PACKED BED REACTOR SYSTEM STUDY ON THE BIOSORPTION OF Cr(VI) FROM AQUEOUS SOLUTION USING CORN COB POWDER

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May, 2015

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BY

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M.Sc/Science/31859/2012-2013

A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES AHMADU BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN BIOCHEMISTRY

DEPARTMENT OF BIOCHEMISTRY,
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA

MAY, 2015

DECLARATION

I,UKUWA, Stellahereby declare that this thesis entitled “Packed Bed Reactor System Study on the Biosorption of Cr(VI) from Aqueous Solution Using Corn Cob Powder” has been carried out by me in the Department of Biochemistry. The information derived from the literature has been acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

…… …… ……

Stella UKUWASignature Date

CERTIFICATION

This thesis entitled "PACKED BED REACTOR SYSTEM STUDY ON THE BIOSORPTION OF Cr(VI) FROM AQUEOUS SOLUTION USING CORN COB POWDER" by UKUWA, Stellameets the regulations governing the award of the of masters of science degree in biochemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dean School Of Postgraduate Studies Date ……..

DEDICATION

This project report is hereby dedicated to the Almighty God for His mercies, grace and sustenance and also to my ever loving parents Mr. and Mrs. Ukuwa for being there for me at all times.

ACKNOWEDGEMENT

My gratitude goes to my ever loving parents Mr. and Mrs. Ukuwa for being there for me at all times, their love and care which they lavished on me during the period and all stages of my life, and I can't thank them enough. Special thanks go to my family for their unflinching support and concern. And to my dear husband Martin UkwuruAgi, thank you so much.

I would also love to acknowledge my supervisors Prof. I.A Umar, and DrD.B James for their, academic and moral support which they gave relentlessly, and also to Dr A.B Sallau, I am grateful for his immense contribution and support.

My sincere gratitude goes to the members of staff of the Department of Biochemistry, especially my Lecturers: Prof. H.M Inuwa, Prof. D.A Ameh, Prof. S.E Atawodi, Prof. H.C Nelebe, Prof. Sani Ibrahim, Mr. Owolabi, Prof. Onyike, Dr. Kola Anigo, Mr. G.C Njoku, Dr. Auwal Ibrahim, and Dr Mrs. Abdulazeez Mansura. They all illuminated my path to knowledge of Biochemistry.

Special thanks go to the staff of Institute for Agricultural Research (IAR) whose help and assistance cannot go unmentioned and to Mr. Edward I say thank you.

My sincere appreciation goes to my guardian parents: Prof. and Dr. (Mrs.) Mangut, Prof. Oyedeleand his lovely wife for taking me as their own I say. Also to the chaplain Rev. I.G Baba and members of the chapel of redemption and Fellowship Of Postgraduate Christian Student for their prayers, fellowship and spiritual and moral support.

Very special thanks go to Oloche Matthew and Jeremiah Alika; you are true friends to me. And finally to all my colleagues and well wishers I say a big thank you. I am glad is completed and all glory be to God.

ABSTRACT

The current method used in the treatment of Cr(VI) uses biosorbents that are expensive hence the need for cheaper available biosorbent. In this study,potential use of corn cob powder biomass, as a bioremediation agent for the removal of Cr(VI) was investigated in a packed bed column bioreactor. The effects of the operating parameters such as influent Cr(VI) concentration, pH, biomass concentration, flow rate and temperature, on the Cr(VI) removal were investigated in the continuous system using a packed-bed reactor. Percentage removal curves were obtained for different flow rate, pH, temperature, biomass concentration and initial concentration of Cr(VI). It was found that the adsorption of Cr(VI) to the biomass was strongly dependent on these parameters, as expected. In particular, the influent pH and temperature were most significantly affected leading toa high percentage removal of Cr(VI); a decrease in the influent pH of 2, and an increase in the temperature up to 70°C enhanced the Cr(VI) reduction in the column significantly ($P<0.05$) up to 70 ± 11.39 %. A flow rate of 5min/ml was optimum for higher removal percentage. FTIR spectra analysis carried out on the biosorbent showed the presence of some functional group; hydroxyl (OH), carboxylic (COOH), ethyne (CH), and ethane (CH_2) groups which are responsible for the biosorption reaction in the column. Both Langmuir and Freundlich adsorption isotherms fitted reasonably well with the data and showed high correlation coefficient (R^2) values of 0.993 and 0.985 respectively. These results show that, the adsorbent can be used as a low cost alternative in biosorption of wastewaters containing lowerconcentrations of Cr(VI).Finally, the potential of the column packed with corncobbiomass for Cr(VI) detoxification has been

found to be a good biosorbent in removal of Cr(VI) from aqueous solutions and also in the treatment of Cr(VI) containing industrial waste

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LIST OF ABBREVIATION

ANOVA	Analysis of Variance
FTIR	Fourier Transform Infrared Spectroscopy
KBr	Potassium Bromate
NARICT	National Research Institute for Chemical Technology
NILEST	National Institute of Leather Science and Technology
pH	Potential of Hydrogen Ions
PAC	Powdered Activated Carbon
SD	Standard Deviation
SPSS	Statistical Package for the Social Science
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Over the last three decades there has been increasing global concern over the public health impacts attributed to environmental pollution. The World Health Organization (WHO)estimates that about a quarter of the diseases facing mankind today occur due to prolonged exposure to environmental pollution (WHO, 2002).

Pollution by heavy metals is one of the serious environmental threats as a result of various industrial discharges (Wang and Chen, 2009). Hexavalent chromium Cr (VI) is released into the environment by many industrial activities such as leather tanning, chrome plating, stainless steel welding, pigment production and nuclear weapon production (Gonzalez *et al*., 2003). Chromium exists in two oxidation states Cr(III) and Cr(VI), and the most toxic form is Cr(VI), which has been implicated in causation of liver damage, pulmonary congestion and oedema (Babu and Gupta, 2008; Raji and Anirudhan, 1998).

Pollution of water due to presence of certain heavy metal ions is a severe socio-environmental problem caused by the discharge of industrial wastewater. In view of their toxicity, non-**biodegradability and persistent nature, their removal becomes an absolute necessity.** However, such processes are not only expensive and highly energy intensive, but also lead to production of harmful by-products and end-products, the ultimate disposal of which again causes secondary pollution (Sen and Ghosh, 2010).

Rapid industrialization and urbanization have resulted in increased discharge of heavy metals such as lead, chromium, mercury, selenium, zinc, arsenic, gold, silver, copper, nickel, etc. into aquatic ecosystem which has become a matter of concern over the last few decades due to pollutant's, carcinogenic and mutagenic nature(Ayres, 1992). These toxic materials are generated during mining operation, refining ores, sludge disposal, fly ash from incinerators, and the process of radioactive metal plating or the manufacture of electrical materials, metal equipment, paints, alloys, batteries, pesticides or preservatives (Trivedi, 1989).The untreated effluent from electroplating industries contains approximately 100mg/L chromium (VI) which is much higher than the permissible limit of 0.05-1mg/L (Deilippis and Pallaghy, 1994).

The process of removing heavy metal by a biological material is known as Biosorption and the biological materials used are called biosorbents. Several methods have been employed in the removal of heavy metals and other contaminants.Biological processes (biosorption, bioaccumulation and biodegradation) have been proposed as potential methods for the removal of heavy metals from the environment. However, bioaccumulation and biodegradation have been linked with some disadvantages such as resistance to microbial activity, production of by-product and/or other metabolites with higher toxicity than primary substrate (Ramsay and Nguyen, 2002). Thus, biosorption is considered to be one of the promising processes for removing hazardous and environmentally undesirable chemicals (Hu *et al*., 2010). Mohanty*et al*. (2005) showed some of the advantages of biosorption method, which include removal of both organic and inorganic constituents even at very low concentrations, its relative ease and safe to operate, usage of both batch and continuous equipment with no sludge formation, and the

adsorbent can be regenerated and reused.

Various biosorbents like bacteria, fungi, yeast, agricultural by product, industrial wastes, etc. have been used for biosorption (Gadd, 1993). Biosorption of toxic metals is based on a non-enzymatic process such as adsorption. Adsorption is due to the non-specific binding of ionic species to cell surface associated or extracellular polysaccharides or proteins (Volesky, 1990). Bacterial cell wall, the polysaccharides and proteins present in the corn cob powder are efficient metal biosorbent that bind charged group.

The use of biosorption technology using granular and powdered activated carbon has been carried out. However, prohibitive costs limit their extensive utilization especially in developing countries. Because of growing interest, the low-cost, easily available and environment friendly agricultural residues have been tested as metal biosorbents and a number of agro-based plant waste materials, such as papaya wood (Saeed*et al*., 2005), and rice husk (Tarley and Arruda, 2004), coconut fibers (Espinola*et al*., 1999) black gram husk (Saeed and Iqbal, 2003) have been reported as potential biosorbents.

This report focuses on the investigation of the potential of corn cob also known as*Zea mays* cob for the removal of chromium VI ions from aqueous solution. The polysaccharides and protein present in *Zea mays* cob were reported to be efficient metal biosorbent that bind to the charged group of these toxic metal. (Gibson and Benson, 2002).

The abundance of corn cob in most developing countries as well as its composition and cost effectiveness make it a strong candidate to be used as an adsorbent for removal

of many pollutants from aqueous solutions. The current economic values of corn cob are less than the apparent cost of collection, transportation and processing for beneficial use (Tsai *et al*., 2001). Thus, corn cob has been used as fertilizer and soil conditioners by land application, as animal and poultry bedding, as fiber and roughage in animal feed (Bagby and Widstrom, 1987) and as energy source by combustion (Lin *et al*., 1995). However, direct utilization of corn cob as metal biosorbent may be economical, practical and useful.Thus thisstudy aims at exploring the feasibility of using corn cob as an adsorbent for the uptake ofChromium (VI) from aqueous solution. Also, the effects of various factors including pH, contact time, temperature and adsorption isotherms on the uptake will be investigated.

1.2 Statement of Research Problem

Chromium is one of the major pollutants in the environment and is frequently present in wastewaters from various industrial units. Chromium is a toxic metal of widespread use and it exists in several oxidation states. Among the several oxidation states, Cr (VI) is considered to be the most toxic. It is usually associated with oxygen as chromate ($Cr0_4^{2-}$) or dichromate ($Cr0_7^{2-}$) ions. The Hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties (Helmer and Bartley, 1971). The untreated effluent from electroplating industries contains approximately 100mg/L chromium (VI) which is much higher than the permissible limit of 0.05-1mg/L (Deilippis and Pallaghy, 1994).

The persistent nature of Cr (VI) makes it accumulate in the food chain which with time reaches harmful levels in living beings resulting in serious health hazards such as irritation in lungs and stomach, cancer in digestive tract, low growth rates in plants and death of animals(Park *et al*.,

2004). Therefore, removal of Cr(VI) from wastewater, prior to its discharge into natural water systems, adjoining landmasses and sewer systems, requires serious and immediate attention. The contaminated corn cob powder can now be properly disposed in such a way as to prevent it from being introduce into natural waters and accumulating in the food chain. Also, it can be recycled and channeled into other means of chemical production.

1.3 Justification

Corn is a staple food in the northern part of Nigeria; it is produced in large quantity which leads to the availability of corn cobs in large quantity that could always be put into use.It contains cellulose and hemicelluloses, which have adsorption and biosorption properties; hence can bind to Cr(VI) ions. Corn cobs are common wastes found in our environment; hence can help convert waste into useful form. Cr(VI) adsorption has been carried out using other biosorbent e.g. Neem saw dust (Vinodhini and Nilanjana, 2009) hence the need to investigate the ability of corn cob powder in adsorption of Cr(VI) is imperative. Continuous reactors are generally able to cope with much higher reactant concentrations due to their superior heat transfer capacities(James*et al*., 1975). Continuous reactors make higher mixing rates possible. The output from a continuous reactor can be altered by varying the run time. This increases operating flexibility for manufacturers.Despite the demonstration of the efficiency of corncob to bioremediateCr (VI) using batch process (Sallau*et al*., 2012), there is no information of the biosorption of Cr(VI) using corn cob in a continuous process. Therefore, this study may create a method that will assist industries in reducing toxicity of waste water containing Cr (VI).

1.4 Aim and Objectives

1.4.1 Aim

The aim of this study was to examine the potential of corncob powder in the biosorption of chromium (VI) in aqueous solution in a continuous bioreactor process.

1.4.2 Specific Objectives

The specific objectives of this study are:

I. To investigate the effect of some operating parameters such as mass of corn powder, flow rate, influent solution pH and temperature on chromium (VI) removal by corn cob powder in the column

II. To compare the absorptive properties of corncob powder with activated carbon, a standard synthetic adsorbent used in industries

III. To compare the potentials of corncob powder in removal of chromium (VI) from synthetic chromium (VI) Solution and industrial waste containing chromium (VI).

IV. To carry out Fourier transform infrared spectroscopy (FTIR) of the biosorbent before and after biosorption

V. To carry out adsorptionisotherm studies of the biosorption process.

CHAPTER TWO

LITERATURE REVIEW

2.1 Biosorption

Biosorption can be defined as the removal of metallic ions by means of passive adsorption, or complexion by living biomass or organic waste (Davis and Volesky, 2003). Other definition of biosorption is the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). Biosorption is a process in which solids of natural origin are employed for binding heavy metals/radionuclide species in biomass (Saravanan and Brindha, 2009). More specifically, the metal binding in biosorption may be due to a combination of several sequestering mechanisms such as complexing, coordination, chelation, adsorption ion exchange or micro-precipitation (as metal or metal salt) (Eneida and Ravagnani, 2002). This process is less disruptive and can be often carried out on site, eliminating the need to transport the toxic materials to treatment site (Lokeshwariand Josh, 2009). Biosorption is proven to be quite effective for removing metal ions from contaminated solutions in a low cost and environment-friendly manner (Jamila and Hussan, 2009). Biosorption of toxic metal is based on non-enzymatic processes such as adsorption. Adsorption is due to the non-specific binding of ionic species to cell surface associated or extracellular polysaccharide (cellulose and hemicellulose) (Volesky 1990).

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate

species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases (Park*et al.,* 2006). Bacterial cell walls and envelopes, and the polysaccharides present in the maize cob are efficient biosorbent that bind charge groups (Volesky 1990).Biosorption technology is based on the interaction between toxic metals and the binding structural group on the cell structure of microorganisms and plants.

2.1.1 Mechanisms of Biosorption

The biosorptionmechanisms are various and are not fully understood. Based on the adsorption by a biomass they may be classified according to various criteria.

Physical adsorption: In this category, physical adsorptiontakes place with the help of vanderWaals' forces. Kuyucakand Volesky(1988) hypothesized that uranium, cadmium, zinc, copper and cobalt biosorption by dead biomasses ofalgae, fungi and yeasts takes place through electrostaticinteractions between the metal ions in solutions and cell wallsof microbial cells. Electrostatic interactions have beendemonstrated to be responsible for copper biosorption bybacterium *Zoogloearamigera*and alga *Chiarella vulgaris*(Aksu et al. 1992), for chromium biosorption by fungi*Ganodermalucidum*and *Aspergillusniger*.

Ion Exchange: Cell walls of Agricultural biomass and microorganism containpolysaccharides and bivalent metal ions exchange with thecounter ions of the polysaccharides. For example, thealginates of marine algae occur as salts of

K^+,Na^+,Ca^{2+},andMg^{2+}.These ions can exchange with counter ions such as$C0^{2+}$,Cu^{2+},$Cd^{2+}$and Zn^{2+}resulting in the biosorptive uptakeof heavy metals (Kuyucak and Volesky 1988). Thebiosorption of copper by fungi *Ganodermalucidium*(Muraleedharan and Venkobachr, 1990) and *Aspergillusniger*was also uptaken by ion exchange mechanism.

Complexation: The metal removal from solution may alsotake place by complex formation on the cell surface afterthe interaction between the metal and the active groups. Aksuet al. 1992 hypothesized that biosorption of copper by C.*vulgaris* and Z. *ramigera*takes place through both adsorptionand formation of coordination bonds between metals andamino and carboxyl groups of cell wall polysaccharides.Complexation was found to be the only mechanismresponsible for calcium, magnesium, cadmium, zinc, copperand mercury accumulation by *Pseudomonas syringae.* Microorganismsmay also produce organic acids (e.g., citric, oxalic,gluonic, fumaric, lactic and malic acids), which may chelatetoxic metals resulting in the formation of metallo-organicmolecules. These organic acids help in the solubilisation of metal compounds and their leaching from their surfaces.Metals may be biosorbed or complexed by carboxyl groupsfound in microbial polysaccharides and other polymers.

2.1.2 Factors Affecting Biosorption

The following factors affect the biosorption process:

I. Temperature seems not to influence the biosorption performances in the range of 20-35 CC (Aksu*et al.*, 1992)

II. pH seems to be the most important parameter in the biosorptive process, it affects the solution chemistry of the metals, the activity of the functional groups in the

biomass and the competition of metallic ions (Friis and Myers-Keith, 1986, Galun*et al*., 1987)

III. Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake(Gadd*et al.*, 1988; Fourest and Roux, 1992). Suggesting that an increase in biomass concentration leads to interference between the binding sites. Fourest and Roux, 1992 invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. Hence this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.

IV. Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions. For example: Uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of manganese, cobalt, copper, cadmium, mercury and lead in solution (Sakaguchi and Nakajima, 1991). In contrast, the presence of Fe^{2+} Zn^{2+}wasfound to influence uranium uptake by *Rhizopusarrhizus*(Tsezos and Volesky, 1982) and cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper (Sakaguchi and Nakajima, 1991).

2.1.3 Advantages of Biosorption

The major advantages of biosorption over conventional treatment method include low-cost, high efficiency of metal removal from dilute solution, biosorbent regeneration and metal recovery, Potentiality, minimization of chemical and/ or biological sludge, no

additional nutrient requirement and regeneration of biosorbent and the possibility of metal recovery.(Sara *et al.,* 2009).

These advantages of biosorption are seen over conventional treatment method such as the physical and chemical processes available for removal of heavy metals. These method include chemical coagulation using aluminum and ferric salts (Fatoki and Ogunfowokan, 2002), and cationic (Evans and Li, 2003), electro-chemical precipitation, ultrafiltration, ion exchange and reverse osmosis (Nomanbhay and palanisamy, 2005).

2.2 History of Corn

Corn is a grain domesticated by indigenous peoples in Mesoamerica in prehistoric times. Its main classification is vegetable, yet it is a technically a fruit. Between 1700 and 1250 BCE, the crop spread through much of the Americas after the European contact with the America's, in the late 15^{th} and early 16^{th} centuries, explorers and traders carried corn back to Europe and introduced it to other countries through trade. Spread corn to the rest of the world due to its popularity and ability to grow in diverse climates. (Lance andGarren, 2002). In Nigeria corn is a staple food that is mainly grown in the northern part, therefore it produces large volume of waste (corn cob)(Woranart , 2008).

2.2.1 Classification of Corn

Kingdom – Plantae

Sub-kingdom – Tracheobionta

Super-division – Spermatophyta

Division – Magnoliophyta

Class – liliopsida

Sub-class - Commelinidae

Order – Cyperales

Family – poaceae

Genus – Zea

Species – Zea*mays*

(Gibson and Benson, 2002).

2.2.2 Biosorbent Properties of Corncob

Biosorption of toxic metal is based on non-enzymatic processes such as adsorption. Adsorption is due to the non-specific binding of ionic species to cell surface associated or extracellular polysaccharide (cellulose and hemicellulose) (Mullen *et al*., 1989; Volesky 1990).The polysaccharides present in the maize cob are efficient biosorbent that bind charge groups. Corn cobs are rich in cellulose and hemicellulose which comprise about 80% of the dry matter which are converted into metal ion adsorbent for waste water treatment. (Sharma and Forster, 1994).Maize cobs are recyclable, organic and natural, virtually dust free and non-sparkling. (Raoand Venkobachar, 1993). Corn cobs are rich in cellulose and hemicellulose which comprises 80% of the dry matter, which are converted into metal ion adsorbent for waste treatment. (Patterson and Fendorf, 1997).Corn cob powder possesses various functional groups predominantly large proportions of polysaccharides (OH group) on the surface after drying process (Khemani*et al*., 2011), hence can be used as a biosorbent.

2.3 Chemistry and Characteristics of Chromium

In nature, chromium generally occurs in small quantities associated with other metals, particularly iron. Its atomic weight is 51.996.Chromium has six oxidation states. Most

chromate (Cr(VI)) results from man-made production, as the form is rare in nature (Barceloux, 1999). Hexavalent chromium reduces readily to Cr(III); the rate increases with decreasing pH (Barceloux, 1999).The hexavalent state is one of the three most stable forms in which chromium is found in the environment (U.S. EPA, 1988). The other two of these forms are the 0 (metal and alloys), and the +3 (trivalent chromium, Cr(III)) valence states. . Hexavalent chromium, in contrast to the trivalent form, exists as highly-oxidizing species (IARC, 1990). As noted by NTP (2008), Cr(VI) is usually "present in complexes with halide (chromyl chloride) and oxygen ligands (chromium trioxide, chromate, dichromate)." There are numerous Cr(VI) compounds. Some examples are potassium chromate, dichromate, sodium chromate, chromium trioxide, and lead chromate. Hexavalent chromium compounds can vary considerably in their water solubility and other physical properties.

2.4 Hexavalent Chromium (Chromium VI)

Chromium VI as one of the major pollutants of the environment is available in nature as an odorless, steel grey hard metallic element. It is the seventh most abundant element on the earth and twenty first most abundant elements in the rocks (McGrath and Smith, 1990). Elemental chromium is not usually found pure in nature and principally occurs as the mineral chromite $FeOCr_2O_3$or chrome iron stone in which form it is extremely stable. Chromium exists in nature as stable hexavalent and trivalent forms (Sen and Ghosh, 2010). The hexavalent form of chromium is more toxic than trivalent chromium and is often present in wastewater as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). This is of serious environmental concern as Cr (VI) persists indefinitely in the environment complicating its removal (Sen and Ghosh, 2010).

Hexavalent chromium (chromium VI) refers to Chromate, a chemical compound that contain the element chromium in the +6 oxidation state. Virtually all chromium ore is processed via hexavalent chromium, specifically the salt sodium dichromate. Approximately 136,000,000 kilograms (300,000,000 lb) of hexavalent chromium were produced in 1985 (Gerd*et al.*, 2005.) Other hexavalent chromium compounds are chromium trioxide and various salts of chromate and dichromate. Hexavalent chromium is used for the production of stainless steel, textile dyes, wood preservation, leather tanning, and as anti-corrosion and conversion coatings as well as a variety of niche uses. (David and Volesky, 2003).

Hexavalent chromium is recognized as a human carcinogen via inhalation. Workers in many different occupations are exposed to hexavalent chromium. Problematic exposure is known to occur among workers who handle chromate-containing products as well as those who arc weld stainless steel. Within the European Union, the use of hexavalent chromium in electronic equipment is largely prohibited by the Restriction of Hazardous Substances Directive (Kadirvelu*et al*., 2001).

2.4.1 Toxicity of Chromium (VI)

Relying on chemical, toxicological, and epidemiological evidence, Chromium (VI) is both a powerful epithelial irritant and a confirmed human carcinogen. Additionally, chromium (VI) is toxic to many plants, aquatic animals, and bacteria. (Gregory and Rudolph, 2002).

Chromium (VI) can act as an oxidant directly on the skin surface or it can be absorbed through the skin, especially if the skin surface is damaged. Interestingly enough, irritation

of the skin a most frequently reported human health effect from exposure to Cr (VI), taking the form of skin ulceration (dermatosis) and allergic sensitization (dermatitis) (Khitrov and Jaeger,2002).

Respiratory cancer is the health effect of most concern and is the basis for the regulation of chromium (VI). There is also some indication that chromium (VI) may cause cancer of the upper airways and upper gastrointestinal tract, such as the esophagus, larynx, trachea, and stomach. Chromium (VI) appears to be a contact carcinogen to the respiratory system. It has not been implicated in skin cancer, where there is far more frequent and intense contact than for any other part of body (Gregory and Rudolph, 2002).

Autopsy studies of human lungs show that inhaled chromium builds up in the lungs. Chromium concentration in the lungs was found to increase with age for both occupationally and environmentally exposed individuals. The upper lobes tended to have higher concentrations than lower lobes and cancerous portions of lungs showed the highest chromium concentrations. The study on environmental exposure in Hudson County, New Jersey, showed elevated urine chromium levels among residents living on or near landfills containing chromium; the chromium levels in urine also correlated with chromium content of household dust, but the exposure appears to have resulted from ingestion (Stern *et al.,* 1992). Likewise, a similar study in Lecheria, Estado de Mexico, Mexico found elevated concentrations of chromium in the urine of residents around a chromate manufacturing plant. Respirable airborne particles, contaminated water, and contaminated soil were all possible exposure routes (Rosas *et al.*, 1989).

In several epidemiological studies slightly elevated incidence of stomach cancer were reported. In these cases, the route of exposure was inhalation, not ingestion. This may indicate that the chromium reaches the stomach via clearance of the mucous membranes lining the airways. However, these results are not definitive, and it is not widely accepted that chromium (VI) is a carcinogen in the stomach (Gregory and Ruldolph, 2002).

There is vast literature documenting the mutagenic and cytogenic effects of various chromium compounds, which are reviewed by (Levis and Bianchi, 1982; Cohen *et al*., 1993). Various studies have shown various chromium (VI) compounds cause many kinds of genetic damage in the laboratory. However, in a field study (Gao*et al.*, 1994) found no increased DNA damage to lymphocytes among exposed chromium workers when compared with an unexposed group, even though the exposed group had elevated blood, plasma, and urine chromium concentrations. On the other hand (Taioli*et al.*, 1995) found slightly elevated numbers of chromate-specific DNA-protein cross links among residents of Hudson County (New Jersey) with elevated chromium urine concentrations when compared with a control population. Both of these studies used white blood cells (WBCs) for DNA testing; however, because chromates are not associated with any white blood cells or even circulatory disorders. Another theory holds that chromium (VI)-induced damage to cells causes the release of hydrolytic enzymes from the lysosomes(Khitrov and Jaeger,2002).

2.4.2 Chromium (VI) and the Environment

Chromium VI can be found in air, soil, and water after release from the manufacture, use, and disposal of chromium-based products.Chromium VI does not usually remain in the atmosphere, but is deposited into the soil and water.Chromium VI can easily change from

one form to another in water and soil, depending on the conditions present (Kratochvil and Volesky, 1998):

2.4.3 Health Hazards of Chromium (VI)

Breathing high levels of chromium (VI) can cause irritation to the lining of the nose, nose ulcers, runny nose, and breathing problems, such as asthma, cough, shortness of breath, or wheezing. The concentrations of chromium in air that can cause these effects may be different for different types of chromium compounds, with effects occurring at much lower concentrations for chromium (VI) compared to chromium (III) (Sen and Dastidar, 2010).

The main health problems seen in animals following ingestion of chromium (VI) compounds are irritation and ulcers in the stomach and small intestine and anemia. Chromium (III) compounds are much less toxic and do not appear to cause these problems (Gregory and Jaeger, 2002).

Sperm damage and damage to the male reproductive system have also been seen in laboratory animals exposed to chromium (VI).Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted(Khitrov*et al.,* 2000).

2.5 Packed Bed Column Reactor

The most effective apparatus for continuous operation is a column reactor, which handles product as a flowing stream, much like that used for ion exchange. A column reactor is also a kind of bioreactor which is a vessel in which a chemical process is carried out, it

usually involves organisms or a biochemically active substance. Thus, many researchers have used a column packed with various biomasses capable of removing heavy metals (Volesky*et al.,* 2003). Meanwhile, many mathematical models have been used to study column systems, and their dynamic behavior has also been well established (Figueira*et al., 2000*). All these models have been mainly originated from research on activated carbon sorption, ion exchange or chromatographic applications. However, in the case of Cr (VI) removal in the column, a few studies have been reported, but no theoretical model has been proposed to predict the experimental breakthrough data (Park*et al.*, 2006).Biosorbent packed in a column appears to be the most appropriate device for effective and continuous removal of heavy metals (Kratochvil and Volesky, 1998). Various parameters affect the biosorption process in column such as, mass of biosorbent, flow rate of influent, temperature, initial concentration of influent and pH.

2.5.1 Benefits of Continuous Reactors

I. The rate of many chemical reactions is dependent on reactant concentration. Continuous reactors are generally able to cope with much higher reactant concentrations due to their superior heat transfer capacities. Plug flow reactors have the additional advantage of greater separation between reactants and products giving a better concentration profile.

II. The small size of continuous reactors makes higher mixing rates possible.

III. The output from a continuous reactor can be altered by varying the run time. This increases operating flexibility for manufacturers.

2.6 The Adsorption Isotherm of Metal Removal

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and solid phase, when the adsorption process reaches equilibrium state. The equilibrium of the biosorption process of heavy metals is often described by fitting the experimental points with the model (Gadd*et al*., 1988). The Freundlich and Langmuir models were used to describe the biosorption equilibrium.

2.6.1Freundlich Adsorption Study

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by the equation.

$q_e = K_F C_e^{1/n}$ qe

WhereK_F and n are Freundlich constants characteristic of the system.K_F and n are indicators of adsorption capacity and intensity, respectively. The equation can be linearized in logarithmic form and Freundlich constants can be determined.

The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model(Donmez*et al.*, 1999). The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the powder and the linear form is represented by equation :

$lnq_e = ln\ K_f + {}^{1}/_{n} ln\ C_e$

Where; q_e (mg/g) is the metal ion uptake per unit weight of maize cob powder; C_e is the concentration of metal ions in solution at equilibrium (mg/dm^3); $K_f$and $_n$ are the Freundlich constants. The value of $K_f$is a measure of the degree of adsorption and n

indicates the affinity of the sorbent toward the powder. For *1/n* less than unity, adsorption is the predominant process taking place otherwise desorption becomes predominant (Matakaet *al*, 2010).

A plot of lnq_e against $\ln C_e$ in equation above, yielding a straight line indicates the confirmation of Freundlich adsorption isotherm. The constants, *n* and $K_f$can be obtained from the slope and intercept respectively.

2.6.2Langmuir Adsorption Study

The Langmuir equation which is valid for monolayer sorption onto a surface a finite number of identical sites and is given by below:

$q_e = K_L 1/q_{max} Ce/1 + 1/q_{max} C_e$

where K_L is the maximum amount of the metal ion per unit weight of cell to form a complete monolayer on the surface bound at high C_e (mg g^{-1}) and$1/q_{max}$is the constant related to the affinity of the binding sites, K_L represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. $K_L$and$1/q_{max}$can be determined from the linear plot of C_e/q_eversus C_e (Matakaet *al*, 2010).

The linearized form of the equation after arrangement is given by:

$C_e/q_e = 1/q_{max} K_L + C_e/q_{max}$

Where K_L (dm^3 g^{-1}) is a constant related to the adsorption energy and $q_{max}$is the maximum sorption upon complete monolayer saturation of the powder surface. The experimental

data were fitted to equation 1 for linearization by plotting C_e/q_eagainst C_e to obtain a straight line graph.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Biosorbent

The biosorbent used are corn cobs, obtained from a local farm at Samaru located in Zaria, Kaduna state. The corn cobs were identified at the herbarium in the department of Biological Science,Ahmadu Bello University Zaria, and it was assigned a voucher number 2399.

3.1.2 Reagents and Equipment

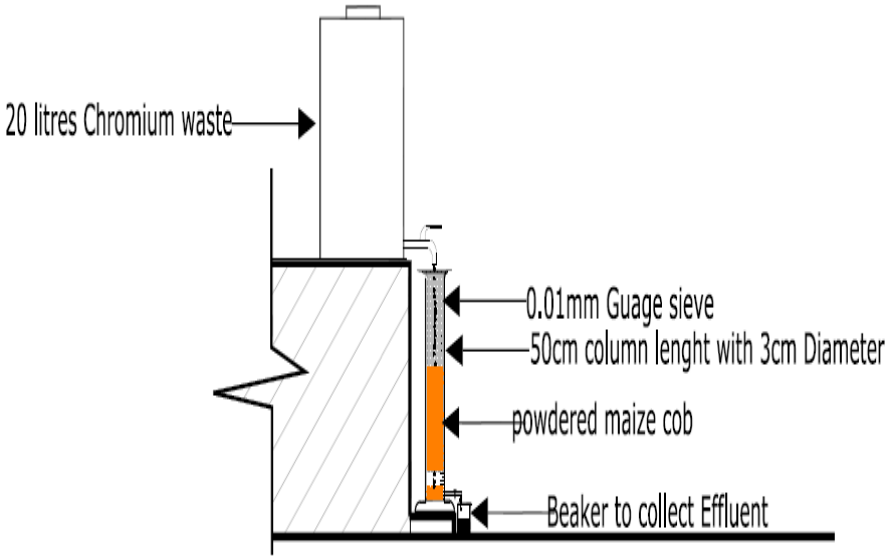
The chemicals and reagent used were of analytical grade and are as follows: Potassium dichromate (Sigma-Aldrich), Absolute Ethanol (Merck) 1, 5 diphenylcarbazide (Sigma-Aldrich), concentrated sulphuric acid (Sigma-Aldrich), monobasic sodium phosphate (Sigma-Aldrich), Acetic acid (Sigma-Aldrich), and Sodium hydroxide (Sigma-Aldrich).

The equipment used are as follows: a continuous bioreactor (laboratory scale),Jenway 6305 UV/VIS Spectrophotometer (S/N 20307),Laboratory milling machine (S/N 285307), weighing analytical balance (S/N 8030151073), water bath Grant JB Series, (S/N 630314002),Jenway pH meter (S/N 32609), SHIMADZU FTIR – 8400S Fourier Transform Infrared Spectroscopy.

3.1.3 Continuous Reactor System

The continuous reactor system used in this study consist of 10 L of chromium waste as a flowing stream and a 50 cm long and 3cm internal diameter plastic column, the column

was densely packed with a known amount of powdered maize cob. The process was operated in a down flow mode, and set at constant temperature with the aid of a water bath. The chromium waste was continuously fed into the reactor and emerges as continuous stream of product. The effluent was collected at the bottom of the column and quantified. Each experiment was carried out until the effluent Cr (VI) concentration (*Ct*) were close to the influent concentration (*C*0), *Ct*/*C*0=0.90. Continuous experiments were performed in triplicate and the mean values are presented with a maximum deviation of 5% in all the studied cases.



Fig, 3.1 A Continuous Bio-reactor setup

To quantify the removal capacity of each column under given operating condition, a graph of effluent concentration was plotted against the operating time, as well as a graph showing percentage removal against time.

3.2 Methods

3.2.1 Pre-treatment of Biosorbent

Maize cobs weighing 1200g was washed in acetone to disinfect them and then rinsed in deionized water; it was then dried in the lab for 7days at room temperature (Park*et al.*, 2006). The already treated maize cob was then broken into smaller pieces using a mortar and pistle to allow the laboratory machine to grind it.

3.2.2 Preparation of Chromium (VI) Solution

In the preparation of chromium (VI) stock solution, potassium dichromate was used as the source of chromate. Potassium dichromate (100mg) was weighed and dissolved in 10 liter of deionized waterto give a final solution of 10mg/L.

3.2.3 Preparation of DiphenylCarbazide Solution (Developing Reagent)

1, 5 diphenylcarbazide (0.1g) was weighed and dissolved in 47.5 ml of absolute ethanol by shaking in a volumetric flask (solution A).Sulphuric acid (0.5ml) was measured and added to 2ml of deionized water (solution B). Solutions A and solution B were then mixed together and stored in a brown bottle. Diphenylcarbazide is an organic reagent which forms red violet complex with chromium (VI)(Park*et al.*, 2006).

3.2.4 Determination of Chromium (VI) Concentration

A colorimetric method, as described in the Standard Methods was used to measure the concentrations of chromium (VI) ions in solution (Clesceri et al., 1998). The absorbance of the pink colored complex formed by the reaction of 1, 5-diphenycarbazide with Cr(VI) in acidic solution was readspectrophotometricallyat 540 nm.

The concentration of Cr (VI) in the liquid samples was determined spectrophotometrically.Diphenylcarbazide solution (1ml) was pipette into a test tube, and 1ml of varying concentrations of chromium VI solution were added and allowed to stand for 10 minutes in a dark area, and the absorbance was taken at 540nm using a spectrophotometer(Park *et al.*, 2006). Color formation was based on the reaction of Cr (VI) with 1, 5-diphenylcarbazide (DPC) in an acidic solution. The Cr (VI) is reduced to Cr (III) by the DPC which is, at the same time, oxidized to 1,5diphenylcarbazone forming a red-violet complex with the Cr(III) (Najdeker, 1971) .

3.2.5 Preparation of Standard Curve

This was done by taking 1ml of varying concentrations of chromium solution and adding to 1ml of diphenylcarbazide solution and then allowed to stand for 10 minutes in a dark area. The absorbance was taken at 540nm using a spectrophotometer. The respective absorbance values were then plotted against corresponding concentrations to obtain a standard curve.

3.2.6 Determination of the Effect of Mass of Corncob Chromium (VI) Removal

120g and 60g of corncob powder was weighed separately, and each mass was packed into the column of the same length and thesynthetic Cr (VI) solution was allowed to flow into the column at a flow rate of 10 ml min^{-1}, the effluent was filtered using an inbuilt sieve in

the column and Cr (VI) concentration was determined in the filtrate, as described byPark*et al.*,(2006).

3.2.7 Determination of the Effect of flow rate on Chromium (VI) Removal

The mass of corn cob powder at which maximum adsorption of chromium wasobserved was packed into the column and the flow rate range from 5 to 20ml min^{-1} was used at different runs while maintaining the influent Cr (VI) concentration constantly at 100 mg L^{-1}, and filtered using an inbuilt sieve in the column. The effluent concentration was quantified in accordance with the method described by Park*et al.*,(2006).

3.2.8 Determination of the Effect of Temperature on Chromium (VI) Removal

Under a temperature range of 30°C to 80°C, using a water bath to regulate the temperature, synthetic Cr (VI) solution was allowed to flow at a flow rate of 10 ml min^{-1} into the column packed withthe mass of corn cob powder at which adsorption was found to be optimum and the residual chromium VI ion concentration of the effluent was determined(Park*et al.,* 2006).

3.2.9 Determination of the Effect of Initial $K_2Cr_2O_7$ Concentration on chromium (VI)Removal

To evaluate the effect of the influent Cr (VI) concentration on its removal in the column, the mass of corn cob powder at which adsorption is maximal was packed into the column and the concentration of influent Cr (VI) was increased from 100 to 200 mg L^{-1} under the same operating condition,and the effluent Cr (VI) was filtered using an inbuilt sieve in the column, and the effluent chromium (IV) ion was quantified (Park*et al.,* 2006).

3.3.0 Determination of the Effect of pH on Chromium (VI) Removal

At a pH of 2 and 5, using hydro chloric acid and 20.0mmol/dm^{-3} sodium hydroxide to regulate the pH, Synthetic Cr (VI) wastewater was allowed to flow at a flow rate of 10 ml min^{-1} into the column packed with mass of corn cob powder at which adsorption is maximal. The filtered effluent chromium (VI) concentration was then quantified (Park*et al.,* 2006).

3.3.1 The Use of activated carbon which is Standard Adsorbent used in Industry

All procedures done above were repeated but the absorbent used to reduce the synthetic chromium (VI) waste was activated carbon a standard adsorbent used in industry.

3.3.2 The use of sample Waste Water containing Chromium (VI) from Leather Tanning Industry

All procedures done in earlier experiment was repeated using maize cob powder as the adsorbent to reduce industrial chromium VI waste from leather tanning industry NILEST Zaria.

3.3.3 FTIR Analysis of Biosorbent

Characterization of the chemical surface of the corncob powder was done by Shimadzu 8400S Fourier transform infrared spectrometer at NARICT (National Research Institute for Chemical Technology). The unexposed and Cr (VI) exposed corncob powder were each mixed with 100mg KBr (Potassium bromate). The powdered mixture was pressed in a mechanical die press to form pellet by a pressure of 1200 psi for 5min. The pellet formed was then inserted into the instrument and the absorption spectral was recorded from 400 to 4000 cm^{-1}.

3.3.4 Statistical Analysis

Data obtained in this study was analyzed using statistical package for the social sciences (SPSS), version 20. The results were expressed as mean ± standard deviation except where otherwise stated. The data was analyzed by analysis of variance (ANOVA). The difference between the various groups were compared using the Duncan Multiple Range Test. P values less than 0.05 ($P<0.05$) were taken as significant.

CHAPTER FOUR

RESULTS

4.1 Effect of Mass of Corn Cob on Chromium (VI) Removal

Figure 4.1 presents the effect of the mass of biosorbent (60g and 120g) on the percentage (%) removal of Cr (VI) ions from aqueous solutions. The plot depicts the biosorption potential of corncob powder based on its mass. From the result, the percentage removal of Cr (VI) is higher when a biomass of 120g of corncob powder was packed in the column (70 ± 11.39 %) and a lower percentage removal (55 ± 5.05 %) was obtained with a biomass of 60g.

4.2 Effect of Flow Rate on Chromium (VI) Removal

The effect of flow rate on the percentage removal of Cr (VI) ion from aqueous solution is shown in Figure 4.2. Flow rates of 5, 10,15 and 20ml/min were investigated respectively; it was found that the percentage removal of Cr (VI) was 77 ± 5.25 %, 70 ± 11.39 %, 40 ± 9.56 % and 39 ± 7.56 % respectively. Thus the flow rate of 5ml/min was shown to have the highest percentage removal of Cr (VI) of up to 77 ± 5.25 %.

4.3 Effect of Temperature on Chromium (VI) Removal

Figure 4.3 shows the result of the effect of temperature on the percentage removal of Cr (VI) from aqueous solution. Temperature of 30°C, 40°C, 50°C, 60°C, 70°C and 80°C were investigated, and a percentage removal of 57 ± 3.03 %, 58 ± 0.84 %, 67 ± 7.45 %,69

± 2. 64 %,70 ± 11.39 % and 46 ± 7.45 % were obtained respectively. The temperature of 70°C was shown to have the highest percentage removal of 72%.

4.4 Effect of Initial $K_2Cr_2O_7$ Concentration on Chromium (VI) Removal

The effect ofinitial $K_2Cr_2O_7$ concentration on the percentage removal of chromium VI from aqueous solution is illustrated in Figure 4.4. There was a higher percentage removal of about 70 ± 11.39 %, when a concentration of 100mg/L potassium dichromate was allowed to pass through the column packed with a constant biomass of 120g. A lower percentage removal of 30 ± 8.67 % was observed when the concentration of potassium dichromate was increased to 200mg/L, keeping the mass of the biomass constant at 120g.

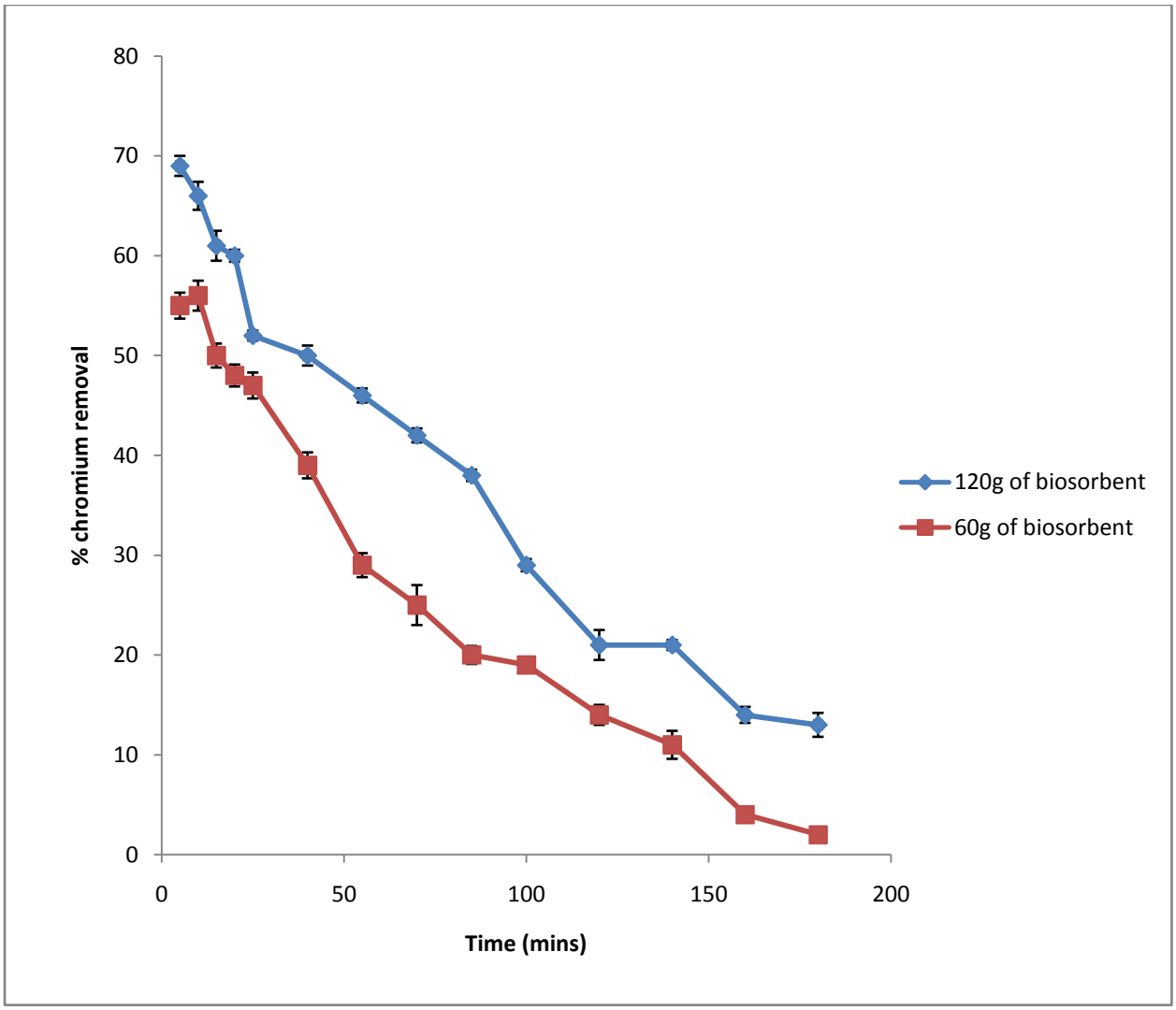


Fig 4.1.Effect of Mass of Biosorbent on Percentage Removal of Cr (VI) in the Column.

Table 4.1. Effect of Mass of Biosorbent on Percentage Removal of Cr (VI) in the Column

Time of continuous Biosorption (mins)	**Effect of mass on % of Chromium (VI) removed using Corn cob powder adsorbent**	
	60 (mg)	120 (mg)
5	55 ±5.05[a]	70 ±11.39[a]
10	56 ±2.54[a]	66 ±9.44[b]
20	48 ± 3.03[b]	60 ±8.34[c]
40	39 ± 2.43[c]	50 ±5.03[d]
70	25 ± 1.34[d]	42 ±8.36[e]
100	19 ± 4.24[e]	29 ±8.02[f]
120	14 ±3.65[f]	21 ±4.45[g]
140	11 ±2.03[f]	21 ±4.23[g]
180	4 ± 0.45[g]	14 ±1.65[h]

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

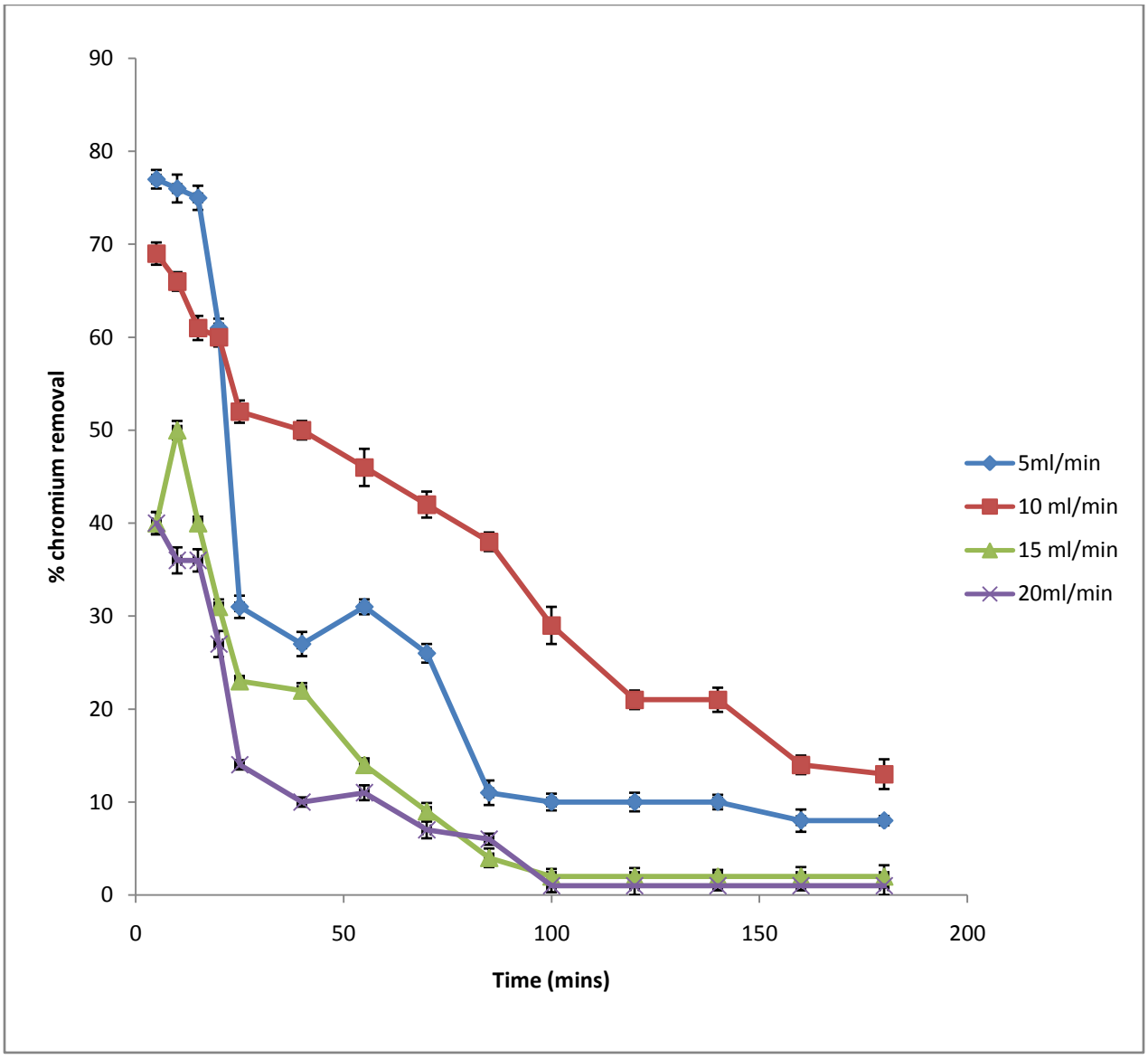


Fig 4.2 Effect of Flow Rate on the Percentage Removal of Cr (VI) in the Column.

Table 4.2 Effect of Flow Rate on the Percentage Removal of Cr (VI) in the Column.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**			
	5 (min/ml)	10 (min/ml)	15 (min/ml)	20 (min/ml)
5	77 ± 5.25^{a}	70 ± 11.39^{a}	40 ± 9.34^{a}	39 ± 7.56^{a}
10	76 ± 4.87^{b}	66 ± 9.44^{b}	50 ± 4.53^{b}	36 ± 5.05^{b}
20	61 ± 2.56^{c}	60 ± 8.34^{c}	31 ± 5.95^{c}	27 ± 5.54^{c}
40	27 ± 1.04^{d}	50 ± 5.03^{d}	22 ± 3.34^{d}	10 ± 2.43^{d}
70	26 ± 4.45^{e}	42 ± 8.36^{e}	9 ± 2.06^{e}	8 ± 1.56^{e}
100	16 ± 3.29^{f}	29 ± 8.02^{f}	5 ± 0.89^{f}	4 ± 0.18^{f}
120	10 ± 3.23^{g}	21 ± 4.45^{g}	2 ± 0.56^{g}	1 ± 0.05^{g}
140	8 ± 0.98^{h}	21 ± 4.23^{g}	2 ± 0.97^{g}	1 ± 0.12^{g}
180	8 ± 1.67^{h}	14 ± 1.65^{h}	2 ± 0.94^{g}	1 ± 0.56^{g}

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

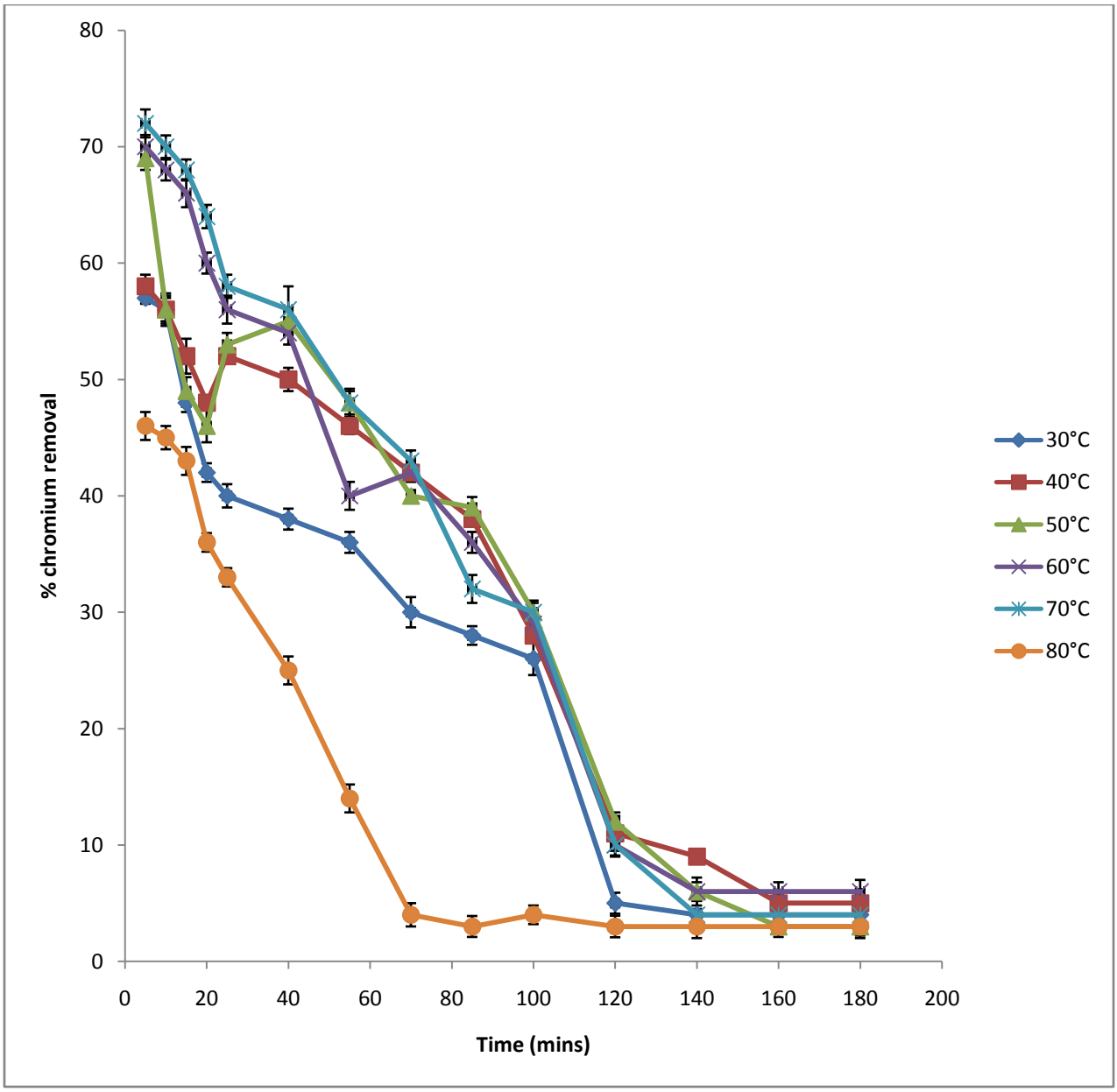


Fig 4.3.Effect of Temperature on the Percentage Removal of Cr(VI) in the Column.

Table 4.3 Effect of Temperature on the Percentage Removal of Cr (VI) in the Column.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**					
	30 (°C)	40(°C)	50(°C)	60(°C)	70(°C)	80(°C)
5	57 ±3.03[a]	58 ±0.84[a]	67 ± 7.45[a]	69 ±2.64[a]	70 ± 11.39[a]	46 ± 7.45[a]
10	56 ±2.34[b]	56 ± 6.45[b]	56 ±1.34[b]	68 ± 10.21[b]	66 ± 9.44[b]	45 ± 7.02[b]
20	42 ± 4.23[c]	48 ± 11.56[c]	46 ± 4.45[c]	60 ± 12.34[c]	60 ± 8.34[c]	36 ± 4.35[c]
40	38 ± 9.45[d]	50 ± 12.24[d]	55 ± 6.54[d]	54 ± 9.45[d]	50 ± 5.03[d]	25 ± 2.75[d]
70	30 ± 6.45[e]	42 ± 6.34[e]	40 ± 8.34[e]	42 ± 7.93[e]	42 ± 8.36[e]	10 ± 2.20[e]
100	26 ± 7.05[f]	28 ± 3.43[f]	30 ± 5.43[f]	29 ± 4.53[f]	29 ± 8.02[f]	6 ± 1.45[f]
120	5 ± 0.56[g]	11 ± 2.87[g]	12 ± 3.67[g]	10 ± 2.34[g]	21 ± 4.45[g]	4 ± 0.56[g]
140	4 ± 0.46[h]	9 ± 3.43[h]	6 ± 0.93[h]	6 ± 0.56[h]	21 ± 4.23[g]	3 ± 0.02[h]
180	4 ± 0.65[h]	5 ± 0.34[i]	3 ± 0.15[i]	6 ±0.13[h]	14 ±1.65[h]	3 ± 0.12[h]

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

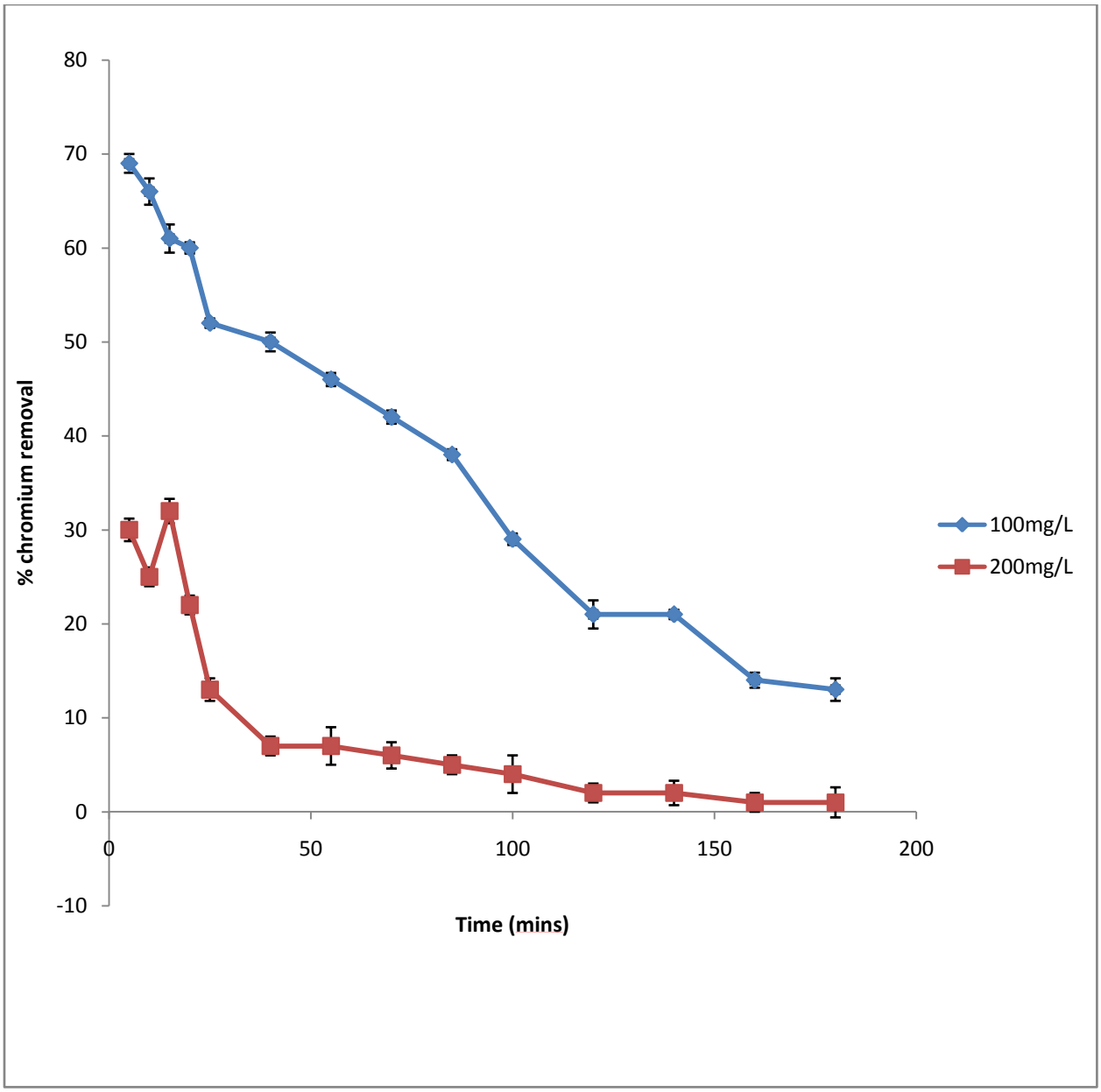


Fig 4.4 Effect of Initial Concentration of Cr(VI) in synthetic waste on the Percentage Removal of Cr (VI) in the Column.

Table 4.4 Effect of Initial Concentration of Cr(VI) in synthetic waste on the Percentage Removal of Cr (VI) in the Column.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**	
	100 (mg/L)	200 (mg/mL)
5	70 ± 11.39^{a}	30 ± 8.67^{a}
10	66 ± 9.44^{b}	25 ± 7.49^{b}
20	60 ± 8.34^{c}	22 ± 6.87^{c}
40	50 ± 5.03^{d}	23 ± 6.39^{d}
70	42 ± 8.36^{e}	15 ± 1.98^{e}
100	29 ± 8.02^{f}	10 ± 1.09^{f}
120	21 ± 4.45^{g}	6 ± 0.86^{g}
140	21 ± 4.23^{g}	4 ± 0.67^{h}
180	14 ± 1.65^{h}	2 ± 0.12^{i}

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

4.5 Effect of pH on Chromium (VI) Removal

The result of the effect of pH on the percentage removal of Cr (VI) ions from aqueous solutions is shown in Figure 4.5. This plot depicts the biosorption potential of corncob powder in the column at a pH of 2 and 5. It was found that using a constant biomass of 120g, at pH 2 a higher percentage removal of about 98 ± 1.63 % was obtained and at a pH of 5, a percentage removal of 70 ± 11.39 % was obtained. But when 60g of the biomass was packed in the column the percentage removal of 82 ± 3.37 % was observed at pH 2.

4.6 The Use of Activated Carbon which is Standard Adsorbent Used in Industry

The percentage removal of Cr (VI) ions from aqueous solution using activated carbon packed in the column was compared with the percentage removal observed when corncob powder was packed in the column, as illustrated in Figure 4.6. The percentage removal obtained using activated carbon as the biosorbent was found to be 85 ± 3.37 % while the percentage removal observed using corncob powder as the biosorbent was found to 70 ± 11.39 %.

4.7The Use of Sample Waste Water Containing Chromium (VI) From Leather Tanning Industry

Figure 4.7 shows the result obtained when corncob powder was used to treat an industrial waste, comparing it with its ability to treat Chromium in solution. It was found that the percentage removal of Cr (VI) ions from the industrial waste using corncob powder as biosorbent was 40 ± 7.94 %, while the percentage removal of Cr (VI) ions from the chromium solution using the same amount of corncob powder was 70 ± 11.39 %.

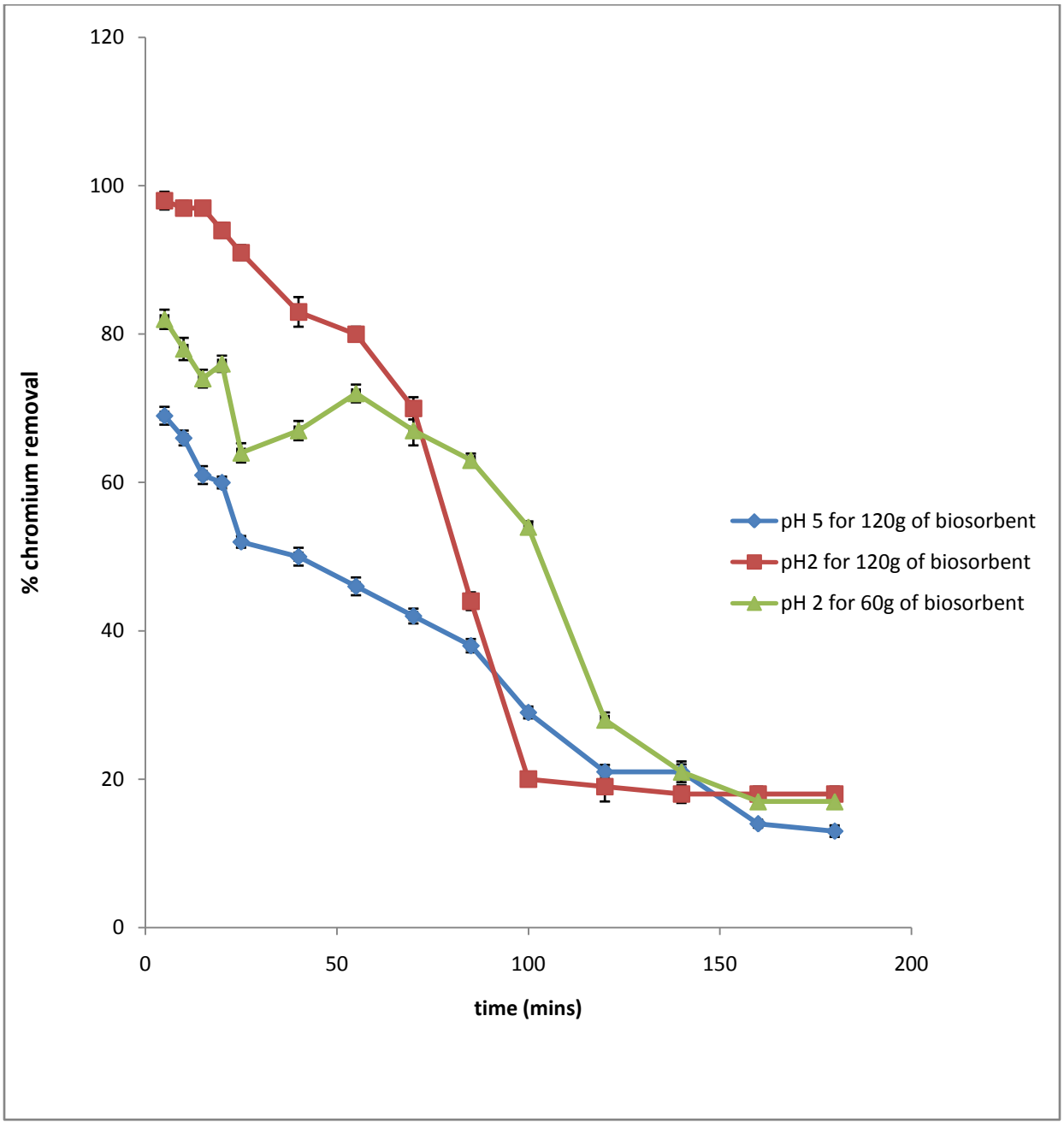


Fig 4.5 Effect of pH on the Percentage Removal of Cr (VI) in the Column.

Table4.5 Effect of pH on the Percentage Removal of Cr (VI) in the Column.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**		
	pH 5 for 120g	pH 2 for 120g	pH 2 for 60g
5	70 ± 11.39^{a}	98 ± 1.63^{a}	82 ± 3.37^{a}
10	66 ± 9.44^{b}	97 ± 8.29^{ab}	78 ± 5.94^{b}
20	60 ± 8.34^{c}	94 ± 7.26^{bc}	76 ± 5.48^{bc}
40	50 ± 5.03^{d}	83 ± 3.26^{d}	67 ± 4.95^{c}
70	42 ± 8.36^{e}	70 ± 6.37^{e}	54 ± 3.05^{d}
100	29 ± 8.02^{f}	20 ± 2.38^{f}	28 ± 6.47^{e}
120	21 ± 4.25^{g}	19 ± 5.23^{fg}	21 ± 5.86^{f}
140	21 ± 4.03^{g}	18 ± 4.23^{g}	17 ± 3.75^{g}
180	14 ± 1.65^{h}	18 ± 4.67^{g}	10 ± 2.98^{h}

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

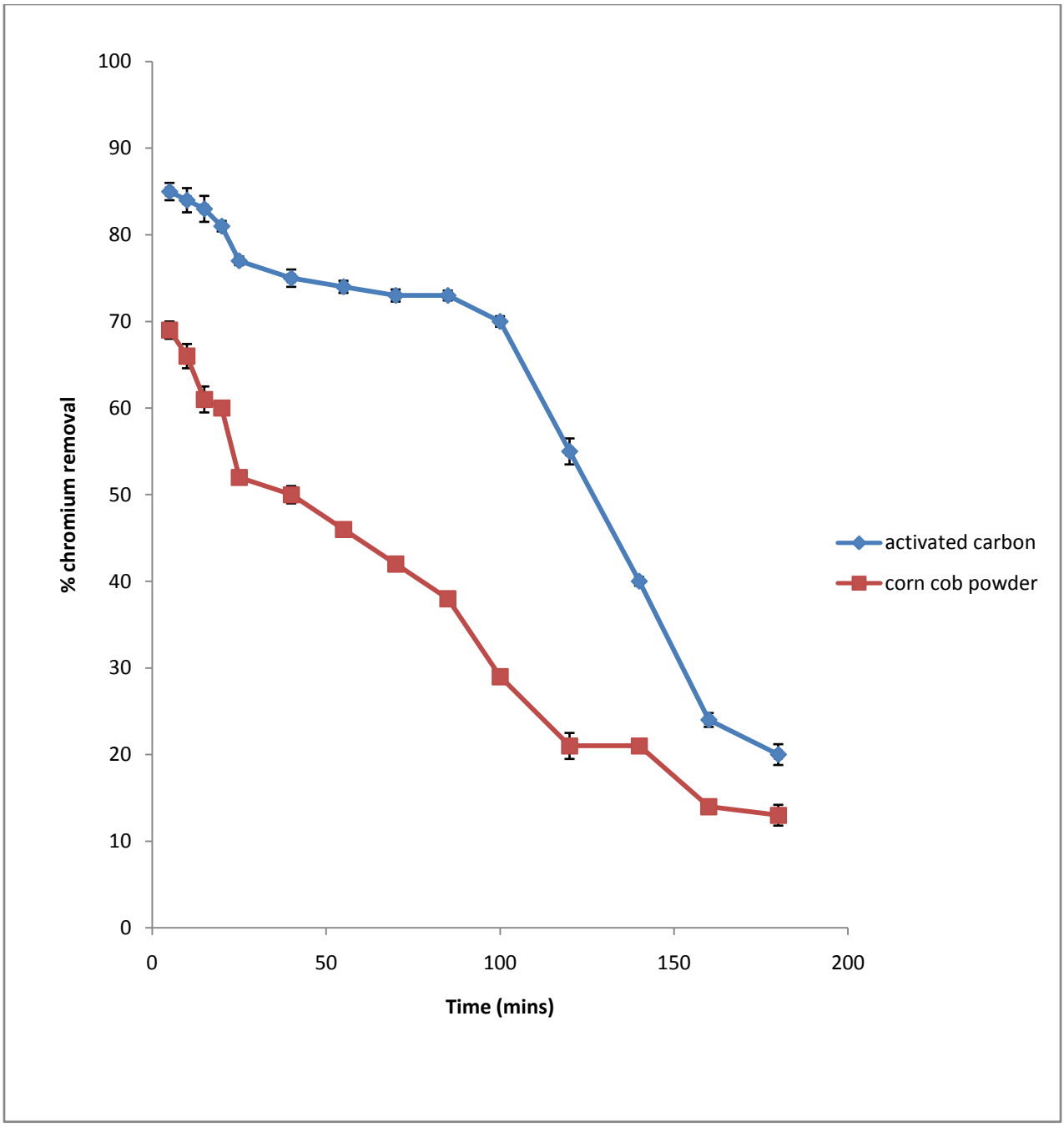


Fig 4.6 Percentage Removal of Cr(VI) from Cr(VI) Solution Using an Industrial Biosorbent and Corn Cob Powder.

Table 4.6 Percentage Removal of Cr(VI) from Cr(VI) Solution Using an Industrial Biosorbent and Corn Cob Powder.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**	
	Industrial Biosorbent	Corncob Powder
5	85 ±3.73[a]	70 ± 11.39[a]
10	84 ±4.29[a]	66 ± 9.44[b]
20	81 ± 4.37[b]	60 ± 8.34[c]
40	75 ±8.27[c]	50 ± 5.03[d]
70	73 ±9.02[c]	42 ± 8.36[e]
100	70 ±2.34[d]	29 ± 8.02[f]
120	55 ±3.38[e]	21 ± 4.45[g]
140	40 ±6.39[f]	21 ± 4.23[g]
180	20 ±1.48[h]	14 ±1.65[h]

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

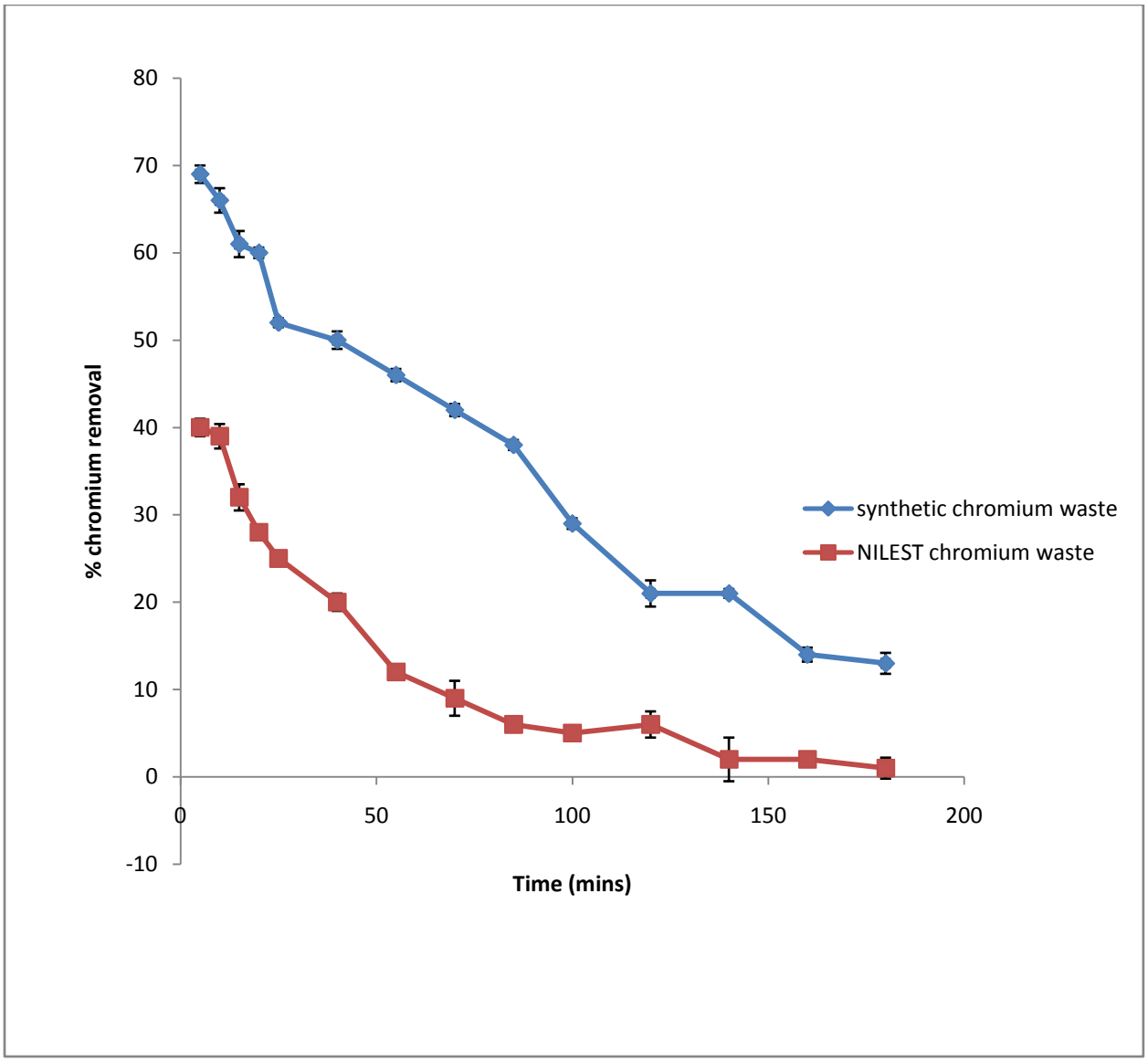


Fig 4.7 Percentage Removal of Cr(VI) by Corn Cob powder From a Cr(VI) solutionand an Industrial Waste.

Table 4.7 Percentage Removal of Cr(VI) by Corn Cob powder From a Cr(VI) solutionand an Industrial Waste.

Time of continuous Biosorption (mins)	**% of Chromium (VI) removed using 120 g of adsorbent**	
	Synthetic Chromium (VI) solution	Industrial waste from NILEST
5	70 ± 11.39^{a}	40 ± 7.94^{a}
10	66 ± 9.44^{b}	39 ± 7.04^{b}
20	60 ± 8.34^{c}	32 ± 3.12^{c}
40	50 ± 5.03^{d}	25 ± 3.75^{d}
70	42 ± 8.36^{e}	20 ± 2.34^{e}
100	29 ± 8.02^{f}	12 ± 1.87^{f}
120	21 ± 5.45^{g}	9 ± 1.04^{g}
140	21 ± 4.23^{g}	2 ± 0.45^{h}
180	14 ± 1.65^{h}	1 ± 0.91^{i}

Results are presented as mean ± SD. Values with different superscripts down the column are significantly different from each other at $P<0.05$.

4.8 FTIR Analysis

In order to determine which functional groups are responsible for metal uptake, FTIR spectra of the biosorbent, before and after Cr (VI) uptake, were carried out. The spectra of adsorbent were measured in the range of 400–4000cm^{-1}. As can be seen in Fig. 4.8, the spectra showed a number of absorption peaks, indicating the complex nature of the material studied. The FTIR spectrum of corn cob powder exhibits a broad peak at 3407.37cm^{-1}, 2854 cm^{-1}, and 1388.79cm^{-1}. There was a decrease in peak intensity at 2929.97 cm^{-1}, Bands around 1654.98cm^{-1} and 1730.21cm^{-1} , 1030.02–1141.90cm^{-1} were observed.

4.9 The Adsorption Isotherm of Biosorption Process

The linear graph showing the adsorption isotherm of Cr (VI) as shown in figure 4.9 was obtained at room temperature at a pH of 2. The Freundlich and Langmuir adsorption constants evaluated from the isotherm with their correlation coefficients are also represented in appendix 5, and high correlation coefficients where found for both studied model which are 0.985 and 0.993, respectively.

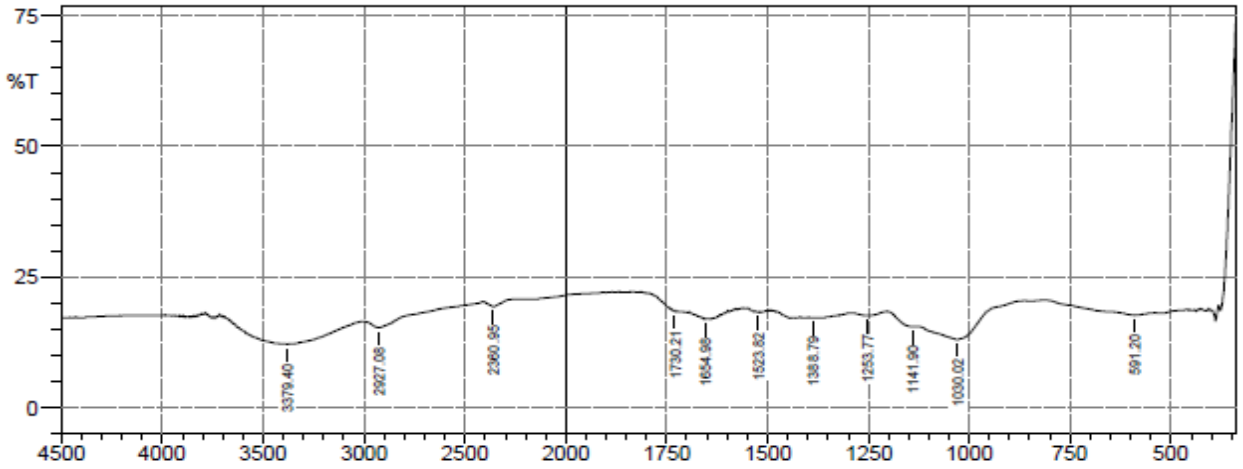


Fig 4.8a. FTIR Spectra of Corn Cob Powder

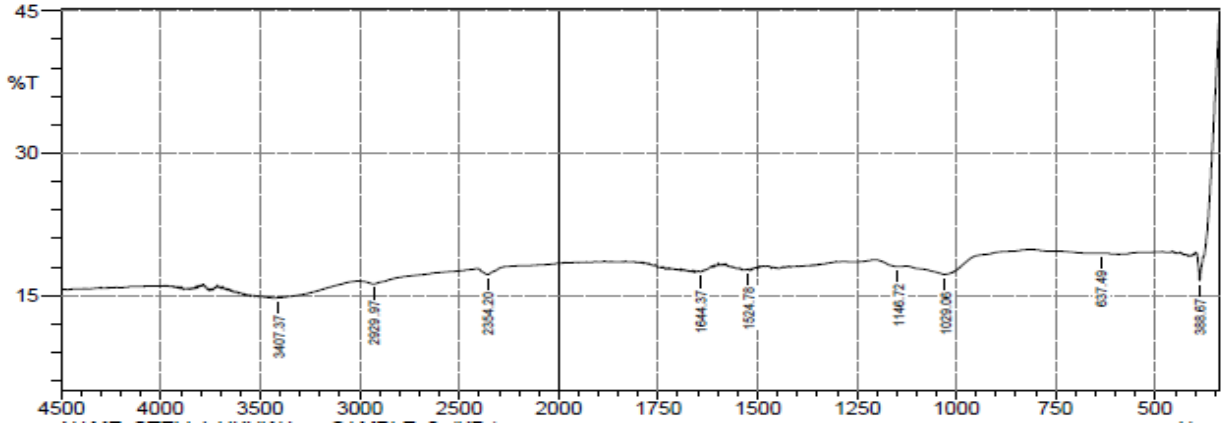


Fig 4,8b. FTIR Spectra of Corn Cob Powder Exposed To Cr (VI)

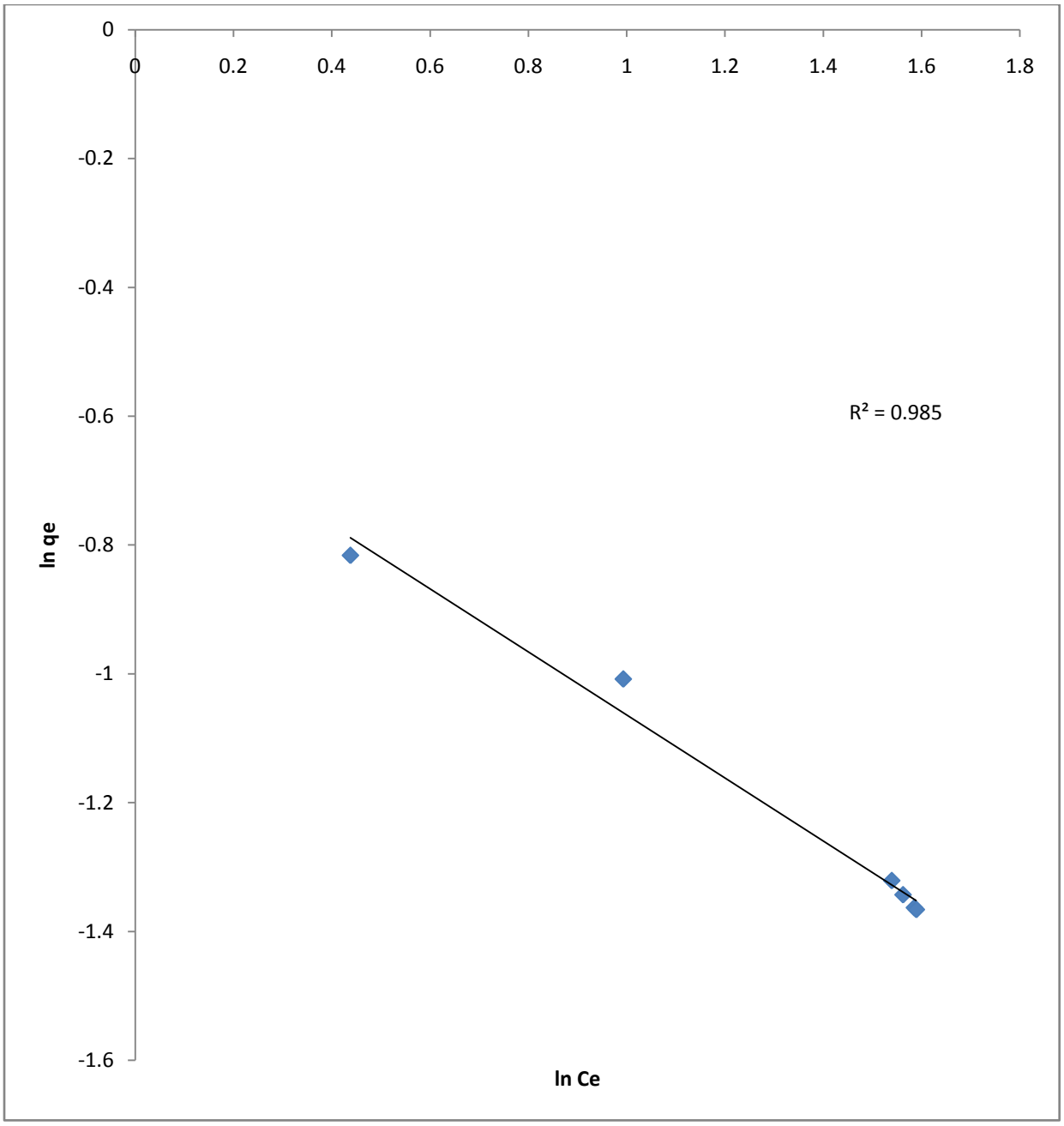


Figure 4.9a: Freundlich isotherm fits for chromium (VI) adsorption on corncob powder.

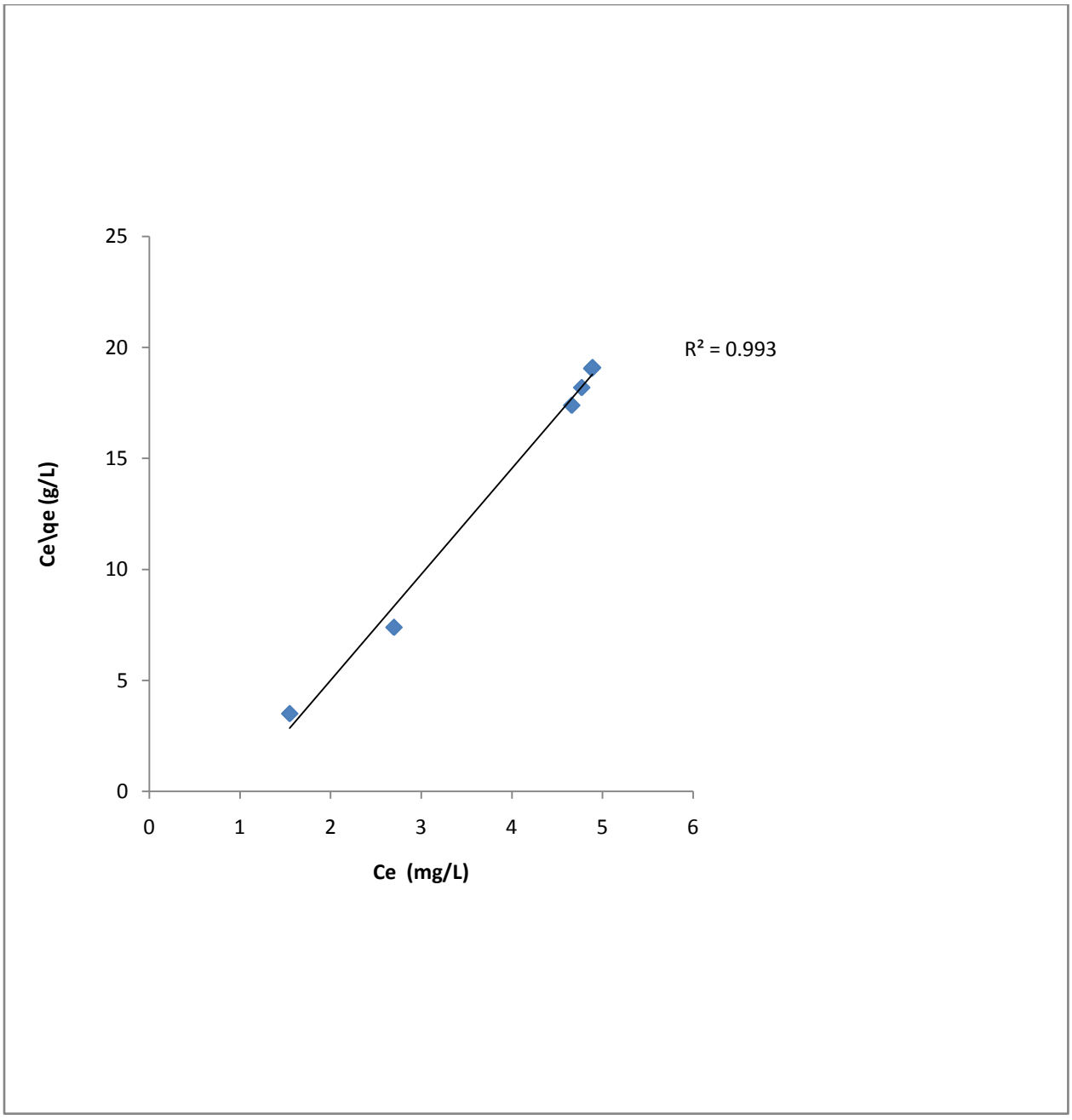


Figure 4.9b: Langmuir isotherm fits for chromium (VI) adsorption on corncob powder.

CHAPTER FIVE

DISCUSSION

The effect of the mass of biosorbent on chromium (VI) removal in the column revealed that on increase of the mass there was a higher percentage removal of chromium (VI) and vice versa, when the biomass concentration was decreased from 120 to 60 g L^{-1}, there was a reduction of Cr (VI) removal observed.The maximum percentage removal of Cr (VI) was 70 ± 11.39 % when a biomass concentration of 120 g L^{-1} was used, and a maximum percentage removal of 55± 5.05 % was obtained when a biomass concentration of 60 g L^{-1} was used (Fig 4.1). A similar result was observed in work carried out by Park et al., (2006) where the biomass concentration was decreased from 140 to 70 g L^{-1},This decrease in biomass concentration caused decreases in the Cr (VI) percentage removal, due to the lack of the electrons and the functional groups responsible forCr (VI) adsorption and binding (Park et al., 2004). The result of decrease in biomass concentration caused decreases in the reduction of Cr (VI) and total Cr removal efficiencies by the column.

The results of the percentage removal of Cr (VI) Showed that the lower the flow rate the longer the retention time, which allows for maximum binding and hence more biosorption of Cr (VI). The graph shows that the maximum percentage removal of Cr(VI) was 39± 7.56 % at a flow rate of 20mLmin^{-1}, 40± 9.34 % at a flow rate of 15mLmin^{-1}, 70 ± 11.39 % at a flow rate of 10mLmin^{-1}, 77± 5.25% at a flow rate of 5mLmin^{-1} (Fig 4.2). Earlier saturation and a lower Cr (VI)-removal efficiency were observed at flow of 15 and 20mLmin^{-1}. The two main reasons for this behavior are the insufficient reaction

time inside the column and the diffusion limitation of the Cr (VI) ions onto the surface of the biomass (Park *et al*,.2006)

Temperature is a thermodynamic parameter which affects the adsorption process. The effect of temperature on Cr (VI) removal was also examined in the column, and it was observed thathigher temperatures gave higher percentage removal. Using a temperature range of 30 - 80 ^{o}C, an increasing trend of Cr(VI) removal with increase in temperature was observed (Fig 4.3) . Thus, about 70 ± 11.39 % was realized as the maximum percentage removal of Cr (VI) at the 70 ^{o}C. This result was supported by previous batch experiment (Sallau*et al*., 2011). In general, increase in temperature increases the rate of a redox reaction (Wittbrodt and Palmer 1996) Das et al., (2000) and Guo et al., (2002) suggested that high temperature results in creation of some new sorption sites on the adsorbent surface by increasing the rate of intra particle diffusion of sorbate ions into the pores of adsorbent at higher temperature, since diffusion is often endothermic. However, at a temperature of 80°C the trend changed as the maximum percentage removal was 46 ± 7.45 % this may be due to damage of the physical properties of the biosorbent that interferes with binding of ionic species to it. Temperature, which usually enhances biosorptive removal of adsorptive pollutants when increased by increasing surface activity and kinetic energy of the adsorbate, but which may also damage the physical structure of the biosorbent(Park et al., 2010)

To evaluate the effect of the influent Cr(VI) concentration on its removal in the column, the concentration of it was increased from 100 to 200 mg L^{-1} under the same operating condition (Fig 4.4). The change in the influent Cr(VI) concentration significantly affected the bioadsorption and removal of Cr(VI) by corncob powder , as the maximum removal

percentage at an initial concentration of 200 mg L^{-1} was 30 ± 8.67 %, compared with the 70 ± 11.37 % obtained at an initial concentration of 100 mg L^{-1}, this could be due to a higher driving force for mass transfer ; hence, the adsorbent achieved saturation more quickly, which resulted in a decrease in exhaustion time and adsorption zone length (Baral*et al*., 2009) As expected, the higher the influent Cr(VI) concentration at a constant biomass concentration the lower the percentage removal, due to exhaustion of electrons required for Cr (VI) reduction and functional group required for binding the initial pollutant concentration (Yu *et al*., 2003). Initial concentration of influent, when increased increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases removal efficiency (Fomina and Gadd 2014).

The most important single parameter influencing the Cr(VI) reduction is the solution pH. The pH of the system controls the adsorption capacity by influencing the surface properties of adsorbent and ionic forms of the chromium in solutions, (Garg et al., 2007). The batch experimental study had shown that the reduction rate of Cr(VI) from aqueous solution increased with decreasing pH, due to the consumption of protons during Cr(VI) reduction(sallau*et al.,* 2012). In this study, it was observed that the higher the influent pH, the poorer the Cr(VI)-reduction efficiency(Fig 4.5) ; the percentage removal was 98± 1.63 % after the first 5min at pH 2 while at pH 5 it was 70± 11.39% removal after the first 5mins . The reasons for maximum adsorption of most adsorbent at acidic pH were explained by Gupta et al. (2010) based on the fact that Cr(VI) exists in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} in acidic medium, as such low pH causes the surface of the adsorbent to be protonated resulting in a strong attraction between these oxyanions of Cr(VI) and the positively charged surface of the adsorbent. As the

pH increases, there exists some negatively charged hydroxyl ions available in aqueous solution, which may cause repulsion of negatively charged ions ($HCrO_4$-, $Cr_2O_7^{2-}$ and CrO_4^{2-}) and negatively charged adsorbent, causing a decrease of adsorption. Several experiments have indicated maximum percent adsorption under acidic pH. Park *et al*., (2006) found the maximum adsorption at pH 2.00 to 2.10 using brown seaweed *Ecklonia* biomass as adsorbent. In the case of soya cake, adsorption of Cr(VI) increased with decreased in pH. Thus, Daneshvar*et al*., (2002) indicated that an inverse relationship exists between the adsorption of chromium by soya cake and pH.

Activated carbon is one of the most effective media for removing a wide range of contaminants from industrial and municipal waste waters. Hence it is employed by most industry to treat their waste water. Using this industrial adsorbent powder activated carbon (PAC), to reduce the synthetic Cr(VI) solution used in this study, it was found that its maximum chromium percentage reduction was about 85 ± 3.73 % while the corn cob powder was about 70 ± 11.39 % (Fig 4.6). This shows that the potential of corncob powder as an industrial adsorbent is very promising.

Using corncob powder to treat an industrial waste obtained from NILEST, showed a removal percentage of 40± 9.34 % as compared to when it was used to treat synthetic chromium waste which showed a removal percentage of 70± 11.39 % (Fig 4.7). This could be due to other pollutant effects in competing for binding sites or other interferences, therefore increasing concentration ofcompeting pollutants will usually reduce biosorptive removal of the target pollutant. Achi*et al* (2012), has indicated that Chromium is as much as 1% of the constituent of leather tanning waste from NILEST, and concentrations of As, Ba, Br, Co, Fe,La, Na, Sb, Sc, Sm and Zn in the sample are

also present. Other elements found in the chrome shavings (Mg,Ca, *etc.*) can be attributed to the use of the salts of these elements for the basification of chrome tanned leathers. Also, the presence of other elements like Ca, Na, *etc*can be linked to the use of alkali in the pre-tanning treatment of hides skins (Achi*et al*., 2012).

However, cation loading of biomass may enhance biosorption of another cation because of pH buffering effects. Calcium-saturated fungal biomass showed enhanced Zn biosorption, for example (Fourest et al., 1994). In some cases, cations may increase biosorption of anionic species by enhancing binding of negatively charged anions (Gadd, 2009). Anionic effects on metal biosorption capacity depend on metal speciation, co-existing metal(s) and the nature of the biosorbent. For example, inhibitory orders for the biosorption of Cr(VI) and Cr(III) ions were, respectively: NO_3^- >Cl^- > SO_4^{2-},and SO_4^{2-} >Cl^- ≈ NO_3^- (Michalak et al., 2013). Anions like CO_3^{2-} and PO_4^{2-} may clearly affect biosorption through the formation of insoluble metal precipitates while chloride may influence biosorption through the formation of complexes, e.g. $CdCl_3$ (Gadd, 2009).

FTIR spectra of the biosorbent, before and after Cr (VI) uptake, were carried out. This is done, to determine which functional groups are responsible for metal uptake.FTIR spectrum of corn cob powder exhibits a broad peak at 3407.37cm^{-1}, which corresponds to the O–H stretching vibrations of cellulose, pectin, absorbed water, hemicellulose, and lignin (Feng*et al*., 2009). The OH stretching vibrations occur within a broad range of frequencies, indicating the presence of free hydroxyl groups and bonded OH bands of carboxylic acids (Namasirayam and Kavith, 2006),(Boucheltа*et al*., 2008). The band at 2927.08 cm^{-1} indicates symmetric or asymmetric CH stretching vibration of aliphatic acids. The peak at 2854 cm^{-1} was the symmetric stretching vibration of CH_2 due to CH

bonds of aliphatic acids. Bands around 1654.98cm^{-1} and 1730.21cm^{-1} are indicative of the existence of free and esterified carboxyl groups, respectively (Arslanoglu et al., 2008). The peak at 1388.79cm^{-1} may be assigned to symmetric stretching of –COO−. The bands observed at 1030.02–1141.90cm^{-1} were assigned to C–O stretching of alcohols and carboxylic acids (Sari et al., 2008). Similar FTIR spectra were obtained by Lodeiro*et al*,.(Lodeiro*et al*., 2008) with orange peels. When the biomass was loaded with chromium, differences in the positions of the absorbance peaks appeared. Band shifting and possible involvement of hydroxyl groups were observed around the broad peak at 3407cm^{-1} in the sorption process. In the spectrum of the chromium-loaded biomass, there was a decrease in peak intensity at 2929.97 cm^{-1} due to the interaction between chromium ions and different C–H groups in the biomass. The shift of the asymmetric and symmetric C-O bands (1644–1524 cm^{-1}) indicates a degree of carboxyl bonding.

Besides, Cr(VI) sorption results in a relative decrease in free carboxyl band intensity (1644cm^{-1}) in relation to esterified carboxyl band intensity (1730.21 cm^{-1}). From these spectra it seems that carboxyl and hydroxyl groups are the main functional groups involved in Cr (VI) bonding to the corn cob powder. The importance of these groups has been shown in experiments carried out with this biomass with the mentioned functional groups blocked (Perez Martin *et al*., 2009).

Classical adsorption models (Langmuir and Freundlich) have been used to describe the equilibrium established between adsorbed metal ions on the biomass (*q*e) and metal ions remaining insolution (*C*e) at a constant temperature. The experimental results obtained for the adsorption ofchromium on corn cob powder at optimum temperature under pre-defined conditions of pH, adsorbent dose and incubation period obeyed the Langmuir

andFreundlich adsorption isotherms based on the highest correlation coefficient (R^2) values of 0.993 and 0.985, respectively (Fig. 4.9). Thus, the present adsorption studies fitted reasonably well with Langmuir isotherm which is mainly applicable for monolayer adsorption onto a surface containing a finite number of identical sites, with the assumption that adsorption surfaces possess uniform energies and no transmigration of adsorbate in the plane of the surface (Garg*et al*., 2007).

CHAPTER SIX

SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

I. From this present study, a pH of 2, temperature of 70°C as well as flow rate of 5ml/min, are optimal conditions for maximum removal of Cr (VI) from aqueous solutions in a continuous packed bed reactor.

II. Increase in the mass of a biosorbent results in higher percentage removal as a mass of 120g gave a percentage removal of 70% while a mass of 60g gave a percentage removal of 55%.

III. The higher the influent Cr (VI)concentration at a constant biomass the lower the percentage removal. An initial concentration of 200mg/L gave percentage removal of 30% while the initial concentration of 100mg/L gave a removal percentage to 70%.

IV. Also using the corncob powder to treat an industrial waste containing Cr (VI) was found to have a percentage removal of40%, this could be due to other metals present in the industrial waste that interfere with the chromium biosorption, or competes with the Cr (VI) for binding site on the corncob powder.

V. Using activated carbon to treat the synthesized Cr (VI) waste, a percentage removal of 85% was obtained and comparing it with our corncob powder which gave a percentage removal of 70%,it showed that corncob powder though not as effective as the industrial adsorbent has a good potential for use as a natural biosorbent in industry.

VI. The FTIR spectra of corn cob powder, before and after uptake of Cr VI, shows that the following functional groups; OH, CH, $CH_{2,}$ COO, are present and they are responsible for binding and removal of Cr (VI), making it a good biosorbent.

VII. The two adsorption models (Langmuir and Freundlich) were used for the description of the adsorption of Cr (VI) ions and it was found that the adsorption equilibrium data fitted well with both models, giving an R^2 value of 0.993 and 0.985.

6.2 Conclusion

A packed bed continuous reactor study on the biosorption of Cr (VI) from aqueous solution showed that corncob is a good biosorbent for treatment of chromium (VI) containing waste, because it contains functional group that can bind and remove chromium VI, also optimum condition for the biosorption process was found to be at a pH of 2, a flow rate of 5ml/min and a temperature of 70°C.Hence,the use of corncob powder asbiosorbent seems to be an economical and promising alternative over conventional methods.

6.3 Recommendation

I. Corncob powder is a goodbiosorbent for removal of Chromium (VI)in a continuous packed bed reactor, at a pH of 2, temperature of 70°C and a flow rate of 5ml/min. However more work should be carried out in this area.

II. A study on the chromium (VI) recovery from the column and reuse of the biomass should be carried out

III. A study on the effect of stirring time in the column on the removal of chromium VI from aqueous solutions should be carried out.

REFERENCES

Achi, S. S.,Adeyemo, D. J.,Maj C. and Tagang, J. (2012) analysis of chrome tanned leather shavings using neutronactivation analysis,*Chemical Science and Technology*, 1(1):45-52.

Aksu, Z., Donmez, G.C., Ozturk, A. and Kutsal, T. (1992).The biosorption of copper (II) by C.vulgaris and Zramigera.*Environmental Technology Letters*,13:579-586.

Ayres, R.U. (1992) Toxic heavy metals: materials cycle optimization, *Proceedings of the National Academy of Science*. 89:815–820.

Babel, S. and Kurniawan, T.A.(2004). Cr (VI) removal available adsorbents from synthetic wastewater using coconut shell.*Advances in Environmental Research*, 6:533-540.

Babu, B. V. and Gupta, S. (2008). Adsorption of Cr(VI) using activated neem leaves: Kinetic aqueous solution by agricultural waste biomass. *Journal of Hazardous Material*,140: 60-68

Bagby, M. O. and Widstrom, N. W. (1987). Biomass uses and conversions. In: Watson, S. A., and Ramstad, P. E. (Eds).*Corn: Chemistry and Technology*. pp. 575-590.

Bansal, M., Garg, U., Singh, D. and Garg, V. K. (2009). Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *Journal of Hazardous Material*, 162:312-320.

Baral, S.S., Das, N., Ramulu, T.S.,Sahoo, S.K., Das, S.N. and Chaudhury, G.R. (2009). Removal of Cr(VI) by thermally activated weed Salviniacucullata in a fixed-bedcolumn. *Journal of Hazardous Material*.161:1427–1435.

Barceloux, D. G. (1999).Chromium.*Journal of Toxicology Clinical Toxicology*37(2):173-194.

Bouchelta,C.,Medjram, M.S., Bertrand, O. and Bellat, J.P. (2008).Preparation and characterization of activated carbon from date stones by physical activation with steam.*Journal of Analytical and Applied Pyrolysis*,82(1):70–77.

Brierly, C.L, (1990). Bioremediation of metal, contaminated surface and ground water. *Geomicrobiology Journal*.8:201-223.

Shekar C.K. (1998). Removal of metal ions using an industrial biomass with reference to environmental control.*International Journal of Miner Process*,53:107-120.

Clesceri, L.S., Greenberg, A.E. and Eaton, A.D. (1998). *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, pp. 366–368.

Cohen, M.D., Kargacin, B., Klein, C.B. and Costa, M. (1993).Mechanisms of chromium carcinogenicity and toxicity,*CRC Critical Reviews in Toxicology*.23:255-281.

Daneshvar, N., Salari, D. and Aber, S. (2002). Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake. *Journal of Hazardous Materials*, 94:49-61

Das, D.D., Mahapatra, R., Pradhan, J., Das, S.N. and Thakur, R.S. (2000). Removal of Cr(VI) from aqueous solution using activated cow dung carbon. *Journal of Colliod and Interface.Science.*,232:235-240.

Davis, T.A. and Volesky, B. (2003).A review of biochemistry of heavy metal biosorption.*Water Research*,37:4311-4330.

Deilippis, C.K. and Pallaghy P.K. (1994).Heavy metal and radionucIide by fungi and yeasts.*In* Norris, P.R. and Kelly, D.P. (Ed), *Biohydrometallurgy.* 54:29-33

Donmez, G.C.,Aksu, Z.,Ozturk, A. and Kutsal, T. (1999). A comparative study on heavy metal biosorption characteristics some algae, *Process Biochemistry*,34:885–892.

Eaton, A.D., Clesceri, L.S. and Greenberg, A. E. (1995).*Standard Methods for the Examination of* Water *and Wastewater*. American Public Health Association (APHA), AWWA, WPCF, Washington, DC, pp. 225-257.

Eneida, S.C. and Ravagnani, T.M.K. (2002).Biosorption of chromium (III) by sargasum specie. Biomass. *Electronic Journal Biotechnology*,5:2

Espinola, A., Adamian, R., and Gomes, L.M.B. (1999). An innovative technology: Natural coconutfibre as adsorptive medium in industrial wastewater cleanup. *Waste Treatment Clean Technology Process*,3:2057-2066.

Evans, C.V. and Li, Z. (2003).*Removal of heavy metal and radionuclides from soil using cationic surfactant flushing*. University of Wisconsin water resources institute. pp 1-15.

Fatoki, O.S. and Ogunfowakan A.O. (2002).Effect of coagulant treatment on the metal composition of raw water.*Water South Africa*28(3):293-298.

Feng, N.,Guo, X., and Liang, S. (2009) Adsorption study of copper (II) by chemically modified orange peel, *Journal of Harzadous Materials*,164(2–3):1286–1292.

Figueira, M.M., Volesky, B.,Azarian, K. and Ciminelli, V.S.T. (2000).Biosorption column performance with a metal mixture.*Environmental Science Technology*,34:4320–4326.

Fomina, M. and Gadd, G.M. (2014).Biosorption: current perspectives on concept, definition and application. *Bioresource Technology*,160:3-14.

Fourest, E. and Roux, J.C. (1992). Heavy Metal Biosorption by Fungal Mycelia by products: Mechanism and influence on pH.*Applied Microbiology and Biotechnology*3:399-403.

Friis.N. and Myers, K. (1998).Biosorption of uranium and lead by Streptomyces longwoodensis.*Biotechnology and Bioengineering*,28:21-28.

Gadd, G.M. (1993).Microbial formation and transformation of organometallic and organometalloid compounds, *FEMS Microbiology Reviews*,11:279-310.

Gadd, G.M. (2009). Biosorption: critical review of scientific rationale, environmental importanceand significance for pollution treatment. *Journal of Chemical Technology and Biotechnology*,84:13-28.

Galun, C.M Muraleedharan, T.R. and Venkobachar,C. (1987).Mechanism of biosorption of copper (II) by Ganodermalucidum.*Biotechnology and Bioengneering*.35:320-325.

Gao, M., Levy, L.S., Faux, S.P., Aw, T.C., Braithwaite, R.A. and Brown, S.S. (1994). Use of molecular epidemiological techniques in a pilot study on workers exposed to chromium, *Occupational and Environmental Medicine*, 51:663-668.

Garg, U. K., Kaur, M. P., Garg, V. K. and Sud, D. (2007).Removal of hexavalent chromium from aqueous solution by agricultural waste biomass.*Journal of Hazardous Materials*,140:60-68.

Gerd, A., Jost, H., Klaus, H., Christopher, S., Ulrich, K., Herbert, K., Peter, S. and Manfred, O. (2005). *Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim.pp 209-211.

Gonzale, A.R.,Ndung'u, K. and Flegal, A.R. (2005)."Natural Occurrence of Hexavalent Chromium in the Aromas Red Sands Aquifer, California. .*Environmental Science and Technology*,39(15):5505–5511.

Gonzalez, C.F., Ackerley, D.F., Park, C.H. and Martin, A. (2003). A soluble flavoprotein contributes to chrome reduction and tolerance by *Pseudomonas putida*. *ActaBiotechnologica*,23:233-239.

Guo, Y., Qi, J., Yang, S., Yu, K., Wang, Z. and Xu, H. (2002). Adsorption of Cr(VI) on micro and mesoporous rice husk-based active carbon. *Materials Chemistry and Physics*,78: 132-137.

Gupta, V.K., Rastogi, A. and Nayak, A. (2010). Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. *Journal of Collective Interface of Science*,342:135-141 .

Hay, R.W. (1984). *Bio-inorganic chemistry*. New york, Ellis Horwood p 210.

Helmer,I.G. and Bartley,E.E. (1971).Progress in the utilization of urea as a protein replacer for ruminant dairy.*Journal of physical Chemistry*,2:54-25.

Herrera, I., Torresdey, J.L., Tiemabnn, K.J., Peralta, J.R., Armendariz, V. and Parsons, J.G. (2003).Biomass binding of silver ions by alfafa biomass (Medicago sativa).Batch, time, temperature and ionic strength studies. *Journal of Hazardous Substance Research*,4(1): 1-16.

Hu, K.B., Wang, Y.L., Li, C.R. and Zheng, Y.Q. (2010). Fractal characteristics of adsorption of mesoporous rice husk-based active carbon. *Materials Chemistry and Physics*,78:132-137.

International Agency for Research no Cancer (1990). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Chromium, Nickel and Welding. Lyon, France. 49:183.

James C.Y., Robert B.E. and Danny J.W, (1975).*Packed bed Reactor for Secondary Effluent, BOD and Ammonia Removal*. Vol. 47, pp 46-56.

Jamila, A.A. and Hussan,A.Z.(2009).Biosorption of lead (II) and copper (II) from aqueous solutions. *Journal of biological resource technology*, 35(1):69-81.

Kadirvelu, K., Thamaraiselvi, K. and Namasivayam, C. (2001). Removal of Heavy Metal from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste. *Bioresource Technology.*,76:63-65.

Kashefi, M., Salaryan, P., Hazeri, N., Valizadeh, J., Abdi, A.andMohammadnia, M. S. (2012). Biosorption of Cr(VI) from aqueous solutions using *Carumcopticum* stem. *International Journal of Chemistry and Biochemistry Science*,1:48-53.

Khitrov, G., Blumenberg, M. andFreedberg, I. (2002). Removal of Heavy Metal from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste. *Bioresource*Technology, 76:63-65.

Kimani, N.G. (2005). *Environmental Pollution and Impacts on Public Health: implications of the Dandora municipal dumping site, Nairobi Kenya.* Report summary in cooperation with United Nations Environment Programme and the St. John Catholic Church, Korogocho.p 34.

Kratochvil, D., Pimentel, P. and Volesky, B. (1998).Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent.*Environmental Science and Technology*,32(18):2693-2698.

Lance, G. and Garren, B.(2002).*Origin, History, and used of Corn (Zea mays)*.Iowa State University, Department of agronomy.p 181.

Levis, H. and Bianchi,B. (1982)."Chromium occurrence in the environment and methods of its speciation.".*EnvironmentalPollution*, 107(3):263–283.

Lin, J.L., Keener, H.M. and Essenhigh, R.H. (1995). Pyrolysis and combustion of corn cobs in a fluidized bed: Measurement and analysis of behavior. *Bioresource Technology,100*:271-282.

Lodeiro, P., Fuentes, A. and Herrero, R. (2008).Cr(III) binding by surface polymers in natural biomass: the role of carboxylic groups.*Environmental Chemistry*.5:355–365.

Lokeshwari,N. and Josh, K. (2009).Biosorption of heavy metal (chromium) using biomass.*Global Journal of Environmental Resource*.3(1):29.

Mataka, L.M., Sajidi,S.M.,Masamba, W.R.L. and Mwatseteza, J.F. (2010). Cadmium sorption by *Moringastenopetale* and *Moringaoleifera*seed powder: batch, time, temperature, pH, and adsorption isotherm studies. *International Journal of Water Resources and Environmental Engineering*,2(3):50-59.

McGrath, S.P. and Smith, S. (1990). Chromium and nickel, *In:*Alloway,B.J. (Ed.), *Heavy Metals in soils.* Willy,New York, pp125-150.

Michalak, I., Chojnacka, K. and Witek-Krowiak, A. (2013). State of the art for the biosorption process-a review.*Applied Biochemistry and Biotechnology*,170:1389-1416.

Mohanty, K., Das, D., and Biswas, M.N. (2005). Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectonagrandis*sawdust by ZnCl2 activation. *Chemical Engineering Journal*,115:121-131.

Najdeker, E. (1971).Reaction mechanisms in the diphenylcarbazone- chromium system.*Proceedings of the Society of Analytical Chemistry*,pp195-197.

Nakano, Y.,Takeshita,K. and Tsutsmi,T. (2000). Adsorption mechanism of hexavalent chromium by redox within condensed-tannin gel.*Water Research*,35(2):496-500.

Namasivayam, C. and Kavitha, I.R. (2006). XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase, *Microchemical Journal*,8:43-48.

Nomanbhay, S.M. and Palanissamy, K. (2005). Removal of heavy metal from industrial waste water using chitoson coated oil palm shell charcoal. *Water Research*,4:34-35.

Park, D., Yun, Y.S. and Park, J.M. (2006).Reduction of hexavalent chromium with the brown seaweed *Ecklonia*biomass.*Environmental Science Technol*ogy,38:4860–4864.

Park, D., Yun, Y.S. and Park, J.M. (2010).The past, present, and future trends of biosorption. *Biotechnology and Bioprocessing*,15:86–102.

Patterson, P.R.S. and Fendorf,M. (1997).Reduction of hexavalent chromium by amorphous iron sulfide.*Environmental science technology*, 31:20-39.

Pehlivan, E., and Altun, T. (2008).Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *Journal of Hazardous Materials*,155: 378-384.

Pérez, A.B.,Marín, J.F.,Ortu˜no, M.I., Aguilar, V.F.,MeseguerSáez, J. and Lloréns M. (2009). Use of chemical modification to determine the binding of Cd(II), Zn(II) and Cr(III) ions by orange waste, *Chemical Engineering Journal*, 155:199-206.

Raji, C. and Anirudhan, T.S. (1998).Batch Cr(VI) removal by polyacrylamide grafted sawdust: Kinetics and thermodynamics. *Water Research*,32:3772-3780.

Ramsay, J.A., and Nguyen, T. (2002).Decoloration of textile dyes by *Trametesversicolor* andits effect on dye toxicity. *Biotechnology Letters*,24:1757-1761.

RaoIyengar, L. and Venkobachar, C. (1993). Sorption of heavy metal from aqueous phase by waste biomass.*Journal of Environmental Engineering*119:369-377.

Reddy, A.R.and Reddy, K.H. (2003). Heavy metal ion uptake properties of polystyrene supporting chelating polymer resins.*Proceedings of Indian Academy of Science-chemical science*, 153(3):155-160.

Rich, G. and Cherry,K. (1987).*Hazardous Waste Treatment Technologies*, Pudvan Publishers, New york. pp35-46.

Rosas, J.E., Hernandez, R.M., Gascon, A.R., Iguata, M., Guzman, J.L., Patarroyo, M.E. and Pedraz, J.L. (1989).*Biodegrable PLGA micospheres as a delivery system for toxicity of heavy metal synthetic peptide*.vol.20 p.4445.

Saeed, A. and Iqbal, M. (2003).Bioremoval of cadmium from aqueous solution by black gram husk (*Cicerarientinum*). *Water Research*,37:3472-3480.

Saeed, A. Iqbal, M. and Akhtar, M.W. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *BioresourceTechnology.*, 45:25-31.

Sakaguchi, T. and Nakajima,A. (1991). Accumulation of heavy metals such as uranium and thorium by microorganisms*In* : Smith,R.W. and Misra,M. (Ed), *Mineral Bioprocessing*. The Minerals, Metals and Materials Society, 1:34-36.

Salina, E., Orellando.M.E., Rezza, I., Marchesvky, E. andTosset, M.S. (2000).Removal of cadmium and lead from dilute aqueous solution by *Rhoditorularubra.Bioresource Technology.*72:107-112

Sallau, A.B. Salihu, A. and Stella, U. (2012).Biosorption of Chromium (VI) from Aqueous Solution by Corn Cob Powder:*International Journal of Environment and Bioenergy*,4(3):131-140.

Sara, K.J., Anwar, M., Hassan, R., FarooHafza, B., Fatima, M. and Khalid, H.N. (2009).RemovalofChromuim VI by biosorption of Eucalyptus Bark.*World Applied Sciences Journal*,6(12):1818-4952.

Saravanan, A. and Brindha,V.(2009).An evaluation of chromium and zinc biosorption by a seaweed (sargassumspp) under optimized conditions. *Indian Journal of Science and Technology*,2:21-23.

Sari, A.,Mendil, D.,Tuzen, M. and Soylak, M. (2008).Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomiumsplendens*) biomass: equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*. 144(1):1–9.

Sen, M. and GhoshDastidar M. (2010).Chromium removal using various biosorbent.*Iran Journal Environmental Health Science*, 7(3):182-190.

Sharma, D. and Forster, C.F. (1994).A preliminary examination into the adsorption of hexavalent chromium using low cost adsorbents.*Bioresource Technology*, 47:257-264.

Stern, H.N., Gerlach, K. and Bloomer, H. (1992). Combination activin and its resceptors during Gastrulation studies in Later phasesAdsorption, *Bioresource Technology*,14:85-92.

Taioli, E., Zhitkovich, A., Kinney, P., Udasin, I., Toniolo, P. and Costa, M. (1996).Increased DNA-protein cross links in lymphocytes of residents living in chromium-contaminated areas, Biomarker. *Journal of Science and Technology*,1:86-93.

Tarley, C.R.T. andArruda, M.A.Z. (2004). Biosorption of heavy metals using rice milling by- products: Chracterisation and application for the removal of metals from aqueous effluents. *Chemosphere*,54:987-995.

Tewaria, N., Vasudevana, P. and Guhab, B.K. (2005).Study onbiosorption of Cr(VI) by *Mucorhiemalis*. *Biochemical Engineering Journal*,23:185-192.

Trivedi, R.K. (1989).Pollution Management in Industries, Environmental Publications.*Bioresource Technology*,47:30-35.

Tsai, W.T., Chang, C.Y., Wang, S.Y., Chang, C.F., Chien, S.F. and Sun, H.F. (2001).Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob.*Research in Conservational Recycling*,32:43-53.

Tsezos, M. and Volesky.B. (1982).The mechanism of uranium biosorption by *Rhizopusarrhizus*.*Biotechnology and Bioengineering*, 24:385-340.

United State Environmental Protection Agency (1988). Toxicological Review of Trivalent Chromium In Support of Summary Information on the Integrated Risk Information System (IRIS).Washington, DC, U.S. Environmental Protection Agency.(CAS No. 16065-83-1).

United State Environmental Protection Agency (1991). Guidelines for Developmental Toxicity Risk Assessment. R. A. Forum. Washington, D.C. EPA/600/FR-91/001
.

Vinodhini, V. and Das, N. (2009).Mechanism of Cr (VI) Biosorption by Neem dust.*American –Eurasian Journal of Scientifiv research*,4(4):324-329.

Volesky, B., Weber, J. and Park, J.M. (2003).Continuous-flow metal biosorption in a regenerableSagassumcolumn, *Water Resourses*, 37:297-306.

Wang, J. and Chen, C. (2009).Biosorbentsfor heavy metals removal and their future. *BiotechnologyAdvances*,27:195-226.

Wittbrodt, P.R. and Palmer, C.D. (1996). Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances, *Environmental Science Technol*ogy,30:2470–2477.

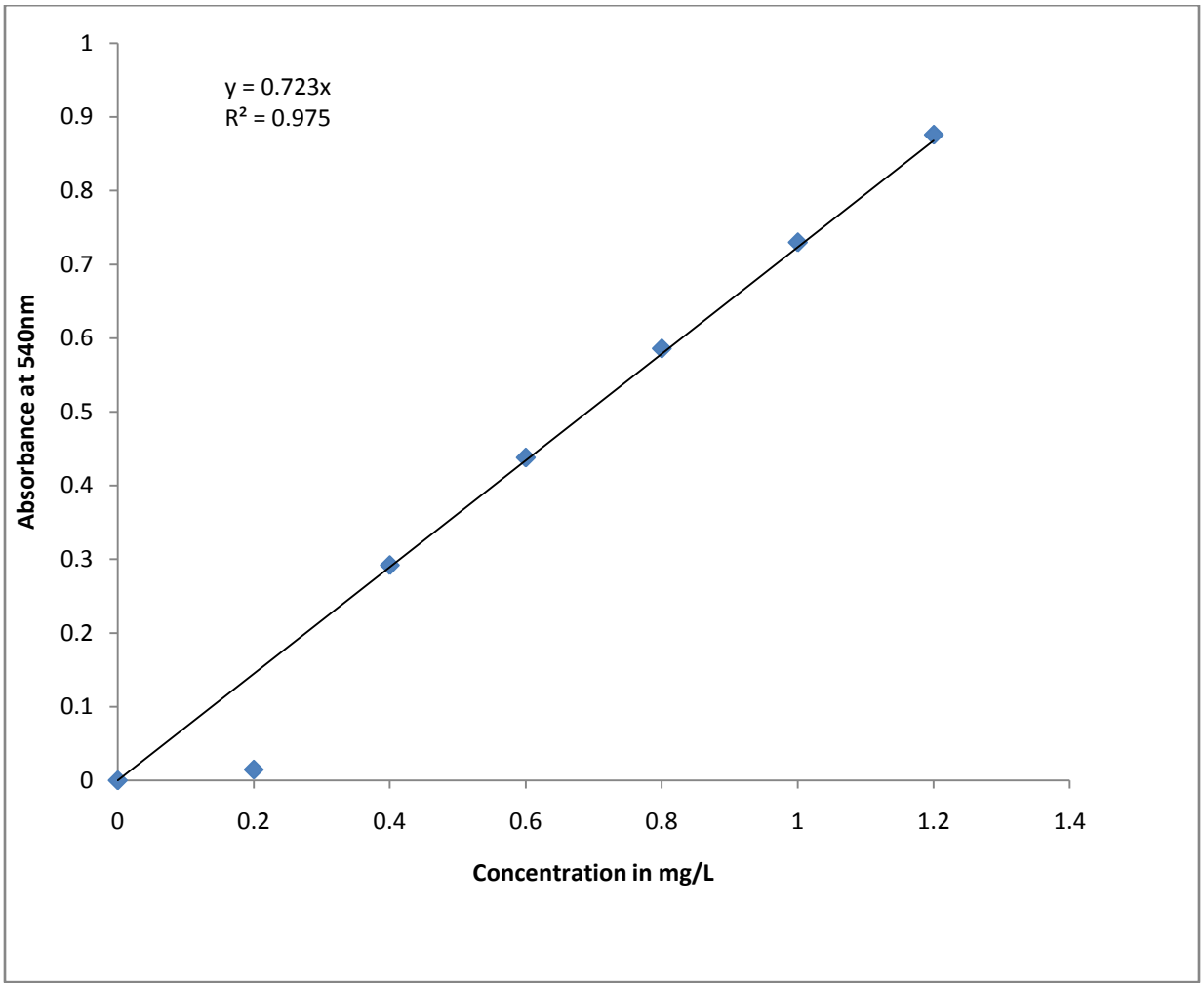
Woranart, J. (2008). *Grains Grown in Northern Nigeria*, Department of Agriculture, Divisionalcoll Revised January. p 181.

World Health Organization. (2002). *The World Health Report: Reducing Risk and Promoting Healthy Lifestyle*, Geneva; WHO

Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A.and Margrave, J.L. (2003). Adsorption of chromium from aqueous solutions by maple sawdust.*Journal of Hazardous Materials.*100:53-63.

APPENDICES

Appendix 1



Appendix 1: Standard curve showing varying concentration of Chromium VI and its correspondingabsorbance at 540nm.

Appendix 2

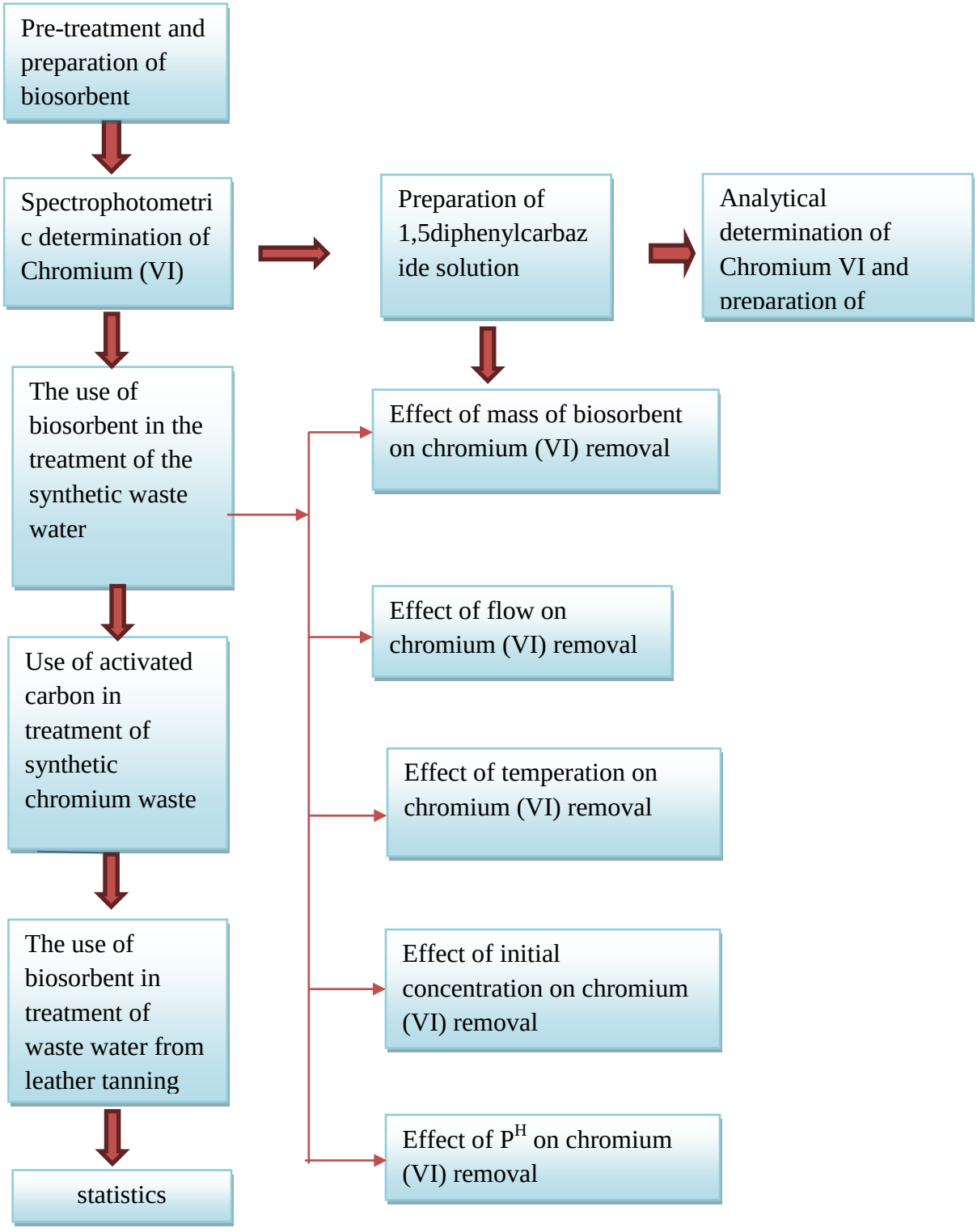


Fig 3.a flow chart of my experimental design.

Appendix 3

Calculations used in analysis

$$q_e = \frac{(Co - Ce)\, v}{M}$$

V = volume of metal ion

M = mass of adsorbent

Co = initial concentration of metal ion

Ce = final concentration of metal ion.

$$\frac{\text{Concentration}}{\text{Initial concentration}} \times 100 = \text{percentage of metal ion left in solution}$$

Therefore, percentage adsorbed = 100 – percentage of metal left in solution

Appendix 4

Table 1: Operating conditions of the column reactor

	[Cr(VI)] (mg L−1)	[A] (g L−1)	pH (−)	*B* (mL min−1)	Temperature (◦C)
Run 1	100	120	5	10	30
Run 2	100	60	5	10	30
Run 3	100	120	2	10	30
Run 4	100	60	2	10	30
Run 5	200	120	5	10	30
Run 6	100	120	5	20	30
Run 7	100	120	5	10	70
Run 8	100	120(activated carbon)	5	10	30
Run 9	100(industrial waste)	120	5	10	30
Run 10	100	120	5	5	30
Run 11	100	120	5	15	30
Run 12	100	120	5	10	40
Run 13	100	120	5	10	50
Run 14	100	120	5	10	60
Run 15	100	120	5	10	80

[A] and*B* represent the concentration of biomass packed within the column and flow rate of influent, respectively.

Appendix 5

TABLE 2: parameters from data of reaction isotherms for the sorption of chromium VI Cob powder at room temperatureon maize.

Langmuir parameters	q_m(mg/g)	K_L (dm^3/mg^{-1})	R^2
	0.210	1.059	0.993
Freundlich parameters	n	K_f (mg/g)	R^2
	2.04	1.78	0.985

Langmuir Parameters:

From equation y = 4.7716x + 4.5407

Slope = 4.7716, therefore q_m = 1/47716 = 0.21

Intercept = 4.5407, therefore $1/q_mK_L$ = 4.5407

$K_L = \frac{4.7716}{4.5407} = 1.059$

R^2 is gotten from the graph = 0.993

Freundlich parameters:

From equation y = 0.4892x + 0.5749

Slope = 0.4892, therefore 1/n = 0.4892

Therefore, n =1/0.4892 = 2.04

Intercept = 0.5749, therefore ln K_F = 0.5749

Therefore, $K_F = e^{0.5749} = 1.78$.

R^2 is gotten from the graph = 0.985