ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDIES

ASSESMENT OF MAERUA SUBCORDATA ROOT AS BIOSORBENT FOR THE REMOVAL OF Cr (VI) IONS FROM TANNERY WASTE WATER

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CIVIL ENGINEERING
(WATER SUPPLY AND ENVIRONMENTAL ENGINEERING STREAM)

By: Mesfin Berecha

Advisor: Dr. AgizewNegusie

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared Spectrometry
UNIDO	United Nations Industrial Development Organization
UNEP	United Nations Environment Programme
APHA	American Public Health Association
UNDP	United Nations Development Programme
LIDI	Leather Industry Development Institute
WHO	World Health Organization
UNICEF	United Nations Children's Fund
MS	Maerua Subcordata
STDEV	Standard Deviation
MCL	Maximum Contaminant Level
rpm	revolution per minute

ABSTRACT

Chromium containing wastes are generated by industries such as leather tannery, electroplating, paint and pigment manufacturing. The form of Cr (VI) is responsible for human carcinogen as well as water and soil pollution. The main objective of the present study was to evaluate the possibility of using Maerua Subcordata as a Biosorbent for the removal of Cr (VI) from tannery waste water and aqueous solution. The study was conducted in Addis Ababa university Environmental science laboratory center and Ethiopian leather industry development institute laboratory center, from January to May, 2015. Maerua Subcordata was collected from South Omo Zone DasenechWoreda and cut in to small pieces, dried in the sunlight and grind to produce the powder, treated with H3PO4 (45%w/w). Physical characterization such as moisture content and bulk density of activated Maerua Subcordata was done and it was found low moisture content which indicates high quality of the biosorbent.The Biosorption of Cr (VI) from aqueous solution and real tannery waste water by activated Maerua Subcordata was studied.

The biosorbent was characterized by FTIR spectroscopy and characterization of the Maerua Subcordata suggested the possible contribution of carboxyl and hydroxyl groups in Cr (VI) Biosorption. The Biosorption efficiency of the Maerua Subcordata was dependent on the pH of the Cr (VI) solution, with pH 3 being optimal. The removal rate of Cr (VI) ions increased with increase in contact time and remained constant after an equilibrium time of 60 min. The removal of Cr (VI) ions increased with increase in biosorbent concentration with the optimal biosorbent dosage at 125 mg/L. Both Langmuir and Freundlich model were followed by adsorption of Cr(VI) on activated MaeruaSubcordata. But Langmuir model best describes the adsorption data with coefficient of determination (r^2) value 0.993.The maximum adsorption capacity obtained from Langmuir model is 4.54mg/g.The RL value obtained from Langmuir model shows the adsorption is favorable. When applying the biosorbent to real waste water 86.5% removal efficiency was obtained. The reduction in efficiency might be due to the presence of interfering ions which compete with Cr (VI) ion for Biosorption.

Therefore, the study revealed that the activated Maerua Subcordata could be used as an excellent biosorbent for the removal of Cr (VI) chromium from Tannery wastewater and aqueous solution.

Key words: Hexavalent chromium, Activated Maerua Subcordata, Biosorption

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Water is one of the most important natural resources, essential for all forms of life. This natural resource is being contaminated every day by various anthropogenic activities such as rapid growth of populations; urbanization and industrialization which have led to increased disposal of wastewater into the environment. This often exceeds the admissible sanitary standards and results in the adverse impact on aquatic environment and ground water consequently on human health. (L. Vasseur et al., 2008)

Tanning industry in Ethiopia is currently believed to be one of the sectors supporting economic development of the country significantly by generating foreign currency and it is also pollutant. Consequently , during the past 20 years the industry has had significant government support and has multiplied throughout Ethiopia. With the ever increasing demand on irrigation water supply, farmlands are frequently faced with utilization of poor quality water. In many parts of Ethiopia, wastewater, which is disposed to wells, ponds, streams and treatment plants, is used as a source of irrigation water as well as for drinking. (EskindirZinabu, 2006)

Industrial effluents which discharged from the textile and tannery contains a higher amount of heavy metals especially chromium, copper and cadmium. These effluents released on the land as well as dumped in to the surface water which ultimately leaches to ground water and lead to contamination due to accumulation of toxic metallic components and resulted in a series of well documented problems in living beings because they cannot be completely degraded .(Malarkodi et. al. 2007).

The heavy metals in water stream represent an important pollutant. Among the toxic heavy metals which present potential danger to human health are Cu, Pb, Cd, Cr and Hg,because these are not biodegradable, react irreversibly with enzymes and proteins and their effective characteristic such as toxicity, accumulation in living organism, strong oxidant capable of being absorbed by the skin hence causing various disorder and diseases. From all the heavy metals, Cr (VI) is one of the most hazardous inorganic water pollutants due to its carcinogenic nature and toxic effect. (Malarkodi M, et al., 2007).

Chromium is a transition metal which occurs in six different forms of oxidation states ranging from Cr (I) up to Cr (+VI), but the two common valence states are trivalent and hexavalent chromium forms (John et al., 2003); however, concerns regarding the presence of Chromium in the environment focus on the potential adverse health effects of Cr (VI)-contaminated soils, groundwater, and drinking water supplies.

Hexavalent chromium is more hazardous, carcinogenic,and mutagenic and the most water soluble which easily enters to living cells (Mina et al., 2011). The contamination of environment by Chromium is a critical problem because of adverse effects on aquatic life and human health (Haruna et al., 2011).

Chromium, while not unique in its properties, is commonly used in various industries because of the characteristics the metal and its compounds. Chromium (VI) compounds known as chromates and dichromate enter water bodies from different industrial processes which are used for chrome plating, manufacture of pigments, leather tanning and wood treatment. The minimum human daily requirements of chromium for optimal health is not known, but a daily ingestion of 50-200 μg/ day (0.0007-0.003 mg/kg of body weight per day) has been estimated to be safe and adequate (Kulkarni et al., 2013).The permissible limits for discharge to surface waters are 2 and 0.1 mg/l as total chromium and Cr (VI), respectively (Wang et al., 2009).

Conventional methods such as chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, electro dialysis, solvent extraction, etc. can reduce the concentration of chromium from contaminated waters(Bhatti et al., 2007, Chowdhury, 2009).However, all of these methods suffer from incomplete metal ion removal, high capital for operational costs, requirements for expensive equipment and monitoring systems, high reagent and energy requirements, membrane scaling, fouling and blocking, or the generation of toxic sludge and other waste products that require disposal (Dhanakumar et al., 2008).

Biosorption is an effective removal technique used in industries especially in water and wastewater treatment and the process has an edge over other methods due to its sludge free clean operation. It is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate).Adsorption is alternative removal mechanism for heavy metals from wastewater which has received considerable attention for the development of an efficient and cheap technology from waste of plant origins (Biswajit et al., 2011).Adsorption is an user-friendly technique for the removal of not only heavy metals but also other contaminants like dyes from wastewater and includes the selective transfer of solute components in the fluid phase onto the surface or onto the bulk of solid adsorbent materials on a suitable interface.

The predominant use of chromium in tannery industry unfortunately introduces an environmental concern implying the primary importance of waste water treatment (Suresh et al., 2012). The removal of chromium from wastewater using bioadsorbent has showed interesting results and generated the new concepts in pollution research (Ansari et al., 2009, Ali, 2010).

1.2 STATEMENT OF THE PROBLEM

The availability and quality of water determines the quality of life. Pure water is not easily available to all. Deprived section of the society consumes contaminated water and takes ill periodically. Water pollution is a large set of adverse effects upon water bodies such as lakes, rivers, oceans and ground water caused by human activities. Water pollution is the result of addition of large amounts of toxic materials. The major causes of water pollution can be classified as municipal, agricultural and industrial wastes. Water pollution by industrial waste water is a major problem in the world due to increase of industrialization. Tannery industries discharge a variety of pollutants in their wastewater including heavy metals, resin pellets, organic toxins, oils, nutrient and solids. (Alebel Abebe, 2010).

Tannery industry uses an extensive amount of water for processing of hides. For 1kg of hide the necessary requirement is 50 - 60 liter of water during the process of tanning. But at present times these tanneries use three times much water than normally required for 1kg of hide (Indira and Ravi, 2006). Tannery Wastewater generally has about 80 gm/l of NaCl. During tanning process, chromium is applied to 90 % of leather produced in the world. Chromium is used to convert the skin into leather, and is used excessively to improve the quality of the tanning process (Bajza et al. 2005). However, only 60 - 80% of chromium is absorbed by the leather and the remaining is usually discharged in sewage system. This metal accumulated in vegetables is toxic and even in small concentrations causes health risks such as cancer, mutation, or miscarriages (Arfaoui et al., 2005; Fahim, 2006).

Chromium ion in liquid tanning wastes occurs mainly in the trivalent form, which gets further oxidized to the hexavalent form (Arfaoui et al., 2005).In humans, Chromium toxicity causes itching and dermatisation and keratinisation of the hands and soles of feet (Huang et al., 2007).The main health effect of chromium can be summarizing in the following table.

Table 1 Health Impacts of chromium

Chromium	damage to skin, respiratory, reproductive and digestive systems,
	cancer
	responsible for toxic and carcinogenic effects

Global populations are increasing rapidly and will reach between nine and eleven billion in 2050, and as population increases so does the production of industries wastewater and the number of people vulnerable to the impacts of severe wastewater pollution will increase. Almost 900 million people currently lack access to safe drinking water, and an estimated 2.6 billion people lack access to basic sanitation (UNICEF, 2010).

Lack of to treat wastewater not only compromises the natural capacity of marine and aquatic ecosystems to assimilate pollutants, but also causes the loss of a whole array of benefits provided by our water ways and coasts that we too often take for granted; safe water for drinking, washing and hygiene, water for irrigating our crops and producing our food for sustaining ecosystems and the services they provide. The financial, environmental and societal costs in terms critical indicators of general human wellbeing are projected to increase dramatically unless tannery waste water treatment is given very high priority and dealt with urgently. (Corcoran et.al, 2010).

In Ethiopia, regulations governing Cr (VI) discharge from tanneries are stringent; all tanneries must thoroughly check their waste streams. Cr (VI) discharge into those streams is one of the components that has to be strictly controlled (Ludvík, 2000). Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. The Maximum permissible set by the world health organization (WHO) limits for Cr (IV) in wastewater and potable are 1.0 mg l^{-1} and 0.05 mg respectively. (Zeleke Abebe, 2011)

It is thus a necessity to remove metal ions from waste water before it can be discharged. In this respect, many physicochemical methods have been developed for the removal of metal ions from aqueous solutions including reduction followed by chemical precipitation, adsorption on activated carbon (Lotfi and Adhoum, 2002),evaporation, electro deposition, ion exchange, membrane separation, coagulation etc.,(Rao RAK, Ikram S. 2011). However these methods have disadvantages such as secondary pollution generation of toxic sludge and or other waste products that require addressing of disposal problems, high capital and operational costs, high energy input, large quantities of chemical reagents or poor treatment efficiency at low metal concentration (Ding Y et.al, 2012). Therefore the Search and development of an efficient and low-cost metal removal processes is of utmost importance.

A thorough literature survey indicated that Maerua Subcordata have been widely studied for pharmaceutical, water coagulation adsorbent for the removal of Cu and Pb other than as biosorbent for the removal of Chromium. But this study was tried to investigate activated roots of Maerua Subcordata removal efficiency for hexavalent chromium considering existing situation. The effects of pH, contact time, biosorbent and adsorbate concentration, and adsorption equilibrium was investigated.

1.3 OBJECTIVE OF THE STUDY

1.3.1General objective

The general objective of the study is to assess the effectiveness of activated Maerua Subcordata root powder as biosorbent in removing of Cr (VI) ions from Tannery Waste Water.

1.3.2 Specific Objective

The specific objectives of the study are:

- To evaluate the adsorption efficiency of activated Maerua Subcordata root powder as biosorbent in removing of Cr (VI) ions.
- To investigate the effect of Biosorbent dose, contact time, Ph and initial Cr (VI) ions concentration using activated Maerua Subcordata.
- To indicate the adsorption model that best fit with experimental data obtained using activated Maerua Subcordata
- To give an insight for further research on Maerua Subcordata

CHAPTER TWO

LITRATURE REVIEW

2.1 Chemistry of Chromium

Chromium occurs in six different forms of oxidation states ranging from Cr (I) up to Cr (+VI), but the two common valence states are trivalent and hexavalent chromium forms .The hexavalent species exists primarily as chromic acid (H2CrO4) and its salts, hydrogen chromate ion (HCrO4–) and chromate ion (CrO42–), depending on the pH. The predominant species present, as a function of the pH, are H2CrO4 at pHs less than about 1, HCrO4–at pHs between 1 and 6, and CrO_4^{2-}at pHs above about 6 (Mollashahi et al.,2011).

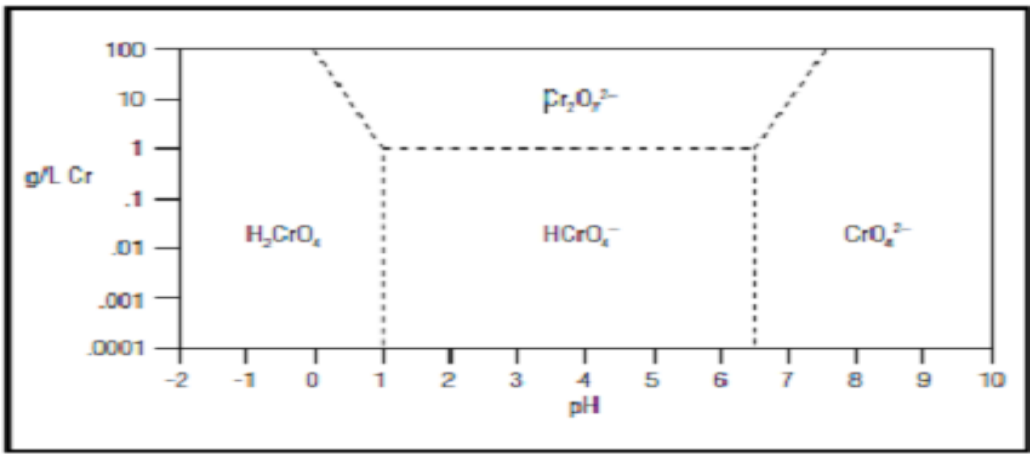

Figure 1 Relative distribution of Cr (VI) species in water as a function of Ph and Cr (VI) Concentration. (Mohan et.al. 2005)

2.2 Sources of Chromium Contaminations

Chromium contamination is primarily owing to its use in numerous industrial processes such as metallurgy, refractory, and chemical manufacturing involving numerous commercial processes like leather tanning, electroplating, manufacturing of dye, paint and paper milling, mining (ore refining), and wood preservation(Kumar,2006).And human-cause done has recently been the focus of much scientific discussion, regulatory concern, and legal posturing. However, relatively high concentrations of naturally occurring dissolved have been observed, usually associated with the very soluble chromates. Thus, both anthropogenic and natural sources of Cr can lead to locally elevated concentrations in soils and waters.

Common and many Cr contamination sites are the questions that continue to arise regarding the safety of the drinking water supply. As with most environmental challenges, questions of science compete with emotional and political responses and financial interests. Chromium from anthropogenic sources is commonly released as Cr-bearing liquid or solid wastes such as chromate byproducts, ferrochromium slag, or Cr plating wastes. The nature and behavior of various forms of Cr found in wastewaters can be quite variable.

The presence, form and concentration of Cr in discharged effluents depend mainly on the Cr compounds utilized in the industrial process, on the pH, and on the presence of other organic and inorganic processing wastes. Chemicals containing Cr (VI) are principally used for metal plating (which uses chromic acid H_2CrO_4) as dyes, paint pigments, and leather tanning.

In waste water where Cr (III) is the most expected form, the red-ox reactions occurring in sludge because of presence of oxidized impurities can increase the concentration of Cr (VI).That is why adsorbents which have both cation and anion-exchangeable possibilities are the objects of many studies.

2.3 Chromium Toxicity

The metals of most immediate concern are chromium, arsenic, mercury and lead of which hexavalent chromium compounds are responsible for the majority of the health problems. If chrome discharges are excessive, the chromium might remain in the solution (Masud et al., 2001). Even in low concentrations, it has a toxic effect upon aquatic life, thus disrupting the food chain for aquatic life and causes underground water pollution. Chromium in soils affects plant growth, it is non-essential for microorganisms and other life forms and when in excess amounts it exerts toxic effect on them after cellular uptake (Singanan et al., 2007).

Chromium has a chronic toxic effect upon aquatic life especially, dichromate are toxic to fish life and rapidly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. Trivalent chromium is an essential nutrient, required for normal energy metabolisms in animals. Ingesting small amounts of chromium will generally not harm, however ingesting above recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, heart burning, respiratory tract infection, sever cough, fever and loss of eyesight. Lung cancer and kidney failure were the reported causes of death in many cases (Perk, 2006). Skin contact may result in systemic poisoning, damage or even severe burns, interference with the healing of cut or scrapes which, if not treated properly, may lead to ulceration and severe chronic allergies. Eye exposure may cause permanent damage. In general, Cr (VI) is more toxic, more soluble, more mobile and hence absorbed into cells more readily than trivalent chromium.

2.4 Description of Tannery Production Process and Wastewater Generation

Leather tanning is a production process in which animal hides and skins are transformed by using of water, chemicals and mechanical process. Therefore, wastewater from the process will contain a high concentration of pollutants. The characteristics of wastewater and the pollution load depend on the type of production process including the source of the tanning. Effluent/wastewater/ management in tanneries require comprehensive approach so that chemicals used in leather processing is optimized, pollution minimized, and water consumption reduced. In most of Ethiopia tanneries effluent management systems are not clearly defined and efficiently installed. Inadequate wastewater management system in tanneries triggers inefficiency in environmental management.(UNIDO, 2003)

Leather production process in tanneries is categorized depending on the type of product, chemicals used, water usage, and machineries employed and other technical specificity. Soaking and washing to remove salt, restore the moisture contents of the hides, and remove any foreign material such as dirt and manure; liming to open up the collagen structure by removing interstitial material; fleshing to remove excess tissue from the interior of the hide; dehairing/dewooling to remove hair/wool either by mechanical or chemical means; bating and pickling to delime the skins, and condition the hides to receive the tanning agents; and tanning to stabilize the hide material and impart basic properties to the hides; (UNEP,2010)

The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant Tanning involves a complex combination of mechanical and chemical processes. The general flow sheet for tanning process is given in Fig. (2).

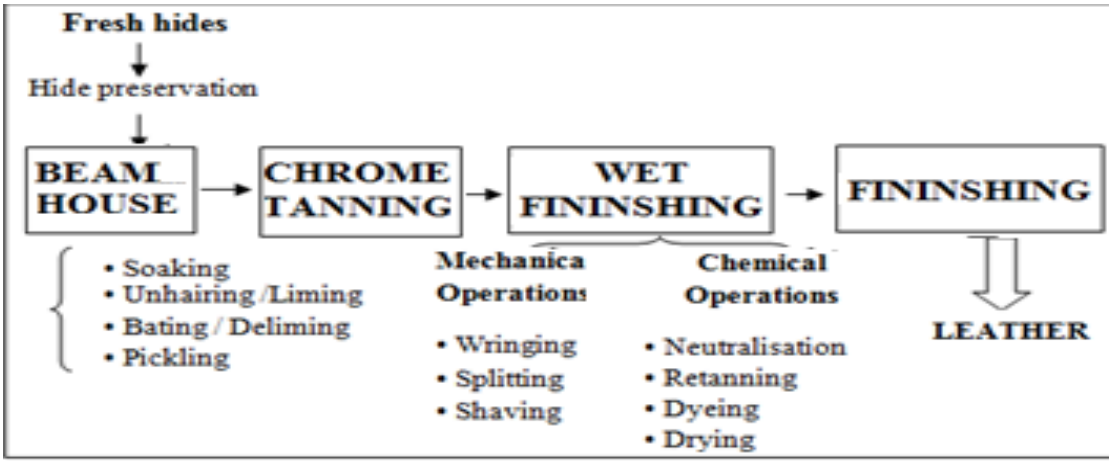

Figure 2 Simplified Tannery Production Chain (source Ilou1,et.al. 2012)

As a result of these processes, effluents (wastewater) or untreated liquid wastes are generated that constitute a major environmental and health hazard. Surveys reveal serious health disorders and environmental problems in the areas where tanneries are located, including contamination of soil, underground water and food (Khan, et.al.2002).

2.5 Chromium from Tannery Effluent

Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution (Ilou1,et.al. 2012) Chromium is highly toxic and carcinogenic to human beings, animals, plants and the general environment (soil and water sediment).Chrome is the primary threat whenever tanning industry comes in to practice. Tannery effluents containing chromium have toxicity as their dissolved $Cr6^{+}$. The Cr^{6+} salts can easily go into the circulation system through the lung, infiltrate cells, combine with big molecules in after being reduced to $Cr^{3+}$and eventually form the "ultimate carcinogen" (O′Brien et. al., 2003; Shakoori et. al., 2004).

If untreated wastewater containing Cr^{6+} is directly discharged to the environment, the environment and ecosystem would be polluted and people's health would be endangered seriously (Trumble and Jensen, 2004).Environmental effects of chromium (Cr) have been extensively reviewed (Steven et al. 1976; Snyder et al. 1977).

Reports from Europe, Scandinavia, Asia, and North America all emphasize the high incidence of lung cancer and other respiratory diseases among workers involved in the manufacture of chromates. Others document that land dumping of wastes from chromate production and electroplating operations have been responsible for groundwater contamination. Discharge of Cr wastes into streams and lakes has caused damage to aquatic ecosystems and that large amounts of Cr^{3+} and Cr^{6+} are reintroduced into the environment as sewage disposal and solid wastes.

2.6 Chromium Removal Technologies

Chromium contamination is common all over the world. For water resources, the impact of this contamination is severe. Hence, it is desirable to remove chromium from the contaminated water. Many treatment processes have been developed to remove chromium from wastewater (Hyder, 2013).

2.6.1. Chemical Precipitation

Chemical precipitation is the method, in which dissolved and suspended metal ions are transformed to the insoluble solid through a chemical reaction. Usually a precipitating agent accelerates this conversion from metal ions into insoluble solid. The commonly used precipitation agents are lime and magnesia (Mahmoodet.al. 2008). This technique has been proven as an effective way to remediate heavy metals including chromium from wastewater. It is a simple, inexpensive, convenient, and safe method. However this technique requires large amounts of chemicals, and excessive toxic sludge is produced. Sludge filtration and disposal increase the overall cost of the process. Sometimes metal precipitation is slow, and aggregation of metal precipitates take place (Kurniawanet.al, 2006).

2.6.2. Reduction

Reduction is a treatment process in which the higher valance state of metal ion is converted or reduced to the lower valance state using reducing agents. This technique offers several advantages such as recovery of metals from contaminated wastewaters; recycle of treated water, and short treatment times.

However, the disadvantages include additional chemicals requirement, and hazardous sludge formation. It is also quite expensive (Martinez & Rodriguez, 2007).

2.6.3. Ion Exchange

Ion exchange is a suitable technique to remove heavy metal from the wastewater and this technique has also been applied as a remediation measure for Cr (VI) (Riveroet.al. 2004). Various ion exchange resins are commercially available which can effectively remove Cr (VI) below the standard limit of Cr (VI) (0.1 mg/L) in wastewater. This process reduces the amount of waste for disposal and the cost of operation is generally lower. However, limitation of this method is that efficiency dependent on the pH of water (Rengarajet.al. 2003).

2.6.4. Adsorption

The adsorption technique has several benefits. It is effective and economical. It can remove the contaminating metals as well as recovery and recycle of sorbet metals from sorbent. It has evolved as the suitable alternative for those metal ions that cannot be removed easily by other techniques.

The removal efficiency is excellent for this process and depends on pH, adsorbate concentration, and adsorbent dosages (Mohan et.al. 2008). Adsorption is the process through which a substance originally present in one phase is removed from that phase by accumulation at the interface between that phase and a separate solid phase. The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid (Mohan et.al., 2008).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements be they ionic, covalent or metallic of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available (Ferrari et.al. 2010).

Adsorption can result either from the universal van der Waals interactions (physisorption) or it can have the character of a chemical process (chemisorptions). Contrary to physisorption, chemisorptions occurs only as a monolayer. Physorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. Chemisorptions occur usually at temperatures much higher than the critical temperature (browskiet.al. 2001).

The sorption mechanism of hexavalent chromium can be described by four different ways which are: 1) anionic sorption, 2) sorption-coupled reduction, 3) anionic and cationic sorption and 4) reduction and anionic sorption. In Anionic sorption, negatively charged chromium species $CrO4^{2-}$ and $Cr2O7^{2-}$ bind to positively charged functional groups on the surface of sorbents. Electrostatic attraction and/or surface complexation provide the binding phenomenon between the opposite charge (Hamadiet.al., 2001). In the anionic sorption mechanism, the sorption of Cr(VI) is increased at low pH whereas at high pH Cr(VI) sorption decreases. At low pH functional groups of the sorbent become protonated, and easily attract negatively charged chromate ions. On the other hand, at high pH de protonation takes place because functional groups of the sorbent become negatively charged and do not attract negatively charged chromium compounds (Hamadiet.al., 2001). Sorption-coupled reduction is the mechanism that deals with the reduction of Cr(VI) to Cr(III) using a sorbent in an acidic medium (Park et.al., 2005; Mohan & Pittman, 2006). Then the resultant Cr(III) is sorbed from the solution. In the anionic and cationic sorption mechanism, part of the Cr(VI) is reduced to Cr(III), and then both the chromium species are sorbed to the surface of sorbent. According to the reduction and anionic sorption mechanism, a part of the Cr(VI) is reduced to Cr(III); afterward Cr(VI) is mainly sorbed by the sorbent while Cr(III) remains in the solution (Bidyut& Chris, 2010; Rengaraj et.al., 2003).

2.7 Mechanisms of Biosorption

Biosorption is a process by which heavy metals are sequestered by dead biosorbent even from very dilute aqueous solution. The understanding of the exact mechanisms of Biosorption process is important, in order to develop the biosorbent for the commercial application of Biosorption process to treat industrial waste water mainly from tannery, for the commercial applications of Biosorption process to treat tannery waste water. The phenomena of heavy metals Biosorption is not bossed on a single mechanism.

It is a complex which involves several mechanisms that quantitatively and qualitatively differ according to the biosorbent types, its origin and its processing. Possible Biosorption mechanisms are physical sorption; chemisorptions, ion exchange, micro precipitation and entrapment of metals ion in inter orintra-fiberillar capillaries and spaces of the structural polysaccharide network of the biosorbent. There are several chemical groups that could attract and confiscate metals in biomass.((Park et.al., 2005)

2.8 Driving force in Biosorption

The phenomena of heavy metals sorption takes place as a result of either solvent motivated force, which is related to the surface tension, or through sorbent motivated force that combines chemical, electrostatic and physical interactions between metals and sorbing surface. (Volesky, 2003

Generally, the Biosorption is driven by a combination of both forces. There are four steps which occur in the process of metals Biosorption by a porous biosorbent.
Step 1- the metals is transported from the stock solution to the boundary film surrounding the biosorbent.

Step 2- the metals is transported from the boundary film to surface of the biosorbent, through external diffusion

Step 3- the metals are transported from the surface to the intra-particle active sites, through internal diffusion.

Step 4- finally in the fourth step uptake of metals at the active sites of the biosorbent occurred, through various mechanisms including, physical sorption, and ion exchange chemical reaction.

These steps are highlighted in figure 3

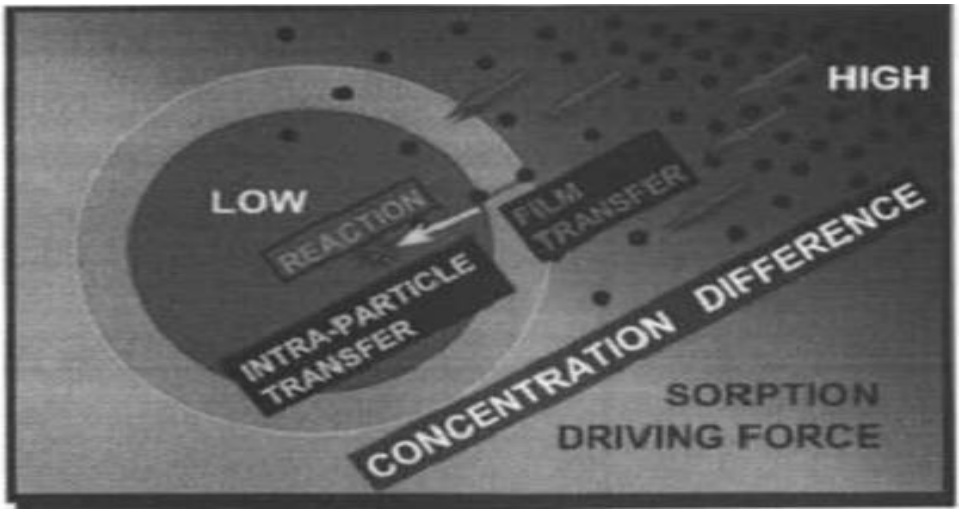

Figure 3 Driving Force for Biosorption(source Volesky, 2003)

2.9 Adsorption Equilibrium

Adsorption is usually described by isotherms which show how much solute can be absorbed by the adsorbent at a given temperature. An adsorption isotherm relates the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with which the adsorbent is in contact. These values are usually determined experimentally, but there are also models to predict them, both for single metal adsorption and multi component adsorption.

Although the Langmuir and the Freundlich adsorption isotherms are the two well established types of adsorption isotherms for single metal adsorption **(**Benavente, 2008).

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm (Ahaylaet.al., 2005).

$$q = \frac{q_{max}\, b\, C_{eq}}{1 + b\, C_{eq}}$$

Where q is milligrams of metal accumulated per gram of the bio sorbent material; Ceq is the metal residual concentration in solution; qmaxis the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates (Ahaylaet.al., 2005).

The Langmuir isotherm is based on the assumptions that metal ions are chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between the ions (Langmuir, 1918). The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation(Ahaylaet.al., 2005**).**

$$1/qe = 1/b\, q_{max}\, Ce + 1/qmax$$

The constants q max and b can be calculated from the slope and intercept of the plot of 1/qe versus 1/Ce (Thamilarasuet.al., 2011). The larger the constant b the higher is the adsorption energy, reflected by a fast increase in adsorption at low concentrations of adsorbent (Samadiet.al., 2009).
The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is defined as:

$$\mathbf{RL = 1/ (1+bCo)}$$

Where b is the Langmuir constant and Co is the initial concentration of Cr(VI). The RL value indicates the shape of isotherm as given (Ahaylaet.al., 2005).

Table 2 Types of Isoterm for Various RL

RL	Type of isotherm	Source
R_L>1	Unfavorable	(Thamilarasu et.al., 2011).
R_L=1	Linear	(Thamilarasu et.al., 2011).
RL between 0and 1	Favorable	(Thilagavathy et.al., 2013).
RL=0	Irreversible	(Thamilarasu et.al., 2012).

The well-known Freundlich isotherm is often used to describe adsorption on heterogeneous surface energy system (Schneider et.al., 2007; Ozacar, 2003).The Freundlich isotherm can be derived by assuming a logarithmic decrease in enthalpy of adsorption with the increase in the fraction of occupied sites. The isotherm model is commonly expressed by the following nonlinear equation.

$$q_e = K_f C_e^{1/n}$$

A linear form of this expression is,

$$\text{Log } q_e = \log K_f + 1/n \log C_e$$

Where Kf is the freundlich constant and n is the freundlich exponent. Kf and n can be determined from the linear plot of log qe versus log ce , n values between 1 and 10 indicates beneficial adsorption (Thilagavathy et.al., 2013). The closer the n value of freundlich is to zero the more heterogeneous is the system. The high values of Kf showed easy uptake of Cr(VI) ions from wastewater with high adsorptive capacities of sorbents (Aksu et.al., 2002). Both of the parameters Kf and 1/n affect the adsorption isotherm. The larger the Kf and 1/n value, the higher the adsorption capacity (Samadiet.al., 2009).

2.10 Factors Affecting Adsorption Capacity of Biosorbent

2.10.1. Initial Adsorbate Concentration

Initial adsorbate concentration is one of the important factor which affects adsorption capacity. According to Ahaylaet.al.(2005).As chromium concentration increased the percentage of chromium bio sorption on the adsorbents of treated saw dust, bengal gram husk, and sugar beet bagasse respectively progressively decreased. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for the complexation of Cr ions at higher concentration levels. At lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 100% adsorption. At higher concentrations, more Cr(VI) ions are left unabsorbed in solution due to the saturation of binding sites.(Samadi et.al, 2009

2.10.2. Biosorbent Concentration

Adsorbent concentration is another factor that affects adsorption capacity. As the adsorbent dosage increases, the adsorption of Cr(VI) also increases. This is due to the fact that an increase in adsorbent dosage increases the number of active sites available for adsorption (Samadi et.al, 2009).

Optimum removal of chromium about 94% was achieved for an adsorbent dosage of 2 g of coconut husk. Beyond the optimum dosage, negligible increase in adsorption occurred (Veenaet.al., 2012).

2.10.3. PH

The adsorption of metal ions depend on solution pH, which influences electrostatic binding of ions to corresponding metal groups. Chromium exhibits different types of pH dependent equilibrium in aqueous solutions. As the pH is shifted, the equilibrium will also shift; in the pH range 2 - 6, HCrO4- and Cr2O72-, ions are in equilibrium. At lower pH values, Cr3O10- and Cr4O132- species are formed. according to (Ahayla et.al., 2005**) ,** The optimum initial pH for biosorption of Cr(VI) on bengal gram husk was observed at pH 2.0 which indicates the formation of more polymerized chromium oxide species with decreased pH . 99.6% of Cr(VI) ions were adsorbed from a solution of 10 mg/l at pH 2.0, whereas a 23% reduction in bio sorption was observed as the pH shifted from 2.0 to 4.0. At the optimum sorption pH 2.0, the dominant species of Cr(VI) ions in solution are HCrO4-, Cr2O72-, Cr4O132- and Cr3O102-. These chromate anions interact strongly with the negatively charged ions of the bghmatrix. (Garg et.al., 2004) reported that the maximum percentage removal about 99.7%, 86.6% and 62.2% of Cr(VI) was observed at the initial pH of 3.0 by ACR (commercially prepared activated carbon), SDC (sulphuric acid treated saw dust) and SD (formaldehyde treated saw dust) respectively and decreased at lower and higher initial pH values. At initial pH of 3.0, the adsorbent surfaces might be highly protonated which favor the uptake of Cr(VI) in the predominant anionic form (HCrO4-) (Srinivas Rao et.al., 1992). With increase in pH from 3 to 10, the degree of protonation of carbon surfaces reduced gradually and hence removal was decreased.

2.10.4. Contact time

According to (Yu et.al., 2002) , the removal of Cr(VI) by saw dust increases with time and attains saturation in about 100 – 200 min, Basically, the removal of sorbate is rapid but it gradually decreases with time until it reaches equilibrium (Rengaraj et.al., 2003).

2.10.5. Temperature

Temperature is one of the most important factors which affect the rate of adsorption. The rise in adsorption capacity with temperature is because of the rise in kinetic energy of the sorbent particles. Thus the collision frequency between adsorbent and adsorbate increases, resulting in the enhanced sorption onto the surface of the adsorbent. Secondly, at higher temperatures due to the rupture of bonds of the functional groups on adsorbent surface, there may be an increase in the number of active sorption sites, leading to enhanced sorption (Thamilarasu.et.al, 2011).

2.10.6 Shaking Speed

According to Ahaylaet.al.,(2005) result a 30-40% increase in adsorption of Cr(VI) by bengal gram husk was observed in agitated samples during 120 rpm of Biosorption. This is because agitation facilitates proper contact between the metal ions in solution and the biomass binding sites and there by promotes effective transfer of sorbet ions to the sorbent sites.

At 60 and 180 rpm, the adsorption rates monitored were found to be slightly lower than that at 120 rpm. These results indicate that the contact between solid and liquid is more effective at moderate agitation 120 rpm.

Maximum of 97.77 % Cr(VI) removal by activated carbon prepared from coconut shell was achieved at 200 rpm. The effect of chromium adsorption on low and high agitation speed was observed. An increase in adsorption was observed from 66.66 % to 97.77 %, when the agitation speed was increased from 90 to 200 rpm. Due to agitation, proper contact was developed between metal ion in solution and the binding sites, which promoted effective transfer of adsorbate ions onto the adsorbent sites (Ahaylaet.al., 2005)).

2.11 MaeruaSubcordata

Maerua Subcordata is a wild shrub that is indigenous to many tropical countries and common in east Africa. It has coagulant properties and used in traditional water purification (Verdcourt and Trump, 1969). During the observation made on March 21, 2009 at Old Omokebele in Dasenechworeda, theplant has small leaves and yellow flowers (Fig. 4). It was known from local villagers that the fruit has coffee color and edible with sweet taste. (GedewonTeka, 2009)

There are some communities that have been using the root for clarification of turbid water in many African countries. Jahn (1981, 1986) reported that the Pokomo communities in the Tana District of Kenya use M.subcordata branches and roots for drinking water clarification.

Figure 4 MaeruaSubcordata (gluf) plant

According to Edwards et al. (2000), M. subcordata is a low shrub, 1-2 m, and grows on rocky ground or on well-drained sandy soil; and also in grassland burned every few years and grazed by cattle. It grows in Ethiopia in Kefa, GamoGofa, and Sidama as well as in Tanzania, Uganda, Kenya, Sudan and Somalia. The massive rootstock is pounded and mixed with muddy water to clear it for drinking and washing (Edwards et al., 2000).

Maerua subcordata juice extract seems to provide a coagulant, forming flocs through chemical or biochemical processes.According to Mavura et al. (2008) the pH of fresh juice was determined to be 3.5. This is quite acidic. However, the pH of fresh water after adding the juice was slightly basic (pH of 8.1). The juice has characteristic smell, which is consequently transferred to treated water.The results from metal analysis of M. subcordata indicates that there was practically no aluminum in the plant extract, and therefore the coagulation of turbid water is not caused by aluminum salts as it happens with alum. It is also apparent that the coagulation is not caused by iron salts.The concentration of protein was found to be an average of 289 mg/mL of M. subcordata juice (Mavura et al., 2008).

M.subcordata contains relatively large amounts of polysaccharides, 300 mg/L, mostly amylopectin which is a branched molecule. Special polysaccharides in the roots of M. subcordata are responsible for the flocculation of colloidal particles. These molecules form bridges between particles, increasing their mass as a consequence, thus causing precipitation (Mavura et al., 2008).
During the past few years, some research articles were published reporting the successful use of different kinds of bioserbent in the removal of heavy metals ions from aqueous solution.Munagapati et al. (Munagapati VS, Yarramuthi V, Nadavala SK, Alla SR, Abburi K 2010). reported the use of *Acacialeucocephala*bark powder as an effective, low cost, and environmental friendly biosorbent for the removal of Cr(II), Cd(II) and Pb(II) ions from aqueous solution with sorption capacities of 147.1, 167.7 and 185.2 mg/g; Cork waste biomass has been proved to be an efficient biomaterial useful for Cd(II) and Pb(II) removal from aqueous solutions(López-Mesas M, Navarrete ER, Carrillo F, Palet C 2011). The maximum uptake of Cu (II) and Cr (III) ions by peanut shells was found to be 25.39 mg/g and 27.86 mg/g; respectively (Witek-Krowiak A, Szafran RG, Modelski 2011) .

Historically, Verdcourt and Trump (1969) during their work on “Common Poisonous Plants of East Africa” have mentioned the traditional uses of the root of Maeruasubcordata for water treatment.A preliminary study on water 19 Clarification properties of M. subcordata and Moringastenopetela was done by Hund and Adam (1991).
The roots of Maerua genus have been widely studied for pharmaceutical and toxicity reasons and water coagulation other than as biosorbent for the removal of Heavy metals. As described by Henry and Grindley (1949), McLean et al. (1996) and Henry (1984), roots of M. Subcordata contain poisonous tetramethyl ammonium compounds in lesser concentration that cannot cause health risks to humans.
This study will provide options of low cost Cr (VI) treatment technology from locally available MaeruaSubcordataRoot Tuber which will decrease the cost of importing advanced waste water treatment technologies. And it will have a contribution in decreasing the carcinogenic impact of Cr (VI) to human and the environment in general.

CHAPTER THREE

METHODOLOGY

3.1 Study Design and Period

An experimental study design was used to assess adsorption efficiency of Maerua SubcordataRoot to remove Cr (VI) from aqueous solution and tannery waste water at different working parameters. The study was conducted in Leather Industry Development Institute Environmental laboratory and Addis Ababa university Environmental science laboratory center from January to May, 2015.

3.2 Study Variables

3.2.1 Dependent Variable

- Cr(VI) Biosorption efficiency

3.2.2 Independent Variable

- Biosorbent dose
- Initial Cr(VI) concentration
- Contact time
- pH

3.3 Data Quality Control

In order to control the quality of the experiments, all the batch tests were replicated three times following standard procedure using analytical reagent grade chemicals prepared fresh and experimental blanks were run in parallel. All the synthetic samples were prepared, preserved, and analyzed with carefulness, patience, and accuracy. The instrumental operating errors were eliminated by checking the calibration regularly. Glass wares and syringes used in the tests were pre soaked in 2N HNO3 solution for 1hr.And then washed properly with tap water. Then, rinsed thoroughly with deionized water and dried in oven.

3.4 Experimental Set Up

Activation unit is the place where the processing of Maerua Subcordata to change to activated was taking place then the activated Maerua Subcordata obtained was mixed with Cr(VI) ion in Biosorption unit. Finally the filtrate which contains Cr(VI) obtained after mixing is measured in uv-vis spectrophotometer.

Figure 5 Process of Batch Adsorption Experiment

3.5 Preparation of the Biosorbent

Maerua Subcordata root was obtained from south omo zone DasenechWoreda where the rural community uses it for clarification of turbid water.

The root tubers were cut in to small pieces, dried in the sunlight and grinded to produce the powder. The powder was sieved using a mesh size of 0.5mm in order to attain similar particle size. And dried in oven at 60oc for 8 hrs to gain a constant weight. The Powder was treated with 45% (w/w) H3PO4 in the ratio of 2.3 H3PO4 to1 Maerua Subcordata then it was mixed thoroughly and the mixture was left soaked overnight.Then it was dried at 110°c for 1.5h (liuet.al., 2010) and soaked with deionized water until the solution pH become stable.Finally, the samples here after called activated (treated).

Figure 6 Preparation of Activated Maerua Subcordata

3.6 Characterization of Activated Maerua Subcordata

Characterization is an important task to control the quality of activated biosorbent. Physical characterization such as moisture content and bulk density was carried out.

3.6.1 Moisture Content

Moisture content is an important property which affects the weight of activated biosorbent. The moisture content of activated biosorbent was determined by the loss in mass of wet sample after drying in an oven at 110 °c for 60 minutes. About one gram of activated biosorbent prepared from Maerua Subcordata was taken in a previously weighed crucible. The crucible was placed in an electric hot air oven maintained at about 110°C. After one hour the crucible is taken out, cooled in desiccators and weighed again. The loss in weight of the biosorbent reported on percentage basis gives moisture content in the sample and calculated using the following equation (ASTM D 2974-87).

$$\text{moisture content (\%)} = \frac{(W1+W2) - W3}{W2} * 100$$

Where, W1= weight of crucible,

W2 = weight of activated MaeruaSubcordata

W3 =weight of residue after drying at 110°c

3.6.2 Bulk Density

Bulk density is an important parameter of solids depends on physical structure of adsorbent and degree of compaction. Its determination was by volume which filled by dried biosorbent. About 10g of activated Maerua Subcordata was filled in 50ml measuring cylinder and then amount of activated Maerua Subcordata taken by the cylinder was calculated as shown (Veenaet.al. 2013).

Bulk density = M/V,

Where; M= gram of activated Maerua Subcordata placed in the cylinder;

V= volume of the cylinder taken up by the activated Maerua Subcordata powder.

3.7 FTIR (Fourier Transform Infrared Spectrometry)

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material when IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in identification of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. (Dulaet.al. 2014). FT- IR analysis of Maerua Subcordata was carried out in order to identify the surface functional groups which can contribute significantly to enhance Biosorption efficiency of the activated Maerua Subcordata.

3.8 Determination of Cr (VI) using Colorimetric Method

3.8.1. Cleaning of Glassware's

Glassware's were soaked in warm, mild detergent solution to remove any residual grease or chemicals. After the initial cleaning the glassware's were soaked in 2N HNO3 for 1hr. Then Rinsed thoroughly with distilled water and dried in the oven (APHA, 1998).

3.8.2. Removal of Reducing Agent from the Extraction Reagent (2% NaOH)

2 ml of 0.1% KMnO4 solution was added using a 5ml pipette to the flask containing 2% NaOH solution and mixed thoroughly. Then the solution was waited for a few second and drop wise addition of 0.1% KMnO4 was continued until a faint pink color was attained which indicates that an excess of KMnO4 was added, thus neutralizing the reducing agent present in the extraction reagent. Then the flask was capped and ready for use (APHA, 1998).

3.8.3. Removal of Reducing Agent from 6N H2SO4

0.75ml of 0.1% KMnO4 was added using a 5ml pipette to the flask containing 6N H2SO4 and mixed thoroughly. Then the solution was waited for a few second and drop wise addition of KMnO4 was continued until a faint pink color was attained which indicates that an excess of KMnO4 was added, thus neutralizing the reducing agent present in the extraction reagent. Then the flask was capped and ready for use (APHA,1998).

3.8.4. Preparation of Stock Solution

A stock solution of Cr (VI) (1000mg/l) was prepared by dissolving 2.8287g analytical reagent grade potassium dichromate (K2Cr2O7) in 1000ml distilled water (APHA, 1998). The solution color turned to yellowish as shown in fig 5. The stock solution was then diluted to the required working solution prior to use in batch tests.

Figure 7 Potassium Dichromate Solution

3.8.5. Preparation of Standard Curve for Hexavalent Chromium

1ml of the chromium stock standard solution was taken and added into a 100 ml volumetric flask and diluted to the mark with distilled water. This solution contains 10mg/l of Cr+6. Then the flask was stoppered and inverted several times to mix the solution thoroughly. Six 100 ml conical flasks which contains 25 ml of the extraction reagent and 7.8ml of H_2SO_4, previously treated with dilute 0.1% KMnO4 solution was prepared.

Then 0ml, 0.5ml, 1ml, 2ml, 4ml and 10ml of the chromium working standard solution which respectively contains 0,0.05,0.1,0.2,0.4 and 1mg/l was added to each flask and shacked well to remove the carbon dioxide gas. Then 2 ml diphenyl carbazide solution was added to each flask, and diluted to the mark with distilled water. After that the flasks was capped and mixed thoroughly by inverting several times.

Then the mixture was allowed to stand for 10 minutes for full color development. Finally the absorbance of each standard was read in uvvis spectrophotometer at 540 nm after setting the instrument to zero with the reagent blank. At the end absorbance vs. mg Cr(VI) /l was plotted using Microsoft excel (APHA,1998).

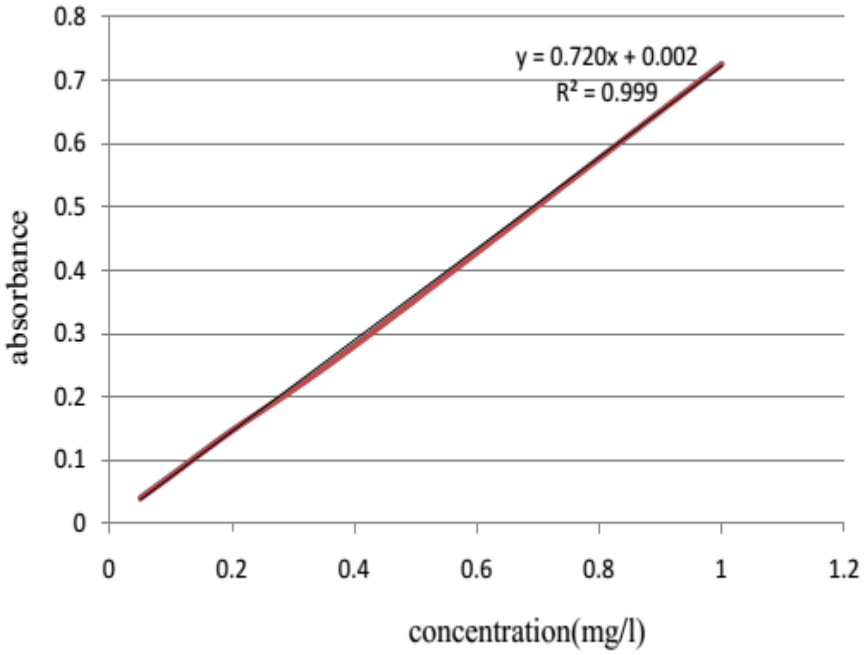

Figure 8 Standard Calibration Curve for Hexavalent Chromium

3.9 Batch Adsorption Experiment Procedure

➢ In the batch test 50 ml of required Cr(VI) solution was added in the 100 mL conical flask. The pH of the adsorbate solution was adjusted to the desired value by adding 0.1M H_2SO_4 and NaOH solution and measured by a micro-processor pH meter model 210 as shown in (fig.9).

Figure 9 PH Adjustment using Hanna PH 210 Micro Processor PH Meter.

➢ Before adding sorbent into the sorbate solution, a sample was collected to measure the initial Cr (VI) concentration. Then the required amount of sorbent (activated Maerua Subcordata powder) was measured in digital balance model E42S-B and mixed with the adsorbate solution in the conical flask.

➢ After that, the conical flask was placed in the thermostat water bath shaker for mixing the solution properly for known minutes by setting the instrument at shaking speed of 200 rpm. The mixing of adsorbate and adsorbent in shaker is shown in (Fig.10).

Figure 10 Mixture of Adsorbent and Adsorbate in Thermostat Water Bath Shaker Model No GFL 1083

➢ The samples of this mixture were collected, filtered using what man No. 41 filter paper and stored in the 100 ml volumetric flask. Then 25 ml extraction solution (2% NaOH) and 7.8ml H_2SO_4 was added to the flask.

➢ These stored samples were analyzed colorimetric ally using 1,5diphenylcarbazide solution to identify the Cr(VI) concentration at a wave length of 540 nm using Agilent cary 100 Uv-vis spectrophotometer(APHA,1998). The Cr(VI) concentration measurement using Uv-vis spectro photometer is shown in (Fig.11). All the batch tests were conducted in the laboratory using similar manner described above.

Figure 11 Agilent Carry 100 UV- vis Spectrophotometer

3.10 Data Analysis and Presentation

3.10.1 Analysis of Adsorption Data

Adsorption data of removal efficiency(R) and adsorption capacity (qe) of activated Maeru Subcordata was calculated using an equation R= (Co - Ce/Co)*100 and q = (Co - Ce)/m*v respectively for different initial Cr(VI) concentration, MaeruaSubcordata, PH and contact time ,. Where; R = % removal efficiency; Co = initial Cr(VI) concentration in mg/l; Ce= final Cr(VI) concentration in mg/l; q = Adsorption capacity in mg/g; V= volume of the solution in ml; m = mass of the adsorbent in g (Thamilarasu et.al., 2011).

3.10.2. Analysis of Adsorption Isotherm Data

Analysis of the isotherm data is important in order to develop an equation which accurately represents the adsorption capacity of activated Maerua Subcordata and which could be used for design purposes .There are a number of models which describe the adsorption process. Out of which the Langmuir and Freundlich models given by the equation 1/qe= 1/qmax.b.1/Ce+ 1/qmax and Log qe= logKf+1/n log Cerespectively were used for this study. These models are selected because, in most of the studies of single metal adsorption by carbonaceous materials Langmuir and Freundlich models shows best fits than others (Ahayla et.al., 2005).

3.10.2.1 Langmuir Isotherm

The Langmuir isotherm represents the equilibrium distribution of metal ions between the liquid and solid phase given by the linear equation 1/qe=1/qmaxCeb +1/qmax. where; qe is the adsorption capacity; qmax is the maximum site specific adsorption in mg/g; b is the rate of adsorption to desorption in l/mg and Ce is the equilibrium Cr(VI) concentration left in the solution in mg/l .The assumptions are; metal ions are chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between the ions. The values of Langmuir constants, qmaxand b was determined from the slope and intercept of the plot 1/qevs1/ce . RL is one of the characteristics of Langmuir model which describes the shape of the isotherm. RL value between 0 and 1 indicates beneficial adsorption and was calculated using an equation RL=1/ 1+bCo (Thamilarasuet.al., 2011). Langmuir isotherm adsorption data was obtained by varying the initial Cr(VI) concentration from 2 to 10 mg/l while keeping other parameters such as adsorbent dose, pH, contact time and shaking speed values of 0.125g,3,60 minutes,200rpm respectively.

3.10.2.2 Freundlich Isotherm

The well-known Freundlich isotherm is a special case applied to non-ideal sorption on heterogeneous surfaces and also to multilayer sorption, suggesting that binding sites are not equivalent and/or independent. The Freundlich model is described by the linear equation Lnqe =1/n lnCe+ lnKf.where; Kf indicates the adsorption capacity in (mg1-1/n L1/n g-1) and 1/n is Freundlich constant related to the adsorption intensity. Kf and n are empirical constants and were determined from the linear plot of lnqe versus lnCe.Freundlich isotherm adsorption data was also obtained by varying the initial Cr(VI) concentration from 2 to 10 mg/l while keeping other parameters at optimum values. Finally, the data obtained from the isotherms was analyzed using Microsoft excel sheet 2007 and the one which better fits (having high r2 value) was selected as a general equation for extrapolation and generalization of the result . Finally the result was presented using tables and figures.

3.11 Application to Tannery Wastewater

The adoptability of the technique enlarged with the activated MaeruaSubcordata for chromium removal was undertaken with some actual effluent samples. Chrome tanning effluent was collected from Ethiopian leather Industry development Institute (LIDI) and Batu Tannery PLC, which is a private leather tanning industry in Addis Ababa, at discharge point. The chrome tanning liquor from Batu Tannery Leather Development institute had pH of 3.5 and 4.12 chromium concentration of 2370.2 mg/land 2085.2 mg /l respectively which was measured before application with adsorbent. In order to study the efficiency of the activated Maerua Subcordata for the actual sample, the effluent was digested with concentrated Nitric acid and then filtered through Whatmann No.41 filter paper. The resulting solution was dissolved at different time intervals, and at optimum conditions of activated Maerua Subcordata dose, stirring speed and with actual adsorbate concentration.

Finally, the solutions were subjected to atomic absorption spectroscopy for extraction of total chromium as Cr (VI).

3.12 Experimental Procedures for Digestion

The sample digestion and extraction procedures necessary to give values for dissolved (free) Cr (VI) or total chromium as Cr(VI).The chrome waste of 100ml was transferred to a beaker and 5ml HNO3 (conc.) was added with a few boiling chips. Then this was subjected to a slow boiling and evaporated in a hood to the lowest possible volume of 20ml before precipitation occurs. Since digestion is not complete after final volume of 20ml, 5ml of HNO3 (conc.) was added until a clear solution was observed. This was then cooled and filtered through 100ml cylinder using Whatmann No.41 filter paper. To oxidize Cr (III), a portion of digested filtrate sample was taken into 125ml conical flask by adding several drops of methyl orange indicator, then NH4OH (conc.) was added until solution just begins to turn yellow. Then after, 1+1 H2SO4 was added 17 drop wise until it becomes acidic and the volume was adjusted to 40ml followed by adding boiling chips and subjected to heat for boiling. When two drops of KMnO4 solution was added, the solution became faded then an excess of two drops of KMnO4 solution was added and this gave a dark red color. This was boiled for 5 minutes, and then 1ml sodium azid solution was added and boiled for a minute gently. Since red color didn‘t fade completely after boiling for a minute, another 1ml sodium azid solution was added and continued boiling for 1minute until color had faded completely and allowed to cool. The final solution was subjected to atomic absorption spectroscopy for total chromium concentration as Cr (VI) ions.

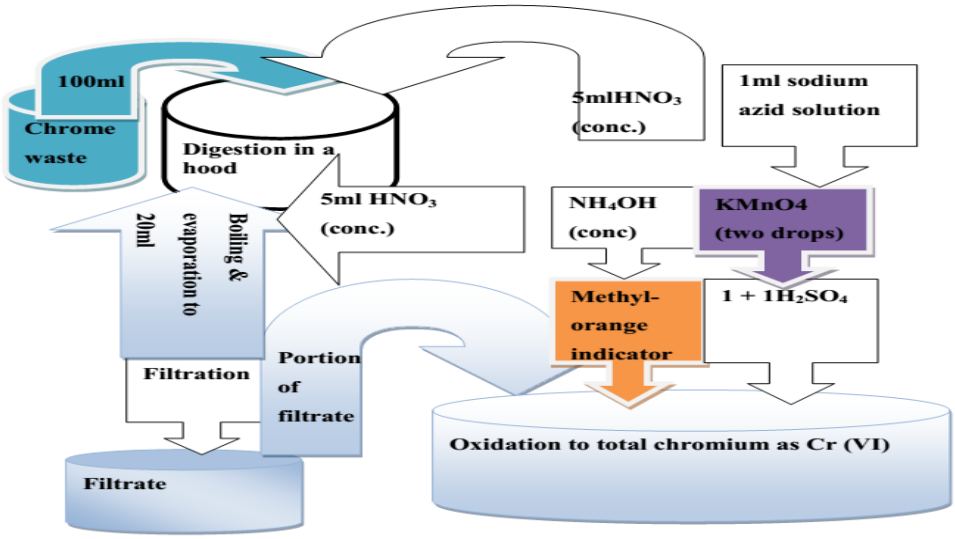

Figure 12 Flow Chart of Experimental Procedures for Digestion and Oxidation of Wastewater Sample

CHAPTER FOUR

RESULT

4.1 Physical Characteristics of ActivatedMaeruaSubcordata

Table 3 Results of proximate Analysis of Activated MaeruaSubcordata

No	Physical characteristics	unit	value
1.	Moisture content	%	1.8
2.	Bulk density	g/ml	0.588

It is confirmed from the proximate analysis that the moisture content of activated MaeruaSubcordata is 1.8% while its bulk density 0.588 g/ml. (Table 3)

4.2 Fourier Transform Infrared Spectrophotometer (FTIR) Test

The spectra of activated MaeruaSubcordata were measured at 400 - 4000Cm-1. FTIR test of activated MaeruaSubcordata displays a number of absorption peaks as shown in fig. 13

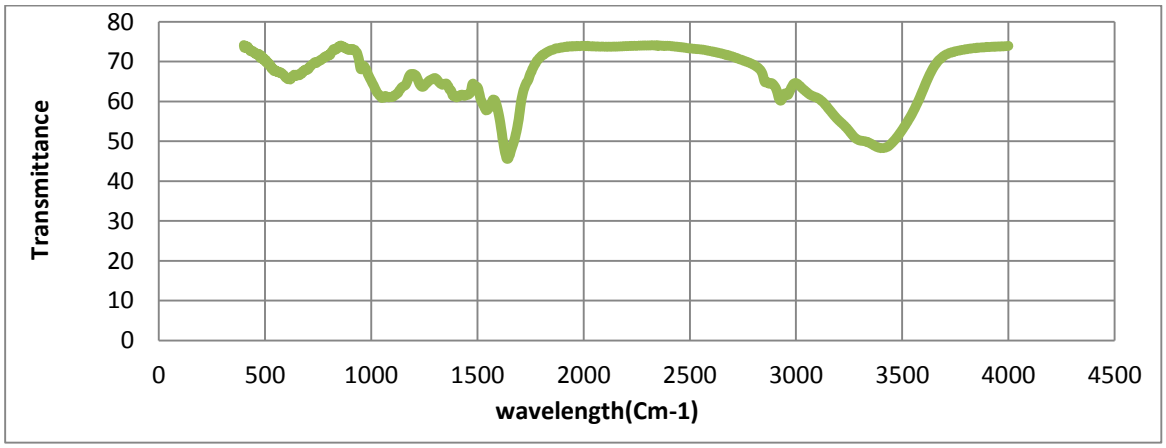

Figure 13 FTIR (Fourier Transform Infrared Spectrophotometer) spectra of activated Maerua Subcordata

Table 4 Frequencies and respective functional groups present on the surface of activated MaeruaSubcordata

Frequencies(Cm)	Bond	Functional group
3500-3200	O-H stretch, H-bonded	Hydroxyl
3000-2850	C-H Stretch	Alkanes and Aldehydes
1760-1665	All C=O Stretch	Carbonyls
1680 - 1640	–C=C– stretch	Alkenes
1500 - 1400	C–C stretch	Aromatics

It can be seen from (Table 4), the broad absorption peak between 3200 - 3500cm-1 was indicative of Hydroxyl (O-H stretching).The dominant absorption peak between 2850-3000cm-1 indicates the presence of alkanes and aldehydes (C-H stretching). The strong absorption peak between 1665-1750cm-1 was assigned to carbonyls(C=O stretching).The medium absorption peak between 1640-1680cm-1 indicates –C=C– stretch alkenes. The absorption peak between1400-1500cm-1 was assigned to C–C stretching of aromatics.

4.3 Batch Adsorption Experiment Results

4.3.1 The Effect of Biosorbent Dose

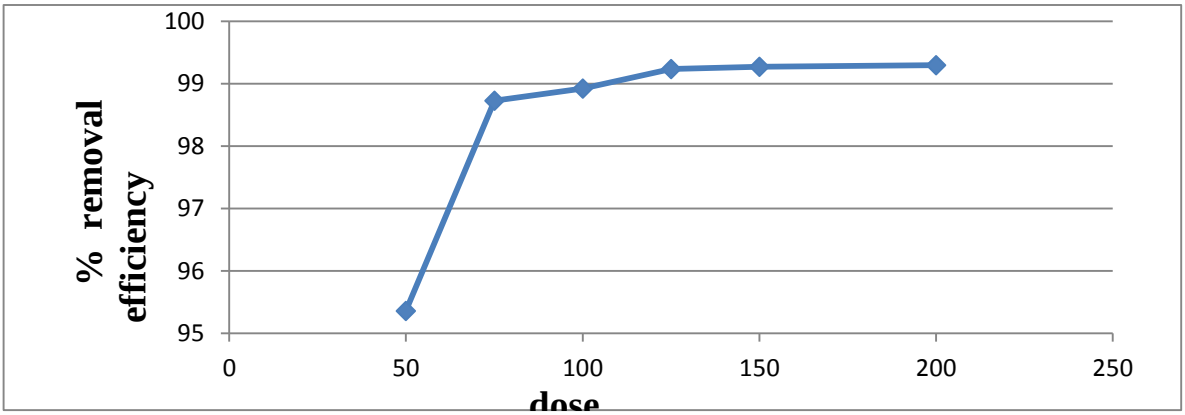

Figure 14 The effect of adsorbent dose on removal efficiency at initial conditions of Cr(VI) concentration = 6mg/l, pH = 2, contact time =100 minute, Agitation speed = 200rpm.

It is evident from (Fig.14) that, as MaeruaSubcordata dose increases, the efficiency for removal of Cr(VI) ion from aqueous solution was increased. The removal efficiency for biosorbent doses of 50mg, 75mg, 100mg, 125mg, 150mg and 200mg were 95.36% 98.7%, 98.9% and 99.24%, 99.27%, 99.29% respectively. The results indicate that there was a sharp increase in removal efficiency from 95.3% to 98.7% when the adsorbent dose was increased from 50 to 75mg. The increase in removal efficiency was continued up to 200mg adsorbent dose.

Maximum about 99% removal efficiency was obtained at 125mg Maerua Subcordata which is the optimum dose. Further increase in adsorbent dose was not shown significant improvement in removal efficiency.

4.3.2 The Effect of Initial Cr(VI) Concentration

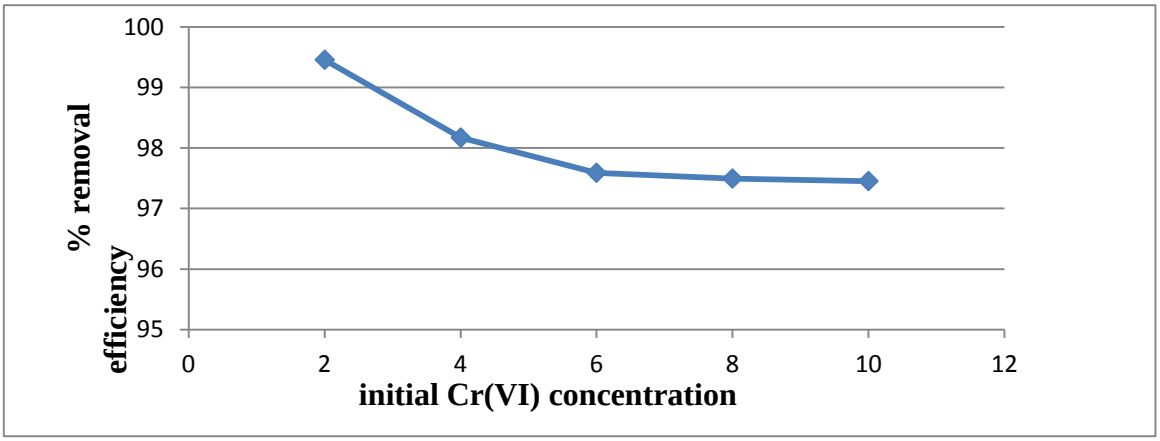

Figure 15The effect of initial cr (VI) concentration at initial conditions of adsorbent dose =0.125g,pH =2,contact time = 100 minute, Agitation speed =200rpm

(Fig.15). Shows the effect of initial Cr(VI) concentration on the removal efficiency of MaeruaSubcordata. The removal efficiencies for 2mg/l, 4mg/l, 6mg/l, 8mg/l and 10mg/l were 99.45%, 98.17%, 97.59%, 97.49%, 97.45% respectively. It can be seen from the figure, as initial Cr(VI) concentration increased from 2 to 10 mg/L, the adsorption removal efficiency decreased from 99.45% to 97.45%. The decrease in removal efficiency from 99.45 to 97.4 was observed when the initial Cr(VI) concentration was increased from 2 to 6 mg/l but further increase in initial concentration from 6 to 10mg/l was not show significant effect. Maximum removal efficiency about 99.45% was obtained at lower initial Cr (VI) concentration of 2mg/l.

4.3.3 The Effect of Ph

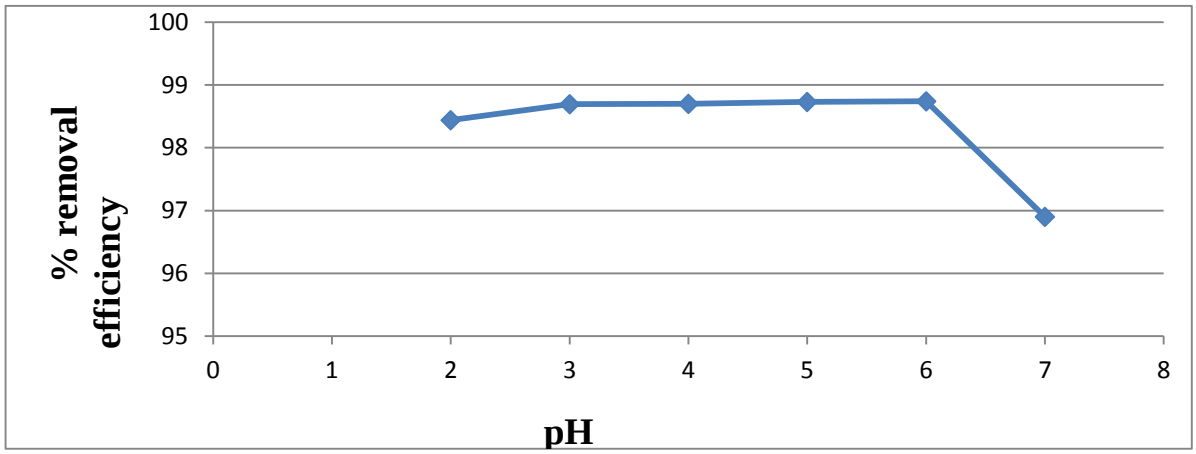

Figure 16 The effect of pH at initial conditions of Cr(VI) concentration = 6mg/l ,adsorbent dose = 0.125 g,contact time = 100 minutes, shaking speed = 200 rpm

The removal efficiency of Maerua Subcordata at pH 2, 3, 4, 5, 6, 7 were 98.44%, 98.69%, 98.70%, 98.73%, 98.74%, and 96.89% respectively. About 98% removal efficiency was obtained between pH range 2 to 6 and further increase in pH from 6 to 7 shows decrease in removal efficiency from 98.7% to 96.89%. Maximum removal efficiency about 98.7% was obtained at pH 3 further increase in PH from 3 – 6 show insignificant effect.

4.3.4 The Effect of Contact Time

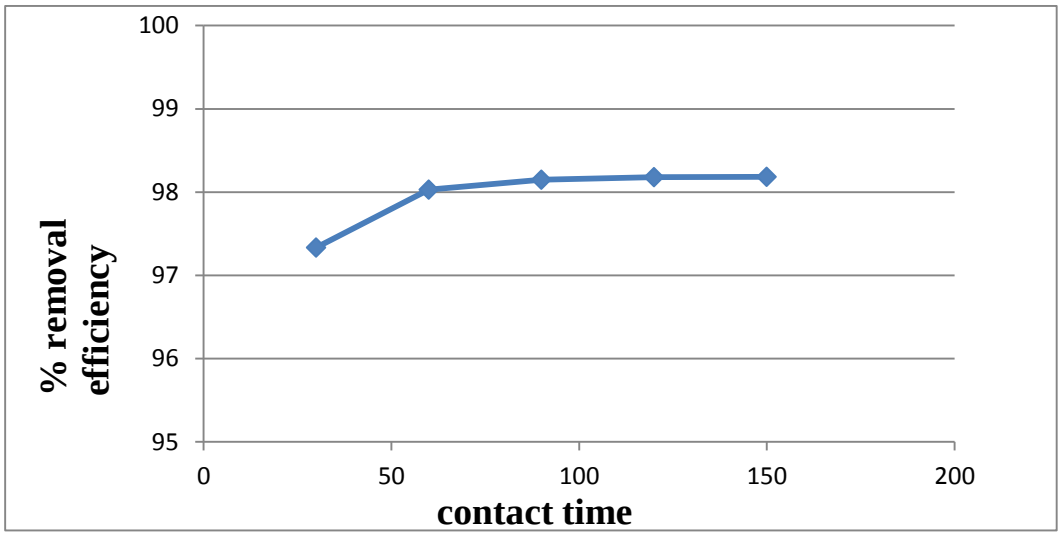

Figure 17 The effect of contact time at initial conditions of Cr(VI) concentration =6mg/l, adsorbent dose=0.125g,pH=3, contact time=60 minutes, shaking speed =200 rpm.

(Fig.17).Shows the effect of contact time on the removal efficiency of Maerua Subcordata. The removal efficiency of MaeruaSubcordata at contact time of 30, 60, 90, 120 and 150 minutes were 97.3%, 98.03% ,98.15%, 98.18%, 98.18% respectively. When contact time increased from 30 to 150 minute, the adsorption of Cr(VI) on to Maerua Subcordata was also increased from 97.3% to 98.18%. The results indicate that the rate of adsorption in the first 30 minutes was fast and then decreases until it reaches equilibrium. About 97% of removal efficiency was obtained at contact time of 30 minute.Between 30 to 60 minute the amount of Cr(VI) removed from the solution was increased from 97% to 98%. After that further increase in contact time was not shown any significant effect on the removal efficiency. Maximum removal efficiency about 98.03% was obtained at 60 minute.

4.4 Adsorption Isotherm Analysis

4.4.1 Langmuir Isotherm

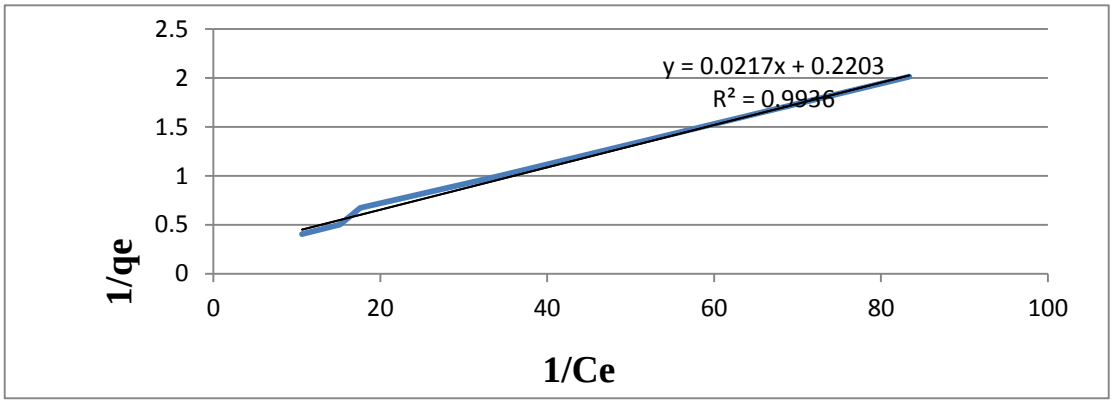

Figure 18 Langmuir plot for the adsorption of Cr(VI) at optimum conditions of Biosorbent dose = 0.125g, pH =3, contact time = 60 minute, shaking speed =200rpm.

The values of langmuir parameters qmax and b obtained from the slope and intercept of 1/Ce vs.1/qe were 4.54mg/g and 0.095 respectively. Whereas the coefficient of determination (r^2) value was 0.993.The value of RL, one of the characteristics of langmuir isotherm was in the range 0.513-0.84.

4.4.2 FreundlichModel

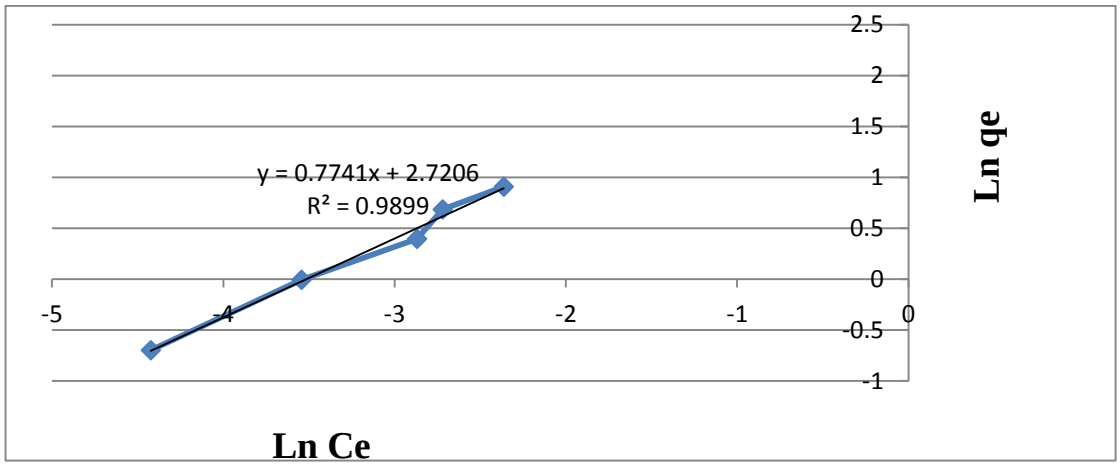

Figure 19 . Freundlich plot for the adsorption of Cr(VI) at optimum conditions of adsorbent dose =0.125g,pH =3,contact time=60 minutes, shaking speed=200rpm

The values of freundlich parameters 1/n and Kf obtained from the slope and intercept of the plot Lnqe vs LnCe were 0.774 and 15.18 respectively.

4.5 Application to Tannery Waste Water

The suitability of the bioadsorbent materials for the removal of Cr (VI) was tested with the tannery industry wastewater. It has been found that increase in contact time up to the equilibrium time increased the percentage adsorption.The data reveals that the treatment of Cr (VI) in tannery wastewater is significantly good. Almost complete removal 86.5 % efficiency was obtained at 6g Maerua Subcordata and 200 rpm shaking speed for 60 minutes at room temperature. Thus, the results are in good agreement with the results obtained from the batch experiments conducted for the Cr (VI) removal in synthetic wastewater samples. This demonstrates that the selected bioadsorbent can be successfully used for the removal of Cr (VI) from tannery industry wastewaters.

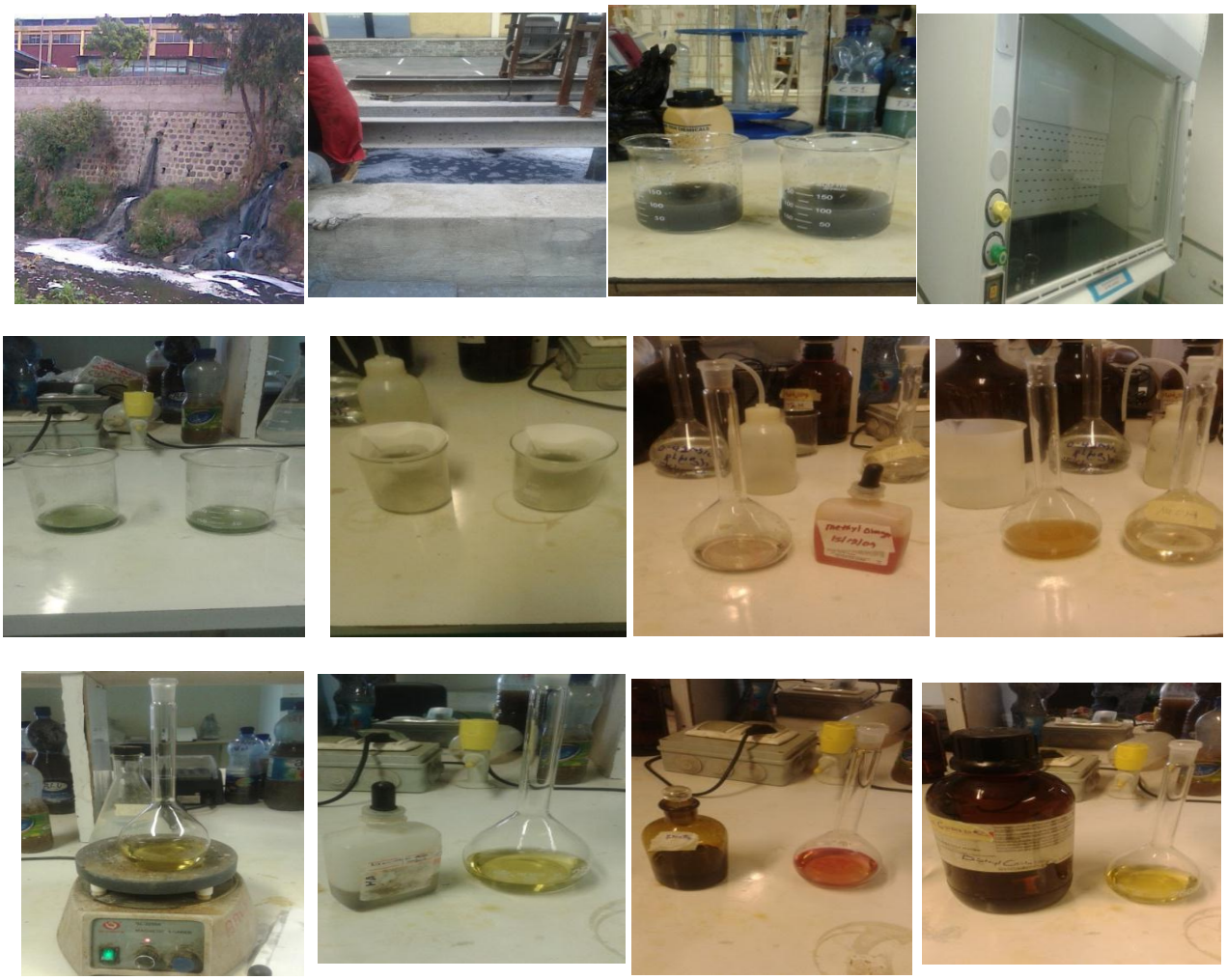

Figure 20Tannery Waste Water Digestion picture taken at AAUES Laboratory on March 2015

CHAPTER FIVE

DISCUSSIONS

5.1 Physical Characteristics of Activated Maerua Subcordata

About 1.8% and 0.588g/ml of moisture content and bulk density respectively were obtained for activated Maerua Subcordata which contributes for higher (99%) removal of Cr (VI) from aqueous solution. Maximum about 93.28% Cr (VI) removal efficiency having moisture content of 3.195% is reported for activated rice husk treated with formaldehyde by (Bishoniet.al., 2009). Compared to activated rice husk , one possible reason for the better efficiency of activated Maerua Subcordata could be due to its low moisture content resulted from the difference chemical activation method employed since sulfuric acid treated raw material has a better yield than phosphoric acid treated raw material with respect to production of high porosity according to (Hoong, 2013).This can be explained as moisture content increases, some adsorption sites within the pores are filled with water and interferes with pore structure development as a result prevents the diffusion of Cr(VI) ion on to the adsorbent site (Veena et.al., 2013).The lower the bulk density value indicates that the highly branched and porous with more void space. The American water work association has set a lower limit at 0.25gm/l for activated adsorbent to be of practical use. Therefore the bulk density obtained from this study satisfies the condition.

5.2 FTIR (Fourier Transform Infrared) Result

The adsorption capacity of activated Maerua Subcordata depends upon porosity as well as chemical reactivity of functional groups at the adsorbent surface. The FTIR spectrum analysis of treated Maerua Subcordata displays a number of functional groups on its surface indicating the complex nature of the biosorbent. According to (Gottipati, 2012) who studied the removal efficiency of Cr(VI) by phosphoric acid treated bael fruit shell reported C-H stretching (aldehydes) observed at the peak 2850-3000Cm-1 played a very important role in Cr (VI) adsorption. A result by (Ramos et.al., 2014) indicates Bonded -OH (hydroxyl) and C=O (Carbonyls) were strongly involved in Cr(VI) adsorption by phosphoric acid treated rice husk .Therefore, the broad and dominant absorption peak observed at 3500-3200Cm-1 and 1760-1665Cm-1 such as –OH (Hydroxyl) andC=O (Carbonyls)mainly involved in Cr(VI) biosorption on to activated MaeruaSubcordata.

5.3 The Effect of Biosorbent Dose

The removal of Cr(VI) ions increased with increase in adsorbent concentration and equilibrium was attained after 125mg of adsorbent dosage. The highest about 99.24% of Cr(VI) removal was achieved at 125mg of MaeruaSubcordata for 6mg/l initial Cr(VI) concentration at pH 2 . According to Thamilarasu et.al., (2011) result about 81.96% removal was obtained from activated carbon prepared from sulfuric acid treated cajanuscajan (L) milp at 300mg optimum adsorbent dose for the same Cr(VI) concentration and pH.

The highest removal efficiency of activated Maerua Subcordata compared to this adsorbent might be due to high porosity and surface area. Increase of removal efficiency as activated Maerua Subcordata dose increased might be due to increment of surface area and availability of more vacant active binding sites for adsorption.

5.4 The Effect of Initial Cr (VI) Concentration

Removal of Cr (VI) was decreased when initial Cr (VI) concentration was increased. Maximum removal efficiency about 99.45% was obtained at lower initial concentration of 2mg/l at adsorbent dosage of 125mg .The same optimum value was obtained by (Thamilarasuet.al., 2011) and who studied the efficiencies of sulfuric acid treated cajanus cajan(L) milp seed shell and got 83.27% removal. The difference in efficiency observed between these adsorbents and activated Maerua Subcordata might be due to difference in the nature of the starting material and the method of activation employed. At lower Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of the initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration .This can be interpreted as when initial Cr(VI) concentration is low, Maerua Subcordata could sorbs all the Cr(VI) ions due to higher availability of the active sites on activated Maerua Subcordata and with increase of initial Cr(VI) concentration, the sorption efficiency decreases as the adsorbent might be saturated with Cr(VI). **(**Thamilarasuet.al., 2011 and Hyder et.al., 2013).

5.5 The Effect of Contact Time and Ph

As shown in (fig. 17), when contact time increases, removal efficiency of activated Maerua Subcordata was increased. Similar result was reported byactivated coffee husk (Veenaet.al., 2013). Maximum % removal of 98.03 was achieved at equilibrium contact time of 60 minutes. The higher % removal as time increases was due to prolonged contact between the Cr(VI) ion and activatedMaeruaSubcordata. The rate of Cr(VI) binding in activated Maerua Subcordata was greater in the initial stages, then gradually decreased after an equilibrium time. The fast adsorption at the initial stage may be due to the fact that a large number of surface sites are available for adsorption. After equilibrium time, the remaining surface sites are difficult to be occupied because of the repulsion between the solute molecules of the solid and bulk phases.The same result was reported by (Veenaet.al., 2013, Yu et.al., 2003 and Samadi et.al., 2009).

PH influences the adsorption of Cr(VI) ions on the adsorbate since it affects the solubility of metal ions and hence the electrostatic binding of metal ions. With increase in pH, the degree of protonation of the surface reduces gradually and the solution becomes basic, increasing the concentration of OH- ions in the solution which hinder the diffusion of Cr (VI) ions.It is evident in figure 16, that between pH 3 and 6 the adsorption is maximum.

About 98.7% removal efficiency was obtained at PH 3. About 86.6% removal was reported by (Garget.al., 2004) at the same optimum pH for sulfuric acid treated saw dust at initial Cr(VI) concentration and adsorbent dosage of 100mg/l and 400mg respectively.

5.6 Adsorption Isotherm Analysis

Figure 18 and 19 indicates adsorption data of Cr (VI) on activated Maerua Subcordata using Langmuir and Freundlich equation respectively**.** The values of Langmuir constants b and qmax obtained from slope and intercept of the plot of 1/qevs 1/ce were, 0.095 and 4.54 mg/g respectively. Higher maximum adsorption capacity (qmax) was obtained by activated Maerua Subcordata compared to rice straw, sugarcane bagasse (Garget.al., 2007), saw dust (Memon et.al.,2005)which respectively has 3.15 mg/g, 0.63 mg/g, 0.28 mg/g, of qmax value. The value of RL, one of the characteristics of Langmuir isotherm which describes the shape of the isotherm obtained from the result indicates favorable adsorption. The coefficient of determination (r 2 = 0.993) which can be seen from Langmuir plot shows adsorption of Cr(VI) on activated Maerua Subcordata obeys the assumption of Langmuir model monolayer adsorption. The values of Freundlich constants Kf and n obtained from the slope and intercept of the plot Lnqe vs LnCe where 15.8 and 0.744.

Higher kf value of 15.8 compared to wool, sawdust, olive cake, coal, cactus which respectively has 2.23,0.489,0.877,0.207,0.094 Kf values (Dakiky et.al., 2002) indicates that higher adsorption capacity of activated Maerua Subcordata. The coefficient of determination (r2 = 0.989) shown in Freundlich plot obeys Freundlich assumption of heterogeneous adsorption. But when both isotherms were compared Langmuir isotherm gives a better fit due to higher r2 value. And qmax predicted from Langmuir isotherm was 4.54 mg/g where as the one obtained from experimental result was 3.93 mg/g,the deviation of Langmuir model from the experimental result was 15%.

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The removal of Cr (VI) in synthetic wastewater and tannery wastewater by using Maerua Subcordata plant was studied in batch experimental systems. The experimental result shows that Maerua Subcordata is an excellent alternative for the removal of Cr(VI) from aqueous solutions.

Adsorption of Cr (VI) was highly pH dependent and the results showed that the removal efficiency increased, as decreasing pH, increasing the adsorbent dose and contact time. Maximum adsorption about 99% removal percentage of Cr (VI) ions using activated Maerua Subcordata as biosorbent was achieved within 60 minutes, at pH 3 and shaking speed, 200 rpm.

Both Langmuir and Freundlich model were followed by adsorption of Cr(VI) on activated Maerua Subcordata. But Langmuir model best describes the adsorption data .The maximum adsorption capacity obtained from Langmuir model is 4.54mg/g .The RL value obtained from Langmuir model shows the adsorption is favorable. The value of Freundlich constants n and Kf were 1.29 and 15.18 respectively. The removal efficiency of Cr (VI) 86.50 % was obtained from the adsorbent when applied to real tannery waste water. The present biosorbent can be recommended for the removal of high concentration of Cr (VI) at the industrial scale before discharging it to the environment. Maerua Subcordata can replace the expensive activated carbon in the adsorption process. Most of the electroplating and tannery effluents contain chromium as one of the major contaminant, which can be removed in a cost effective and efficient manner by Maerua Subcordata.

6.2 Recommendation

- A future study is necessary to examine the removal efficiency of chromium on this biosorbent following continuous method by packing the adsorbent in consecutive column.

- The main objective of this study was to prevent pollution of the environment by chromium. Therefore, chromium loaded Maerua Subcordata has to be managed by doing desorption experiments to recover chromium from the biosorbent surface.

- The effect of temperature on the removal efficiency should also be studied as asorbtion is affected by temperature even keeping other parameters constant.

- The effect of other competing anions on the removal efficiency should also be studied as the real waste effluents are composed of a number of other ions.

CHAPTER SEVEN

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Annexes

Annex 1. Calculation of moisture content

$$\text{Moisture content} = \frac{(W1+W2) - W3}{W1} * 100$$

Where, W1= weight of dish = 64.66915g
W2 = weight of sample = 1.00485g
W3 =weight of residue after drying at 110°c (W1+W2) = 65.65545
Moisture content = (64.66915+1.00485) - 65.65545 *100 = 1.85%
= 1.00485g

Annex 2. Calculation for the preparation of 2N HNO3 from 69% stock standard solution of HNO3

$$\text{Morality of 69\% } HNO_3 = \frac{10*\%*\text{density}}{\text{M.wt}} = \frac{10*69*1.415\text{g/l}}{63.01\text{g/mol}} = 15.495\text{M}$$

Given
C1=15.495M C2 = 2M(required concentration
V1=? V2 =500ml(required volume) Note.
In this case normality = Morality since HNO3 has one hydrogen ion.
C1V1=C2V2
15.495M*V1 =2M*500ml
V1=64.52ml
Therefore, 64.52ml was taken from the stock , added to 500ml conical flask and diluted to the mark.

Annex 3. Calculation for the Preparation of 2%NaOH

20g of NaOH pellet was dissolved by distilled water in 1000ml conical flask.

Annex 4. Calculation for the preparation of 0.1% KMnO4

0.1g of KMnO4 was dissolved in 100ml conical flask and dilute to the mark

Annex 5. Calculation for the Preparation of 6 N H2SO4 from 98% stock standard H2SO4

$$\text{Molarity} = \frac{10*\%\text{ of stock } H_2SO_4*\text{density}}{\text{M.wt}}$$

Annex 6.Calculation for the preparation of 45%(w/w) H3PO4

45g of H3PO4 in 100ml of water since the density of water is 1g/ml
Density of H3PO4 =1.692g/ml
1ml =1.692g 45g =?
$\frac{45g*1.692}{1.692} = 26.6ml$
Therefore, take 26.6ml of H3PO4 from the stock and dilute to 100ml with distilled water to the mark.

Annex 7. Calculation of Potassium Dichromate Requirement to Prepare 1000 mg/LofCr(VI) Stock Solution

Calculate how much K2Cr2O7 is required to get concentration of Cr (VI) stock solution of 1000mg/L (1g/l).

Potassium dichromate (K2Cr2O7) has molecular weight = 2*39 + 2*52 + 7*16 = 78 + 104 + 112
= 294 g/mol

104 g Cr (VI) is available in = 294 g of K2Cr2O7

1 g Cr (VI) is available in = (294/104)*1 = 2.8269 g of K2Cr2O7

Annex 8.calculation of Cr (VI) standard solution.

Concentration of stock Cr (VI) solution=1000mg/l Preparation of Concentration of standard chromium working solution from stock Cr (VI) solutionnitial

Cr (VI) C1=1000mg/l (1mg/ml) mass of stock solution=mass of diluted solution

V1=1ml C1V1=C2V2 V2=100ml C2 = C1V1/V2=1000mg/l*1ml/100ml=10mg/l C2=?

Preparation of different initial Cr (VI) standard solution from Cr (VI) standard workingsolution

Volume of extraction solution=25ml Initial concentration of Cr (VI) standard working solution,

C1=10mg/l Initial volume of Cr(VI) solutionV1=(0ml,0.5ml,1ml,2ml,4ml,10ml) Required diluted solution volume of Cr (VI) V2=100ml

Required diluted concentration of Cr (VI) C2=?

C1V1 =C2V2;

C2=C1V1/V2 C2

=(10mg/l *0ml)/100ml =0mg/l

The same procedure was followed to calculate required diluted concentration of Cr(VI) C2 for 0.5ml,1ml,2ml,4ml,10ml and their respective concentrations are 0.05mg/l,0.1mg/l,0.2mg/l,0.4mg/l,1mg/l

Volume of distilled water =Total volume - (initial volume of Cr (VI) +volume of extraction solution)

= 100 - (0ml +25ml) =75ml

Table 1 Standard hexavalent chromium working solution.

Working standard chromium solution (ml)	Concentration of chromium in mg/l	Absorbance
Blank	0	0
0.5	0.05	0.0409
1	0.1	0.0761
2	0.2	0.1475
4	0.4	0.2815
10	1	0.7259

Annex 9. Dilution of Cr(VI) Stock Solution from 1000 mg/L to the Required Working Concentrations

Initial concentration of stock solution of Cr (VI), C1 = 1000 mg/L Initial volume of stock

Solution of Cr (VI), V1 =?? [Have to find out]

Required diluted concentration of Cr (VI), C2 = (2 mg/l, 4mg/l, 6mg/l, 8mg/l, 10mg/l)

Required diluted solution volume of Cr (VI), V2 = 50 mL [can vary to required volume]

According to the mass balance equation, we know

Mass of stock solution=mass of diluted solution

C1V1=C2V2 V1=C2V2/C1 V1=2mg/l*50ml/1000mg/l=0.1ml

Required deionized water= Total volume of solution - initial volume of Cr (VI)

50ml - 0.1ml = 49.9ml

The same procedure is followed to calculate for other required Cr (VI) concentration and their respective initial volumes and required deionized water are 0.1ml, 0.2ml, 0.33ml, 0.4ml, 0.5ml and 49.8ml, 49.67ml, 49.6ml, 49.5ml

These initial volumes will be taken from Cr (VI) stock solution using 5ml pipette and added to 50ml volumetric flask and the remaining portion will be filled up by deionized water.

Table 2 Calculations of removal efficiency and Biosorption capacity at various Biosorbent Dose

Biosorbent dose(mg)	Co	Ce	Ce*Df	V in liter	R in (%)	qe in mg/g
50	6	0.27847	0.556944	0.05	R =((Co-Ce)/(Co)*100) R=((6-0.2785)/(6)*100) R = 95.3588%	qe =((Co-Ce)/(m)*v) qe=((6 - 0.278)/(0.05)*0.05) qe = 5.722
75	6	0.07615	0.152314	0.05	98.73071	2.961921
100	6	0.06453	0.129074	0.05	98.92438	1.978488
125	6	0.04574	0.091482	0.05	99.23765	1.488565
150	6	0.043738	0.087476	0.05	99.27103	1.191252
200	6	0.042176	0.084352	0.05	99.29707	0.992971

Where, Co = initial Cr (VI) concentration before Biosorption

Ce = equilibrium concentration of Cr (VI) left in the solution after Biosorption

M = mass of Activated Maerua Subcordata

V = total volume of solution

R = removal efficiency of activated Maerua Subcordata

qe =Biosorption capacity of Activated Maerua Subcordata

- The same procedure was followed to calculate R and qe for 75mg,100mg,125mg,150mg and 200mg Maerua Subcordata .

Table 3 Calculations of removal efficiency and adsorption capacity at various initial Cr (VI) Concentration

Co	M	Ce	Ce*Df	V in liter	R in (%)	qe in mg/g
2	0.125	0.0109	0.0218	0.05	R =((Co-Ce)/(Co)*100) R=((2-0.0109)/(2)*100) R = 99.45663	qe =((Co-Ce)/(m)*V qe=((2-0.0109)/(0.125)*0.05) qe = 0.79564
4	0.125	0.073234	0.14647	0.05	98.16915	3.926766
6	0.125	0.14457	0.28914	0.05	97.59043	5.855426
8	0.125	0.20056	0.40112	0.05	97.49389	7.799511
10	0.125	0.255	0.51	0.05	97.45068	9.745068

- The same procedure was followed to calculate R and qe for initial Cr (VI) concentrations of 4, 6,8 and 10 mg/l.

Table 4 Calculations of Removal Efficiency and Biosorption capacity at various PH

PH	Co	M	Ce	V in liter	R in (%)	qe in mg/g
2	6	0.125	0.0935	0.05	R =((Co-Ce)/(Co)*100) R=((6-0.0935)/(6)*100) R = 98.44%	qe =((Co-Ce)/(m)*v) qe=((6 - 0.0935)/(.125)*0.05) qe =5.9065
3	6	0.125	0.0782	0.05	98.69522	5.921713
4	6	0.125	0.0780	0.05	98.70139	5.922083
5	6	0.125	0.0762	0.05	98.73071	5.923843
6	6	0.125	0.0753	0.05	98.74383	5.92463
7	6	0.125	0.1860	0.05	96.89969	5.813981

- The same procedure was followed to calculate R and qe for PH 3, 4, 5, 6, 7.

Table 5 Calculations of Removal Efficiency and Biosorption capacity at different Contact Time

Contact time	Co	M	Ce	V in liter	R in (%)	qe in mg/g
30	6	0.125	0.160046	0.05	R =((Co-Ce)/(Co)*100) R =((6-0.1600)/(6)*100) R = 97.33333	qe =((Co-Ce)/(m)*v) qe= ((6-0.160)/(.125)*0.05) qe = 5.839954
60	6	0.125	0.118148	0.05	98.03086	5.881852
90	6	0.125	0.111157	0.05	98.14738	5.888843
120	6	0.125	0.109306	0.05	98.17824	5.890694
150	6	0.125	0.108935	0.05	98.18441	5.891065

- The same procedure was followed to calculate R and qe for contact time of 60, 90, 120 and 150 minutes

Annex.11.calculation of Langmuir and Freundlich sorption isotherm parameters for Cr (VI) sorption onto Maerua subcordata

Table 6 Langmuir Isotherm Parameters.

Co	Parameters							
	Ce	1/Ce	qe	1/qe	b	qmax	R2	RL
2	0.012	83.4	0.49	2.012	0.095	4.54	0.993	0.513 – 0.834
4	0.029	34.6	0.99	1.007				
6	0.057	17.6	1.49	0.673				
8	0.066	15.2	1.98	0.504				
10	0.094	10.6	2.45	0.404				

$1/qe=1/bq_{max}*1/Ce+1/q_{max}$

Y =0.021x +0.220

1/qe =Y ,1/b qmax =0.220 , 1/Ce = x ,1/qmax =0.220

1/qmax =0.220 qmax=1/0.220 = 4.54

1/b qmax =0.021 b=1/0.021S*1/4.54 =0.095

RL =1/1+bCo ,where Co =2,4,6,8,10 mg/l

=1/(1+(0.095*2)) =0.84 ,1/(1+(0.095*4)) = 0.725 ,1/(1+(0.095*6)) =0.64
= 1/(1+(0.095*8) =0.568 ,1/(1+(0.095*10)) = 0.513
= 0.513-0.84

Table7.Freundlich Isotherm Parameters

Initial Cr(VI). concentration(mg/l)	Parameters						
	Ce	LnCe	qe	Lnqe	1/n	Kf	R2
2	0.012	-4.423	0.49	-0.699	0.774	15.18	0.989
4	0.029	-3.544	0.99	-0.007			
6	0.057	-2.868	1.49	0.396			
8	0.066	-2.719	1.98	0.685			
10	0.094	-2.362	2.45	0.907			

Calculation of the Freundlich isotherm parameters (Kf and 1/n)

$$\text{Ln } qe = 1/n \text{ Ln } Ce + \text{Ln } Kf$$

$$Y = 0.774x + 2.720$$

Ln qe =Y , 1/n =0.774 , Ln Ce = x ,Ln Kf =2.720

1/n =1.144 ,n =1/0.774 = 1.292

Ln Kf = 4.315

$Kf = e^{2.720} = 15.8$

APPROVAL FORM

Submitted by:

Mesfin Berecha		
Student	Signature	Date

Approved by:

1. | | | |
|---|---|---|
| Advisor | Signature | Date |

2. | | | |
|---|---|---|
| Chairman, Dep.'s | Signature | Date |

Graduate Committee

3. | | | |
|---|---|---|
| Chairman, Faculty's | Signature | Date |

Graduate Committee

4. | | | |
|---|---|---|
| Dean, Graduate School | Signature | Date |