the test solution

C_2 Final concentration of the test solution

V_1	Initial volume of the test solution
V_2	Desired final volume of test solution
mg/g	Milligrams per gram
mg/l	Milligrams per litre
RMM	Relative Molecular Mass
RAM	Relative Atomic Mass
Temp	Temperature
TDS	Total Dissolved Solids
UK	United Kingdom
AR	Analytical Reagent

CHAPTER ONE

INTRODUCTION

1.1   Background

Pollutants enter water systems through various pathways, including sewage discharge, industrial, urban and run-off from firms, as well as deposition from air. Pollutants present in water systems commonly consist of various metallic and organic compounds (Förstner and Wittmann, 2012).

Over the recent past, there has been an increase in heavy metal discharge into the environment as a result of expansion of industries and technology which means increased use of energy and waste production from household and industrial sources. Heavy metals are particularly toxic due to their capability in binding with proteins and prevent DNA replication (Sahoo and Kar, 1992). These have made many waters harmful and unsafe to man and other living organisms (Kanu and Achi, 2011). The discharge of these heavy metals causes a considerable danger to the environment and public health since they are toxic, and also have the ability to bioaccumulate and persist in the environment (Akpor and Muchie, 2010).

Effluents with metals leads to increased quantities of minerals in water bodies (Asamudo *et al*., 2005). This therefore increases the richness of sediments especially if they are essential metals leading to eutrophication, oxygen deficiency and death of aquatic life (Asamuda *et al*., 2005).

Water polluted with metals may cause many health issues. Lead hinders enzyme activities and formation of red blood cells. It can have effect on both nerves and brain at low concentrations (Förstner and Wittmann, 2012). Heavy metals like mercury, cadmium and chromium can bio-accumulate through the food chain to deadly levels in man. Cadmium causes kidney disease and osteomalacia (Asamudo *et al*., 2005). Cadmium and zinc if present in high concentrations, interferes with regulation of ions (Igwe and Abia, 2007). Cadmium and manganese are also known to affect calcium absorption, skeletal calcification and also long term effect on fish and other aquatic lives (Asamudo *et al*., 2005). Chromium is carcinogenic and copper toxicity leads to Wilson's disease (Jomova and Valko, 2011).

The threat of these heavy metals calls for their urgent and efficient removal from such water bodies. Research has led to development of many methods with the aim of removing heavy metals from industrial effluents and these include Coagulation/flocculation processes, membrane filtration, oxidation process, activated carbon adsorption, reverse osmosis, ion exchange and solvent extraction (Bolong *et al*., 2009). These methods however, are disadvantagious in that they are linked with unpredictable metal ion removal, high cost of materials and the production of toxic waste that is not easy to handle most of the time. These processes also consume a lot of time and require skilled labour and are also complicated (Amuda and Ibrahim, 2006). Coal-based activated carbons are also expensive. Findings from research have shown several disadvantages of using synthetic coagulants-based removal processes, with arguments that they can cause diseases like Alzheimer's disease; alum has carcinogenic effects and residual Iron salts are also associated with health problems (Yang *et al*., 2010).

Recent research targets bioremediation processes to alleviate the current problems of water decontamination as they are considered cheap and ecofriendly. Many researchers have investigated the use of cheaper adsorbents such as agricultural wastes (Bousher *et al*., 1997), saw dust (Garg *et al*., 2003), banana pith (Namasivayam *et al*., 1998), cotton waste, rice husk (Ramakrishna *et al*., 1997), bentonite clay (Dogan *et al*., 2004), powdered activated sludge and sewage sludge (Bhattacharyya and Sharma, 2005), orange peels, bamboo dust, coconut shell, groundnut shell, rice husk and straw (Kannan and Sun-daran, 2001), wood, nut shells, peat and bone which have been processed into activated carbons (Amuda *et al*., 2007), maize cob and husk (Igwe *et al*., 2005), sawdust, cassava waste and coconut fibre have also been used. Biomateriales such as *Aspergillus tereus* and other biomaterial materials have also been reported to be efficient heavy metal adsorbents and therefore used in removing metals and organic compounds from urban and industrial wastewaters (Emmanuel, *et al*., 2014). Among these materials, adsorption of methylene blue was investigated by (Kannan and Sundaran, 2001), (Walker and Weatherly, 1998), (Waranusantigul *et al*., 2003), (Otero *et al*., 2003) and (McKay et al., 1985), among others.

The leather division in KIRDI receives leather from SMME in wet blue form, i.e partially tanned form. Tanning is the process of turning hides and skins into leather and during this process large

quantities of water and chemicals are added, with the main chemical being chrome. Leather then passes through various processes as follows:

Step 1. Samming – Here, excess water is removed from leather and this water contains chrome and other chemicals which had been added ealier in the tanning process like lime and sodium sulphide. This wastewater is directed to a collection pit awaiting treatment.

Step 2. Splitting – Leather is splitted into layers since it swells during liming process.

Step 3. Shaving – This is done inorder to achieve uniform thickness and during this process a lot of chrome containing particles are released.

Step 4. Retaning- Chrome is added again, and the wastewater containing chromium is directed to a collection pit. After these processes, the wastewater from the collection pit is treated by first aerating it to help in biological oxidation of organic matter. The effluent is then transfered to a dosing tank where aluminium sulphate is added to bring about precipitation of chromium in the form of chromium sulphate. This wastewater is then discharged into the sewer line.After this, leather is then rinsed severally with water and the process repeated i.e wastewater is directed to the collection pit, passed through aeration tank, to the dosing tank and finally discharged into the main Nairobi county sewer line.

In this project biosorption technology was employed where *Luffa cylindrica* was used as an adsorbent. *Luffa cylindrica* is a cucurbit and is made up of, 30% hemicelluloses, 60% cellulose, and 10% lignin (Oboh and Aluyor, 2009). Mature dry luffa sponge was used in this study. Luffa grows in many parts of Kenya especially Western and Eastern regions and is readily available in local markets and supermarkets where it is sold as a bathing sponge because of its fibrous nature (Barirega and Damme, 2014). Luffa plant is a climbing tree that grows without much attention; it is not eaten in Kenya and therefore does not jeopardize food security. Earlier studies on luffa have proved that luffa sponge can adsorb methylene blue dye (Abdelwahab and Ami, 2013).

1.2   Statement of the Problem

Human activities like industrial processing and use of metals, metallic compounds and alloys increase the natural background levels of metals in the environment. Effluents from textile,

leather, electroplating and cosmetic industries in most cases contain heavy metals. Such effluents alter habitat integrity of natural water bodies if untreated or allowed to accumulate leading to heavy metal poisoning (Kumar, 2015). The immediate treatment and disposal of wastewater containing heavy metals is desirable and also important in an industrializing country.

Increasing awareness on environmental issues and strict rules are putting pressure on industries to ensure that their effluents are treated to reduce the levels of contaminants to acceptable limits before discharge into waterways. The government of Kenya through NEMA (National Envoronmental Management Authority) has come up with maximum allowable quantities of chromium and copper in drinking water as 0.05mg/l and in effluent as 2mg/l and 1mg/l, respectively. This therefore necessitates treatment of wastewater.

A lot of research work is now being carried out to determine biomaterials that can be employed as adsorbents in removing heavy metals and other contaminants from effluents in a more cost effective and safe manner. And this is the basis of the work reported in this thesis.

1.3   Objectives

1.3.1   Overall Objective
To investigate metal adsorption properties of *Luffa cylindrica* and possibility of its use as an affordable adsorptive material for the removal of chromium and copper ions from wastewater.

1.3.2   Specific Objectives
   i.   To study the effects of particle size, pH, duration of contact, initial metal ion concentration in test solution, effect of biomaterial dosage and change in temperature on the removal of copper and chromium ions from aqueous solution in the batch mode of operation.

  ii.   To prepare activated carbon from *Luffa cylindrica* and compare its efficacy with that of luffa in the removal copper and chromium ions.

 iii.   To assess the possibility of regenerating the spent *Luffa cylindrica* with HCl, EDTA and H_2SO_4.

iv. To subject the regenerated luffa to some tests to prove its reusability and compare with that of unused luffa.

v. To assess the practicality of using *Luffa cylindrica* in the removal of chromium from effluent from Kenya Industrial Research and Development Institute (KIRDI)'s leather division.

1.4   Justification

Toxicity of heavy metals has resulted in a lot of research work being done inorder to find the most cost effective and efficient method for their removal. A large number of physico-chemical methods earlier used are associated with many drawbacks hence research on adsorption technology. Adsorption technology has been found to be fast, inexpensive and universal compared to other technologies. This research was based on adsorption technology employing *Luffa Cylindrica* as a biomaterial for removing copper and chromium ions from wastewater systems. Luffa species have several advantages over other adsorbents: it is locally available in Kenya, it is a climbing tree, it can withstand unfavourable weather conditions like drought, it is not eaten in Kenya and therefore doesn't jeopardize food security.This is good for a developing country like Kenya because it is cost effective. Removal of loaded metal from biomaterial is important as it ensures that the material is re-used and this leads to cost cutting. The regeneration of used biosorbent is therefore an important factor in assessing the ability of the biosorbent to be used commercially. Activated carbon was also made from luffa and its efficacy compared with that of fresh luffa.

Chromium is of concern since the leather division in KIRDI (Kenya Industrial Research and Development Institute) uses a lot of chromium sulphate in the tanning process and this necessitated this research in finding out the best way to reduce chromim levels in wastewaters. At the Water and Wastewater laboratory in KIRDI, quite a number of industries bringing their wastewater for copper analysis have shown high levels of copper even in treated effluents hence the motivation in this research for copper and chromium removal.

CHAPTER TWO

LITERATURE REVIEW

2.1   Wastewater

 Wastewater is basically a combination of liquid or water carrying waste matter from residential, institutional and industrial entities. Every living thing produces some amount of waste. As human population increase in a given locality, the waste generated increases and becomes a real danger to our health and well-being (Asthana *et al*., 2017). This waste needs to be collected, treated and disposed well otherwise it may cause enironmental damage, affect plant life and cause illness and even death. There is therefore great need to treat wastewater so as to protect people from waterborne diseases such as cholera, dysentery, typhoid, as well as other illnesses which may develop from coming into contact with untreated sewage. Treatment also protect natural water bodies like rivers, seas and even coral reefs, from the destructive effects of wastewater that has not been treated (Asthana *et al*., 2017).

2.2   Heavy Metals

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples include, cadmium, chromium, thallium, mercury, lead, copper and arsenic (Duruibe *et al*., 2007).

Heavy metals are naturally found on the Earth's surface. They cannot be degraded. They enter our bodies through food, water and air. Some heavy metals like copper, selenium and zinc are essential in human body as they maintain metabolism. They can however, cause poisoning at higher concentrations resulting from drinking contaminated water, e.g water passing through lead pipes (Wuana and Okiemen, 2011). Poisoning can also result from high concentrations in the air near sources of emission or intake through the food chain.

Heavy metals are dangerous since they tend to bioaccumulate in the food chain (Uysal *et al.,* 2009). Bioaccumulation reffers to increase in concentration of a chemical in an organism compared to its concentration in the environment over a period of time. If a compound is

excreted or broken down at a slower rate compared to the rate at which it is taken up and stored, they will tend to build up in the tissues of living things.

Heavy metals get their way into water supply via wastes from homes and industries. Acidic rain also breaks down soil and heavy metals are released into lakes, streams, rivers and groundwater.

2.2.1 Heavy Metals Removal

Many physical and chemical processes that employs the use of coagulation, reverse osmosis, ion-exchange, and flocculation with wide range of synthetic coagulants like aluminum, iron salts, soda ash, etc., have been used in the removal of heavy metals. However, the methods have many drawbacks such as unpredictable removal of metal ion, high material cost, and difficulty in managing generated toxic sludge (Bolong *et al.*, 2009). Removal of heavy metals from wastewater is therefore a major environmental concern, with many researchers trying to come up with various technologies which are affordable and environmentally friendly. Biosorption technology is a more recent research technology on trial; it is fast, inexpensive and universal compared to other wastewater treatment methodologies. In this thesis the efficacy of *Luffa Cylindrica* as an adsorbent in removing copper and chromium from wastewater system is reported.

2.3 Copper

Copper was initially mined from Cyprus by the Romans who called it aescyprum meaning from Cyprus, the name from which the Latin version cuprum and the symbol Cu were coined (Thompson, 2006). Copper exists chiefly as ^{63}Cu at 69.09%, ^{64}Cu at 30.91% and ^{65}Cu in trace amounts (Massey, 1973). Copper is the 25th most abundant element in the earth's crust and is a constituent in biological systems, soil solutions, organic fossils and natural waters (Boyles, 1979). The chief ores are chalcopyrite ($CuFeS_2$) and the chalcocite (CuS_2) (Massey, 1973). Copper is mostly found as sulphide deposits together with Pb, Zn and Cd. It is lustrous, malleable, ductile, tough, corrosion resistant and conducts both heat and electricity and is widely used in industry. Copper is mainly found in effluents from electroplating industries, mining and

in metallurgy. It forms Cu (I) and Cu (II) compounds with few Cu (III) species. It was the first metal to be used by man for practical purposes (Massey, 1973).

Copper is only second to zinc in environmental pollution but is twice as toxic (Leeper, 1978). Although the amount required by plants seldom exceeds 30ppm (Harter, 1983), 500 ppm copper content has been reported in some farmlands especially in Western Europe (Leeper, 1978).

The 2.2 million tons of world copper pollution have been attributed to the extensive use of copper-based agrochemicals, wood and fossil fuel combustion, and inefficient industrial wastewater treatment procedures (Leeper, 1978) among others. Copper pollution has been reported in central highlands of Kenya owing to extensive use of copper-based fungicides in the coffee plantations in that region (Kariuki, 2008) and in horticultural products in Tanzania (Lema *et al.*, 2014). Copper is extensively distributed in the environment and body tissues contain it in traces, but the high amounts of copper is found in the brain and liver (Osredkar and Sustar, 2011). Ceruloplasmin, a protein complex in blood plasma is found to contain about 95% of copper, and 5% loosely bound to a different protein, albumen (Luza and Speisky, 1996). Most of the copper in the body is excreted through the bile and feacal matter (Luza and Speisky, 1996; Cox, 1999).

In man, Copper is needed for the formation of melanin in the skin as well as transportation of electrons in the body. It helps in maintaining the strength of the myelin sheath that covers the nerves. Copper is also important in phospholipid synthesis and also necessary together with iron in the formation of hemoglobin in the blood. It is also found in enzymes that oxidizes fatty acids and is important for the growth of healthy hair. High intake of copper leads to toxicity and can cause hepatitis, nerve disorders and kidney malfunction (Ashish *et al*., 2013).

In plants, Copper is an important constituent of enzymes that helps in regulating the rate of many biochemical reactions. These enzymes helps in the growth of plants. Copper helps in production and formation of seeds and also helps in formation of chlorophyll and is essential for proper enzyme activity (Soetan *et al*., 2010).

Toxicity of copper has been blamed for soil ammonification, demineralization of nitrogen, deceleration of soil enzyme activities, depopulation of soil microorganisms and insects and

copper-induced plant nutrient deficiencies (Hunt *et al*., 2006) among other hazards. In people, Copper toxicity has been associated with inflammation of pulmonary organs, respiratory, gastrointestinal, cardiovascular, neurological and skin dysfunctions (Gaetke and Chow, 2003).

2.4   Chromium

Chromium is one of the metals that has been of a major focus in the treatment of water and wastewater. Chromium ion exists both in trivalent and hexavalent states, but the hexavalent one is more harmful due to its carcinogenicity (Karthikeyan *et al*., 2005). Chromium has been ranked among the top 16 toxic pollutants and has become a major health concern due to its carcinogenic and teratogenic characteristics (Torresday *et al.*, 2000).

Chromium is found in the earth's crust with chromite as the most important ore containing about 68% of chromium oxide and 32% iron oxide. Chromium is used in the manufacture of stainless steel and other alloys (Iyaka, 2009). The trioxide is used in plating, copper stripping, photography and corrosion inhibition. Chromium sulphate is used in textile industry, leather tanning, paints, inks, and glazes for porcelein. Chromium acetate is used in dyeing and tanning. Chromium is also used in explosives and for preservation of wood (Campbell *et al.*, 2009).

Waste from the above industrial units can be a source of pollution from soluble chromate salts. Chromium is found mainly in effluents from leather and textile industries and also in mining and metallurgy (Campbell *et al.*, 2009). Chromium is mainly removed from wastewater by chemical precipitation, but it leads to formation of sludge containing chrome which is difficult to manage. Ion exchange as well as membrane separation are also used but the methods are relatively expensive (Sharma *et al.*, 2007).

Consumption of contaminated water and inhalation of contaminated air leads to exposure to chromium, and also when chromium and chromium - containing compounds come into contact with the skin (Campbell *et al.*, 2009). Chromium levels in air and water is usually low, but contaminated well water may contain chromium (IV) which is dangerous and the hexavalent chromium (Campbell *et al.*, 2009). The main uptake route of chromium (III) is through consumption of vegetables, fruits, meats, yeasts and grains. Chromium content of foods can be

altered by how the food is prepared and stored (Campbell *et al.*, 2009). Storing foods in steel tanks or cans may lead to increase in the concentrations of chromium (Campbell *et al.*, 2009).

Chromium (III) is an important nutrient for humans and its deficiency may cause heart conditions, metabolic disruptions and diabetes (Iyaka, 2009). High intake on the other hand leads to toxicity and this in some cases is observed as skin rash. Chromium (VI) is dangerous to human health and mainly affect those who work in the steel and textile industries (Iyaka, 2009). Higher exposure to chromium also affects those who smoke tobacco. Chromium (VI) is also known to cause other health effects like stomach upset, respiratory problems, weak immune system, kidney and liver damage, alteration of genetic material, Lung cancer and even death (De Flora, 2000).

2.5   Luffa

2.5.1   *Structure and uses of Luffa*

The luffa, sometimes called loofah, or lufah are tropical and subtropical vines comprising the class Luffa. Two species commonly grown in many parts of the world are angled luffa called *Luffa acutangula* and the smooth fruited version called Luffa *aegyptiaca (Luffa cylindrica)* (Pandey *et al.,* 2014). *Luffa cylindrica* is a warm season, cold sensitive genus originating from India where it is harvested when still young and eaten (Oboh and Aluyor, 2009).

Luffa has also found extensive use as a sponge in bathing, washing utensils, cars, etc., because of its fibrous nature. Luffa grows in many parts of Kenya especially Western and Eastern regions and is readily available in local markets and supermarkets. In Kenya, it is mainly used as dish and bathing sponge.

Luffa cylindrica is a cucurbit and is made up of 10% lignin, 60% cellulose and 30% hemicellulose (Mazali and Alves, 2005). The structures of those components are as shown below:
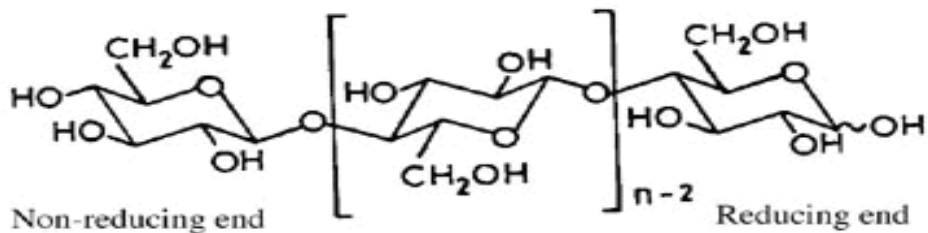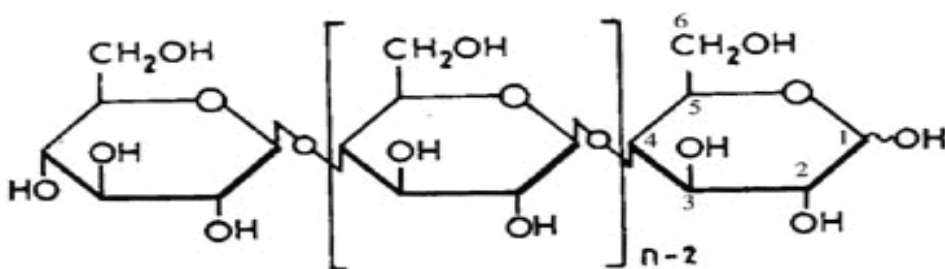
Figure 1: **Structure of cellulose**

From the above figure, it is clear that cellulose has –OH groups as functional groups and deprotonation of such groups yields a negative charge where positively charged ions can be attracted to. Lignin on the other hand is mainly made from three monomers (figure 2)
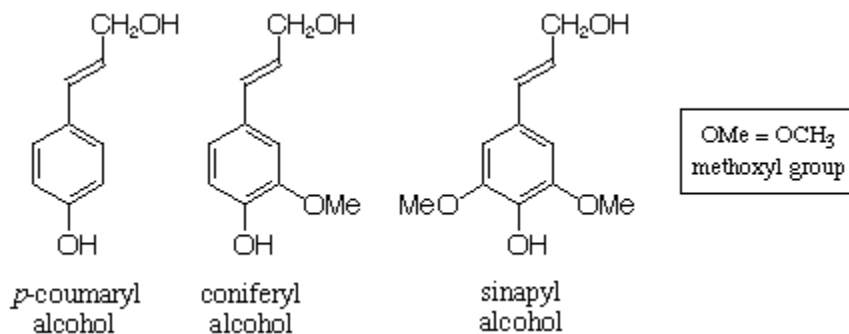
Figure 2: **Structure of lignin**

Lignin is composed of –OH groups as well as -OCH_3 groups which exhibits a negative charge when the methyl group leaves.This makes it possible for cationic cleavage. Hemicelluse also

exhibits tendency to attract cations due to deprotonation of –OH group and C-O- that is found in the monomer unit.The structure appears as shown in figure 3
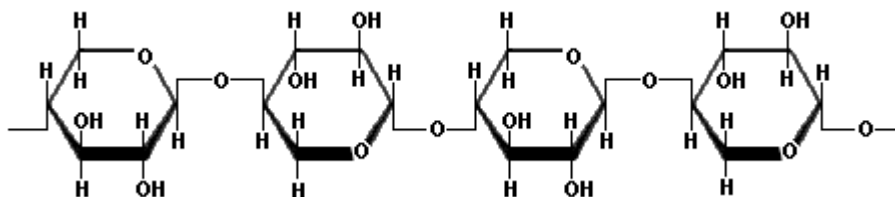
Figure 3:   **Structure of hemicellulose**

2.5.2 Luffa tree

Luffa tree is a climbing vine with leaves lobed like those of cucumber and yellow flowers as shown in figure 4. The fruit has fibrous interior which makes it useful as a rough sponge for cleaning and scouring. Mature seeds are black in color. Smooth luffa fruits are shaped like cucumbers but are larger. Luffa fruits are characterized by sharp elevated ridges running the length of the pods as shown in figure 4 (Oboh and Aluyor, 2009).

Figure 4:   **Fresh green luffa**

2.5.3 *Luffa sponge*

Luffa sponge has fibrous structure with very high porosity (79-93%), low density of between 0.02 g/cm^3 and 0.04 g/cm^3 and high specific pore volume ranging from 21-29 cm^3/g (Saeed and Iqbal, 2013). Luffa sponge is eco-friendly, cost effective and has been successfully used as a biotechnological tool in several systems and applications (Saeed. and Iqbal, 2013). Figure 5 shows a dry peeled luffa sponge.

Figure 5:   Peeled dry Luffa sponge

The cross sectional view depicts a network of xylem fibres which is responsible for the course texture, making the sponge suitable for scrubbing. See figure 6 below

Figure 6: **Cross-section view of Luffa sponge**

Peeled dry Luffa sponge can also be used to make activated carbon as was the case in this project (see Figure 7 below)

Figure 7: **Activated carbon from dry Luffa sponge**

2.6   Activated Carbon

In recent years, awareness campaigns and concerns about the quality and safety of water for drinkingr has made more people to turn to point-of-use devices to treat water to their own preferred quality levels. The indicator being the increased demand for domestic home water

filters, intended to remove odors, organic contaminants and unpleasant tastes from water (Smith, 2011).

These water filters employs the use of activated carbon which is known to be efficient in removing impurities (Baughman, 2002). Activated carbon has an incredible capacity to adsorb, high affinity for a wide range of dissolved organic compounds and chlorine, and capacity to be custom-made to suit particular applications (Baughman, 2002).

Any organic material with high content of carbon like wood, coal, coconut shell, peat, etc are good for making activated carbon. To make granular activated carbon, the biomaterial is ground, appropriate binding agent added, compacted and crushed to the right size (Bagreev *et al.*, 2001).

Thermal decomposition of the biomaterial in a furnace under controlled environment leads to formation of activated carbon. The activated carbon has an exceptionally large surface area per unit volume, and a network of small pores where adsorption occurs (Eltom *et al.,*2012).The surface of the pores provides the molecules neccesary for adsorption to take place.

Activated carbon acts to remove pollutants from water through physical adsorption which is the primary means (Eltom *et al.,*2012). The porous nature of carbon provides a large surface area for pollutants (adsorbates) to attach. In other words, physical adsorption takes place because the molecules, especially the ones at the surface of a solid (pore walls of carbon) exert attractive forces and thus seek other molecules to adhere to (Eltom *et al.,*2012).

The large internal surface area of carbon provides many sites that have the capacity to attract other molecules (Eltom *et al.,*2012). Attractive forces on the surface of carbon adsorbs water contaminants. Differences in concentration of the adsorbate in solution and in the carbon pores causes adsorption. The adsorbate moves from the solution via the pore channels to the area where the strongest attractive forces are (Smith, 2011). Water contaminants become adsorbates since the attraction of the carbon surface for them is stronger than the attractive forces that keep them dissolved in solution and therefore they get adsorbed on carbon surface (Singh *et al*., 2008). For adsorbates to be adsorbed onto activated carbon through the process of physisorption, they

need to be in solution and they should be small in size so that they can go through the pores of the activated carbon and accumulate (Smith, 2011).

Apart from physical adsorption, chemical reactions can occur on the surface of carbon. An example of such a reaction is the removal of chlorine from water where chlorine reacts with carbon to form chloride ions. This reaction is significant as chlorine to chloride conversion is the basis for the removal of some common unpleasant tastes and odors from drinking water and therefore important for Point of Use (POU) treatment. Activated carbon is also available commercially but it is very expensive. The figure below illustrates a sample of commercial activated carbon.

Figure 8:   Commercial Activated carbon

2.7   Adsorption

Adsorption occurs when a gas or a solute in a liquid accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate) (Aydin *et al.*, 2008). Absorption on the other hand occurs when a substance diffuses into a liquid or solid. The term sorption includes both processes, while desorption on the other hand is the reverse process. Adsorption occurs naturally in most physical, biological, and chemical systems, and is widely

used in industrial applications such as water purification (Onyeji and Aboje, 2011; Owabor *et al*., 2012).

Just like surface tension, adsorption is as a result of surface energy (Huck-Iriart *et al.*, 2016). All the bonding requirements whether ionic, covalent or metallic bonding of the   atoms constituting bulk material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not fully surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever is available for bonding. The material being adsorbed is known as the adsorbate while the solid material being used as the adsorbing phase is known as the adsorbent. The exact nature of the bonding depends on the nature of the species involved, but the adsorption phenomenon can be generally classified either as physisorption or chemisorption (Huck-Iriart *et al.*, 2016).

Physisorption also known as physical adsorption occurs when the adsorbate attaches itself to the surface only through weak intermolecular forces called Van der Waals forces, which also explains the non-ideal behavior of gases (Huck-Iriart *et al.*, 2016).

In chemisorption however, a molecule adheres to a surface through the formation of a chemical bond. Adsorption is usually described through functions (isotherms) which connect the amount of adsorbate on the adsorbent, with its pressure if it is in gaseous form or concentration if it is in liquid form. (Onyeji and Aboje, 2011).

Adsorption has been applied in wastewater treatment since it has several advantages over other methods of wastewater treatment. It can remove even very low concentrations of pollutants which may not be possible through other means, can make use of low cost biomaterials which lowers the cost of water treatment, (Owabor *et al*., 2012).

2.8   Adsorption Isotherms

Adsorption isotherms are graphs that are used in studying adsorption processes. That is the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. Adsorption isotherms describe how adsorbates interact with adsorbent and thus is important for optimizing the adsorption mechanism pathway. It also expresses   surface

characteristics and capacities of adsorbents, and efficient design of adsorption system (Foo and Hameed, 2010)

A number of theories have been advanced to explain the sorption phenomena involving solutes from solutions. In this work two of these theories have been adopted and are discussed below:

2.8.1 Langmuir Theory of Monolayer Adsorption

Langmuir theory proposed by Irving Langmuir assumes that adsorption takes place at specific homogeneous sites within the adsorbent (Amosa *et al*., 2016). Further assumption is that once a metal ion occupies a site, no further adsorption can take place at that site (Foo and Hameed, 2010). The rate of adsorption to the surface should be proportional to a driving force and the available area of free sorptive sites. The driving force is the concentration in the solution, and the area is the amount of bare surface.

If the fraction of the covered surface area is *f*, the rate of adsorption r_a, per unit surface is given by;

$$r_a = k_a C(1 - f) \tag{1}$$

Where C is the adsorbate concentration and k_a the rate constant.

The simultaneous metal desorption from the surface is proportional to the amount of adsorptive surface already covered by metal ions thus the corresponding rate of desorption r_d is given by;

$$r_d = k_d f \tag{2}$$

Where k_d is the respective desorption rate coefficient and *f* is the fraction of the surface covered

at equilibrium. The two rates are equal at equilibrium and therefore it can be shown that, (Amosa *et al*., 2016);

$$f = \frac{k_a C_e}{k_d + k_a C_e} \tag{3}$$

And the overall equilibrium constant,

$$b = \frac{k_a}{k_d} \qquad\qquad (4)$$

Since the adsorbed solute at equilibrium, q_{eq} is proportional to f, it can also be shown that

$$f = \frac{q_{eq}}{q_{max}} \qquad\qquad (5)$$

The Saturated monolayer adsorption capacity $q_{max,}$ can be obtained when f approaches unity, since q_{eq} approaches q_{max}. Thus saturated monolayer isotherm can be represented as;

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \qquad\qquad (6)$$

The above equation can be rearranged to the following linear form by taking reciprocal on both sides;

$$\frac{1}{q_{eq}} = \frac{1}{b q_{max} C_{eq}} + \frac{1}{q_{max}} \qquad\qquad (7)$$

Where C_{eq} is the equilibrium concentration (mg/l), q_{eq} the amount of metal ion sorbed (mg/g) , q_{max} is q_{eq} for complete monolayer coverage of the material by the adsorbate (mg/g), and b sorption equilibrium constant (l/mg). A plot of $1/q_{eq}$ versus $1/C_{eq}$ should indicate a straight line of slope $1/bq_{max}$ and intercept of $1/q_{max}$ from which both the adsorption capacity q_{max} and the equilibrium constant b representing the thermodynamic stability of the adsorption constant between the surface and the solute can be determined. In essence therefore, this theory postulates an irreversible adsorption process with high enthalpies in the order of those in the actual stoichiometry of the interacting groups and is monolayer (Foo and Hameed, 2010).

2.8.2   *Freundlich Adsorption Theory*

This theory concerns physical non-ideal adsorption. Freundlich studied the sorption of a material onto animal charcoal (Freundlich, 1906). He found that if the concentration of solute in the solution at equilibrium C_e (mg/l) was raised to a power $1/n$, where n is the adsorption intensity,

the amount of metal ion adsorbed per gram of the adsorbent (mg/g) being q_e, then $C_e^{\frac{1}{n}}/q_e$ is constant subject to temperature. This isotherm can be used for non-ideal sorption of metal ions onto an adsorbent and is expressed by the equation (Freundlich, 1906)

$$q_e = K_F C_e^{\frac{1}{n}} \tag{8}$$

The equation is conveniently used in the linear form by taking logarithm of both sides, i.e,

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{9}$$

Thus a plot of $log q_e$ against log C_e is a linear graph of gradient 1/n and vertical intercept equal $log k_f$. Adherence of adsorption data to the Freundlich isotherm therefore postulates multilayer physical and completely reversible adsorption based on weak van der Waals type of interaction between the sorbent and the adsorbate particles.

According to Mohan *et al.*, (2006), the values of constants k_f and q_{max} lead to the same conclusion about correlating the experimental data with the sorption model. The Langmuir isotherm assumes monolayer formation. In contrast, while the surface reaches saturation, the Freundlich isotherm does not predict surface saturation by the adsorbate. Therefore, the surface covering is mathematically unlimited. In conclusion q_{max} is the monolayer adsorption capacity while k_f is the relative adsorption capacity.

CHAPTER THREE

MATERIALS AND METHODS

3.1   Biomaterial Preparation

Luffa Cylindrica was bought in bulk from Gikomba and Kenyatta markets in Nairobi – Kenya. The seeds were removed and the material chopped into large pieces and washed severally with distilled water. It was then dried in the oven for 24 hrs, removed and cooled in a dessicator for 5hrs. The chopped pieces were then ground and washed again severally with distilled water until the elutriate got clear. The ground samples were passed through sieves with different pore sizes; 425 um, 710um and 850um to separate them into three different size populations. Particles with size <425 were classified as size A, <710 and >425 as size B and those that are >710 and < 850 as size C.

3.2   Apparatus

All weights were taken using electronic balance 320-4 model. The agitation was done using an orbital shaker model SO1 made in UK. After shaking, the filtration was done using Whatman filter paper No.40. When studying the effect of temperature a thermometer and a waterbath were used. Gallenkamp vacuum oven made in England was used in the carbonization of the biomaterial. In studying the effect of pH, ph/mv/cond./TDS/Temp meter model 86505 from China was used. Laboratory test sieves made in England of mesh sizes 850um, 710um and 425um were used in separating the biomaterial into different sizes inorder to investigate the effect of particle size.   The concentration of metal ions was determined using AAS model AA-6300 Shimadzu, made in Japan. Several flasks, beakers and plastic containers were also used.

3.3   Reagents

All the reagents used were AR grade. Metal ion solutions were prepared by dissolving appropriate quantities of appropriate salts in distilled water. Cr^{3+} solution was prepared from Chromium chloride $CrCl_3$. Cu^{2+} ion solution was prepared from hydrated copper (II) sulphate, $CuSO_4.5H_2O$. 0.1M EDTA used in the regeneration of spent biomaterial was prepared from its disodium salt, $C_{10}H_{14}Na_2O_8.2H_2O$. pH of the test solutions were adjusted using 0.1M HCl, 0.1M

NaOH and 0.1M H_2SO_4, prepared by diluting suitable quantities of the three reagents in appropriate quantities of distilled water. The two acids were also used in the regeneration experiments.

3.4   Properties of the adsorbent

It was important to understand the nature and characteristics of the biosorbent before it was used in the experiments. Thus the pH of 10 % w/v slurry was determined by soaking 10g of biosorbent in water and topping to 100ml.The slurry was left to stay overnight and pH was found to be 5.87 at room temperature. Quantities of copper and chromium present in the biomaterial was also determined using AAS by first ashing the biomaterial in the oven at 550^0C, then digesting it with a mixture of HCl and water in the ratio 1:1. The metal ion quantities were found to be negligible.   From literature, *Luffa cylindrica* is a cucurbit and is composed of 60% cellulose, 30% hemicellulose and 10% lignin (Mazali and Alves, 2005).

3.5   Preparation of stock and working solutions

Stock solutions in ppm were prepared by dissolving the weight of the salt that contains 1g of the metal in 1000ml of distilled water to make 1000ppm. This weight was calculated by using the formular;

$$\frac{RMM}{W}$$

(10)

Where RMM is the relative molecular mass of the salt and W is the weight of the metal in 1.0 mole of the salt.The molar solutions were prepared using the equation below;

$$C = \frac{\% \, purity \, \times sg \, \times 1000}{RMM \, \times 100}$$

(11)

Where C is the concentration of the reagent before dilution, sg is the specific gravity and RMM is the relative molecular mass.

Lower concentrations were obtained by serial dilution of concentrated solution using the formular

$$C_1V_1 = C_2V_2 \tag{12}$$

where

C_1 is the concentration of the stock solution

C_2 is the concentration of the test solution to be made

V_1 is the volume of stock solution to be taken

V_2 is the volume of the test solution to be made

3.6 Adsorption Experiments

The sorption studies were done using batch equilibrium method which involves immersion of pre-determined mass of adsorbent in solution of known concentrations of adsorbate. After sometime, the concentration of the metal ion in the supernatant was determined using Atomic Absorption Spectrophotometer (AAS). The percentage adsorption was then calculated as follows;

$$\% \text{ adsorption} = (C_i - C_f) *100/C_i \tag{13}$$

Where C_i is the initial concentration of test solution and C_f is the final concentration of the test solution. $C_i - C_f$ is therefore the amount of metal ion adsorbed.

3.6.1 Adsorption Studies of Copper

3.6.1.1 Effect of particle size and time of contact

20 ppm copper solution was prepared from 1000ppm stock copper solution prepared from copper sulphate crystals. 0.5g of biomaterial of particle size A was mixed with 30ml of 20ppm copper solution and agitated at the rate of 150 revolutions per minute (rpm) for 10 minutes. The mixture was then filtered and the concentration of copper in the filtrate determined using AAS. This procedure was repeated for 20, 30, 40, 50, 60, 70 and 80 agitation minutes inorder to determine how adsorption changed with time. Standards of 0, 2, 4, 6, 8 and 10 ppm were prepared and used to calibrate the AAS and samples with over range values were diluted appropriately. The same procedure was followed with particle sizes B and C. The % adsorption was then calculated.

23

3.6.1.2 *Effect of biomaterial dosage on copper removal*

30 ml of 50 ppm copper solution was put in 100ml conical flasks and 0.2g, 0.3g, 0.4g, 0.5g, 0.6g, 0.7g, 0.8g, 0.9g, 1.0g, 1.1g, 1.3g, 1.5g, 1.7g, 2.0g, 2.2g, 2.5g and 3.0g of biomaterial of particle size A added to each container and shaken at the rate of 150 rpm for 50 minutes in the orbital shaker. The samples were then filtered and final concentration of copper in the filtrate determined using AAS. The % adsorption was then calculated (see 3.6).

3.6.1.3 *Effect of concentration of copper ions on adsorption*

1000 ppm stock copper solution was diluted serially to 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 ppm concentrations using the formula;

$$C_1V_1 = C_2V_2 \qquad\qquad (12)$$

where C_1 is the concentration of the stock solution

C_2 is the concentration of the test solution to be made

V_1 is the volume of stock solution to be taken

V_2 is the volume the test solution to be made

30 ml of each dilution was put in a conical flask and 0.5g of biomaterial added. The mixture was then shaken on an orbital shaker for 50 minutes at the rate of 150 revolutions per minute. This procedure was repeated with 0.75g, 1g, 1.25g, 2g and 3g of biomaterial of particle size A. The procedure with 0.75g of material particle size A was done six times for each concentration since the spent material was to be used later in desorption studies. The samples were then filtered and final copper concentration in the filtrate determined using AAS. The % adsorption was then calculated.

3.6.1.4 *Effect of temperature on copper adsorption*

30ml of 50 ppm copper solution was put in a plastic container and placed in a waterbath maintained at $30^{o}C$, after equilibrium, 0.5g of the biomaterial was added and shaken at that temperature for 50 minutes; filtered and copper concentration in the filtrate determined using

AAS. The procedure was repeated at 40 ^{o}C, 50°C, 60°C, 70°C and 80°C and each time the samples were filtered and final concentration of copper determined using AAS.

3.6.1.5   *Effect of pH on copper adsorption*

90ml triplicate portions of 50ppm copper solution was put in beakers and pH value of the solution measured and found to be 4.45. The pH value of different portions was then adjusted to 3.03, 3.33 and 3.54 using 0.1M HCl. 30ml aliquot of the copper solution was taken in triplicate from each portion and 0.5 g biomaterial added to each and shaken in the orbital shaker at the rate of 150 rpm for 50 minutes.The solutions were then filtered and copper concentration in the filtrate determined using AAS. This procedure was repeated with 90 ml duplicate portions of copper solution after adjusting their pH values with 0.1M NaOH to 5.10 and 6.31.

3.6.2   *Adsorption Studies of Chromium*

3.6.2.1   *Effect of particle size and contact time on chromium adsorption*

20 ppm chromium solution was prepared from 1000ppm stock chromium solution prepared from chromium chloride crystals. 0.5g of biomaterial of particle size A was mixed with 30ml of 20ppm chromium solution and agitated at the rate of 150 r.p.m for 10 minutes. The mixture was then filtered and the concentration of chromium in the filtrate determined using AAS. This procedure was repeated for 20, 30, 40, 50, 60, 70 and 80 minutes. Standards of 0, 2, 4, 6, 8 and 10 ppm were prepared and used to calibrate the AAS and samples with over range concentration values were diluted appropriately. The same procedure was followed with particle sizes B and C and % adsorption was then calculated (see 3.6).

3.6.2.2   *Effect of biomaterial dosage on chromium adsorpton*

0.3g, 0.4g, 0.5g, 0.8g, 1.1g, 1.4g, 1.7g, 2.0g, 2.2g, 2.5g and 3g triplicate portions of biomaterial was weighed and each portion added to separate 30ml portions of 50ppm chromium (III) solution.The samples were put in the orbital shaker and shaken for 50 minutes at the rate of 150 r.p.m. The samples were then filtered and the concentration of chromium in the filtrate determined using AAS.

3.6.2.3 *Effect of pH on chromium adsorption*

90ml portion of 25ppm chromium solution was put in a flask. The pH was measured and found to be 3.86. The pH of the solution was then adjusted using 0.1M HCl to pH 3.30 and divided into three portions of 30ml each.0.5g biomaterial was then added and agitated at the rate of 150rpm for 50 minutes.The samples were then filtered and final concentration of chromium determined using AAS.This procedure was repeated by adjusting pH values to 2.86 and 2.38 using 0.1M HCl and to 4.5 and 5.87 using 0.1M NaOH.

3.6.2.4 *Effect of concentration on chromium adsorption*

1000 ppm stock chromium solution was diluted serially to 5, 10,15, 20, 25, 30, 35, 40, 45 and 50ppm concentrations using the formula;

$$C_1V_1 = C_2V_2 \tag{12}$$

where C_1 is the concentration of the stock solution

C_2 is the concentration of the test solution to be made

V_1 is the volume of stock solution to be taken

V_2 is the volume the test solution to be made

30 ml of each dilution was put in a conical flask and 0.5g of biomaterial added. The mixture was then shaken on an orbital shaker for 50 minutes at the rate of 150 revolutions per minute. The sample was then filtered and the amount of chromium in the filtrate determined using AAS. This procedure was repeated with 0.75g, 1g, 1.25g, 2g and 3g of biomaterial of particle size A. Each procedure was done in duplicate but the one with 0.75g of material was done six times for each concentration since the spent material was to be used in desorption studies. The % adsorption was then calculated (see 3.6).

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3.6.2.5 *Effect of temperature on chromium adsorption*

30mls duplicate portions of 25ppm Cr^{3+} solution was transferred to 100ml plastic bottles and the temperatures brought to equilibrium with that of water bath maintained at $30^{o}C$. 0.5g of biomaterial was then added and shaken for 50 minutes. The samples were filtered and the final concentration of chromium determined using AAS. This procedure was then repeated with waterbath maintained at $40^{o}C$, $50^{o}C$, $60^{o}C$, $70^{o}C$ and $80^{o}C$ and each time the samples were filtered and chromium concentration in the filtrate determined using AAS.

3.7 Desorption Studies

Regenaration of spent biomaterial was done using 0.1 M HCl, 0.1M EDTA and 0.1M H_2SO_4, separately. The efficacy of the three reagents was analyzed to determine the trend in copper and chromium desorption

3.7.1 Copper Desorption

3.7.1.1 *Desorption of Copper from 0.75g spent biomaterial*

0.75g of spent biomaterial that was previously used to study effect of concentration (section 3.6.1.3) was regenerated seprately using 0.1M HCl, 0.1M H_2SO_4 and 0.1M EDTA. As earlier discussed, the effect of concentration using 0.75g of biomaterial was done six times and the excess copper solution in the spent biomaterial separately blotted using filter papers and the biomaterial was left to dry in the open air. The spent biomaterial was then paired to give duplicate quantities. One pair was each treated with 0.1M HCl, another was treated with 0.1M H_2SO_4 and the final one with 0.1M EDTA. This was done by taking 50ml duplicate portions of 0.1M HCl in a container, separately adding the spent pair of biomaterial. The samples were shaken in the orbital shaker for 50 minutes at 150 r.p.m filtered and the amount of copper in the filtrate determined using AAS. % desorption was then calculated.This procedure was repeated with 0.1M H_2SO_4 and 0.1M EDTA separately. The regenerated biomaterial was kept separately and subjected again to another set of adsorption experiments as discussed in section 3.8.1

3.7.1.2   *Effect of concentration of H$_2$SO$_4$, HCl and EDTA on desorption of Copper ions*

24g of *Luffa Cylindrica* was soaked in 400ml of 50ppm copper ion solution and agitated at the rate of 150rpm for 6 hours .The excess water was drained and the biomaterial rinsed with 200ml portions of distilled water five times and dried in the oven for 5 hours at 105^{0}C. 0.1M HCl, 0.1M H$_2$SO$_4$ and 0.1M EDTA were prepared and serial dilutions done to obtain 0.01M, 0.02M, 0.03M, 0.05M and 0.08M concentrations of each. 30ml duplicate portions of each dilution were taken and 0.5g of the biomaterial added and agitated at the rate of 150rpm for 50 minutes .The samples were then filtered and the concentration of copper in the filtrate determined using AAS. The copper content of the used biomaterial was also determined. 2g duplicate portions of the biomaterial was put in a beaker and ashed at 550^{0}C in the furnace. 20ml of a mixture of water and HCl in the ratio 1:1 was then added and the samples digested in the sand bath upto about half the original volume, filtered and topped to 100ml in a 100ml volumetric flask. The amount of copper was then determined using AAS. Amount of copper adsorbed by 0.5g of the biomaterial was calculated as well as the amount desorbed and % desorption calculated (see 3.6)

3.7.2   *Chromium Desorption*

3.7.2.1 *Desorption of Chromium ions from 0.75g spent biomaterial*

0.75g of spent biomaterial that was previously used to study effect of concentration of chromium on adsorption (section 3.6.2.4) was regenerated seprately using 0.1M HCl, 0.1M H$_2$SO$_4$ and 0.1M EDTA. As earlier discussed the effect of concentration using 0.75g of biomaterial was done six times and the excess chromium solution in the spent biomaterial separately blotted using filter papers and the biomaterial was left to dry in the open air. The spent biomaterial was then paired to give duplicate quantities.One pair was each treated with 0.1M HCl, another was treated with 0.1M H$_2$SO$_4$ and the final one with 0.1M EDTA. This was done by taking 50ml duplicate portions of 0.1M HCl in a container, separately adding the spent pair of biomaterial. The samples were shaken in the orbital shaker for 50 minutes at 150 r.p.m filtered and the amount of chromium in the filtrate determined using AAS. % desorption was then

calculated.This procedure was repeated with 0.1M H_2SO_4 and 0.1M EDTA. The biomaterial was reserved for reusability test.

3.7.2.2 Effect of concentration of H_2SO_4, HCl and EDTA on desorption of Cr^{3+} ions

The procedure used in studying the effect of concentration of the desorbing agents on copper desorption (see section 3.7.1.2) was also used on chromium desorption studies, with 50ppm Cr^{3+} ions solution.

3.8   Reusability Test

The biomaterial that was regenerated was subjected to another set of experiments (see sections 3.8.1 and 3.8.2) to determine if it could be reused in adsorption. The effect of copper and chromium concentration was studied. Comparison was also made between the adsorption by the original biomaterial and by each of the regenerated biomaterial.

3.8.1   Adsorption of Copper by the Regenerated Biomaterial

The regenerated biomaterial (section 3.7.1) was thoroughly rinsed with distilled water until the elutriate tested negative for copper. The excess water was blotted out and the material allowed to dry in the air. Concentrations of 20, 30, 40, 50, 60, 70, 80, 90 and 100ppm copper were prepared.

30ml portions of each concentration of copper ion solution was put in different flasks and the biomaterial previously regenerated by HCl added and shaken in an orbital shaker for 50 minutes. Each portion of the biomaterial was subjected to the same concentration as previously done before regeneration. The samples were then filtered and concentration of copper in the filtrate determined using AAS. The analysis was done in duplicates.This procedure was then repeated with biomaterial previously regenerated by EDTA and by H_2SO_4.

3.8.2   Adsorption of Chromium by the Regenerated Biomaterial

The regenerated biomaterial was thoroughly rinsed with distilled water until the elutriate tested negative for chromium, the excess water was blotted out and the material allowed to dry in the

air. Concentrations of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50ppm chromium were prepared. 30ml portions of each concentration of chromium ions was put in different flasks and the biomaterial regenerated by HCl added and shaken in an orbital shaker for 50 minutes.Each portion of the regenerated biomaterial was subjected to the same concentration as previously done before regeneration. The samples were then filtered and concentration of chromium in the filtrate determined using AAS.The analysis was done in duplicates.This procedure was then repeated with biomaterial regenerated by EDTA and by H_2SO_4.biomas

3.9   Preparation of Activated Carbon from Luffa

Eight, 70g portions of Luffa were heated in a vacuum oven at 200^0C for 24 hrs. The carbonized material was left in the desiccator to cool and sieved through 425um sieve. The activated carbon was then used to study the effect of concentration on adsorption of copper and chromium ions, separately.

3.9.1   Effect of Concentration and activated carbon dosage on copper adsorption

10, 20, 30 ,40, 50, 60, 70, 80, 90 and 100ppm copper solutions were prepared from 1000ppm stock solution. 30ml duplicate portions of each concentration was put in different flasks, 0.5g of carbon added and shaken for 50 minutes at 150 rpm in an orbital shaker.The samples were then filtered and concentration of copper in the filtrate determined. The procedure was repeated with 0.75g and 1g portions of activated carbon. Comparison was made between using *Luffa Cylindrica* as it is and using activated carbon derived from it.b

3.9.2   Effect of concentration and activated carbon dosage on chromium adsorption

5, 10, 15, 20, 25, 30, 35, 40, 45 and 50ppm chromium solutions were prepared from 1000ppm stock solution. 30ml duplicate portions of each concentration was put in different flasks, 0.5g of carbon added and shaken for 50 minutes at 150 rpm in an orbital shaker.The samples were then filtered and concentration of chromium in the filtrate determined. The procedure was repeated with 0.75g and 1g portions of activated carbon.

3.10 Treating Effluent from Kenya Industrial Develoment Institute (KIRDI) Leather Division

The adsorption of possible dissolved chromium ions by the biomaterial was tested on real effluent from KIRDI'S leather division.

3.10.1 Sampling Frequency and Duration

The test samples were collected from KIRDI'S leather division on five consecutive days from 4th February 2013 to 8th February 2013, from the collection pit and also from the dosing tank.The collection for day 1 was done from collection pit after retanning process and also from dosing tank after treating this effluent. As explained in section 3.10, retanning process is followed by rinsing the treated leather with a lot of water for some days and this water passes through the same process of treatment. The collection done in the next four consecutive days was done from both collection pit and dosing tank during this rinsing process.

3.10.2 Sample Preparation

Preliminary digestion of sample solutions for determination of metal ions was done by adding 50ml of concentrated nitric acid into a beaker containing 1000ml sample. The samples were then evaporated in a sand bath up to about 200ml, filtered, and the filtrate transferred to 1000ml volumetric flask and topped to the mark.

3.10.3 Sample analysis

Initial amount of chromium was determined in the samples for each day before treating with *Luffa Cylindrica.* The samples were then treated with 0.5g and 2.0g *Luffa Cylindrica* and final residual chromium concentration determined using AAS.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1   Copper Studies

4.1.1   Effect of Particle Size and Contact Time on Copper Adsorption

Particle size and contact time are important parameters to be considerd in any adsorption processes. Whereas particle size determines the surface area of biosorbent available for sorption, time of contact is also important since the biosorbent and sorbate need to be in contact for enough time for maximum sorption. Tables 1,2 and 3 shows % adsorption of copper ions by *Luffa Cylindrica* of particle sizes A, B and C, respectively.

Table 1:   Effect of contact time on % adsorption of 20ppm copper (ii) ions by 0.5g of particle size A (< 425um).

Time (minutes)	Final concentration in ppm	% Adsorption	Standard Deviation
10	3.0590	84.71	±1.34
20	2.7143	86.43	±1.20
30	2.8422	85.79	±0.30
40	2.8500	85.75	±1.27
50	2.8896	85.55	±0.68
60	2.9145	85.43	±0.91
70	2.8745	85.63	±0.45
80	2.8148	85.93	±1.52

Table 2:   **Effect of contact time on % adsorption of 20ppm copper (II) ions by 0.5g of particle size B (>425um and < 710um).**

Time (minutes)	Final concentration in ppm	% Adsorption	Standard Deviation
10	3.1477	84.26	±0.88
20	3.0140	84.93	±1.96
30	2.9312	85.34	±0.45
40	2.8601	85.69	±0.60
50	2.9061	85.47	±1.49
60	2.9618	85.19	±0.39
70	2.8834	85.58	±1.38
80	2.8861	85.57	±0.09

Table 3: **Effect of contact time on % adsorption of 20ppm copper (II) ions by 0.5g of particle size C (>710um and < 850um)**

Time (minutes)	Final concentration in ppm	% Adsorption	Standard Deviation
10	3.1509	84.25	±0.88
20	3.1166	84.42	±0.91
30	2.9351	85.32	±0.70
40	2.9185	85.41	±0.62
50	2.9100	85.45	±0.20
60	2.8783	85.61	±0.52
70	2.9658	85.17	±0.98
80	3.1509	84.25	±1.32

The results were then illustrated graphically as shown in Figure 9 below;
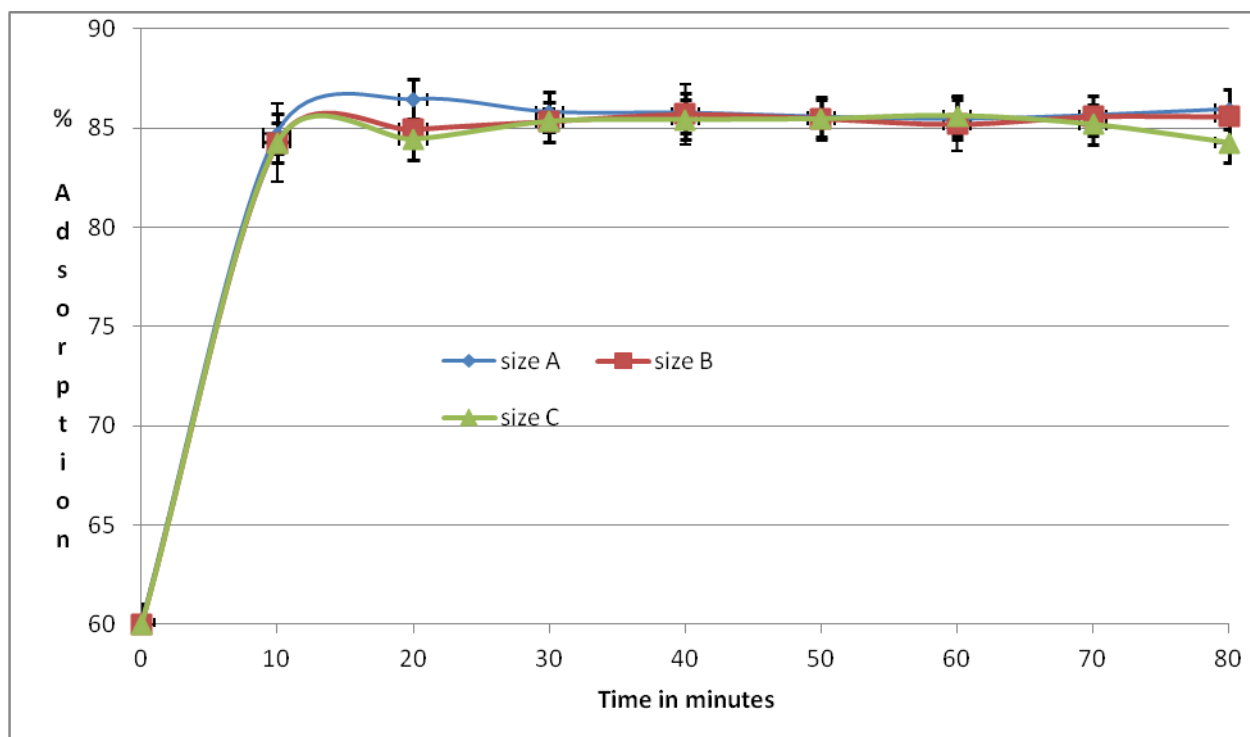
Figure 9: **Plot of % adsorption of 20ppm copper (II) ions against contact time for different particle sizes of 0.5g *Luffa Cylindrica* (size A<425um, 425um<size B<710um, 710um<size C< 850um).**

The study was carried out using 20ppm copper solution and 0.5g biomaterial. It is evident from the plot that there was a rapid uptake of copper during the first 10 minutes and % adsorption seemed to remain constant over the rest of the contact time with particle size A. The order of adsorption beyond 10 minutes mark appeared to be particle size A > particle size B > particle size C. Between 30 to 70 minutes, the equilibrium has already been attained therefore no more adsorption is taking place and biomass weight has become a limiting factor.Desorption is also taking place hence the behavior of particle size C between 70 to 80 minutes. At lower concentrations, the particle size of the biomaterial had no much effect on % adsorption. With 50ppm copper ion concentration, the adsorption profile is as shown in figure 10.
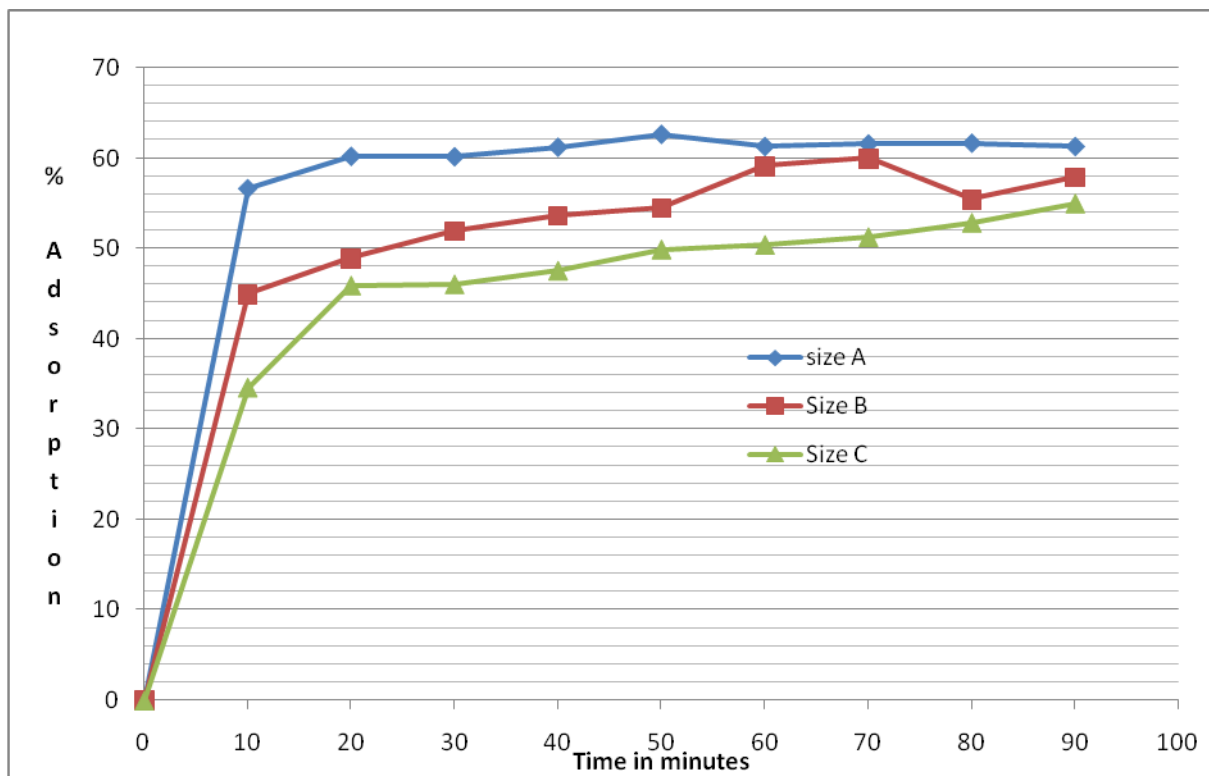
Figure 10: **Plot of % adsorption of 50ppm copper (II) ions against contact time for different particle sizes of 0.5g** *Luffa Cylindrica*

It is clear from the plot that % adsorption decreased with increasing particle size; with particle size A showing greater % adsorption than size B which in turn is greater than size C. This can be attributed to decrease in surface area of the biomaterial exposed for adsorption with increase in particle size (Schiewer and Volesky, 2000). The forces between the solute molecules of the solid and the bulk phase must have made it difficult for Cu^{2+} ions to occupy the remaining vacant surface sites thus minimal change in % adsorption with increase in time (Chand *et al.*, 1994; Saravanane *et al.*, 2002; Bishnoi and Garima, 2004). The decreasing removal with increasing time may be caused by intraparticle diffusion process dominating over adsorption (Deo and Ali, 1992 & Volesky 2003). It is also evident from the two figures that the % adsorptions were relatively lower with 50ppm of Cu^{2+} ions than with 20ppm as would be expected. This can be attributed to the weight of the adsorbent being the limiting factor since the saturation of the adsorption sites by the higher concentration adsorbate solutions would occur much sooner for the

same size and weight of the adsorbent. Particle size A was therefore used as optimal size in all other experiments involving copper (II) ion adsorption.

4.1.2 *Effect of Concentration of Copper (II) Ions on % Adsorption*

Concentration of sorbate ions plays a major role in adsorption since it determines how many ions are competing for available adsorbate sites and this in turn affects % adsorption. Table 4 below shows how % adsorption of copper ions was affected by change of concentration of the metal ions using different biomaterial weight.

Table 4:   Effect of concentration of copper (II) ions on % adsorption by varying weights of adsorbent

Initial Copper conc. (ppm)	Biomaterial weight (grams)	Final copper conc. (ppm)	% Adsorption
10	0.5	0.7878	92.12
	0.75	0.6977	93.02
	1	0.5087	94.91
	1.25	0.4421	95.58
	2.0	0.1433	98.57
	3.0	0.1170	98.83
20	0.5	2.9755	85.12
	0.75	1.9382	90.31
	1	1.8737	90.63
	1.25	1.64325	91.78
	2.0	0.6904	96.55
	3.0	0.5974	97.01

Initial Copper conc. (ppm)	Biomaterial weight (grams)	Final copper conc. (ppm)	% Adsorption
30	0.5	4.52485	84.92
	0.75	3.1087	89.64
	1	2.896	90.35
	1.25	2.55735	91.47
	2.0	1.2057	95.98
	3.0	1.0599	96.47
40	0.5	7.68135	80.80
	0.75	4.28115	89.30
	1	4.22365	89.44
	1.25	4.07315	89.81
	2.0	1.7956	95.51
	3.0	1.7855	95.54
50	0.5	14.6205	70.76
	0.75	5.73115	88.54
	1	5.5909	88.82
	1.25	5.1725	89.66
	2.0	2.2522	95.49
	3.0	2.0609	95.88
60	0.5	18.9820	68.36
	0.75	8.9200	85.13
	1	7.4291	87.62

Initial Copper conc. (ppm)	Biomaterial weight (grams)	Final copper conc. (ppm)	% Adsorption
	1.25	6.8113	88.65
	2.0	3.0911	94.85
70	0.5	26.5795	62.03
	0.75	10.4685	85.05
	1	9.43585	86.52
	1.25	7.99025	88.58
	2.0	4.5164	93.55
	3.0	3.8129	94.55
80	0.5	39.640	50.45
	0.75	20.2685	74.66
	1	11.930	85.09
	1.25	9.78195	87.77
	2.0	7.5655	90.54
	3.0	5.9648	92.54
90	0.5	46.988	47.79
	0.75	28.378	68.47
	1	21.892	75.68
	1.25	18.795	79.12
	2.0	11.627	87.08
	3.0	8,7354	90.29
100	0.5	57.893	42.11

Initial Copper conc. (ppm)	Biomaterial weight (grams)	Final copper conc. (ppm)	% Adsorption
	0.75	35.957	64.04
	1	33.728	66.27
	1.25	29.162	70.84
	2.0	20.284	79.72
	3.0	79.72	86.41

The tabulated results were then represented graphically as shown in Figure 11 below;
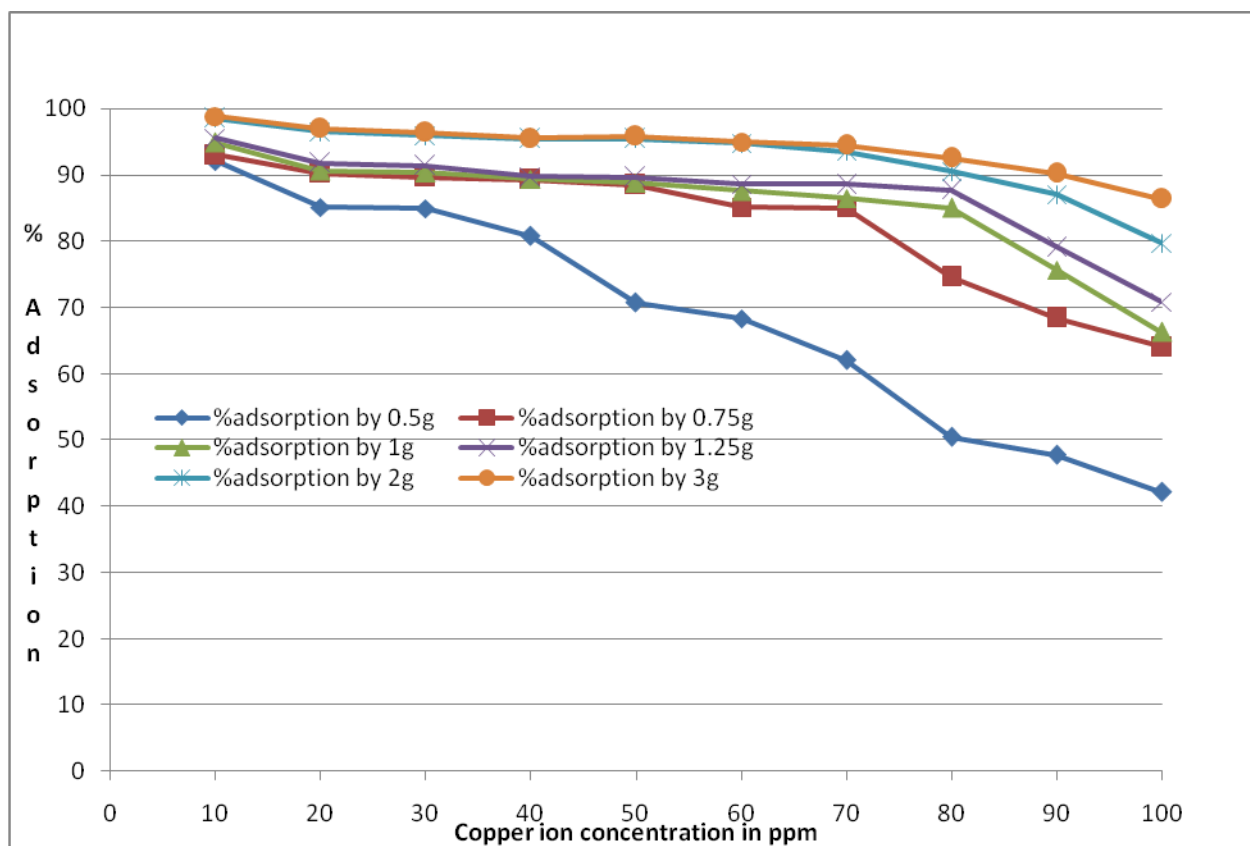
Figure 11: **Effect of initial adsorbate concentration on % copper adsorption using different quantities of *Luffa Cylindrica***

Concentration of metal ions in solution is an important factor when studying biosorption of metal ions in aqueous systems (Matheickal and Yu, 1999). From Figure 11, it is evident that %

40

adsorption was almost 100% with lower copper ion concentrations of the test solution. It is also observed that the % adsorption increased with increase in the weight of the biomaterial. This can be attributed to the fact that increased biomaterial quantity leads to increased number of sites available for adsorption. Each weight however, becomes a limiting factor with increased concentration of copper (II) ions in solution since the number of adsorptive sites remain the same and this explains the downward trend with increase in concentration. It is noted that with weights equal to or above 0.75g, upto nearly 50ppm Cu^{2+} ions in solution can be adsorbed to over 90% level. The higher the ratio of biomaterial to adsorbate concentration the greater the % adsorption of the Cu^{2+} ions in solution. This explains why the plot corresponding to 3g adsorbent shows the highest % adsorption across the entire spectrum of Cu^{2+} ions concentration range from 10ppm to 100ppm.

Langmuir theory postulates monolayer coverage. When q_{eq} i.e, the amount of metal ion sorbed at equilibrium per unit weight of adsorbent (mg/g) is plotted against concentration using 0.5g of biomaterial, the results shown in Figure 12 are obtained.
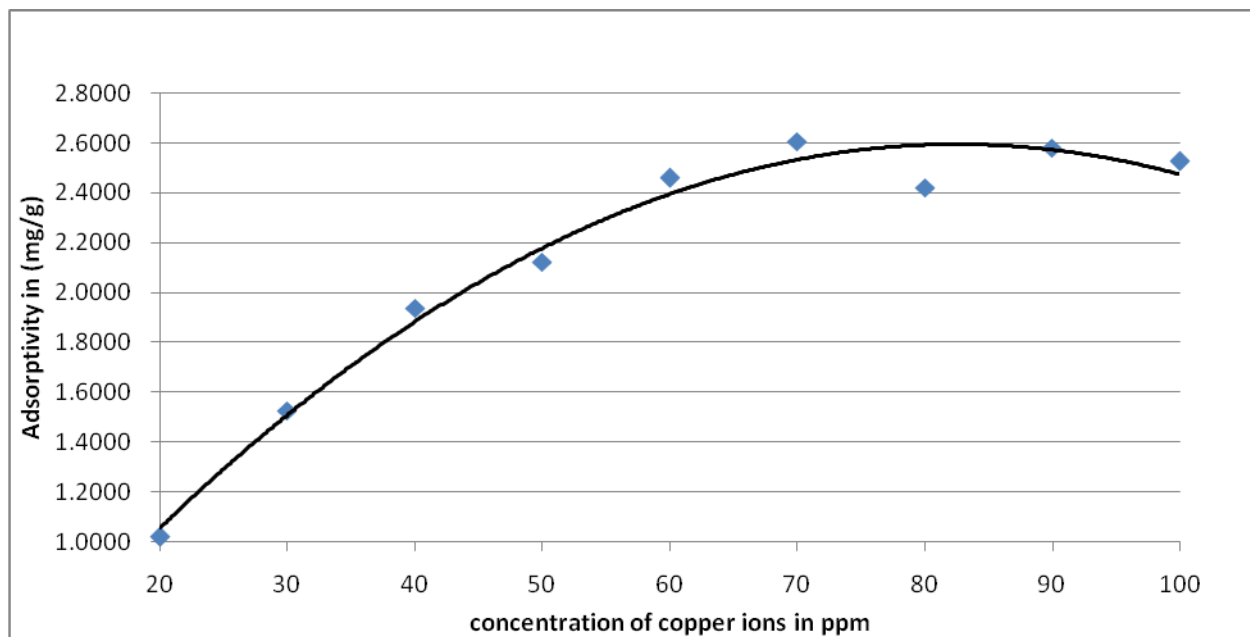
Figure 12: **plot of adsorptivity against initial concentration of Cu2+ ion using 0.5g biomaterial**

It is observed that the adsorption of Cu^{2+} ions per unit weight of adsorbent (mg/g) increases with increase in initial concentration of copper solution. However, after sometime the adsorption is not affected much by increase in concentration which means the surface is saturated and biomaterial weight becomes the limiting factor. This behaviour can be explained from the fact that there is increased metal ion-biosorbent interaction with increased metal ion concentration.

4.1.3   Effect of Temperature on Copper ion Adsorption

Initial temperature of the test solution plays some role in sorption processes. When weak Van der Waal forces of attraction exist between adsorbate and adsorbent, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent (Huck-Iriat *et al.*, 2016). Physical adsorption being an exothermic process occurs more readily at lower temperatures and decreases with increase in temperature (Le-Chatelier's Principle).

Chemisorption or chemical adsorption on the other hand occurs when the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. With the increases in temperature, Chemisorption first increases then decreases.

Table 5 shows how % adsorption of copper (II) ions is affected by changes in temperature. 50ppm copper solution was used with 0.5g of biomaterial.

Table 5: **Effect of temperature on % adsorption of 50ppm copper (II) ion solution by 0.5g of biomaterial**

Temperature in ^{0}C	Final concentration (ppm)	% adsorption	Standard deviation
30	14.414	71.17	±0.56
40	11.627	76.75	±0.89
50	11.217	77.57	±1.59
60	10.2745	79.45	±0.32
70	11.235	77.53	±0.58
80	11.592	76.82	±0.89

The results of Table 5 were then illustrated graphically as shown in Figure 13.
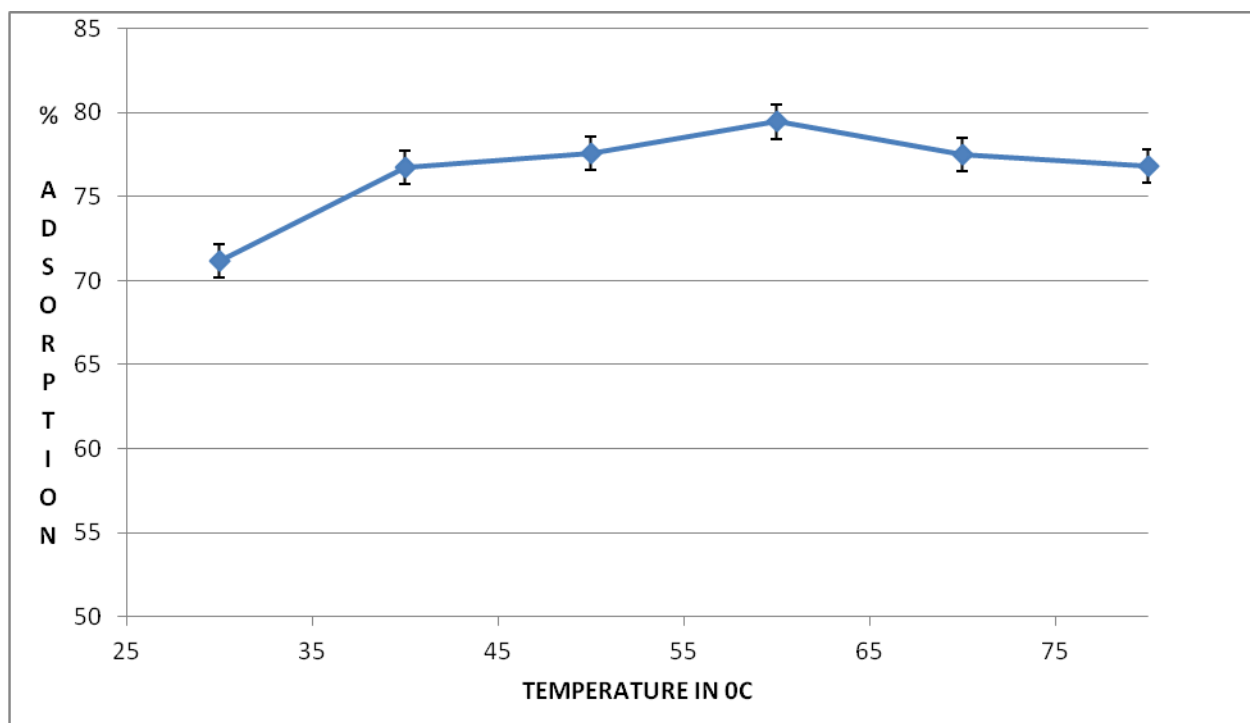
Figure 13: **Plot of % adsorption of copper (II) ions against temperature in ^{0}C**

It is evident from Figure 13 that the percentage adsorption was not affected much by increased temperatures. At higher temperatures beyond 60^0C, the adsorption decreased slightly and this could be attributed to desorption as vibrations and ionic movements increased causing the ions that had been adsorbed to be desorbed. This observation was also made by Aksu and Kutsa, (1991) who stated that molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures. Temperatures above 80^0C were avoided since there was a lot of evaporation. From the discussion in section 4.1.3, it can be said that the adsorption mechanism was partially physisorption and partially chemisorption.

4.1.4   Effect of pH on Copper ion Adsorption

Metal speciation in solution is pH dependent and thus, it was important to determine how pH changes affected the biosorption of copper (II) ions. The pH was adjusted using HCl and NaOH. Use of buffer solutions was avoided as this could have introduced many other ions which could have interfered with the adsorption process. The pH of 50ppm copper solution was found to be 4.45 at 25^oC. Table 6 shows how changes in pH affected percentage adsorption of copper (II) ions using 0.5g biomaterial. This is further illustrated in Figure 14.

Table 6:   Effect of pH of copper solution on % adsorption

$_pH$ value	Final concentration(ppm)	% Adsorption	Standard deviations
3.03	41.403	17.19	±1.76
3.33	31.058	37.88	±0.81
3.54	24.401	51.19	±1.26
4.45(no adjustment)	15.517	68.97	±3.21
5.10	11.319	77.20	±0.65
6.31	8.852	82.29	±0.23
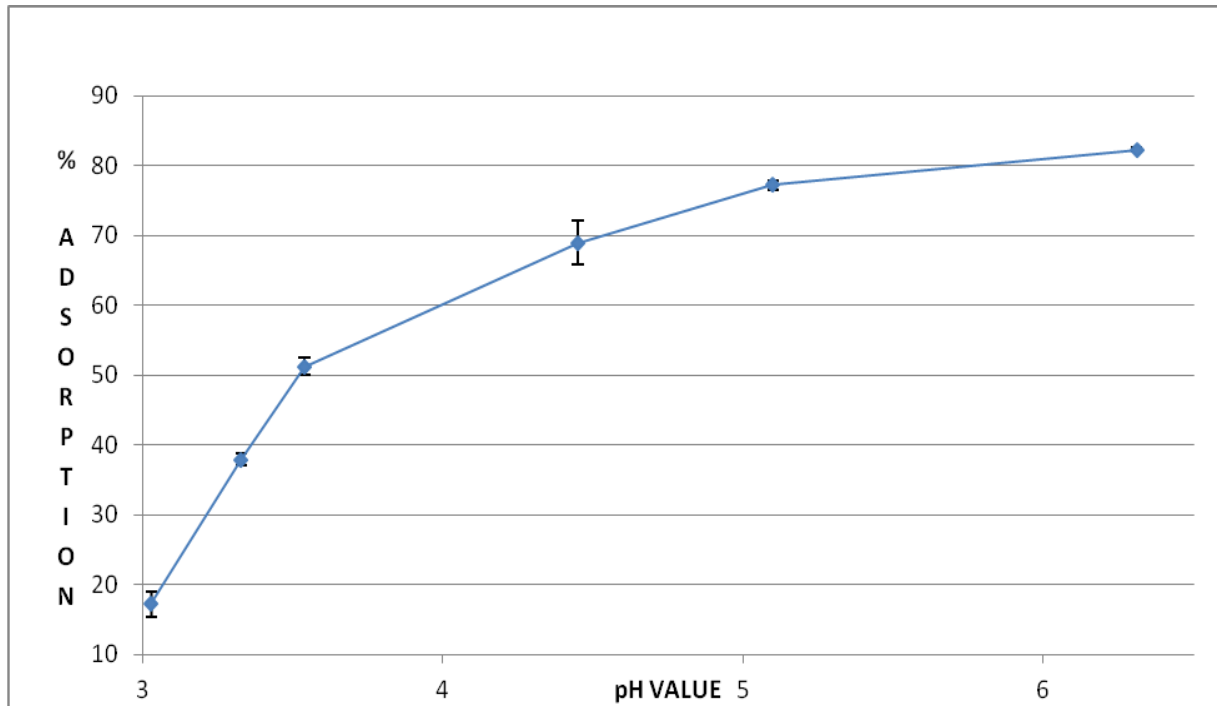
Figure 14:   Effect of pH on % adsorption of copper ions

There was a general increase in % adsorption with increase in pH.Addition of acid to the solution mixture decreases the pH of the solution which consequently caused a decrease in % adsorption. This can be attributed to the fact that at lower pH values, there are more H^+ ions in solution which competes with the Cu^{2+} ions in solution for adsorption sites. On the other hand, introduction of OH^- ions however, led to increased % adsorption and this could be attributed to the fact that the prescence of OH^- ions made the surface charge of the adsorbent to be more negative and this could have increased the electrostatic force of attraction between the biomaterial surface and Cu^{2+} ions hence increased adsorption. An increase in biosorption with increase in pH was also observed and explained by Luef *et al.* (1991) to result in increase in the negative charged group at the surface of the biomaterial. Increased adsorption with increase in pH can also be attributed to the possibility of increased deprotonation of some functional groups in the biomaterial and thereby creating more binding sites. Higher pH values above 7 precipitated copper and was therefore avoided.

4.1.5 Effect of Biomaterial Loading on % Copper (II) ion Adsorption

Biomaterial loading plays an important role in adsorption process as it determines the number of adsorptive sites available for adsorption. The effect of biomaterial loading on copper (II) ion adsorption was studied using biomaterial dosage in the range of 0.2g to 3.0g with 30ml portions of Cu^{2+} ions at different concentrations as shown in Table 7.

Table 7:   **Effect of biomaterial dosage on copper (II) ion adsorption**

Biomaterial dosage (grams)	50 ppm solution		30 ppm solution		25ppm solution		15ppm solution		10ppm solution	
	Final conc. (ppm)	% adsorption	Final conc. (ppm)	% adsorption	Final conc. (ppm)	% adsorption	Final conc. (ppm)	% adsorption	Final conc. (ppm)	% adsorption
0.2	36.22	27.6	13.15	56.2	10.92	59.2	3.647	75.9	1.725	82.76
0.3	26.58	46.9	9.654	67.8	6.631	73.5	2.923	80.5	1.357	86.43
0.4	20.26	59.5	6.296	79.0	4.618	81.5	2.404	85.0	0.988	90.11
0.5	15.09	69.8	4.601	84.7	3.611	85.6	1.558	89.6	0.791	92.09
0.6	7.288	85.4	3.623	87.9	2.798	88.8	1.384	90.8	0.731	92.69
0.7	6.264	87.8	3.232	89.2	2.480	90.1	1.299	91.3	0.702	93.0
0.8	5.711	88.6	3.102	89.7	2.278	90.9	1.198	92.0	0.630	93.7
0.9	5.612	88.8	2.965	90.1	2.165	91.3	1.063	92.9	0.541	94.6
1.0	5.516	89.0	2.877	90.4	2.057	91.8	1.016	93.2	0.473	95.3
1.1	5.239	89.5	2.469	91.8	1.711	93.2	0.938	93.7	0.442	95.6
1.3	3.741	92.5	2.147	92.8	1.538	93.9	0.816	94.6	0.367	96.3
1.5	3.613	92.8	1.700	94.3	1.308	94.8	0.724	95.2	0.314	96.9
1.7	3.273	93.5	1.578	94.7	1.208	95.2	0.545	96.4	0.253	97.5
2.0	2.252	95.5	1.206	96.0	0.997	96.0	0.499	96.7	0.187	98.1
2.2	1.978	96.1	1.089	96.4	0.808	96.8	0.327	97.8	0.210	97.9
2.5	2.013	96.0	1.035	96.6	0.658	97.4	0.283	98.1	0.166	98.3
3.0	2.061	95.9	1.059	96.5	0.647	97.4	0.245	98.4	0.199	98.0

Graphical representation of the data inTable 7 appears as shown below in Figure 15;
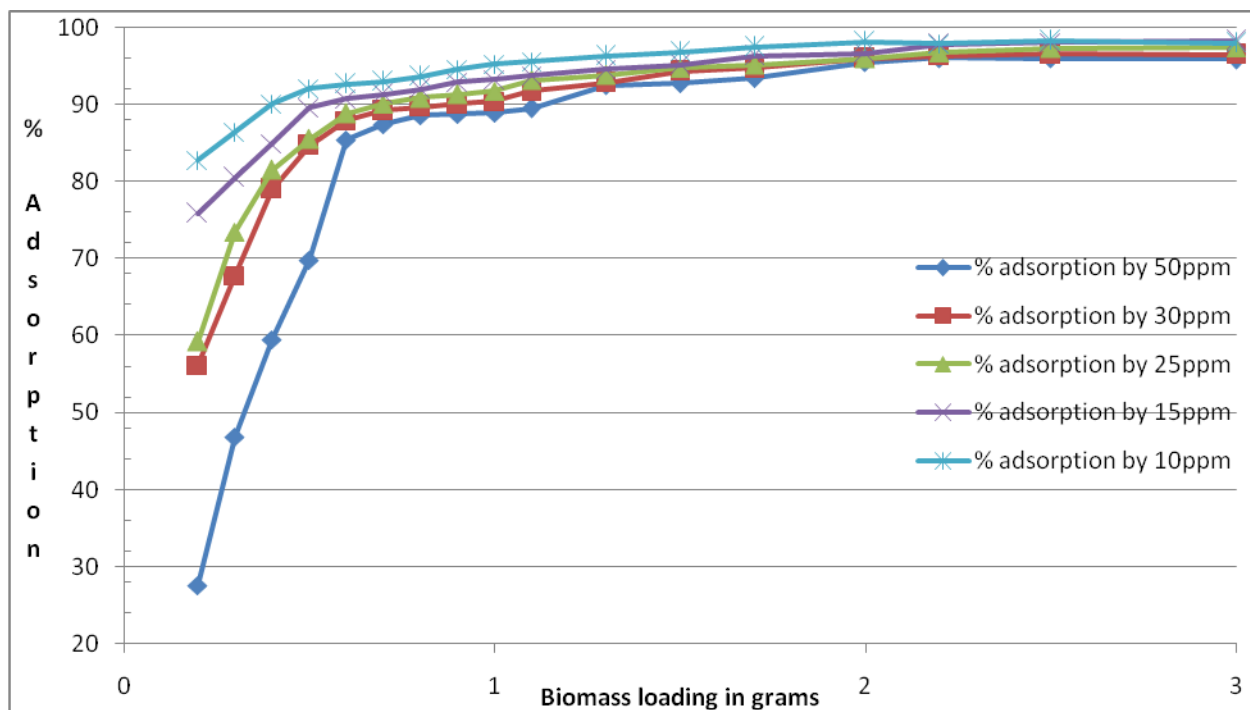
Figure 15: **Plot of % adsorption against biomaterial loading at different Cu^{2+} ion concentration**

There was an increase in % adsorption with increase in biomaterial weight and this can be attributed to the fact that increased biomaterial weight leads to increase in the number of adsorptive sites hence increased adsorption. Biomaterial weight beyond 1g showed only slight change in % adsorption and this can be attributed to the fact that such weights were able to adsorb almost all the copper (II) ions but there was also desorption taking place.There was no limiting factor and 3g almost adsorbed all the copper (II) ions in solution. On the other hand, increase in concentration of Cu^{2+} ions led to decrease in % adsorption. This could be attributed to the fact that increased concentration leads to increased competition for the adsorptive sites thus leading to decreased adsorption with lower weights of sorbent. 0.2g of biomaterial adsorbed about 83% of Cu^{2+} ions in 10ppm copper (II) ion solution while the same weight in 50ppm solution adsorbed only about 28% of the ions. However, when biomaterial weight ceases to be the limiting factor, % adsorption increases and almost reaches 100% irrespective of the concentration of Cu^{2+} ions present in solution.

The effect of biomaterial loading on adsorptivity of Cu^{2+} ions on *Luffa Cylindrica* was also studied and the results tabulated as shown in Table 8.

Table 8: **Effect of biomaterial dosage on copper adsorptivity at different concentrations**

Biomaterial dosage (grams)	Adsorptivity in 50ppm	Adsorptivity in 30ppm	Adsorptivity in 25ppm	Adsorptivity in 15ppm	Adsorptivity in 10ppm
0.2	2.067	2.528	2.112	1.703	1.241
0.3	2.342	2.035	1.837	1.208	0.864
0.4	2.231	1.778	1.529	0.945	0.676
0.5	2.095	1.524	1.283	0.807	0.553
0.6	2.136	1.319	1.110	0.681	0.463
0.7	1.874	1.147	0.965	0.587	0.398
0.8	1.661	1.009	0.852	0.518	0.351
0.9	1.480	0.901	0.761	0.465	0.315
1	1.335	0.814	0.688	0.420	0.286
1.1	1.221	0.751	0.635	0.384	0.261
1.3	1.068	0.643	0.541	0.327	0.222
1.5	0.928	0.566	0.474	0.286	0.194
1.7	0.825	0.502	0.420	0.255	0.172
2	0.716	0.432	0.360	0.218	0.147
2.2	0.655	0.394	0.330	0.200	0.134
2.5	0.576	0.348	0.292	0.177	0.118
3	0.479	0.289	0.244	0.148	0.098

The effect of biomaterial loading on adsorptivity was then represented graphically as shown in figure 16 below;
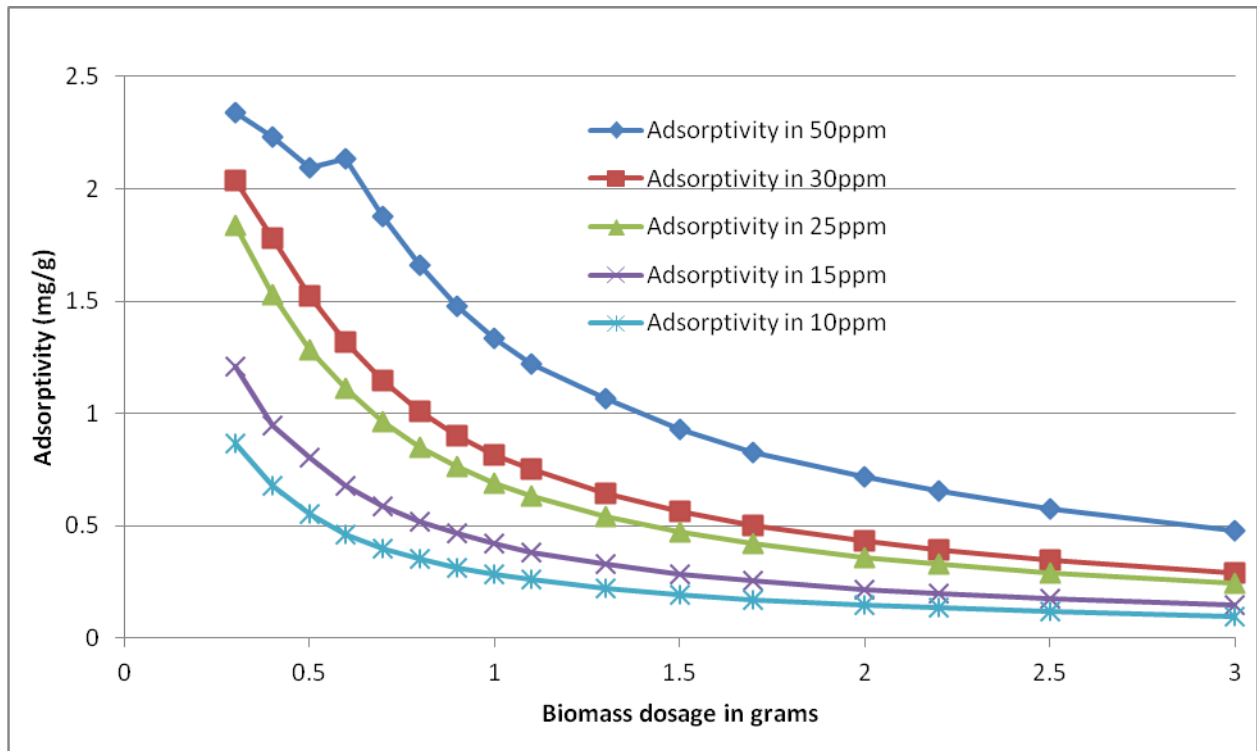
Figure 16: **A plot of copper adsorptivity against biomaterial loading at different Cu^{2+} ion concentrations**

From Figure 16, it is evident that adsortivity decreases with increase in biomaterial dosage. These results are consistent with findings of Potgiere et al., (2006); Low *et al*.,(2004); and Oyelude *et al*., (2017) who independently found that increasing the mass of an adsorbent does not result in subsequent increase in adsorptivity of the adsorbate. Adsorptivity is also found to increase with metal ion-sorbent interaction and this explains why 50ppm copper ion solution had higher adsorptivity values. The highest removal efficiency is therefore achieved with lowest possible amount of sorbent. However, at very low adsorbent loading overall percentage removal efficiencies are low.

4.2   Chromium Studies

4.2.1   *Effect of Particle Size and Contact Time on Chromium ion Adsorption*

Particle size determines the surface area of biomaterial available for adsorption thus plays a major role in adsorption. The particles were categorized as A,B and C where A represents particles with sizes less than 425um, B represents particles with sizes ranging between 425um and 710um and C represents particles with sizes ranging between 710um and 850um.The study was done using 20ppm chromium solution.Time of contact is also important since maximum sorption can only be achieved when sorbent-metal ion interaction is optimized. Tables 9, 10 and 11 shows % adsorption of Cr^{3+} ions by particle sizes A, B and C, respectively.

Table 9:   **Effect of contact time on % adsorption of 20ppm chromium ions on adsorbent of particle size A(< 425um).**

Time in minutes	Final concentration(ppm)	% adsorption	Standard Deviation
10	5.5609	72.20	±0.95
20	4.9787	75.12	±0.90
30	4.8225	75.89	±0.45
40	4.2875	78.56	±1.46
50	4.3751	78.12	±0.77
60	4.4958	77.52	±0.25
70	4.4106	77.95	±1.35
80	4.5384	77.31	±1.27

Table 10: Effect of contact time on % adsorption of 20ppm chromium ions on adsorbent of particle size B (>425um and < 710um).

Time in minutes	Final concentration(ppm)	% adsorption	Standard Deviation
10	7.0569	64.72	±0.89
20	5.1491	74.25	±1.96
30	5.1490	74.26	±0.70
40	5.1349	74.32	±1.36
50	5.0639	74.68	±0.30
60	5.0781	74.61	±1.46
70	4.8793	75.6	±0.60
80	4.9645	75.18	±1.19

Table 11: Effect of contact time on % adsorption of 20ppm chromium ions on adsorbent of particle size C (>710um and < 850um)

Time in minutes	Final concentration(ppm)	% adsorption	Standard Deviation
10	8.3875	58.06	±0.41
20	7.9610	60.19	±1.84
30	6.3989	68.01	±0.93
40	5.6888	71.56	±1.58
50	5.4047	72.98	±0.88
60	5.3479	73.26	±1.56
70	5.0923	74.54	±0.80
80	5.0647	74.68	±0.78

The effect of particle size of the biosorbent and time of contact on adsorption of Cr^{3+} ions from 20ppm chromium (III) ions solution is represented graphically as shown in figure 17;
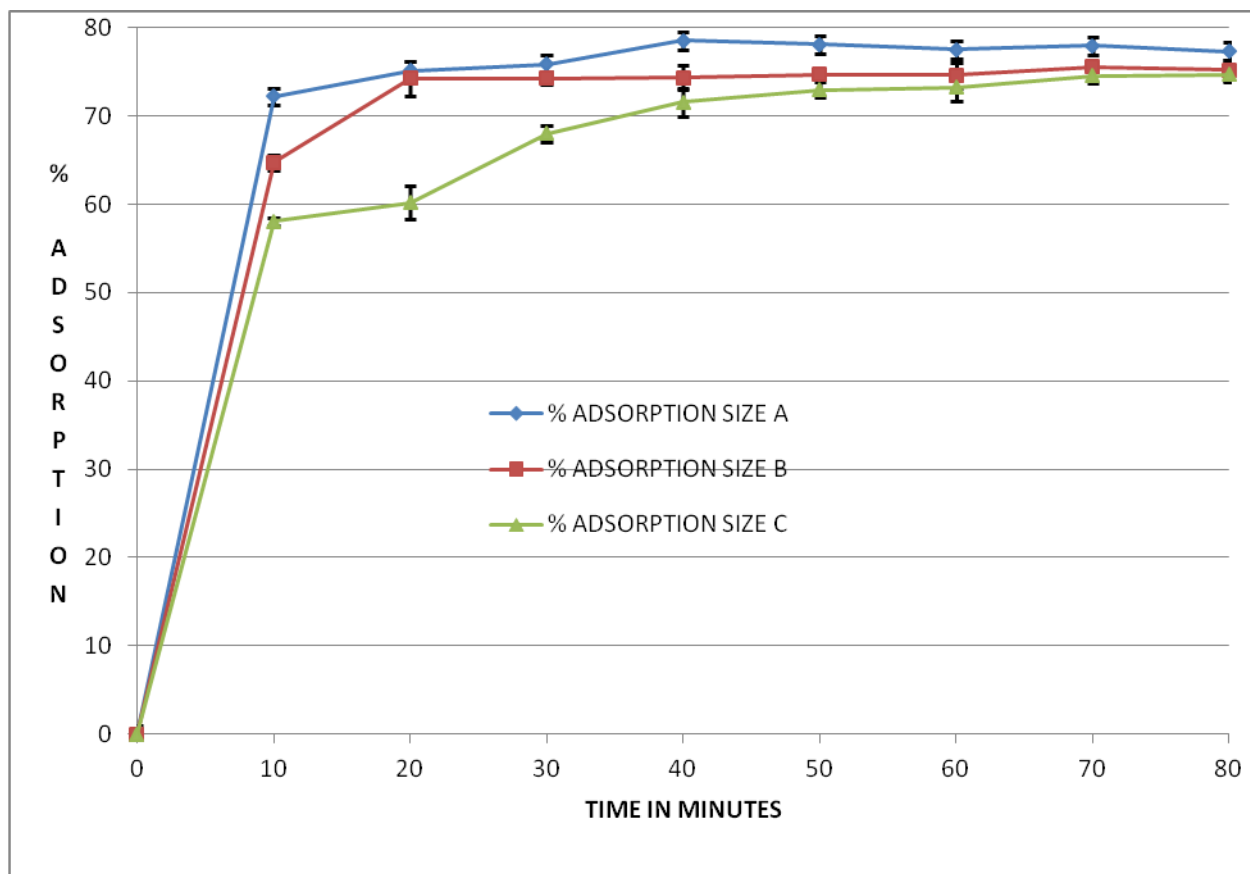
Figure 17: **Plot of % adsorption of 20ppm chromium ions against time for different particle sizes of 0.5g *Luffa Cylindrica***

There was a very high rate of uptake of chromium ions in the first 10 minutes with particle size A showing the highest followed by B and finally C. After 20 minutes, the adsorption was almost complete for all the three particle sizes; which means that there was no more binding sites available for adsorption to take place. The initial rapid uptake within the first 20 minutes was likely due to availability of more binding sites, but after saturation the adsorption was minimal. This therefore means that the weight of the biomaterial was the limiting factor. Higher adsorption percentages were observed with the smaller particle size A.This is attributed to increased surface area. In these studies, the % adsorption never exceeded 80%. This could be

attributed to the lower dosage used (i.e, 0.5g); hence the limiting component in this adsorption process. Particle size A was then used in all further adsorption experiments.

4.2.2 *Effect of Biomaterial Dosage on % Chromium ion Adsorption*

The amount of biomaterial used in adsorption is a major factor to be considerd in adsorption experiments since it determines the number of adsorptive sites available and it also determines the suitability for industrial use of the material in wastewater treatment. Biomaterial weight ranging between 0.3g to 3g was used with different concentrations of chromium ions as indicated in table 12.

Table 12:   Effect of biomaterial dosage on chromium adsorption

Biomaterial dosage (grams)	50 ppm solution		30 ppm solution		25ppm solution		15ppm solution		10ppm solution		5ppm solution	
	Final conc.	% adsorption	Final conc.	% adsorption	Final conc.	% adsorption	Final conc.	% adsorption	Final conc.	% adsorption	Final conc.	% adsorption
0.3	31.662	36.67	13.584	54.72	9.9155	60.34	3.8501	74.33	1.7826	82.17	0.2339	95.32
0.4	29.623	40.75	11.456	61.81	8.1392	67.443	2.9682	80.21	1.3689	86.31	0.1559	96.88
0.5	28.523	42.95	10.378	65.41	7.4047	70.38	2.3171	84.55	0.9230	90.77	0.1384	97.23
0.8	19.417	61.17	3.7071	87.64	3.0950	87.62	1.6943	88.71	0.8870	91.11	0.1223	97.55
1.1	13.979	72.04	3.3537	88.82	2.6418	89.43	1.4187	90.54	0.7935	92.07	0.1208	97.58
1.4	9.7350	80.53	2.7084	90.97	1.8893	92.44	1.0976	92.68	0.7018	92.98	0.1010	97.98
1.7	8.5811	82.84	2.3754	92.08	1.7233	93.11	0.8677	94.22	0.5457	94.54	0.0934	98.13
2.0	7.6130	84.77	2.2050	92.65	1.5322	93.87	0.7714	94.86	0.4544	95.46	0.0794	98.41
2.2	4.315	91.37	1.6686	94.44	1.3320	94.67	0.6659	95.56	0.3228	96.77	0.1141	97.71
2.5	3.8078	92.38	1.3872	95.37	1.0815	95.67	0.6596	95.60	0.2648	97.35	0.0664	98.67
3.0	3.0859	93.83	1.2351	95.88	1.0970	95.61	0.5004	96.66	0.2794	97.21	0.0727	98.55

Figure 18 shows the effect of biomaterial dosage on % adsorption of chromium ions at different concentrations
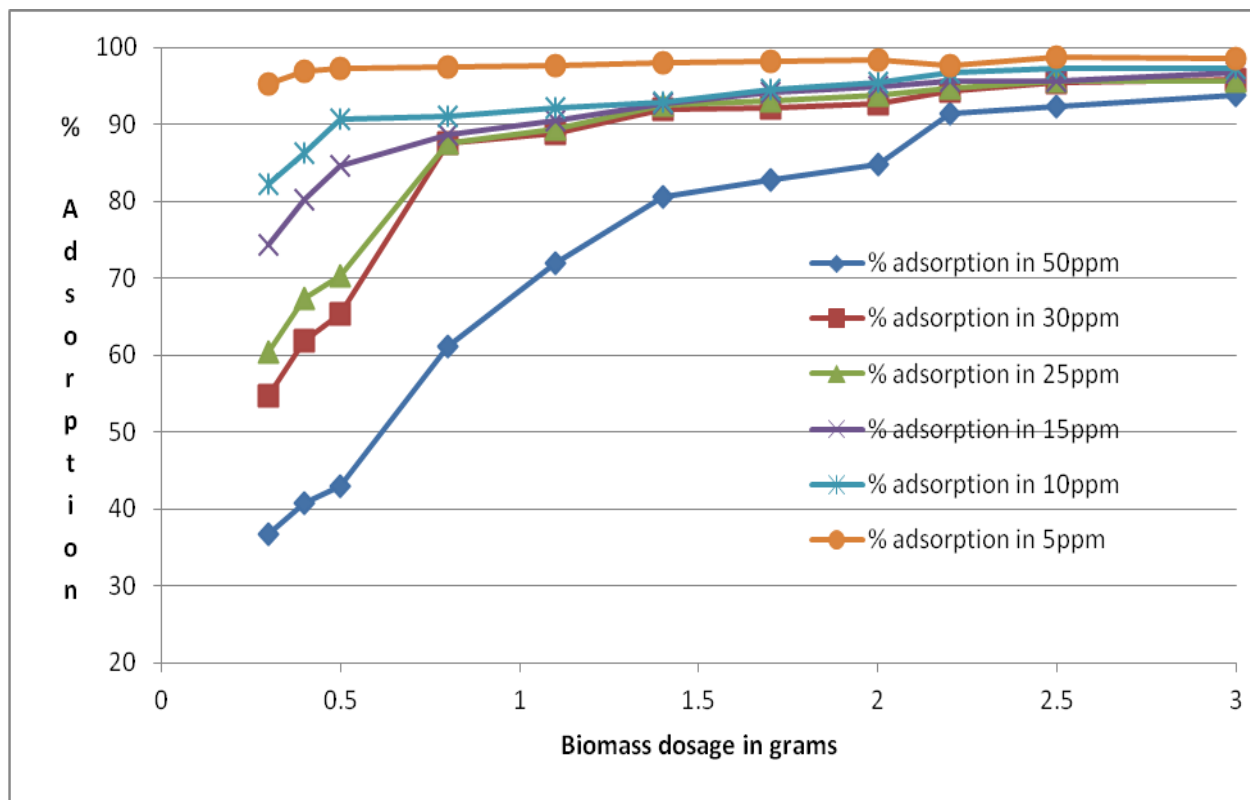
Figure 18: **Plot of % adsorption against biomaterial loading at different Cr^{3+} ion concentration**

From the figure, it is clear that % adsorption increases with increase in biomaterial dosage and this is attributable to increase in the number of adsorptive sites. However, after sometime the % adsorption was almost constant implying surface saturation. 5ppm chromium ion solution showed over 95% adsorption even at low biomaterial dosage of 0.3g while the same biomaterial weight adsorbed only about 36% of chromium ions from 50ppm solution.This means that the higher the biomaterial dosage:chromium ion concentration ratio, the better the interaction and the higher the adsorption. The adsorptivity (mg/g) was calculated for each biomaterial weight for different concentrations of chromium ions and the results are as indicated in Table 13.

Table 13: **Effect of biomaterial dosage on chromium adsorptivity at different concentrations**

Biomaterial dosage in grams	Adsorptivity in 50ppm (mg/g)	Adsorptivity in 30ppm (mg/g)	Adsorptivity in 25ppm (mg/g)	Adsorptivity in 15ppm (mg/g)	Adsorptivity in 10ppm (mg/g)	Adsorptivity in 5ppm (mg/g)
0.3	1.834	1.642	1.508	1.115	0.822	0.477
0.4	1.528	1.391	1.265	0.902	0.647	0.363
0.5	1.289	1.177	1.056	0.761	0.545	0.292
0.8	1.147	0.986	0.821	0.499	0.342	0.183
1.1	0.982	0.727	0.610	0.370	0.251	0.133
1.4	0.863	0.585	0.495	0.298	0.199	0.105
1.7	0.731	0.487	0.411	0.249	0.167	0.087
2	0.636	0.417	0.352	0.213	0.143	0.074
2.2	0.623	0.386	0.323	0.195	0.132	0.067
2.5	0.554	0.343	0.287	0.172	0.117	0.059
3	0.469	0.288	0.239	0.145	0.097	0.049

Figure 19 shows how adsorptivity varies with biomaterial dosage for different concentrations of chromium ions.
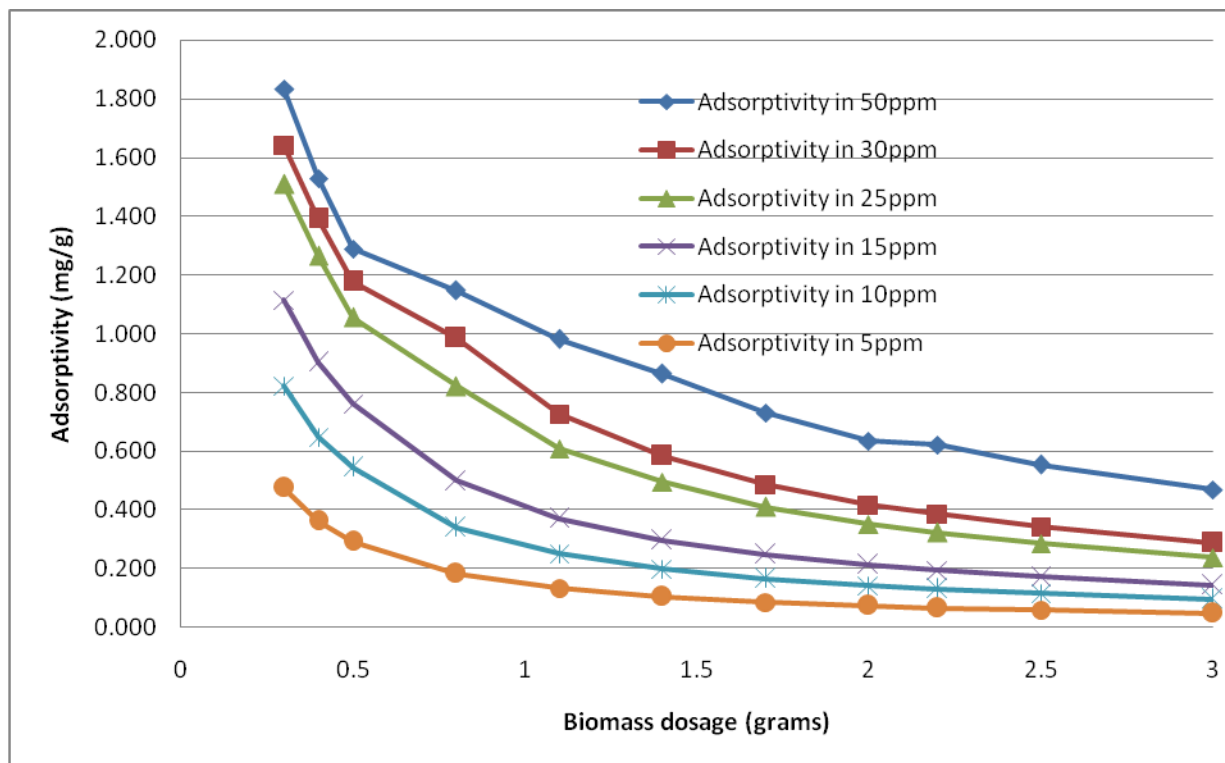
Figure 19:   Plot of chromium ion adsorptivity against biomaterial dosage for different Cr^{3+} ion concentrations.

As observed in the case of copper, adsorptivity decreases with increase in the weight of the biomaterial but increases with increase in concentration.Higher concentrations implies better interaction between metal ion and the sorbent hence higher adsorptivity.

4.2.3   Effect of pH on Chromium ion Adsorption

Solution pH plays an important role in biosorption as it affects the surface charge of the adsorbent.The dissociation of various functional groups on the active sites as well as the degree of ionization are also affected by pH (Wawrzkiewicz and Hubicki, 2009) . In this study, 25ppm chromium solution was used with 0.5g biomaterial. The pH of the 25ppm chromium solution was found to be 3.86 and adjusted to 2.38,2.86,3.30 with 0.1M HCl and to 4.50 and 5.87 higher values with 0.1M NaOH. The results are indicated in the Table 14.

Table 14:   **Effect of pH on chromium ion adsorption**

Initial pH	Final Cr^{3+} concentration In solution (ppm)	% Adsorption	Standard Deviation
2.38	20.238	19.05	±2.34
2.86	15.599	37.61	±0.92
3.30	10.293	58.83	±0.28
3.86(no adjustment)	7.2892	70.84	±0.28
4.5	3.2826	86.87	±0.50
5.87	1.3399	94.64	±0.62

The tabulated results are illustrated graphically as shown in Figure 20 below;
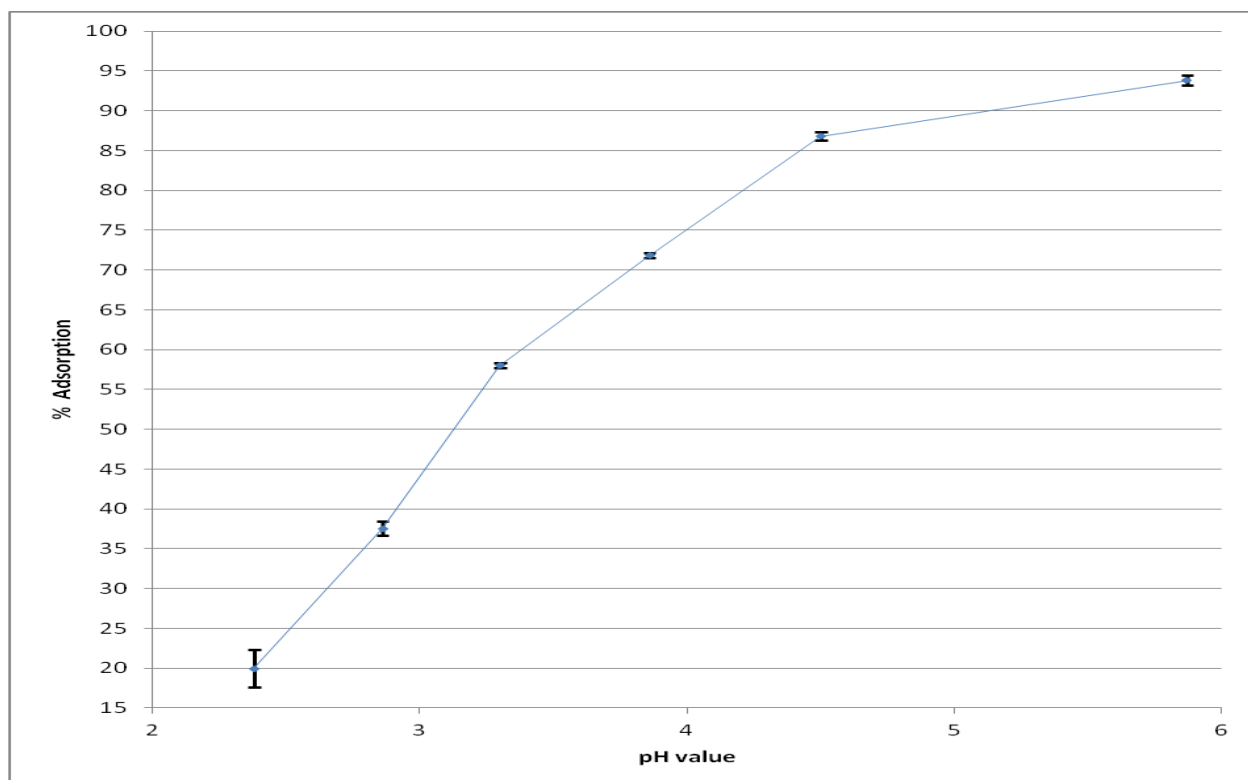
Figure 20:   **Effect of pH on % adsorption of 25ppm chromium ions by 0.5g *Luffa Cylindrica***

There was a general increase in % adsorption with increase in pH. As stated earlier in the case of Cu^{2+} ion, addition of acid introduces H^+ ions into the solution which competes with Cr^{3+} ions for the adsorption sites, hence the decreased % adsorption at much lower pH values. Low efficiency in biosorption of lead at low pH values was also observed by (Krishnan and Anirudhan, 2003) and they attributed it to large amounts of H^+ ions which compete for the adsorption sites. Addition of sodium hydroxide however, led to increased adsorption and this could be attributed to the fact that the OH^- ions starts getting sorbed on the biomaterial surface increasing the negative surface charge hence increased attraction of Cr^{3+} to the surface of the biomaterial. Increased adsorption with increase in pH can also be attributed to possibility of increased deprotonation. An increase in biosorption with pH was explained by (Luef *et al.,* 1991) to be due to an increase in negatively charged groups at the surface of the microbial cells. pH values higher than 6.5 precipitated chromium ions and was therefore not used in this study.

4.2.4 *Effect of Temperature on Adsorption of Chromium ions*

Temperature affects kinetic energy which in turn affects movement of particles. As such, it is an important parameter to be considered in adsorption. Effect of temperature was studied using 0.5g biomaterial with 25ppm chromium ion solution at temperatures indicated in Table 15 below.

Table 15:   Effect of temperature change on adsorption of chromium

Temperature in ^0C	Final Cr^{3+} Concentration in solution	%Adsorption	% Standard deviation
30	7.3548	70.5848	±0.24
40	7.14385	71.4248	±0.90
50	5.67435	77.3026	±1.02
60	3.7237	85.1052	±0.37
70	3.8738	84.5048	±0.02
80	4.57535	81.6986	±0.55

Figure 21 shows how % adsorption changed with increase in temperature.
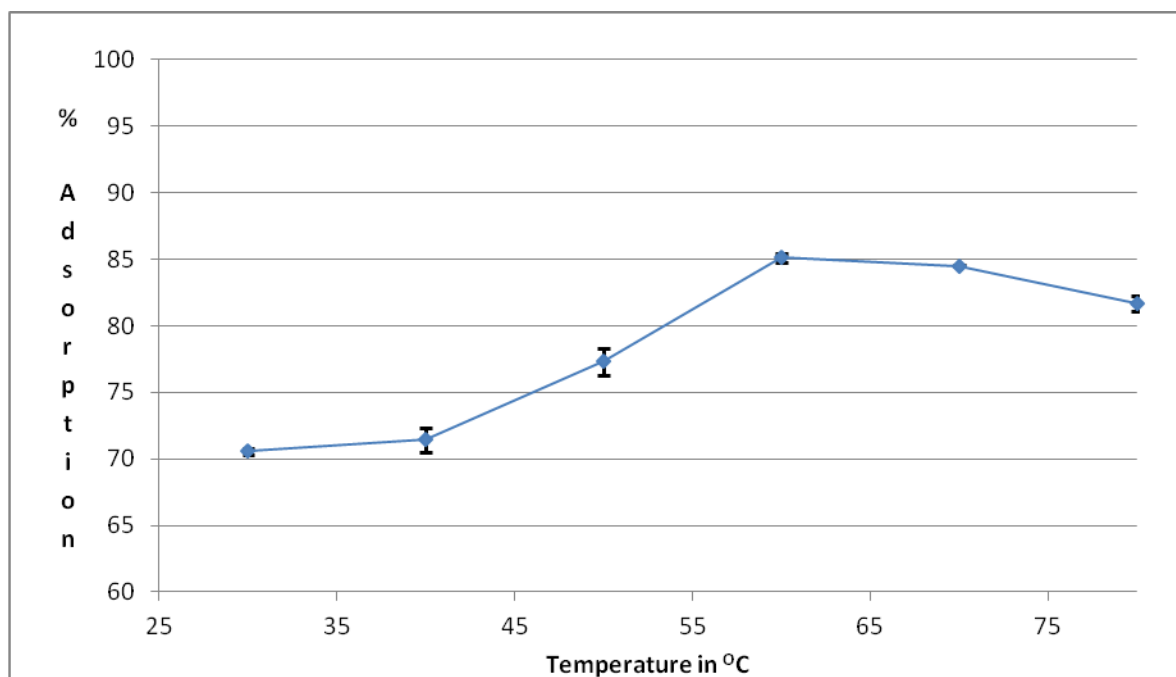
Figure 21: **Effect of temperature on % adsorption of 25ppm chromium using 0.5g biomaterial.**

The percentage adsorption generally increased with increase in temperature upto a maximum % adsorption at about 60^oC; beyond which the % adsorption started to reduce. This could be attributed to the fact that increased temperature increased the kinetic energy of the ions hence increasing their movement and consequently adsorption as the rate of bombardment increased. Higher temperatures might also have led to dissociation of some functional groups in the biomaterial leading to increased number of binding sites hence increased adsorption. At higher temperatures beyond 60^oC, the % adsorption decreased and this could have been due to desorption as vibrations of the bonds between adsorbate and adsorptive sites increased and ionic movements increased causing the ions that had been adsorbed to be desorbed.

4.2.5 Effect of Concentration on Chromium ion Adsorption

A particular quantity of adsorbent can only adsorb a given amount of adsorbate. This therefore means that initial concentration of the adsorbate in solution is an important parameter in

adsorption experiments. This study was done using different concentrations of Cr^{3+} ions in the test solution and different quantities of biomaterial as indicated Table 16.

Table 16:   Effect of concentration of chromium ions on % adsorption

Concentration of chromium (ppm)	Biomass weight (grams)	Final chromium ion conc. (ppm)	% adsorption
5	0.50	0.13845	97.23
	0.75	0.1305	97.39
	1.00	0.1311	97.37
	1.25	0.10335	97.93
	2.00	0.0889	98.22
	3.00	0.0585	98.83
10	0.5	0.9688	90.31
	0.75	0.9073	90.93
	1.00	0.9006	90.99
	1.25	0.8456	92.54
	2.00	0.4232	95.77
	3.00	0.3124	96.88
15	0.50	2.33025	84.46
	0.75	1.7200	88.53
	1.00	1.48215	90.12
	1.25	1.1886	92.08
	2.00	0.8592	94.27
	3.00	0.5534	96.31

Concentration of chromium (ppm)	Biomass weight (grams)	Final chromium ion conc. (ppm)	% adsorption
20	0.50	4.3544	78.23
	0.75	2.4746	87.63
	1.00	2.1950	89.03
	1.25	1.6032	91.98
	2.00	1.2152	93.92
	3	0.7988	96.01
25	0.5	7.3713	70.51
	0.75	3.1244	87.50
	1	2.70635	89.17
	1.25	2.06975	91.72
	2	1.5293	93.88
	3	1.1658	95.34
30	0.5	10.3305	65.56
	0.75	3.83375	87.22
	1.00	3.3225	88.93
	1.25	2.5331	91.55
	2.00	2.2611	92.46
	3.00	1.4663	95.11
35	0.50	14.518	58.52
	0.75	4.5606	86.97
	1.00	4.1213	88.23

Concentration of chromium (ppm)	Biomass weight (grams)	Final chromium ion conc. (ppm)	% adsorption
	1.25	3.3635	90.39
	2.00	3.0287	91.35
	3.00	1.7035	95.13
40	0.50	17.289	56.78
	0.75	6.6236	83.44
	1.00	5.06935	87.33
	1.25	4.1120	89.72
	2.00	3.6476	90.88
	3.00	2.2334	94.42
45	0.50	21.8135	51.53
	0.75	10.493	76.68
	1.00	8.20595	81.76
	1.25	4.7159	89.52
	2.00	4.3781	90.27
	3.00	2.757	93.87
50	0.50	28.685	42.63
	0.75	18.048	57.79
	1.00	14.098	71.80
	1.25	5.3449	89.31
	2.00	7.2785	85.44
	3.00	3.2300	93.54

The tabulated results were further represented graphically as in Figure 22.
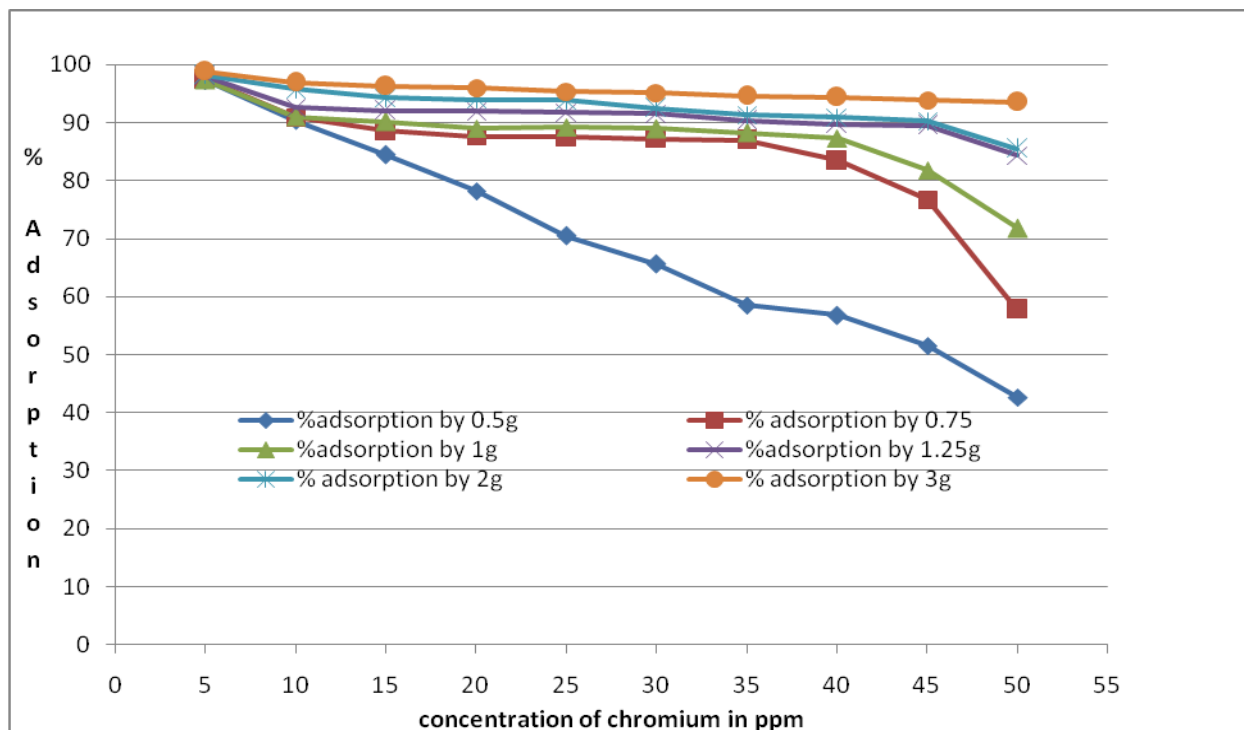
Figure 22:   A plot of % Adsorption against concentration of chromium ions using different weights of Luffa Cylindrica.

The percentage adsorption decreased with increase in chromium ion concentration. Biomaterial weight of 0.5g showed very low adsorption percentages while 3g showed highest adsorption percentages. This can be attributed to the low biomaterial weight : chromium ion concentration ratio in the case of 0.5g and high ratios in the case of 3g of biomaterial weight. The amount of chromium ions in mg adsorbed by 1g of the biomaterial was also plotted against the concentration of chromium ion as shown in Figure 23.
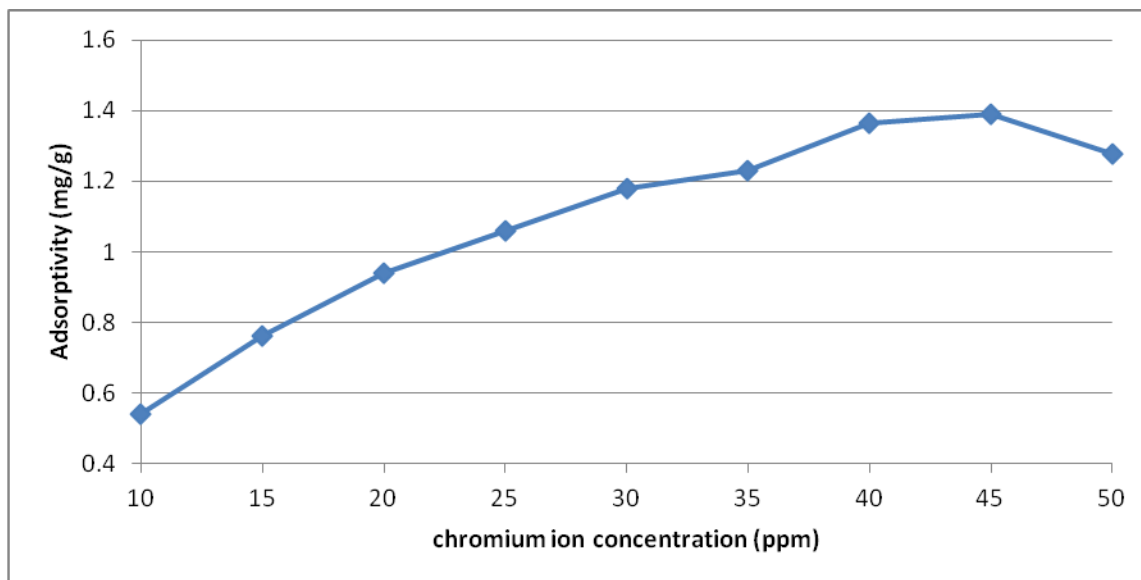
Figure 23:   plot of Chromium ion adsorptivity against initial concentration of Cr^{3+} ion using 0.5g biomaterial

It is observed that amount of Cr^{3+} ions adsorbed per unit weight of the biomaterial increases with increase in initial concentration of chromium ion solution upto a maximum. However, after sometime the change is minimal implying the surface is already saturated or nearly saturated. This increase can be attributed to increase in metal ion-biosorbent interaction.

4.3   Desorption Studies

The ability of an adsorbent to be reused is an important characteristic as this could save on material cost when applied on large scale. Various reagents have been used in desorption studies and in this study the desorption of copper and chromium ions was done using 0.1M HCl, 0.1M H_2SO_4 and 0.1M EDTA separately.

4.3.1   Copper Desorption Studies

Adsorbed copper (II) ions from spent biomaterial was removed using 0.1M H_2SO_4, 0.1M HCl and 0.1M EDTA, separately. This was done by using 0.75g of biomaterial that was previously used in the study of the effect of concentration of copper (II) ions on adsorption.

The concentrations of the desorbing agents was also varied and its effect on desorption analysed.

4.3.1.1 Desorption of copper (II) ions from 0.75g of spent biomaterial

0.75g of spent biomaterial previously used in studying the effect of concentration on adsorption of copper was regenerated using 50ml of each desorbant and the results tabulated as indicated in Table 17

Table 17:   Desorption of copper ions using 0.1M HCl, 0,1M H2SO4 and 0.1M EDTA

Initial concentration in ppm	Amount adsorbed in ppm	Amount desorbed by HCl in ppm	% Desorption	Amount desorbed by H_2SO_4 ppm	% Desorption	Amount desorbed by EDTA in ppm	% Desorption
10	9.3023	7.4716	80.32±1.10	7.6934	82.71±0.57	7.1489	76.85±1.30
20	18.0618	14.062	77.85±0.29	14.522	80.40±0.79	13.684	75.76±1.34
30	26.8913	20.0245	74.53±3.94	21.1725	78.74±1.30	19.9225	74.09±0.22
40	35.7189	24.449	68.45±0.73	24.714	69.19±2.01	23.6415	66.19±1.21
50	44.2689	29.3335	66.26±0.67	29.830	67.38±0.66	29.158	65.87±1.06
60	51.0800	33.312	65.22±0.26	33.9535	66.47±1.26	32.609	63.84±1.02
70	59.5320	37.617	63.19±0.57	38.286	64.31±0.14	37.016	62.18±0.43
80	59.731	37.503	63.55±0.86	37.959	63.55±1.14	36.328	60.84±0.03
90	61.622	38.1600	61.30±0.69	38.579	62.61±0.48	36.309	58.92±0.84
100	64.044	38.965	60.84±0.97	39.287	61.34±1.24	35.901	56.06±1.71

The % desorption of copper ions was then plotted against the concentration of Cu^{2+} ions initially adsorbed on 0.75g spent *Luffa Cylindrica* as shown in Figure 24 .
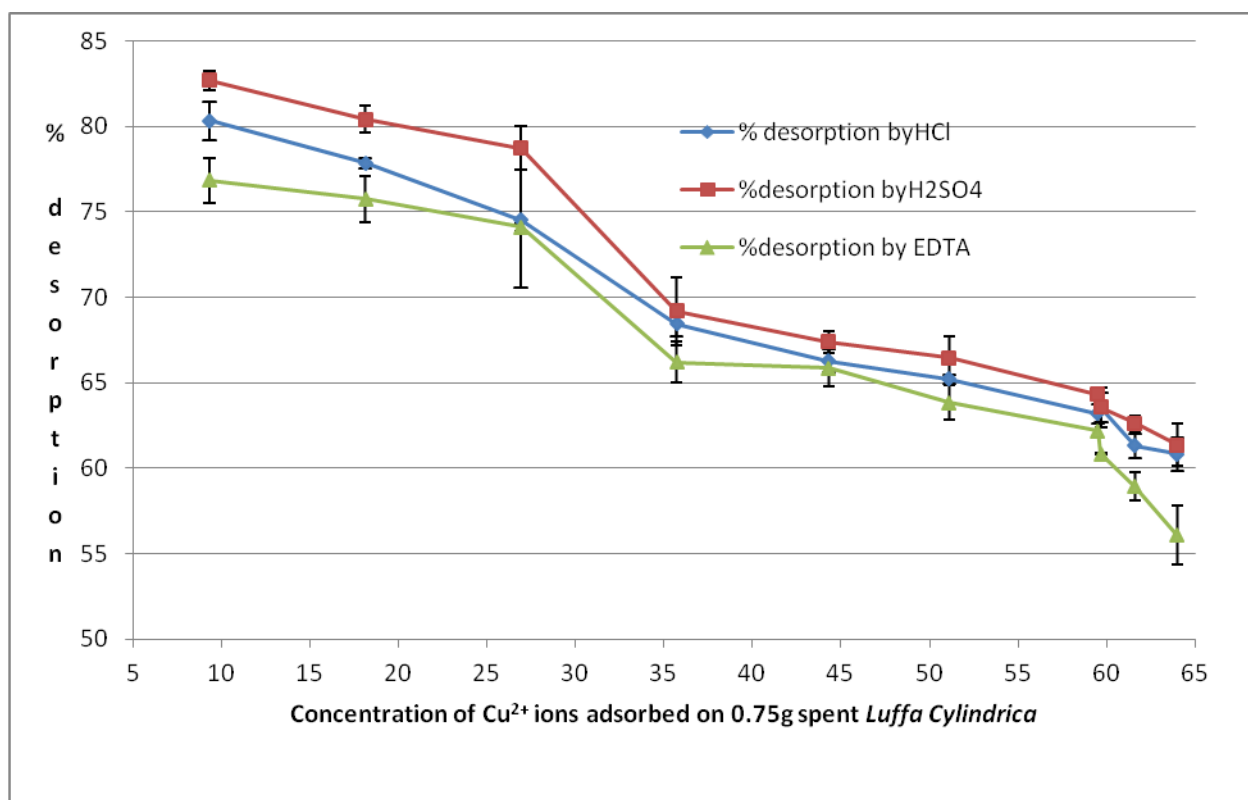
Figure 24: **% Desorption of Cu^{2+} ions adsorbed on 0.75g of spent Luffa Cylindrica by 50ml portions of HCl, H$_2$SO$_4$ and EDTA**

From Figure 24, it is evident that the higher the amount of copper previously adsorbed on the adsorbent, the lower the % desorption realized for a given desorption agent concentration employed. This could imply that the mechanism of adsorption of Cu^{2+} onto *Luffa Cylindrica* is both physical and chemical with chemisorptions being the most prevalent. Sulphuric acid gave higher desorption percentages followed by hydrochloric acid and finally EDTA. The percentage desorptions were however, very close to each other with the two acids giving almost same values. It is likely that the two acids caused the desorption by ion exchange and H$_2$SO$_4$ having two replaceable hydrogen ions per mole was able to perform better. EDTA may have chelated with the already adsorbed copper ions on the surface of the biomaterial and hence gave the lowest recovery of copper.

4.3.1.2 Effect of Concentration of H_2SO_4, HCl and EDTA on desorption of Copper (II) ions from spent biomaterial.

The 2g portion of biomaterial previously soaked in copper ion solution, ashed, digested with HCl and topped to 100ml in 100ml volumetric flask (see section 3.7.7.2) gave a reading of 14.44ppm (14.44mg of copper in one litre of the solution). 0.5g of the biomaterial used therefore contains 0.361mg Cu^{2+}.Table 18 shows desorption by H_2SO_4, HCl and EDTA at different concentrations.

Table 18:   Effect of Concentration of H_2SO_4, HCl and EDTA on Copper Desorption

Concentration of the desorbing agent in moles per litre	Desorption by HCl		Desorption by H_2SO_4		Desorption by EDTA	
	Amount desorbed in mg	% desorption	Amount desorbed in mg	% desorption	Amount desorbed in mg	% desorption
0.01	0.1626	45.17	0.2076	57.66	0.1679	46.63
0.02	0.1979	54.96	0.2186	60.71	0.1694	47.06
0.03	0.2114	58.71	0.2199	61.08	0.1695	47.08
0.05	0.2087	57.96	0.2240	61.29	0.1737	48.25
0.08	0.2138	59.38	0.2246	62.37	0.1794	49.83
0.1	0.2283	63.42	0.2330	64.71	0.1773	49.25

The tabulated results were further illustrated graphically as shown in Figure 25 below.
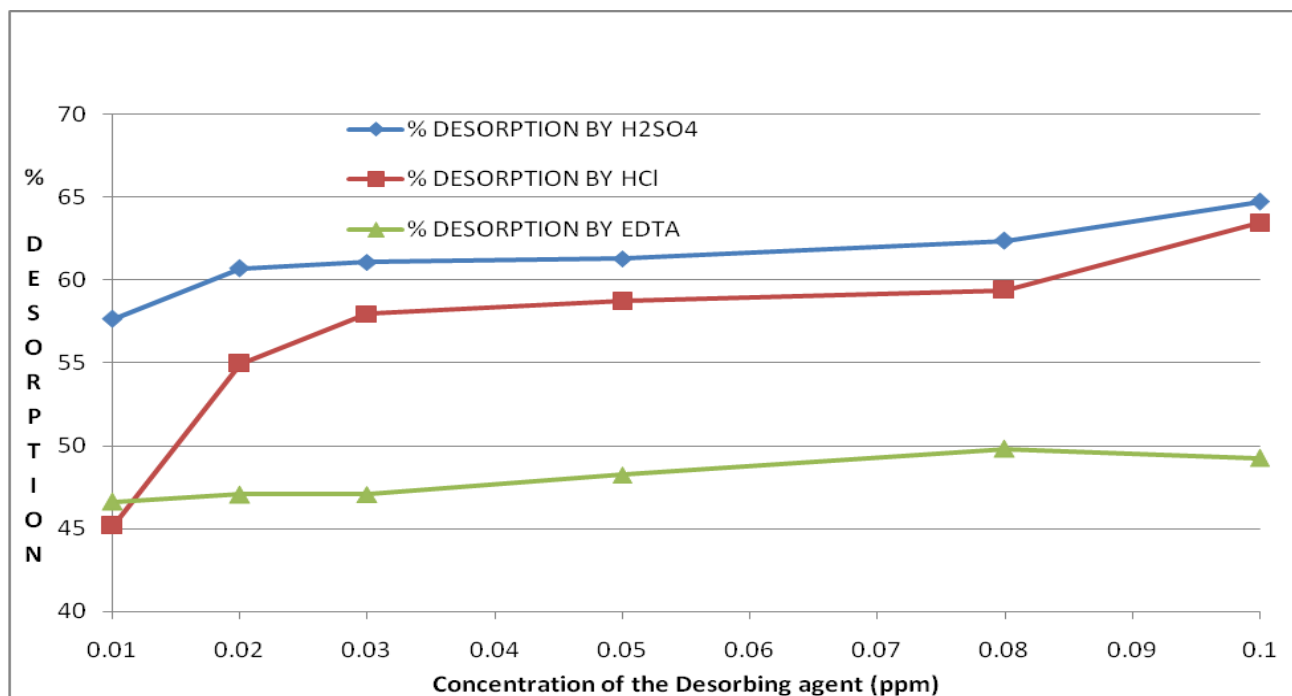
Figure 25: **Effect of concentration of H₂SO₄, HCl and EDTA on % desorption of Cu²⁺ ions**

H$_2$SO$_4$ showed greater capability in desorbing copper from the used biomaterial followed by HCl and finally EDTA. In all the three cases, % desorption was found to increase only slightly with increase in concentration of the desorbing agent with EDTA showing nearly no change at all even as the concentration is changed. H$_2$SO$_4$ and HCl likely desorbed by ion exchange. Desorption by H$_2$SO$_4$ was slightly better than that of HCl, however the % adsorptions were almost equal at concentration of 0.1M. The % desorption was lowest with EDTA and this could be due to the fact that EDTA is chelating with the already adsorbed copper ions on the adsorbent surface without removing most of the ions from the surface into the solution.

4.3.2   Chromium Desorption studies

Like copper, chromium ions were desorbed from spent biomaterial using 0.1M HCl, 0.1M H_2SO_4 and 0.1M EDTA, separately.   The effect of concentration of these three reagents in desorption of chromium ions was also studied and the results shown in the subsequent sections.

4.3.2.1.   Desorption of Chromium ions from 0.75g of spent biomaterial using 0.1M HCl, 0.1M H_2SO_4 and 0.1M EDTA, separately.

0.75g of spent biomaterial that was used in the study of effect of concentration on chromium was subjected to desorption studies using 50ml portions of 0.1M HCl, 0.1M H_2SO_4 and 0.1M EDTA, separately.The results are shown in Table 19 below.

Table 19:   Desorption of chromium using HCl, H_2SO_4 and EDTA

Initial concentration in ppm	Amount adsorbed in ppm	Amount desorbed by HCl in ppm	% Desorption	Amount desorbed by H_2SO_4 in ppm	% Desorption	Amount desorbed by EDTA in ppm	% Desorption
5	4.8695	1.5582	32.18±1.69	2.5721	52.82±1.56	3.0856	77.14±0.55
10	9.0927	2.33665	25.70±1.05	3.76745	41.43±1.87	5.8922	64.80±1.59
15	13.2800	2.39055	18.001±0.94	3.8915	29.03±2.57	6.4195	48.34±2.66
20	17.525	2.56745	14.65±1.44	3.9558	22.57±2.10	7.8869	45.01±1.66
25	21.876	2.8065	12.83±0.84	3.9961	18.27±1.02	8.0634	36.86±1.76
30	26.166	2.92185	11.17±1.27	4.19095	16.06±1.97	8.3856	32.05±2.87
35	30.439	3.1514	10.35±1.03	4.29905	14.12±1.32	8.5977	28.29±2.01
40	33.376	3.1629	9.48±1.01	4.3693	13.09±1.78	8.9601	26.85±2.78
45	34.507	3.2198	9.33±0.80	4.4558	12.91±0.58	9.1406	26.49±1.10
50	31.952	3.2491	9.17±0.84	4.4242	13.85±1.48	9.2600	28.98±2.12

The % desorption was then plotted against the amount of chromium adsorbed in ppm as shown in Figure 26.
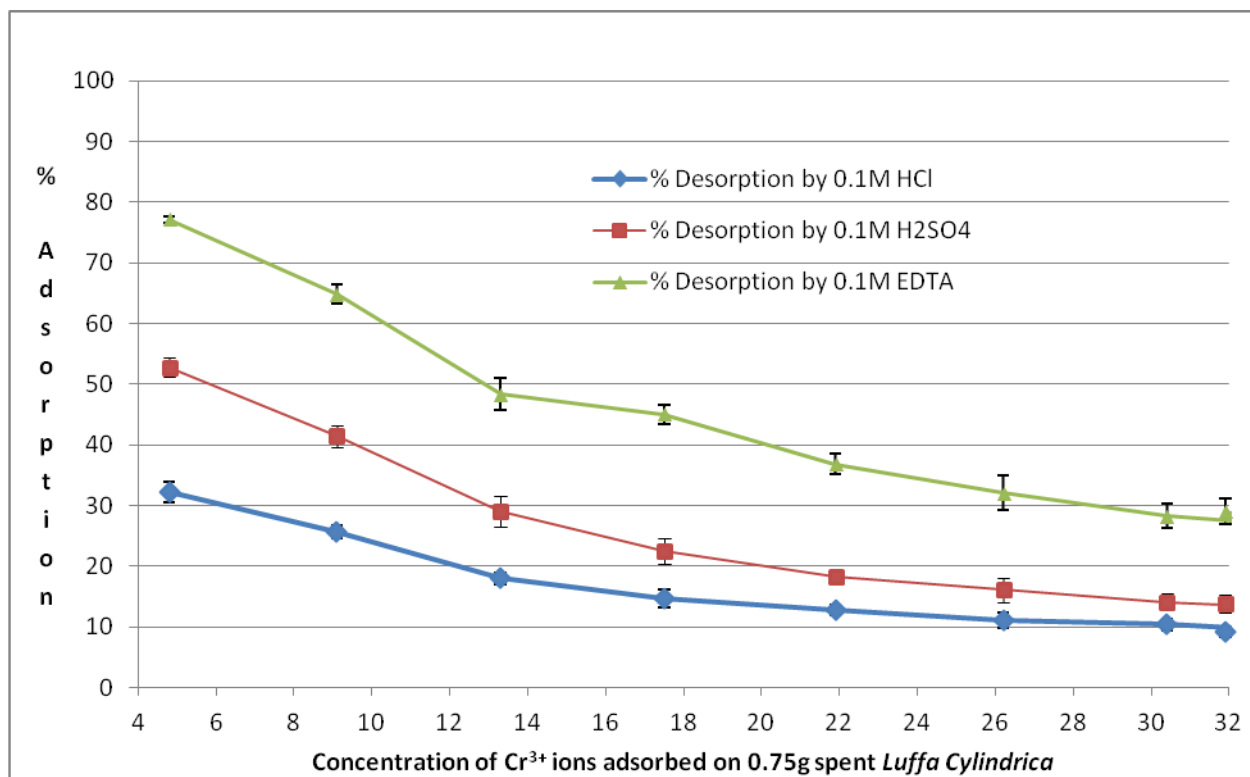
Figure 26:   % Desorption of Cr³⁺ ions adsorbed on 0.75g of spent Luffa Cylindrica by 50ml portions of 0.1M HCl, 0.1M H₂SO₄ and 0.1M EDTA

EDTA had the lowest desorption capability with copper, however with chromium it was the best followed by H_2SO_4 and finally HCl. Just as in the case of copper, sulphuric acid and hydrochloric acid must have caused the desorption by ion exchange. From the experiment it seems like Cr-luffa surface bond is relatively much weaker than Cu-luffa surface bond. Hence luffa having a higher affinity for Cu^{2+} than Cr^{3+}. Therefore it is likely that EDTA has higher chance of displacing Cr^{3+} from the surface than displacing Cu^{2+} from the luffa surface hence greater desorption of Cr^{3+} than Cu^{2+}.

4.3.2.2 Effect of concentration of H_2SO_4, HCl and EDTA, separately on Chromium ion desorption

The 2g of biomaterial loaded with chromium ions in 100ml gave a reading of 11.36ppm (11.36mg of chromium in one litre of the solution). The amount of Cr^{3+} in mg contained in 0.5g of the biomaterial is therefore 0.284mg.

Table 20:   Effect of Concentration of H_2SO_4, HCl and EDTA on % desorption of Chromium

Concentration of the desorbing agent in moles per litre	Desorption by HCl		Desorption by H_2SO_4		Desorption by EDTA	
	Amount desorbed in mg	% desorption	Amount desorbed in mg	% desorption	Amount desorbed in mg	% desorption
0.01	0.0232	8.15	0.0329	11.57	0.0308	10.85
0.02	0.0245	8.64	0.0407	14.32	0.0388	13.65
0.03	0.0286	10.07	0.0463	16.29	0.0410	14.45
0.05	0.0324	11.41	0.0583	20.54	0.045	15.81
0.08	0.0635	22.38	0.0849	29.89	0.046	16.10
0.1	0.1052	37.05	0.1184	41.70	0.0489	16.89

Graphical representation of Table 20 is as shown in Figure 27 below;
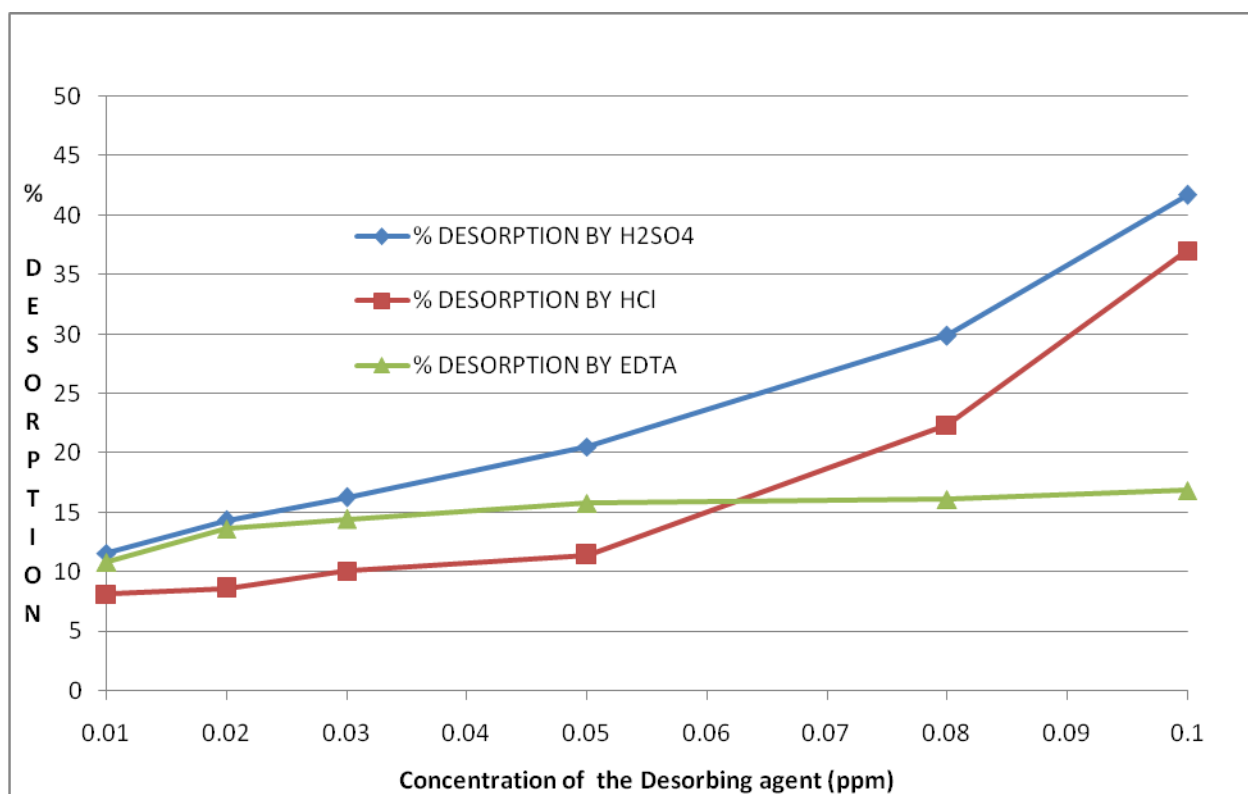
Figure 27: **Effect of concentration of H_2SO_4, HCl and EDTA on Cr^{3+} ions**

Desorption of Cr^{3+} followed almost the same trend as Cu^{2+} desorption with H_2SO_4 being the best followed by HCl as illustrated by Figure 27. EDTA showed just a small increase in % adsorption with increase in concentration. As earlier observed, Cr-luffa surface bond is likely to be a weak bond thus the process of rinsing the biomaterial with water must have led to greater loss of chromium ions especially on the surface of the biomaterial.

4.4   Reusability Test

The possibility of recycling and re-using spent material would be a major achievement in industrial processes as it would lower the cost of production. In this study, the biomaterial that was subjected to desorption studies was used in further adsorption experiments.

4.4.1 Adsorption of Copper using Regenerated Luffa Cylindrica

Inorder to test the possibility of re-using the regenerated spent biomaterial, the effect of concentration on copper ion adsorption was repeated using 0.75g of regenerated biomaterial with each exposed to the same concentration as done ealier before regeneration. Table 21 shows the results obtained.

Table 21:   Investigating the reusability of regenerated biomaterial in copper adsorption

Initial conc. of Cu^{2+} ions	% adsorption by fresh *Luffa Cylindrica*	Spent luffa regenerated with 0.1M HCl		Spent luffa regenerated with 0.1M H_2SO_4		Spent luffa regenerated with 0.1M EDTA	
		Final concentration of Cu^{2+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa	Final concentration of Cu^{2+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa	Final concentration of Cu^{2+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa
10	93.02	0.9479	90.52	0.8831	91.17	0.0834	99.17
20	90.31	2.5354	87.32	2.4119	87.94	0.1787	98.97
30	89.64	6.75225	77.49	6.6679	77.79	0.2210	99.26
40	89.30	15.701	60.75	14.464	63.84	0.34945	99.13
50	88.54	23.335	53.33	21.0335	57.93	0.85345	98.29
60	85.13	33.7665	43.72	32.753	45.41	2.9782	95.04
70	85.05	42.0485	39.93	39.111	44.13	5.793	91.72
80	74.66	52.395	34.51	50.259	37.18	15.9345	80.08
90	68.47	63.924	28.97	60.1645	33.15	28.909	67.87
100	35.96	73.52	26.48	66.348	33.15	32.6745	67.33

Figure 28 below illustrates how the % adsorption of copper ions using fresh Luffa Cylindrica compares with % adsorption obtained using regenerated spent *Luffa Cylindrica* with HCl, H_2SO_4 and EDTA, separately.
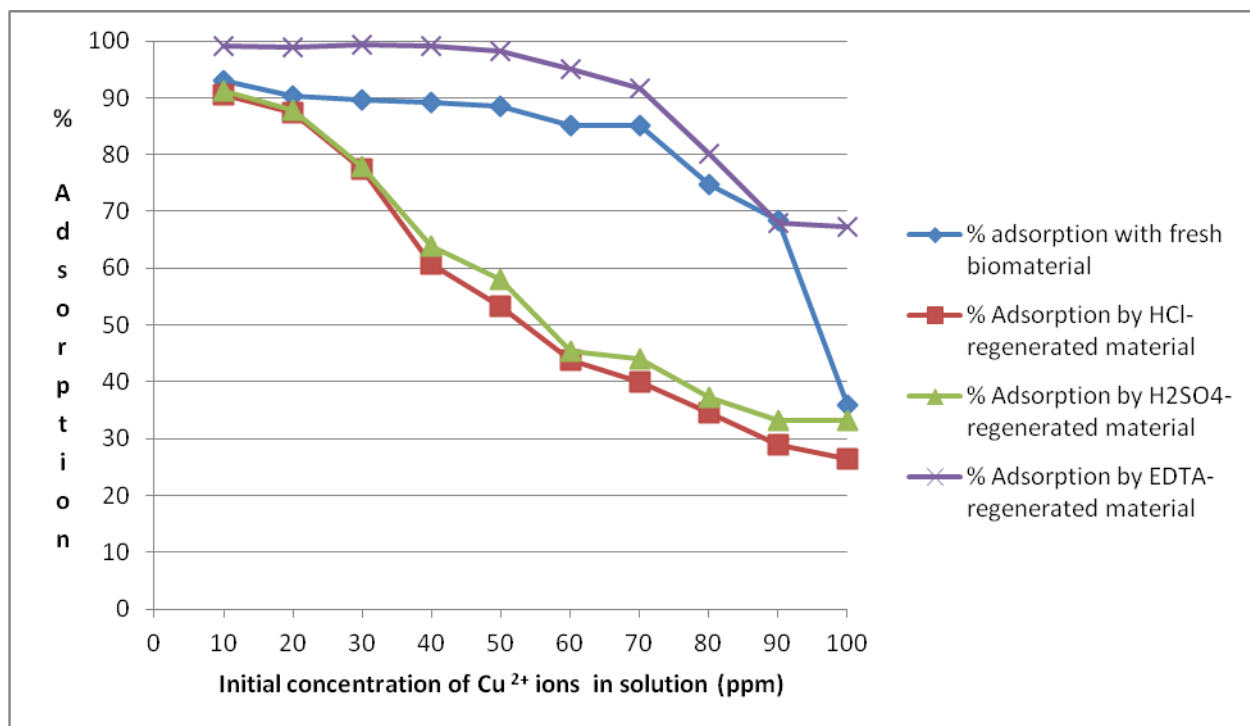
Figure 28:   Comparing the efficacy of regenerated biomaterial and fresh biomaterial in copper ion adsorption

It is noted that the spent material regenerated with EDTA was the best adsorbent compared to those regenerated using either HCl or H_2SO_4. This can possibly be attributed to additional functional groups from EDTA to the biomaterial which enhanced its adsorption capability .This fact also proves that treatment of the biomaterial with EDTA can improve its adsorption capability. It can be postulated that the EDTA upon interaction with the biomaterial surface remains attached to the surface thus availing more functional groups that are able to sequester metal ions from solution. Adsorption by spent material regenerated with H_2SO_4 and HCl were poor adsorbers compared to the original biomaterial possibly because the mechanism of ion exchange through which desorption occurred introduced H^+ ions onto the biomaterial lattice affecting the adsorption of positively charged copper (II) ions.

4.4.2 Adsorption of Chromium using Regenerated Biomaterial

Similar experiments as in section 4.4.1 were conducted inorder to investigate the possibility of using the regenerated biomaterial in the adsorption of Cr^{3+} ions. The effect of concentration on chromium ion adsorption was repeated using 0.75g of the regenerated biomaterial, with each exposed to the same concentration of chromium ions as done ealier before regeneration. 30ml solution of each concentration was used.The results are illustrated in Table 22.

Table 22:   Investigating the reusability of regenerated biomaterial in chromium ion adsorption

Initial conc. of Cr^{3+} ions in solution	% adsorption by fresh *Luffa Cylindrica*	Spent luffa regenerated with 0.1M HCl		Spent luffa regenerated with 0.1M H_2SO_4		Spent luffa regenerated with 0.1M EDTA	
		Final concentration of Cr^{3+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa	Final concentration of Cr^{3+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa	Final concentration of Cr^{3+} in the test solution (ppm)	% Adsorption by the regenerated spent luffa
5	97.39	0.4127	91.75	0.5151	89.69	0.2032	95.94
10	90.93	1.0114	89.89	1.6422	83.58	0.5625	94.88
15	88.53	3.0007	79.99	4.1141	72.57	0.8535	94.31
20	88.50	5.9603	70.20	6.4611	67.69	1.5902	94.12
25	87.50	12.048	51.81	13.023	47.91	1.5075	93.97
30	87.22	21.430	28.57	22.340	25.55	1.8568	93.81
35	86.97	27.961	20.11	29.568	15.52	2.7604	92.11
40	83.44	34.236	14.41	34.436	13.91	3.5672	91.08
45	76.68	39.344	12.57	40.422	10.17	6.0885	86.47
50	57.79	44.451	11.10	45.361	9.28	9.2119	81.58

The tabulated results were represented graphically as shown in Figure 29 below;
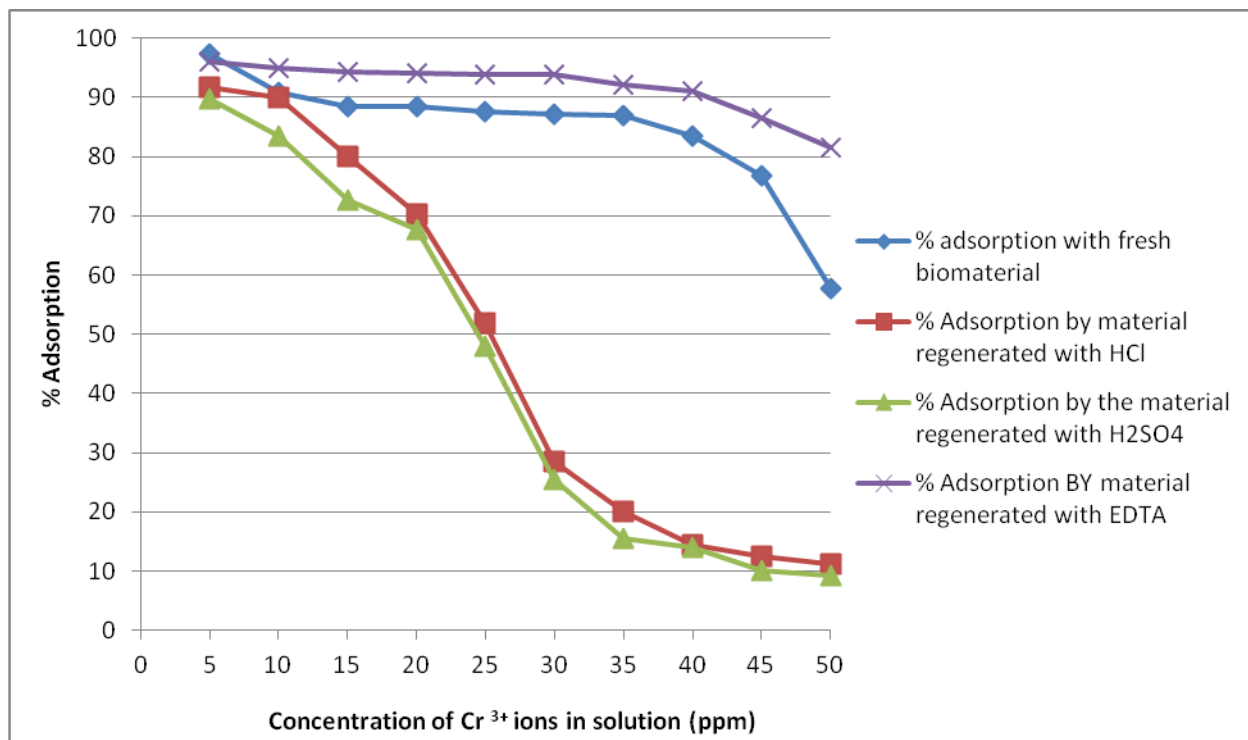
Figure 29:   Comparing the efficacy of regenerated biomaterial and fresh biomaterial in chromium (III) ion adsorption.

The material regenerated with EDTA was the best adsorbent and this can possibly be attributed to the fact that some EDTA molecules remained attached onto the biomaterial surface as much as it was the best desorbing agent with chromium.EDTA being a chelating agent was able to chelate with the metal ions in solution thereby improving the efficacy of the biomaterialThis fact also proves that treatment of biomaterial with EDTA can improve its adsorption capability. Adsorption by materials regenerated with H_2SO_4 and HCl showed decreased sorption capabilities and this could have been caused by interaction of metal ions with functional groups which may have resulted to irreversible masking of adsorptive sites on sorbent surface.

4.5   Adsorption by *Luffa Cylindrica*-Based Activated Carbon

70g portion of the biomaterial weighed 12.8583g after carbonization. Carbonizing   the biomaterial led to weight loss of about 81.6%. Though energy is used in the   carbonization

process, the weight reduction has the advantage of easier transportation, reduced storage space and enhanced adsorption.

4.5.1 *Copper ion Adsorption using Luffa Cylindrica-Based Activated Carbon*

The carbonized *Luffa Cylindrica* biomaterial was used in the study of the effect of initial concentration of the metal ion in the test solution at different concentrations. The results are shown in Table 23.

Table 23: Effect of concentration of copper ions and carbonized *Luffa Cylindrica* dosage on copper ion adsorption

Initial Concentration of Cu^{2+} ions (ppm)	Weight of carbonized material (grams)	Final concentration of Cu^{2+} ions (ppm) in test solution	% adsorption
10	0.5	0.53915	94.61
	0.75	0.38915	96.11
	1	0.2392	97.61
20	0.5	1.3100	93.45
	0.75	0.8711	95.66
	1	0.5690	97.15
30	0.5	2.1867	92.71
	0.75	**1.329**0	95.57
	1	0.9678	96.71
40	0.5	3.3200	91.70
	0.75	2.0921	94.77
	1	1.3960	96.51
50	0.5	4.2920	91.42
	0.75	3.0661	93.87
	1	2.1170	95.76
60	0.5	5.6111	90.65
	0.75	3.9840	93.36
	1	2.9204	95.13
70	0.5	8.5406	87.79
	0.75	6.8140	90.26

Initial Concentration of Cu^{2+} ions (ppm)	Weight of carbonized material (grams)	Final concentration of Cu^{2+} ions (ppm) in test solution	% adsorption
	1	4.7649	93.19
80	0.5	14.944	81.32
	0.75	11.866	85.16
	1	6.2485	92.19
90	0.5	21.561	76.04
	0.75	12.712	85.88
	1	7.8231	91.31
100	0.5	33.658	66.34
	0.75	14.651	85.35
	1	10.572	89.43

Figure 30 shows composite plots of % adsorption versus concentration of copper ions in solution for different weights of the Luffa Cylindrica-based carbonized biomaterial.
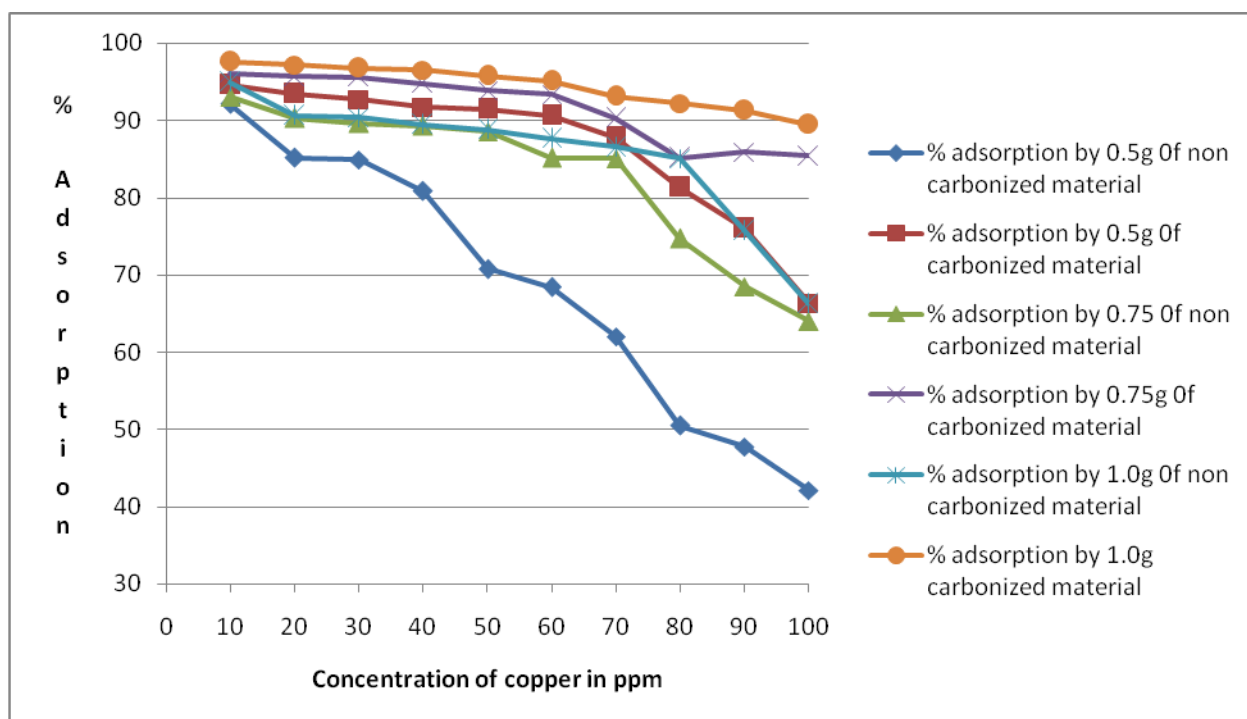
Figure 30; **Comparing adsorption efficacies of *Luffa Cylindrica*-based carbonized biomaterial with non carbonized *Luffa Cylindrica* in the removal of copper ions.**

From the figure it is noted that % adsorption generally decreases with increase in concentration of Cu^{2+} ions in the test solutions. High concentration leads to higher mass transfer resistance reducing metal ion interaction with binding sites hence reduced % adsorption (Aksu and Akipinar, 2000). Similar trend was observed with biomaterial dosage: as one increases the dosage, % adsorption increases. It is also evident from the plots that carbonized luffa provided higher adsorption values than the non-carbonized luffa of similar weights and this could be because carbonizing the biomaterial increases the pore sizes and thus increased adsorption. Carbonizing the material also led to decrease in the size of particles exposing more surface area for adsorption

4.5.2   Chromium ion Adsorption using Luffa Cylindrica-Based Activated Carbon

The efficacy of carbonized *Luffa Cylindrica* in removing chromium ions from aqueous solution was also investigated at different adsorbate concentrations. The results are compared with those of a similar experiment done using non carbonized *Luffa Cylindrica*. The results are tabulated as shown in Table 24 below:

Table 24:   **Table of chromium adsorption using activated carbon at different chromium ion concentration and different weights of carbonized Luffa Cylindrica**

Concentration of chromium (ppm)	Weight of carbonized luffa (grams)	Final concentration of chromium (ppm) in solution	% Adsorption by the *Luffa Cylindrica*-based carbonized biomaterial
5	0.5	0.1067	97.87
	0.75	0.0975	98.05
	1	0.0576	98.85
10	0.5	0.8691	91.31
	0.75	0.773	92.27
	1	0.7231	92.77
15	0.5	2.2767	84.82
	0.75	1.6214	89.19
	1	1.1525	92.32

Concentration of chromium (ppm)	Weight of carbonized luffa (grams)	Final concentration of chromium (ppm) in solution	% Adsorption by the *Luffa Cylindrica*-based carbonized biomaterial
20	0.5	3.0482	84.76
	0.75	2.3341	88.33
	1	1.7454	91.27
25	0.5	3.8732	84.51
	0.75	2.9952	88.02
	1	2.2825	90.87
30	0.5	4.7872	84.04
	0.75	4.5237	87.92
	1	2.9193	90.27
35	0.5	6.0463	82.73
	0.75	4.4311	87.34
	1	3.5910	89.74
40	0.5	8.2640	79.34
	0.75	6.3521	84.12
	1	4.3168	89.21
45	0.5	9.8505	78.11
	0.75	7.3251	83.72
	1	4.9815	88.93
50	0.5	13.163	73.67
	0.75	8.0050	83.99
	1	6.6280	86.74

Figure 31 illustrates the comparison between carbonized luffa and non-carbonized luffa in terms of their efficacy in removing chromium ions at different concentrations and different biomaterial weights.
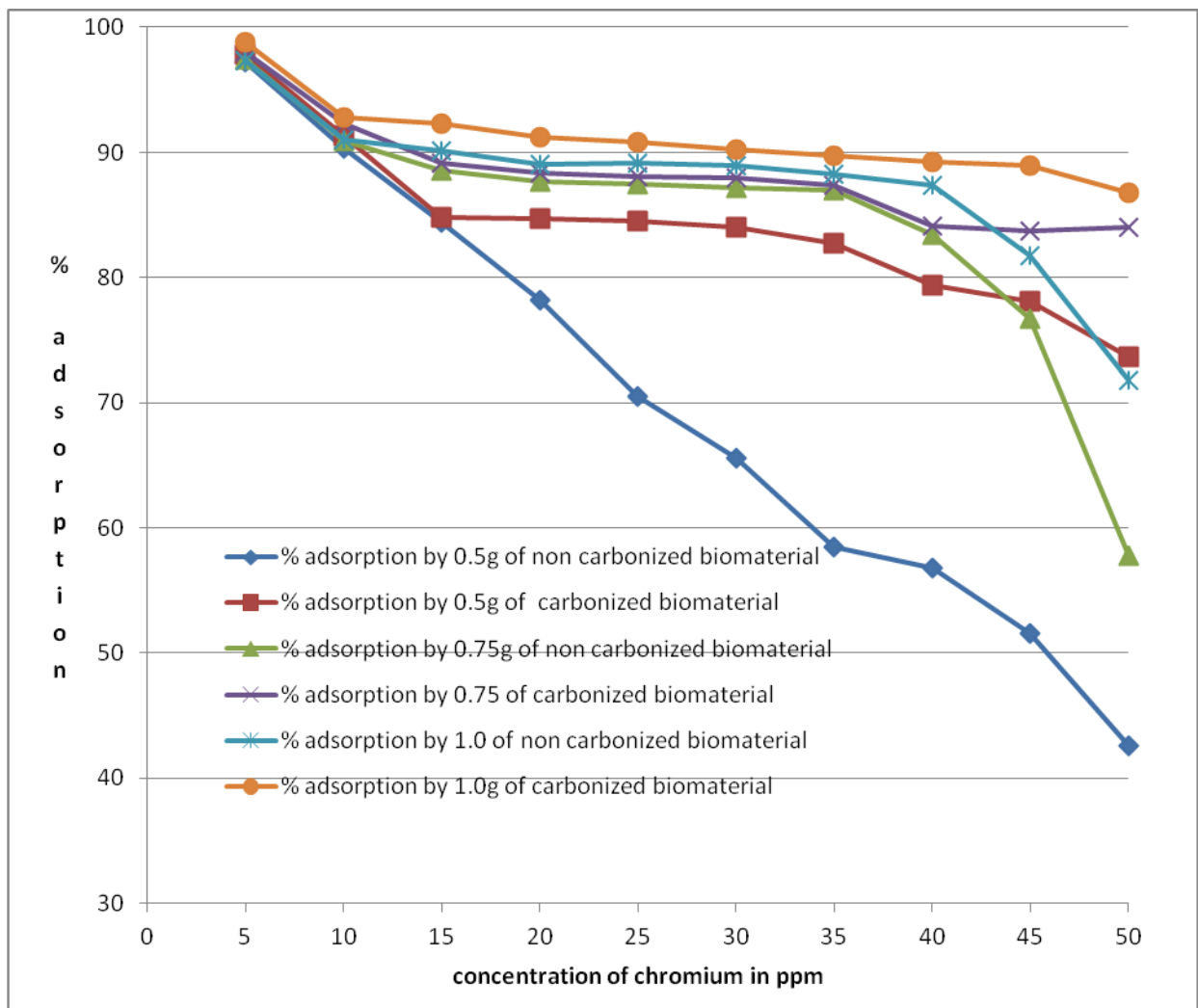
Figure 31: **Comparing the efficacy of carbonized and non-carbonized Luffa Cylindrica in adsorption of chromium ions**

It was noted that carbonized luffa offers higher adsorption percentages than the fresh *Luffa Cylindrica* and this could be because carbonizing the biomaterial under controlled conditions generates activated carbon which is known to have higher adsorptivity for metal ions as it increases the pore sizes and thus increased adsorption. It is also evident from Figure 31 that % adsorption decreases with increase in concentration of the adsorbate in the test solution. Increased biomaterial dosage however, led to increase in % adsorption.

4.6   Comparison Between Copper and Chromium Adsorption using *Luffa Cylindrica*

The possibility for preferential adsorption of one metal ion over the other by *Luffa Cylindrica* was investigated. This was in a bid to determine if there exists any special metal ion characteristics to influence their adsorption by *Luffa Cylindrica*. Effect of contact time on % adsoprtion was considered both for carbonized and non carbonized biomaterial.

4.6.1 Effect of Contact Time on the Adsorption of Copper and Chromium using Non Carbonized Luffa Cylindrica

0.5g of the biomaterial was used with 30ml portions of 20ppm copper and chromium solutions separately, shaken in the orbital shaker at 150rpm for the stated periods of time as shown in Table 25

Table 25:   Comparing copper and chromium ions adsorption using 0.5g of non carbonized *Luffa Cylindrica*

Contact time (minutes)	% Adsorption of Cu^{2+} ions	% Adsorption of Cr^{3+} ions
10	84.71	72.20
20	86.43	75.12
30	85.79	75.89
40	85.75	78.56
50	85.55	78.12
60	85.43	77.52
70	85.63	77.95
80	85.93	77.31

For better illustration of the differences in % adsorption of the two metal ions using Luffa Cylindrica, the data shown in Table 25 was plotted as shown in Figure 32 below;
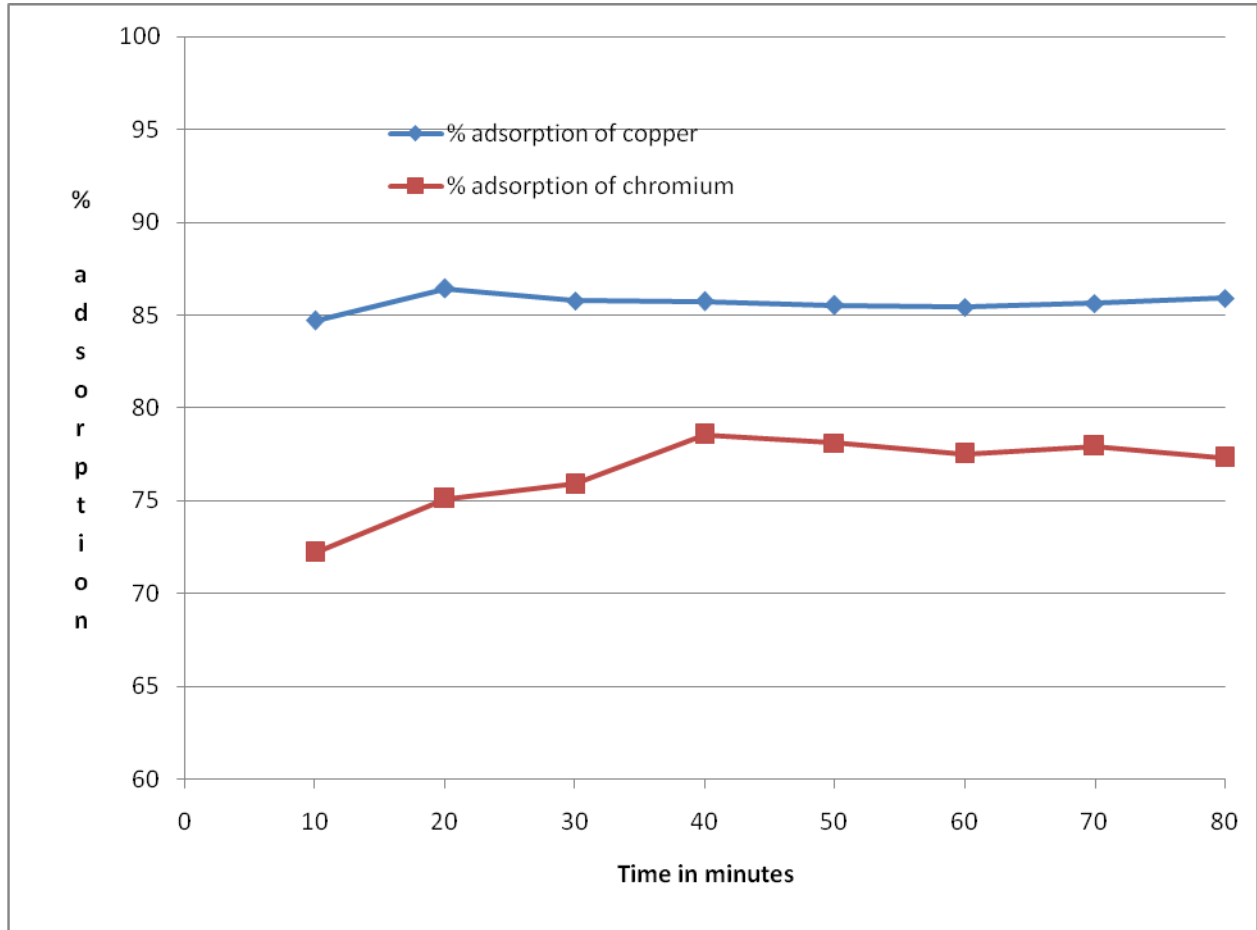
Figure 32: **Comparing copper and chromium ions adsorptions using O.5g non-carbonised *Luffa Cylindrica* at different contact times**

From the figure it is noted that *Luffa Cylindrica* adsorbed Cu^{2+} better than $Cr^{3+.}$ Literature shows that several metal ion properties such as electronegativity, hydration energies, ionic radii e.t.c plays a major role in sorption of the metal ion onto biomaterials but it is also evident from literature that the nature of the biomaterial also plays a role as the observed trend is not always the same for different biomaterials. Lim, *et al.,* (2010) did a study on adsorption of Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+} onto *Chlorella Vulgaris* and discovered that metal with high

83

electronegetivity exhibits higher adsorptive tendency than those with lower electronegativity. This could explain why Cu^{2+} ions which is more electronegative is adsorbed better than Cr^{3+} ions. The ionic radius of Cu^{2+} is 87pm while that of Cr^{3+} is 75.5pm. It is to be expected that the sorption of metal ions with larger ionic radii should be greater than those with smaller ionic radii (Tobin, *et al.*, 1984).

4.6.2   Adsorption of Copper and Chromium using Carbonized Luffa Cylindrica

Comparison was also made between copper and chromium ion adsorptions using the carbonized *Luffa Cylindrica* .The results are tabulated as shown in Table 26.

Table 26:   Comparison between copper and chromium adsorption using 0.50g carbonized *Luffa Cylindrica* at different metal ion concentrations

Concentration (ppm)	% Chromium adsorption	% Copper adsorption
10	91.31	94.61
20	84.76	93.45
30	84.04	92.71
40	79.34	91.70
50	73.67	91.42

The results were then illustrated graphically as shown in Figure 33 below;
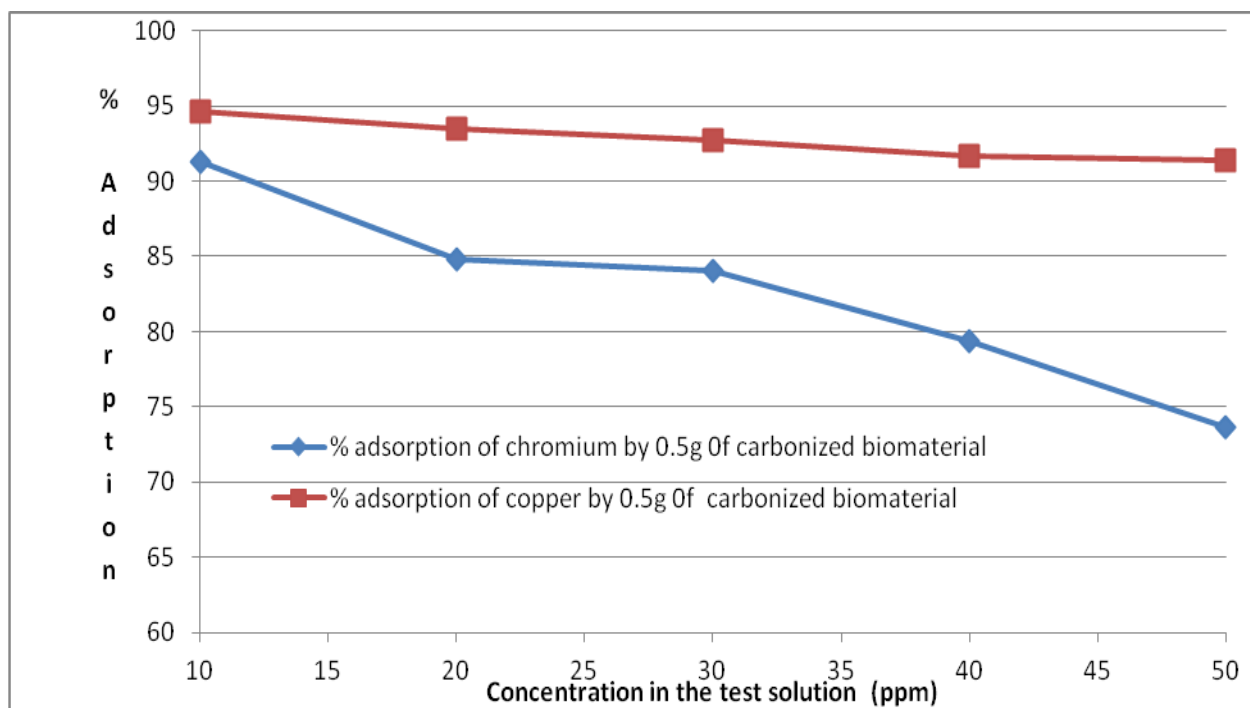
Figure 33:   Comparing adsorption of copper with that of chromium using 0.5g carbonized *Luffa Cylindrica* at different concentrations

Adsorption of copper ions was still better than that of chromium ions when carbonized Luffa Cylindrica was used. The reason for such phenomenon is still likely to be the high electronegetivity of Cu^{2+} ion and its larger ionic radius as discussed under section 4.6.1.

4.6.3   Adsorption of Copper and Chromium using EDTA- regenerated biomaterial

Adsorption of Copper ions using EDTA- regenerated biomaterial was also compared with that of Chromium as tabulated in Table 27.

Table 27: **Comparison between copper and chromium adsorption using 0.75g of the EDTA regenerated *Luffa Cylindrica* at different metal ion concentrations**

Initial concentration in ppm	% Adsorption of chromium by EDTA regenerated biomaterial	% Adsorption of copper by EDTA- regenerated biomaterial
10	94.88	99.17
20	94.12	98.97
30	93.81	99.26
40	91.08	99.13
50	81.58	98.29

The data were illustrated graphically as shown in Figure 34 below;
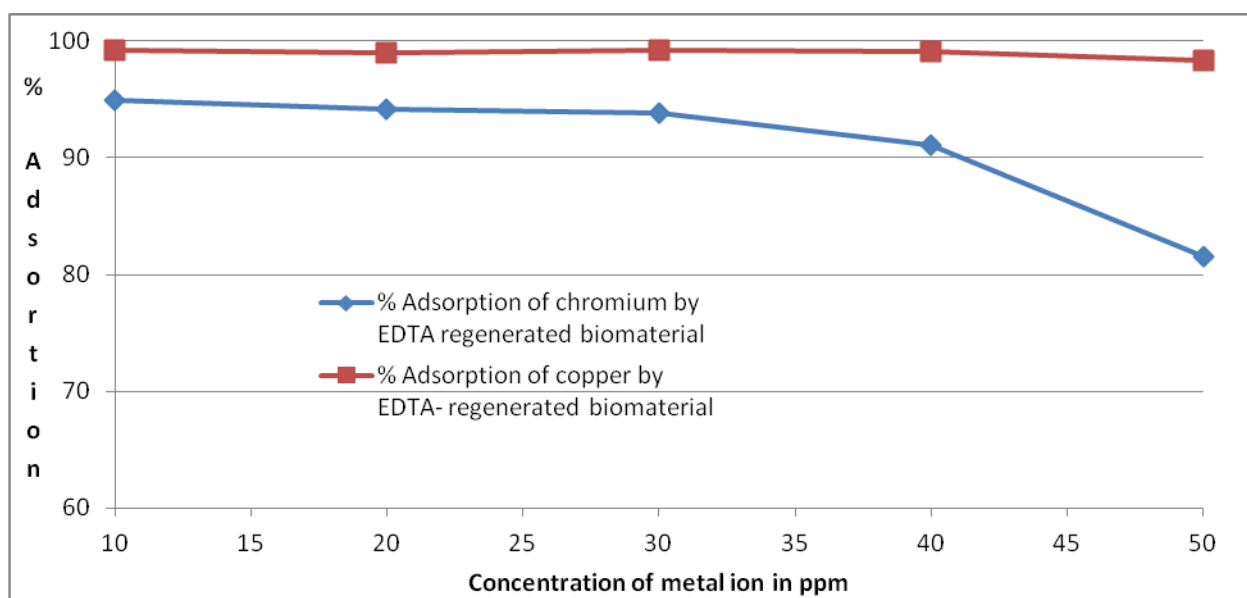
Figure 34: **Comparing adsorption of copper with that of chromium using 0.75g of EDTA- regenerated *Luffa Cylindrica* at different concentrations**

The efficacy of a chelating agent in binding a given metal ion depends on the stability constants of the chelator for the particular metal ion, the concentration of the metal ions and the presence and concentration of other functional groups competing for the metals in question (Waters *et al.,*

2001). From literature the stability constant for Cu-EDTA is 18.8 and that of Cr-EDTA is 13.61. The higher the stability constant the more tightly the metal ion will bond to the chelating agent and the more likely the chelate will be formed (Waters *et al.*, 2001).This therefore explains why adsorption of copper was higher than that of Chromium ions using EDTA-Regenarated Luffa Cylindrica.

4.7 Application of Luffa Cylindrica with Real Wastewater Samples

The ability of *Luffa Cylindrica* to remove chromium ions from real wastewater samples was tested on the effluent from KIRDI's leather division where a lot of chrome is used in the tanning process. The samples were collected from two points (i.e the collection pit where wastewater is directed before treatment and also discharge from the dosing tank where the wastewater is treated). Day 1 samples were collected immediately after addition of chromium in the retaning stage. Immediately after retaning, leather is normally rinsed with alot of water. Samples for the next four days were therefore collected during this rinsing process. Table 28 shows the results of chromium analysis from the wastewater before treatment with aluminium sulphate at the treatment plant and also after treatment.

Table 28: **Chromium analysis before and after treatment at KIRDI treatment plant**

Day	Chromium concentration in Untreated effluent (ppm)	Chromium concentration in Aluminiun Sulphate treated effluent (ppm)	% Removal of Chromium with Aluminium sulphate
I	31.710	3.9171	87.65
2	26.822	2.4611	90.82
3	26.012	2.0097	92.27
4	22.081	1.9771	91.05
5	20.977	1.9752	90.58

From Table 28, it is evident that after treating the effluent at the treatment plant using aluminium sulphate, the levels of chromium in the wastewater are still high, which implies that the treatment

is not efficient; the cost of aluminium sulphate not withstanding. The untreated effluent was then subjected to treatment with *Luffa Cylindrica* directly without going through the normal treatment process at the plant. 0.5g and 2g of *Luffa Cylindrica* were used and the results are as shown in Table 29.

Table 29:   Treatment of untreated effluent with *Luffa Cylindrica*

Day	Initial Cr^{3+} ion concentration	Conc. Of Cr^{3+} after treatment with 0.5g *luffa*	% Adsorption	Conc.of Cr^{3+} after treatment with 2g *luffa*	% Adsorption
1	31.710	11.213	64.64	2.3916	92.45
2	26.822	8.0147	70.11	1.9211	92.84
3	26.012	7.6532	70.58	1.8428	92.92
4	22.081	5.3112	75.95	1.3103	94.06
5	20.977	4.7774	77.23	0.8885	95.76

It is clear from Table 29 that *Luffa Cylindrica* is more efficient in the removal of chromium ions in solution though the dosage seemed to have been a limiting factor when 0.5g Luffa Cylindrica was used. 2g was able to remove over 90% of chromium ions in the effluent solution. Use of *Luffa Cylindrica* therefore can provide an affordable eco-friendly alternative in the treatment of chromium-containing wastewater for a developing country like Kenya.

4.8   Adsorption Isotherm Studies

In order to optimize a design for an adsorption system to remove metal ions from aqueous solutions, it is imperative to establish the most appropriate correlation for the equilibrium curves. The linear, Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinities of the adsorbent.

4.8.1 Freundlich Isotherm for Copper ion Adsorption using fresh Luffa

The adsorption phenomenon of copper ions was studied using the effect of concentration on Cu^{2+} ion adsorption with 0.5g of biomass and 30ml sample solution. The experimental data obtained for testing the aproppriateness of the Freundlich isotherm for the adsorption of copper ion is as shown in table 30 below.

Table 30:   **Table showing the experimental data for Freundlich isotherm on copper adsorption using fresh Luffa**

Concentration (ppm)	C_e	logCe	q_e	$logq_e$
20	2.9755	0.4736	1.0215	0.0092
30	4.5249	0.6556	1.5285	0.1843
40	7.6814	0.8854	1.9391	0.2876
50	14.6205	1.1650	2.1228	0.3269
60	18.9820	1.2783	2.4611	0.3911
70	26.5795	1.4245	2.6052	0.4158
80	39.6400	1.5981	2.4216	0.3841
90	46.9880	1.6720	2.5807	0.4117
100	57.8930	1.7626	2.5264	0.4025

where C_e is concentration of Cu^{2+} ions in the solution at equilibrium (mg/l);

q_e is the amount of Cu^{2+} ions adsorbed per gram of the adsorbent (mg/g);

From the experimental data a plot of Log q_e versus log C_e (see equation 9 page 20) was plotted to test Freundlich isotherm fit as shown in Figure 35.

From the linearized Freundlich equation, a graph of C_e versus q_e (figure 35) was drawn .
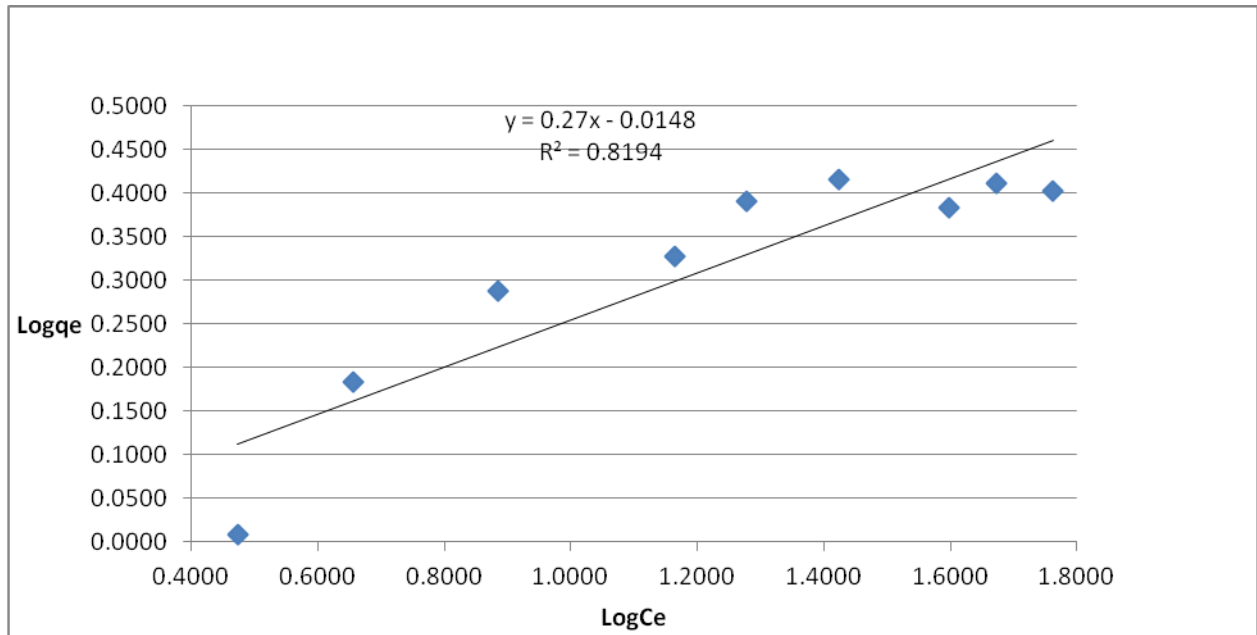
Figure 35: **Freundlich isotherm for copper adsorption onto fresh** *Luffa Cylindrica*

From Figure 35, correlation coefficient R^2 was found to be 0.8194 which is far from 1. It can therefore be concluded that the data is not in conformity with the Freundlich model. As earlier discussed, adherence of adsorption data to Freundlich isotherm postulates multilayer physical and completely reversible adsorption based on weak Van der Waals type of interaction between the sorbate and adsorbate particles (Freundlich, 1906). Adsorption of copper ions by *Luffa Cylindrica* therefore can be said not to adhere to Freundlich isotherm.

4.8.2 Langmuir Isotherm Model for Copper Adsorption using fresh Luffa

The experimental data obtained from the effect of concentration on copper adsorption using 0.5g of biomaterial and 30ml of copper ion solution was tabulated as shown in Table 31 below:

Table 31: Table showing the experimental data for Langmuir isotherm studies on copper adsorption onto fresh Luffa

Concentration(ppm)	C_{eq}	$1/C_{eq}$	q_{eq}	$1/q_{eq}$
20	2.9755	0.3361	1.0215	0.9790
30	4.5249	0.2210	1.5285	0.6542
40	7.6814	0.1302	1.9391	0.5157
50	14.6205	0.0684	2.1228	0.4711
60	18.9820	0.0527	2.4611	0.4063
70	26.5795	0.0376	2.6052	0.3838
80	39.6400	0.0252	2.4216	0.4130
90	46.9880	0.0213	2.5807	0.3875
100	57.8930	0.0173	2.5264	0.3958

Where C_{eq} is the equilibrium concentration of Cu^{2+} ions (mg/l) and q_{eq} is the adsorbed Cu^{2+} ions at equilibrium (mg/g).

From the data in Table 31, a graph of $1/q_{eq}$ versus $1/C_{eq}$ based on linearised Langmuir equation was plotted as shown in figure 36 below:
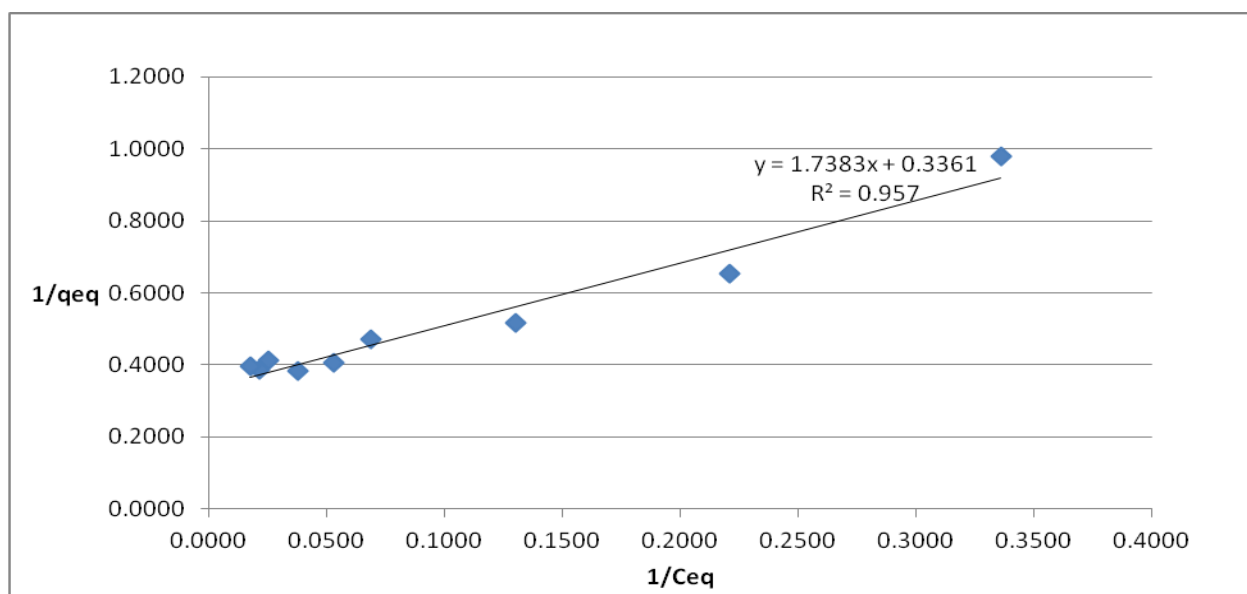

Figure 36: Langmuir isotherm for copper adsorption onto fresh Luffa Cylindrica

The copper adsorption results on Luffa sponge at various concentration was fitted to the linearized Langmuir isotherm (Eq.7)

The Langmuir isotherm gave a good fit with a linear correlation, $R^2 = 0.957$ which means monolayer adsorption was favourable. The basic assumption of the Langmuir theory proposed by Irving Langmuir is that adsorption takes place at specific homogeneous sites within the adsorbent (Langmuir, 1918). The q_{max} value, the monolayer adsorption capacity calculated from this data was found to be 2.9753 mg/g and b, the Langmuir constant was found to be 0.1933l/mg. The q_{max} value for adsorption of copper ions was higher than that of chromium ions (see pg 98). The lower the value of Langmuir constant b, the higher the affinity of sorbent for sorbate (Volesky and Holan, 1995). The Langmuir constant b for copper ion adsorption is compared with that of chromium on page 98.The experimental data gave a good fit to the Langmuir isotherm. This observation has also been made by other researchers studying metal adsorption by other biomaterials (Silveria and Allenoi, 2003; Mesquita and Silva, 2002; Ulmanu *et al*., 2003).

4.8.3   *Langmuir isotherm for copper adsorption using carbonised biomaterial*

The experimental data obtained from the effect of concentration on copper adsorption using 0.5g of carbonised biomaterial and 30ml of copper ion solution was also fitted to Langmuir isotherm as tabulated below;

Table 32: Table showing the experimental data for Langmuir isotherm studies on copper adsorption onto carbonised Luffa

Concentration(ppm)	Ceq	1/Ceq	q_{eq}	$1/q_{eq}$
20	1.31	0.763359	1.1214	0.891742
30	2.1867	0.45731	1.668798	0.599234
40	3.32	0.301205	2.2008	0.45438
50	4.292	0.232992	2.74248	0.364633
60	5.6111	0.178218	3.263334	0.306435
70	8.5406	0.117088	3.687564	0.271182
80	14.944	0.066916	3.90336	0.25619
90	21.961	0.045535	4.08234	0.244958
100	33.658	0.029711	3.98052	0.251223

A plot of $1/C_{eq}$ against $1/q_{eq}$ (as a test to the fit to the linearised Langmuir isotherm) was drawn as shown in Figure 37 below:
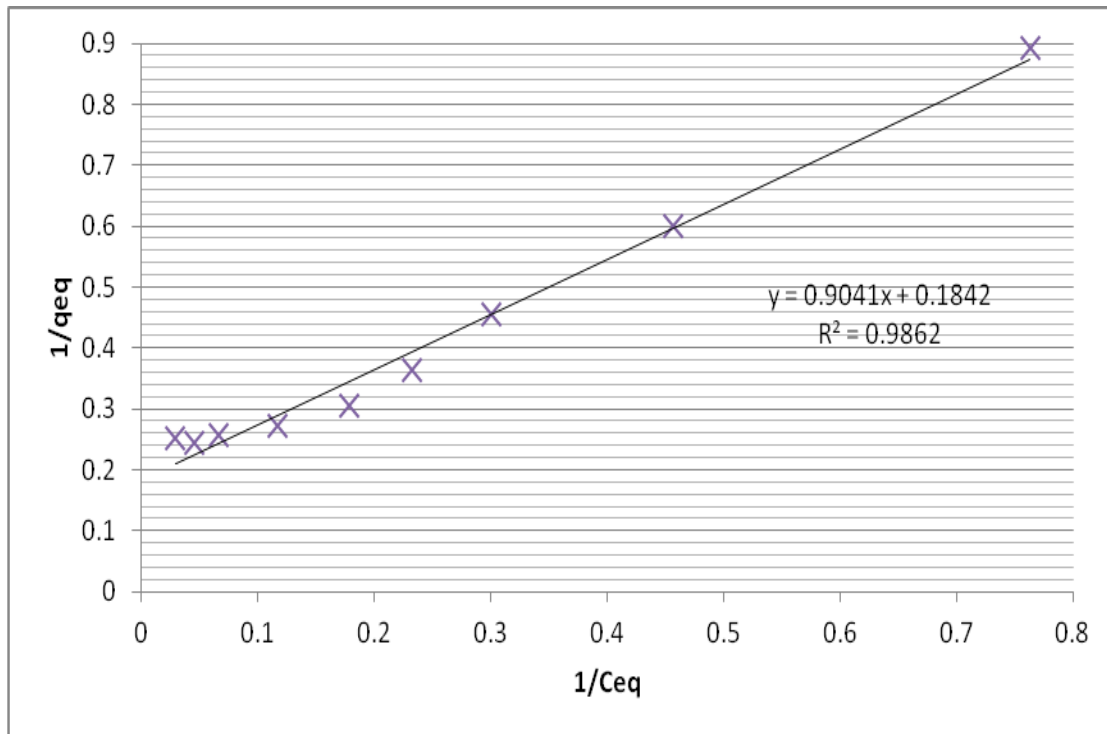
Figure 37: **Langmuir isotherm for copper adsorption onto 0.5g carbonised *Luffa Cylindrica***

The data fitted well giving R^2 value of 0.9862 and q_{max} value of 5.4288mg/g which is 1.8 times that obtained for adsorption using fresh *Luffa Cylindrica*. This implies that monolayer adsorption capacity is improved by carbonisation

4.8.4 Langmuir Isotherm for Chromium Adsorption onto fresh Luffa

The data obtained from the experiment on the effect of concentration of Cr^{3+} ions on adsorption of Cr^{3+} ions by *Luffa Cylindrica* using 0.5g of the biomaterial and 30ml of the solution was fitted to Langmuir isotherm. The adsorption data obtained were tabulated as shown in in Table 33 below:

Table 33: **Table showing experimental data for Langmuir isotherm on chromium ion adsorption using fresh Luffa**

Concentration (ppm)	C_{eq}	$1/C_{eq}$	q_{eq}	$1/q_{eq}$
10	0.9688	1.0322	0.5419	1.8455
15	2.3302	0.4291	0.7609	1.3155
20	4.3544	0.2297	0.9387	1.0653
25	7.3713	0.1357	1.0577	0.9454
30	10.3305	0.0968	1.1802	0.8473
35	14.518	0.0688	1.2289	0.8137
40	17.289	0.0578	1.3627	0.7339
45	21.8135	0.0458	1.3912	0.7188
50	28.685	0.0349	1.2789	0.7819

A plot of $1/q_{eq}$ versus $1/C_{eq}$ from the linearised Langmuir equation was then drawn as illustrated in Figure 38 below.
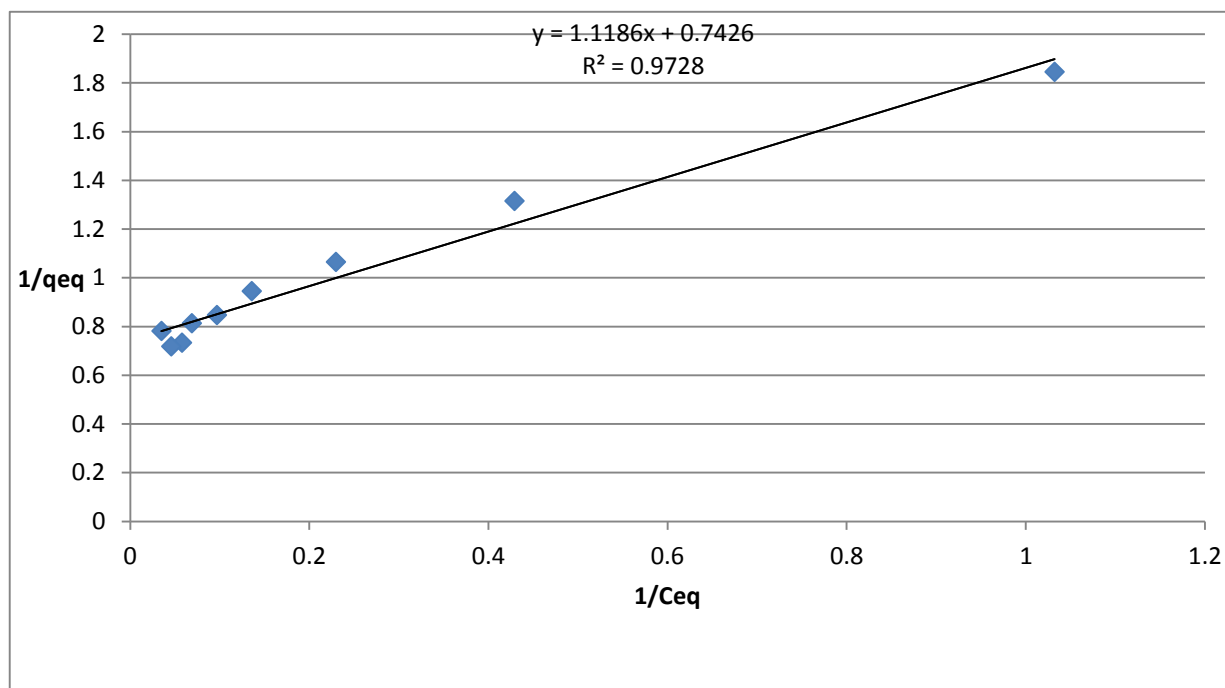

Figure 38: **Langmuir isotherm for chromium adsorption onto fresh *Luffa Cylindrica***

95

The Langmuir isotherm gave a linear correlation, $R^2 = 0.9728$ which means the data was in conformity with the model. Monolayer adsorption was therefore favourable. The q_{max}, the monolayer adsorption capacity calculated from this data was found to be 1.3466mg/g: a value less than half the one for copper. The b value, the langmuir constant, which is a coefficient related to the affinity between the sorbent and the sorbate was found to be 0.6639 l/mg, a value almost three times larger than that obtained with copper ions. The lower the value of b, the higher the affinity of sorbent for sorbate (Volesky and Holan, 1995). It can therefore be concluded that *Luffa Cylindrica* has a higher affinity for Cu^{2+} ions than Cr^{3+} ions since it had a lower value of b, i.e, 0.1933l/mg compared to 0.6639 l/mg obtained with Cr^{3+}.

4.8.5   *Langmuir isotherm for Chromium adsorption onto carbonised biomaterial*

The experimental data obtained from the effect of concentration on chromium adsorption using 0.5g of carbonised biomaterial and 30ml of Chromiumr ion solution was also fitted to Langmuir isotherm. The experimental data is as tabulated in Table 34 below;

Table 34:   Table showing experimental data for Langmuir isotherm on chromium ion adsorption using 0.5g Carbonised Luffa

Chromium concentration in ppm	Ceq	$1/C_{eq}$	q_{eq}	$1/q_{eq}$
10	0.8691	1.150616	0.547854	1.825304
15	2.2767	0.439232	0.763398	1.309933
20	3.0482	0.328062	1.017108	0.98318
25	3.8732	0.258184	1.267608	0.788887
30	4.7872	0.20889	1.512768	0.66104
35	6.0463	0.16539	1.737222	0.575632
40	8.264	0.121007	1.90416	0.525166
45	9.8505	0.101518	2.10897	0.474165
50	13.163	0.075971	2.21022	0.452444

Where C_{eq} is the equilibrium concentration of Cu^{2+} ions (mg/l); .

q_{eq} is the adsorbed Cu^{2+} ions at equilibrium (mg/g).

A graph of $1/q_{eq}$ versus $1/C_{eq}$ was then drawn as shown below in Figure 39.
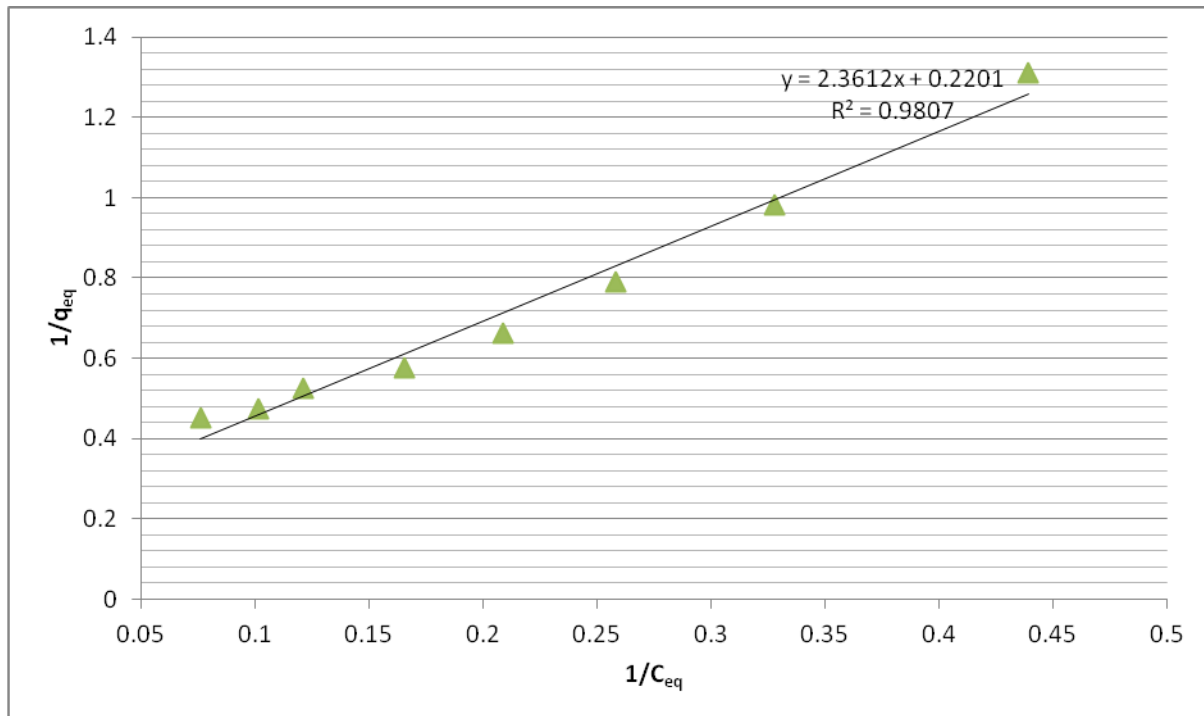
Figure 39: **Langmuir isotherm for chromium adsorption onto Carbonised *Luffa Cylindrica***

The data on Chromium adsorption onto carbonised biomaterial gave Correlation coefficient R2 value of 0.9807 which means it was in conformity with the model. q_{max} value was found to be 4.5433mg/g which is 3.37 times higher than that obtained with fresh *Luffa Cylindrica.* Carbonisation increases the surface area over which adsorption takes place..

4.8.6 *Freundlich Isotherm for Chromium Adsorption onto fresh Luffa*

The adsorption phenomenon of Chromium ions was studied using the effect of concentration on Cr^{3+} ion adsorption with 0.5g of biomaterial and 30ml sample solution. The experimental data obtained for testing the appropriateness of the Freundlich isotherm for the adsorption of Chromium ion is as shown below in Table 33 below;

Table 35;   Freundlich isotherm data on chromium adsorption

Concentration	q_e	C_e	$logC_e$	$log\ q_e$
10	0.5419	0.9688	-0.01377	-0.26608
15	0.7609	2.3302	0.367393	-0.11867
20	0.9387	4.3544	0.638928	-0.02747
25	1.0577	7.3713	0.867544	0.024363
30	1.1802	10.3305	1.014121	0.071956
35	1.2289	14.518	1.161907	0.089517
40	1.3627	17.289	1.23777	0.1344
45	1.3912	21.8135	1.338725	0.14339
50	1.2789	28.685	1.457655	0.106837

A graph of $Logq_{eq}$ against $Log\ C_{eq}$ was then plotted and is shown in Figure 40.
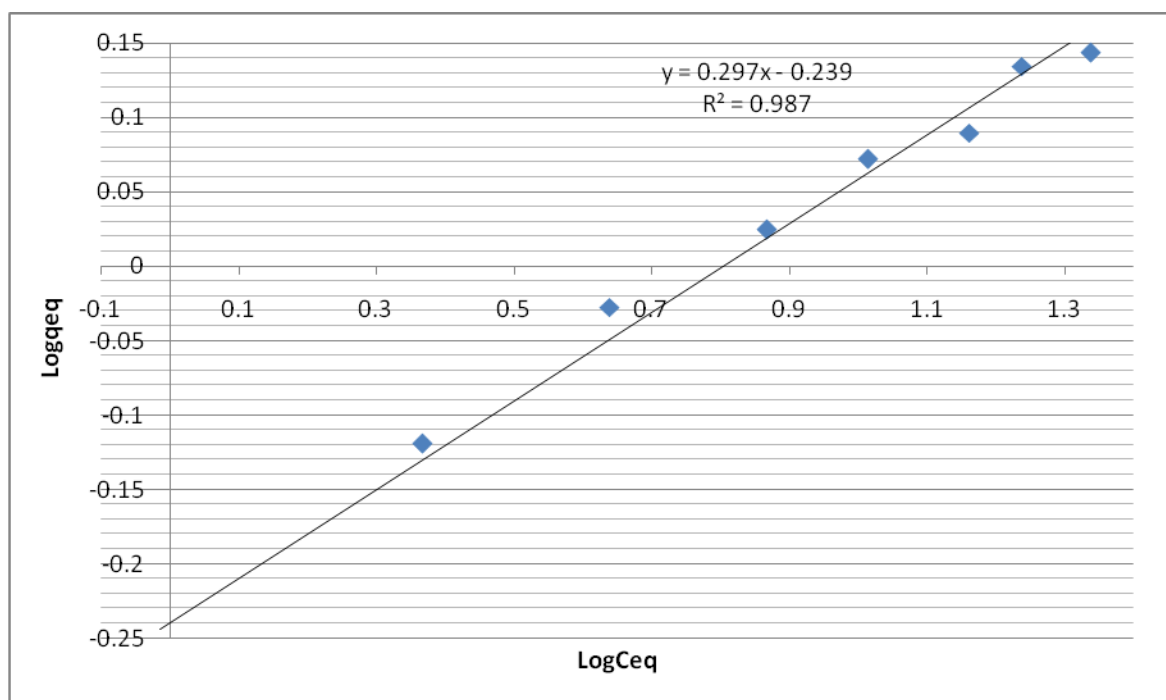
Figure 40:   Freundlich isotherm for chromium adsorption onto fresh Luffa

The correlation coefficient value R^2 was found to be 0.987 which means the data fitted well with the isotherm. From the figure above the value of $1/n = 0.297$ while n=3.367. The values of 'n' ranging from 2-10 indicates good adsorption capacity, 1-2 moderate adsorption capacity and less than one indicates poor adsorption capacity (Treybal, 1981; Hamdaouia and Naffrechoux, 2007). The value of n is 3.367 which therefore implies that Luffa Cylindrica can adsorb chromium well. The approximate adsorption capacity, K_F value for Chromium adsorption onto Luffa Cylindrica was found to be 0.5768 mg/g.

CHAPTER FIVE

CONCLUSION AND RECCOMENDATIONS

5.1   Conclusion

This study whose results are reported in this thesis proved that *Luffa Cylindrica* can adsorb both copper (II) and chromium (III) ions from aqueous solutions.It can also remove   chromium (III) ions from wastewaters. It also proves that the biomaterial can be regenerated using sulphuric acid, hydrochloric acid and EDTA. The regenerated biomaterials however, gave slightly lower adsorption values compared to the original fresh biomaterial except the one regenerated with EDTA which gave higher adsorption. Treating *Luffa Cylindrica* with EDTA thus increases its metal ion adsorption capability. The carbonized biomaterial also showed better adsorption values than the non-carbonized one. Adsorption experiments demonstrated that pH, adsorbent dose, time of contact, concentration of the metal ion in solution, biomass dosage and particle size have significant effects on adsorption of the metal ions. Desorption of already adsorbed copper ions was better with sulphuric acid followed by hydrochloric acid and finally EDTA. It is likely that the acids caused the desoption by ion exchange while EDTA desorbed by chelating with the copper ion already adsorbed and the chelate remaining on the surface of the biomaterial. For chromium ions however, EDTA was the best and this could be because chromium (III) ions are not as strongly attached to the biomaterial as copper and therefore EDTA was able to form chelate and remove the chromium ions from the surface of the biomaterial. Generally, it can be concluded that Luffa Cylindrica can be recycled but the number of cycles may depend on the metal ion adsorbed as well as the regenerant. It was also noted that *Luffa Cylindrica* has a higher affinity for copper ions than chromium ions whether fresh carbonized or regenerated form. Luffa Cylindrica can therefore be used as a low-cost eco-friendly adsorbent for the removal of Chromium ions from wastewaters.

5.2   Recommendations

Following the results obtained from this work, the following recommendations are proposed:

- That since *Luffa Cylindrica* has proved successful in adsorption of chromium ions from wastewater, there is a need to set up a pilot plant to establish its use as an adsorbent on industrial scale.
- Studies should be conducted to remove Copper from real effluents using Luffa Cylindrica.
- That detailed studies should be carried out to evaluate *Luffa Cylindrica's* efficacy in the adsorption of other heavy metal ions such as Pb, Cd, Zn and Hg

REFERENCES

Abdelwahab, O. and Amin, N. K. (2013). Adsorption of phenol from aqueous solutions by Luffa cylindrica fibers: Kinetics, isotherm and thermodynamic studies. *The Egyptian Journal of Aquatic Research*, **39**, 215-223.

Akpor, O. B. and Muchie, M. (2010). Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. *International Journal of Physical Sciences*, **5**, 1807-1817.

Aksu, Z. and Kutsal, T.A A. (1991). Bioseparation process for removing Pb (II) ions from wastewater by using *C. vulgaris*, *Journal of Chemical Technology and Biotechnology*, **52**; 108-118.

Aksu, Z. and Akpınar, D. (2000). Modelling of simultaneous biosorption of phenol and nickel (II) onto dried aerobic activated sludge. *Separation and purification Technology*, **21**, 87-99.

Amosa, M. K., Jami, M. S. and Ma'an, F. R. (2016). Electrostatic biosorption of COD, Mn and H_2S on EFB-based activated carbon produced through steam pyrolysis: an analysis based on surface chemistry, equilibria and kinetics. *Waste and Biomass Valorization*, **7**, 109-124.

Amuda, O. S. and Ibrahim A.O. (2006). Industrial wastewater treatment using natural materials as adsorbent. *African Journal of Biotechnology*, **5**; 1483-1487.

Amuda, O. S., Giwa, A. and Bello, I. A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal*, **36**, 174-181

Asamuda, N.U., Daba, A.S. and Ezeronye, O. U. (2005). Bioremediation of textile effluent using *Phanerochaete chrysosporium*. *African Journal of Biotechnology*, **4**; 1548-1553.

Ashish, B., Neeti, K. and Himanshu, K. (2013). Copper Toxicity: A Comprehensive Study. *Research Journal of Recent Sciences*, **2**; 58-67.

Asthana, M., Kumar, A. and Sharma, B. S. (2017). Wastewater Treatment. In *Principles and Applications of Environmental Biotechnology for a Sustainable Future* (pp. 173-232). Springer Singapore.

Aydin, H., Bulut, Y. and Yerlikaya, C. (2008). Removal of Cu (II) from aqueous solution by adsorption onto low -cost adsorbents. *Journal of. Environmental Management*, **87**; 37-45.

Bagreev, A., Rhaman, H. and Bandosz, T.J. (2001). Carbon; Thermal Regeneration of a Spent Activated Carbon Adsorbent Previously used as Hydrogen Sulphide Adsorbent. **39**; 1319- 1386.

Barirega, A. and Van Damme, P. (2014). Commercialization of Underutilized Plants in Uganda: An analysis of the market chains of Luffa cylindrica (L.) M. Roem. *Ethnobotany Research and Applications*, **12**, 525-533.

Baughman, R. H., Zakhidov, A. A., and De Heer, W. A. (2002). Carbon nanotubes--the route toward applications. *science*, **297**, 787-792.

Bhattacharya, K.G. and Sharma, A. (2005). Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder. *Dyes and Pigments*, **65**; 51–59.

Bishnoi, N.R., Pant, A. and Garima. A. (2004). Biosorption of copper from aqueous solution using algal biomass. *Journal of Scientific and Industrial Research*, **63**; 813–816.

Bolong, N., Ismail, A. F., Salim, M. R. and Matsuura, T. (2009). A review of the effects of emerging contaminants in wastewater and options for their removal. *Desalination*, *239*(1-3), 229-246.

Bousher, A., Shen, X. and Edyvean, R.G.J. (1997). Removal of coloured organic matter by adsorption of dyes onto low cost waste materials. *Water Research*, **31**; 2084 - 2092.

Boyles, E. A. (1979). Copper in natural waters. *Copper in the Environment*, **1**; 77.

Campbell, M.A., Li, L.H., Wu, K.L., Amy Dunn, M.P.H., Lindsey Roth, M.S. and Beaumont, J. (2009). Evidence on the developmental and reproductive toxicity of Chromium (hexavalent compounds). *Reproductive and Cancer Hazard Assessment Section Office of Environmental Health Hazard Assessment California Environmental Protection Agency*, 7-31.

Chand, S., Aggarwal, V.K. and Kumar, P. (1994). Removal of Hexavelent Chromium from the Wastewater by Adsorption. *Indian Journal of Environmental Health*, **36**; 151-158.

Cox, D.W. (1999). Disorders of copper transport. *British Medical Bulletin*, **55**; 544-555.

De Flora, S. (2000). Threshold mechanisms and site specificity in chromium (VI) carcinogenesis. Carcinogenesis, 21(4), 533-541.

Deo, N. and Ali, M. (1992). Use of a low cost material as an adsorbent in the removal of Cr (VI) from the dilute aqueous solution, *International Journal of Environment and Pollution*, **12**; 439-411.

Dogan, M., Alkan, M., Turkyilmaz, A. and Ozdemir, Y. (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Material*, **109**; 141-148.

Duruibe, J. O., Ogwuegbu, M. O. C. and Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. International Journal of Physical Sciences, 2(5), 112-118.

Eltom, A. E., Lessa, M. P. F., da Silva, M. J. and da Rocha, J. C. (2012). Production & Characterization of Activated Carbon Membranes. *Journal of Materials Research and Technology*, *1*(2), 80-83.

Emmanuel, S. D., Adamu, I. K., Mohammed, S. Y., Ejila, A., Amos, Y., Bobai, M. and Agbor, O. (2014). Effect of industrial tannery effluent on soil fungi and fungal protease/cellulase activity on modified rice husk/modified sawdust medium (MRHM/MSDM). *Scientific Research and Essays*, *9*(21), 894-905.

Foo, K.Y. and Hameed, B.H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, **156**; 2-10.

Förstner, U. and Wittmann, G. T. (2012). *Metal pollution in the aquatic environment*. Springer Science & Business Media.

Freundlich, H.M.F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry*, **57**; 385-471.

Gaetke, L. M. and Chow, C. K. (2003). Copper toxicity, oxidative stress, and antioxidant nutrients. *Toxicology*, *189*(1), 147-163.

Garg, V.K., Gupta, R., Yadav, A.B. and Kumar, R. (2003). Dye Removal from aqueous solution by adsorption on treated sawdust. *Bioresource Technology*, **89**; 121-124.

Hamdaoui, O. and Naffrechoux, E. (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon: Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *Journal of Hazardous materials*, **147**, 381-394.

Harter, R. D. (1983). Effect of soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Science Society of America Journal*, **47**; 47-51.

Huck-Iriart, C., De-Candia, A., Rodriguez, J. and Rinaldi, C. (2016). Determination of Surface Tension of Surfactant Solutions through Capillary Rise Measurements: An Image-Processing Undergraduate Laboratory Experiment. *Journal of Chemical Education*, *93*(9), 1647-1651.

Hunt, W. G., Burnham, W., Parish, C. N., Burnham, K. K., Mutch, B. R. I. A. N., & Oaks, J. L. (2006). Bullet fragments in deer remains: implications for lead exposure in avian scavengers. *Wildlife Society Bulletin*, **34**; 167-170.

Igwe, J. C. and Abia, A. A. (2007). Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Eclética Química*, **32**; 33-42.

Igwe, J.C.1., Ogunewe D.N.1. and Abia, A.A. (2005). Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk. *African Journal of Biotechnology*, **4**; 1113-1116.

Iyaka, Y.A. (2009). Chromium in soils: a review of its distribution and impacts. *Continental Journal of Environmental Sciences*, **3**; 13-18.

Jomova, K. and Valko, M. (2011). Advances in metal-induced oxidative stress and human disease. *Toxicology*, **283**; 65-87.

Kannan, N. and Sundaram, M. M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. *Dyes and pigments*, **51**; 25-40.

Kanu, I. and Achi, O. K. (2011). Industrial effluents and their impact on water quality of receiving rivers in Nigeria. *Journal of applied technology in environmental sanitation*, 1; 75-86.

Kariuki, P.M. (2008). Assessment of occupational and environmental safety concerns in pesticide use among small-scale farmers in Sagana, Nyeri District, Kenya MSc. Thesis. Nairobi, Kenya: Kenyatta University.

Karthikeyan, T., Rajgopal, S. and Miranda, L.R. (2005). Chromium (VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon. *Journal of Hazardous Material*, **124**; 192–199.

Krishnan, K.A. and Anirudhan, T.S. (2003). Removal of cadmium (II) from aqueous solutions by steam activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies. *Water SA journal*, **29**; 147-156.

Kumar, B. (2015). Isolation and identification of heavy metal tolerant bacteria from industrial effluent metal dumping sites and wastewater of Solan region.

Langmuir, I. (1918). A new adsorption isotherm. *J. Am. Chem. Soc*, **40**, 1361-1403.

Leeper, G.W. (1978) .Managing the heavy metals on the land. Marcel Dekker Inc., I.S.B.N.0-8247-6661-X. 121.

Lema, E., Machunda, R. and Njau, K. N. (2014). Agrochemicals use in horticulture industry in Tanzania and their potential impact to water resources. *International Journal of Biological and Chemical Sciences*, **8**; 831-842.

Lim, S. L., Chu, W. L. and Phang, S. M. (2010). Use of Chlorella vulgaris for bioremediation of textile wastewater. *Bioresource technology*, **101**, 7314-7322.

Low, K. S., Lee, C. K. and Mak, S. M. (2004). Sorption of copper and lead by citric acid modified wood. *Wood Science and Technology*, *38*(8), 629-640.

Luef, E., Prey, T. and Hubicek, C.P. (1991). Biosorption of zinc by fungal mycelial wastes. *Applied Microbiology and Biotechnolology*, **34**; 688-692.

Luza, S.C. and Speisky, H.C. (1996). Liver copper storage and transport during development: implications for cytotoxicity. *American Journal of Clinical Nutrition*, **63**; 812-820.

Massey, A G. (1973). Copper. In: Comprehensive Inorganic Chemistry. *Pergamon Press, Oxford*, **3**; 1-78.

Matheickal, J. T. and Yu, Q. (1999). Biosorption of lead (II) and copper (II) from aqueous solutions by pre-treated biomass of Australian marine algae. *Bioresource technology*, **69**, 223-229.

Mazali, I.O. and Alves, O.L. (2005). Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (*Luffa cylindrica*). *Academia Brasileira de Ciências*, **77**; 25-31.

Mc-Kay, G., Otterburn, M.S. and Aga, J.A. (1985). Fulters earth and fired clay as adsorbents for dyestuffs-equilibrium and rate studies, *Water Air Soil Pollution*, **24**; 307-322.

Mesquita, M. and Vieira e Silva, J. (2002). Preliminary study of pH effect in the application of Langmuir and Freundlich isotherms to Cu and Zn competitive adsorption. *Geoderma*, **106**; 219–234.

Mohan, D., Singh, K. P. and Singh, V K. (2006). "Trivalent chromium removal from waste water using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloths. *Journal of Hazardous Materials*. **135**; 280-295.

Namasivayam, C., Prabha, D. and Kumutha, M. (1998). Removal of direct red and acid brilliant blue by adsorption onto banana pith. *Bioresource Technology*, **64**; 77-79.

Oboh, I.O. and Aluyor, E.O. (2009). *Luffa cylindrica* - an emerging cash crop. *African Journal of Agricultural Research*, **4**; 684-688.

Onyeji, L.I. and Aboje, A.A. (2011). Removal of heavy metals from dye effluent using activated carbon produced from coconut shell. *International Journal of Engineering Science and Technology*, **3**; 8239-8245.

Osredkar, J. and Sustar, N. (2011). Copper and zinc, biological role and significance of copper/zinc imbalance. *J Clinic Toxicol S*, *3*(2161), 0495.

Otero, M., Rozada, F., Calvo, L.F., Garcia, A.I. and Moran, A. (2003). Kinetic and equilibrium modeling of Methylene Blue removal from solution by adsorbent materials produced from sewage sludges. *Biochemical Engineering Journal*, **15**; 59-68.

Owabor, C.N., Ono, U.M. and Isuekevbo, A. (2012). Enhanced sorption of naphthalene onto a modified clay adsorbent: effect of acid, base and salt modifications of clay on sorption kinetics. *Advances in Chemical Engineering and Science*, **2**; 330-335.

Oyelude, E. O., Awudza, J. A. and Twumasi, S. K. (2017). Equilibrium, Kinetic and Thermodynamic Study of Removal of Eosin Yellow from Aqueous Solution Using Teak Leaf Litter Powder. *Scientific reports*, **7**, 12198.

Pandey, A., Pradheep, K. and Semwal, D. P. (2014). Notes on Luffa (Cucurbitaceae) Genetic Resources in India: Diversity Distribution, Germplasm Collection, Morphology and Use. *Indian Journal of Plant Genetic Resources*, **27**(1), 47-53.

Potgiere, J. H., Potgierer-Vermaak, S. S. and Kalibantonga, P. D. (2006). Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, **19**, 463-470.

Ramakrishna, K.R. and Viraraghavan, T. (1997). Dye removal using low cost adsorbents. *Water Science and Technology*, **36**; 189–196.

Saeed, A., and Iqbal, M. (2013). Loofa (Luffa cylindrica) sponge: Review of development of the biomatrix as a tool for biotechnological applications. *Biotechnology progress*, **29**, 573-600.

Sahoo, D. K., Kar, R. N. and Das, R. P. (1992). Bioaccumulation of heavy metal ions by Bacillus circulans. *Bioresource technology*, **41**; 177-179.

Saravanane, R., Sundararaja, T. and Sivamurthyreddy, S. (2002). Efficiency of chemically modified low cost adsorbent for the removal of heavy metals from wastewater. A comparative study. *Indian Journal of Environmental Health*, **44**; 78-81.

Schiewer, S. and Volesky, B. (2000). Biosorption processes for heavy metal removal. *Environmental Microbe-Metal Interactions*, **14**; 329-362.

Sharma, Y.C., Uma, Srivastava, V., Srivastava, J. and Mahto, M. (2007). Reclamation of Cr (VI) rich water and wastewater by wollastonite. *Chemical Engineering Journal*, **127**; 151–156.

Silveira, M.L.A. and Alleoni, L.R. (2003). Copper adsorption in tropical Oxisols. *Brazilian Archives of Biology and Technology*, **46**; 529-536.

Singh, R. K., Kumar, S., Kumar, S. and Kumar, A. (2008). Development of parthenium based activated carbon and its utilization for adsorptive removal of p-cresol from aqueous solution. *Journal of Hazardous Materials*, *155*(3), 523-535.

Smith, K.M. (2011). Characterization of activated carbon for taste and odour control. MSc. Thesis. University of Toronto.

Soetan, K. O., Olaiya, C. O. and Oyewole, O. E. (2010). The importance of mineral elements for humans, domestic animals and plants: A review. *African Journal of Food Science*, **4**; 200-222.

Thompson, M. (Ed.). (2006). *Base Metals Handbook*. Elsevier

Tobin, J.M Cooper, D.G and Neufield, R.J (1984) Uptake of Metal ions by *Rhizopus Arrhizus*. *Applied and Environmental Biology* **47**, 821-824.

Torresdey, J.L.G., Tiemann, K.J. and Armendariz, V. (2000). Characterization of Cr (VI) binding and reduction to Cr (III) by the agricultural byproducts of *Avena monida* (Oat) biomass. *Journal of Hazardous Material*, **80**; 75-188.

Treybal, R. E. (1981). Adsorption and ion exchange. *Mass transfer operations*, 568-569.

Ulmanu, M., Maranon, E., Fernandez, Y., Castrillon, L., Anger, I. and Dumitriu, D. (2003). Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents. Journal to Water, Air, and Soil Pollution, **142**; 357–373.

Uysal, K.; Köse, E.; Bülbül, M.; Dönmez, M.; Erdoğan, Y.; Koyun, M.; Ömeroğlu, Ç. and Özmal, F. (2009). The comparison of heavy metal accumulation ratios of some fish species in Enne Dame Lake (Kütahya/Turkey). *Environmental Monitoring and Assessment*, **157**; 355-362.

Volesky, B., (2003). Sorption and Biosorption. B V Sorbex: Montreal, QC. 316.

Volesky, B. and Holan, Z.R. (1995) Biosorption of Heavy Metals. *Biotechnology progress* **11**, 235-250

Walker, G.M. and Weatherley, L.R. (1998). Fixed bed adsorption of acid dyes onto activated Carbon. *Environmental Pollution*, **99**; 133-136.

Waranusantigul, P., Pokethitiyook, P., Kruatrachue, M. and Upatham, E.S. (2003). Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*spirodela polyrrhiza). Environmental Pollution*, **125**; 385-392.

Waters, R.S., Bruden, N.A., Patterson, K.Y. and Anderson, R.A. (2001) EDTA Chelation Effects on Urinary losses of cadmium, calcium, chromium, cobalt, copper, lead, magnesium and zinc. *Biological Trace Elements Research* **83**, 207-221

Wawrzkiewicz, M. and Hubicki, Z. (2015). Anion exchange resins as effective sorbents for removal of acid, reactive, and direct dyes from textile wastewaters. *Ion Exchange-Studies and Applications*. InTech, Lublin, Poland, 50-67

Wuana, R. A. and Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. Isrn Ecology, 2011.

Yang, Z. L., Gao, B. Y., Yue, Q. Y. and Wang, Y. (2010). Effect of pH on the coagulation performance of Al-based coagulants and residual aluminum speciation during the treatment of humic acid–kaolin synthetic water. *Journal of Hazardous Materials*, *178*(1), 596-603.