REMOVAL OF HEXAVALENT CHROMIUM FROM INDUSTRIAL WASTE WATER USING ACTIVATED CARBON DERIVED FROM KHAT STEM

By: Tilahun Kebede

Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

Presented in partial fulfilment of the Requirements for the Master Degree of Science in Chemistry (Industrial Chemistry)

Office of graduate studies

Adama Science and Technology University

September, 2021

Adama, Ethiopia

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By: Tilahun Kebede

Major advisor: Dereje Tsegaye (PhD)

Co- advisor: Tegene Desalegn (PhD)

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Declaration

I hereby declare that this Master Thesis entitled “Removal of hexavalent chromium from industrial waste water using activated carbon derived from khat stem” is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation

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I/we, the advisor(s) of this thesis, hereby certify that I/we have read the revised version of the thesis entitled “Removal of hexavalent chromium from industrial waste water using activated carbon derived from khat stem” prepared under my/our guidance by Tilahun Kebede submitted in partial fulfilment of the requirements for the degree of Mater’s of Science in Industrial chemistry.Therefore, I/we recommend the submission of revised version of the thesis to the department following the applicable procedures.

_____	_____	_____
Major Advisor	Signature	Date
_____	_____	_____
Co-Advisor	Signature	Date

Approval Page of M.Sc. Thesis

I/we, the advisors of the thesis entitled “Removal of hexavalent chromium from industrial waste water using activated carbon derived from khat stem” and developed by Tilahun Kebede hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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We, the undersigned, members of the Board of Examiners of the thesis by Tilahun Kebede have read and evaluated the thesis entitled “Removal of hexavalent chromium from industrial waste water using activated carbon derived from khat stem ” and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfilment of the requirement of the degree of Master of Science in Industrial chemistry.

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LIST OF ABBREVIATIONS

ACC	Activated Carbon Clothe
ACF	Activated Carbon Fibrous
ACDKS	Activated Carbon Derived from Khat Stem
ANOVA	Analysis of Variance
ASTM	American Society for Testing Method
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
iTCSD	innovative Technology Center for Sustainable Development
PAC	Powdered Activated Carbon
RPM	Revolution per Minute
SEM	Scanning Electron Microscope
WHO	World Health Organization
XRD	X-ray Diffraction

Abstract

Chromium released from industry lead to massive environmental pollution and have tendency to accumulate in certain parts of the human body and become harmful to life. In this study stems of khat used for preparation of activated carbon collected from East Shoa Zone AdamaKhatterawere investigated as adsorbent for removal of Cr (VI) from industrial effluents. The adsorbent was characterized by Point of zero charge pH, FT-IR, XRD and SEM analysis. Point of zero charge pH and FT-IR test, showed the presence of acidic functional groups on surface. The study was employed with 150µm - 250µm particle size and efficiency of adsorbentwasinvestigated at different parameters such as pH, initial concentration, adsorbent dose and contact time. Optimum parameters pH 2, dose 1g, concentration 50(mg/L) and contact time 180min were obtained. Result revealed that chromium (VI) removal was pH sensitive and 96 % and above removal capacity was recorded at Optimum parameters. Using optimum parameters; isotherm and kinetics of the adsorption process was analysed using different model. The result showed that isotherm model of the process fitted well the Freundlich adsorption isotherm model and kinetics of adsorption is well defined by the pseudo-second-order. The maximum adsorption was found to be 4.8 (mg/g). The efficiency of activated carbon derived from khat stem to remove Chromium (VI) from real sample at optimized condition was 91.004 % and it was identified that ACDKS can be used to remove Chromium (VI) from tannery industry.

Keywords: - Adsorption; Activated carbon; Khat; Hexavalent chromium; Adsorption isotherm; Adsorption kinetics

1. INTRODUCTION

1.1 Background

Water contamination is a common problem all over the world. It can be geological or anthropogenic (man-made). The natural occurring elements present at unacceptable levels and man-made by-products of industry and agriculture including heavy metals like mercury, copper, chromium, lead, and hazardous chemicals, dyes and compounds like insecticides and fertilizers can contaminate water. Improper storing or disposing of household chemicals such as paints, synthetic detergents, solvents, oils, medicines, disinfectants, pool chemicals, pesticides, batteries, gasoline and diesel fuel can lead to also water contamination (Sharma and Bhattacharya,2017)

The environmental issues due to rapid industrialization and globalization are becoming more and more nuisance for human being. Heavy metals released due to improper management have tendency to accumulate in certain parts of the human body in some selected tissues and become harmful to life and toxic on earth and in water (Sureshkumar, 2015) and these metal play important role in water pollution. Continuously released of heavy metal into the aquatic ecosystem from natural process such as volcanic activity and weathering of rocks and from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing, battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies (Indhumathi et al., 2014). Therefore effective and efficient methods are needed for the removal of contaminants from chemical industries.

Chromium is among the heavy metal elements that contaminant the water. It is an odourless and tasteless metallic element that had atomic weight of 51.996 and atomic number of 24 (Gandhi et al., 2017). Chromium is a potential pollutant and it exists in waters either in trivalent or hexavalent states. The trivalent oxidation mainly presence in the aqueous medium under acidic condition (pH 3.5) as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_3$ and $Cr(OH)_4^-$. However, under oxidizing conditions Cr exists as Cr (VI) - Oxo anion species such as $HCrO_4^-$ (pH 4–6) or CrO_4^{2-} (pH 8–10) (Naba and Sambrita, 2019).

The main source of chromium contamination is untreated or ill-treated effluents from chromium based industries such as painting, cement, mining, production of steel and other metal alloys, car manufacturing, textile, electroplating and tannery

industries,photographicmaterial and corrosive painting industries etc. (Sujitha and Ravindhranath, 2018; Davoud et al., 2016; Renu et al., 2017; Veena and Nicky, 2015; Vusumzi et al., 2019; Ramesh et al., 2013). According to WHO the maximum permissible limit of chromium hexavalent for the discharge to inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L (Shen et al. 2010). So that chromium found above this level limit is toxic and have to be removed from water.

So that due to its toxicity undesirable effects of Cr (VI) can be avoided by treating the effluents prior to discharge into water stream. There are various methods used to remove Chromium from waste water such as coagulation flocculation, membrane adsorption, Ion exchange, chemical precipitation etc. (López et al., 2014; Khulbe and Matsuura, 2018; Petr and Jiří, 2016; Pradhan et al., 2017). However, these methods have been found to be limited, since they often involve high capital and operational costs. The above difficulties can be removed by using a high-performance and cost effective technique known as adsorption. Adsorption is viewed as superior to other methods because of its simplicity, cost-effectiveness, and non-hazardous technique, easy operation and simplicity of design (Vusumzi et al., 2019; Şerife and Erol, 2019).

Activated carbon used for adsorption is carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces. It has been known as the most effective and useful adsorbent for removing pollutants from contaminated gas and liquid flow (Andi and Paulus, 2018). These materials are characterized by their extraordinary large specific surface areas, the presence of a wide spectrum of surface functional groups like carboxylic group and well-developed porosity. For these reasons, activated carbons are widely used as adsorbents for the removal of metal ions and organic chemicals of environmental or economic concern from waste water, potable water, air and gases (Al-Qodah and Shawabkah, 2009).

Based on its size and shape, activated carbon is classified into four types: granular-activated carbon (GAC), powder-activated carbon (PAC), activated carbon clothe (ACC) and activated carbon fibrous (ACF). Granular and powdered are most frequently used (Tadda et al. 2016)

Due to the different sources of raw materials, the extent of chemical activation, and the physico-chemical characteristics, each type of activated carbon has its specific application

as well as inherent advantages and disadvantages in wastewater treatment (Mojdeh et al., 2008)

Activated carbon generation reported by many researchers were classified into four main processes which are physical and chemical activation process, pyrolysis process, carbonization and steam/thermal activation. The physical activation includes carbonization and activation step whereby steam and carbon dioxide (CO_2) are the most broadly used reagents, significantly influencing the porosity of the activated carbon (AC). The AC generation using chemical activation entails a single step whereby chemical reagents like nitric acid, phosphoric acid, zinc chloride and potassium hydroxide can simply be used at room temperature. However, depending on the chemical reagents used, impurities like zinc (Zn) and phosphorus (P) can be found in AC product, which at the same time may result in raising the operation cost due to additional of chemical used (Taddaet al. 2016).

Based on this fact the present study was focused on characterize, evaluate the applicability and the efficiency of the activated carbon derived from khat stem as an adsorbents for the removal of hexavalent chromium from waste water. The activated carbon was produced via chemical activation using nitric acid as activating agent and was characterized by several techniques and prepared activated carbon were employed for removal of Cr (VI) from aqueous solutions.

The activated carbon prepared from Khat stem is selected in study for the removal of hexavalent chromium from waste water because it is locally available (in Ethiopia it is cultivated in most parts of the country and distributed to local consumers and in other countries), low cost adsorbent, the author has not encountered research works conducted for removal of chromium from aqueous solutions using khat and using this khat as a source of activated carbon is an alternatively waste management or environmental conservation.

1.2 Statement of the Problem

As a result of different human activities, the world is facing serious threats of water pollutions. Water pollution in particular, has raised severe environmental impacts. In addition to the shortage of resources of water due to drought and misuse, production of large volumes of waste water has put a lot of pressure on the human kind (Abdel and Abdul, 2017).

Water is a media for the metabolic activities of living and living organisms not only require water they need pure water or free from any contaminants (Babatunde et al., 2007). But there are different natural and anthropogenic contaminants that affect the purity of water. Chromium is one of the potential pollutants which are often used in industries such as painting, cement, mining, production of steel and other metal alloys, car manufacturing, textile, electroplating, tannery industries,photographic material, corrosive painting and other. The metal contaminated discharges of these effluents into the environment and water bodies causes serious health problems such as nausea, skin ulcers, mal-functioning of liver, kidneys and lung cancer (Sujitha and Ravindhranath, 2018). So that Chromium have to be removed from water due to reason mentioned above or due to it is considered as top six toxic pollutants next to lead and mercury(Abdel and Abdul, 2017).

In Ethiopia, increasing number of industries which could be source of effluents containing chromium must be treated before discharged to the environment because of its mutagenic and carcinogenic properties. Even though different reports are available on chromium removal using different natural adsorbent; removal of chromium from aqueous solution using activated carbon derived from khat stem (ACDKS) has not been yet reported in Ethiopia. The use of khat (Catha edulis) as a potential source of activated carbon for removal of chromium from the aqueous solution is environmentally friendly and practical waste conservation method. This study is meant to provide information on the efficiency activated carbon derived from khattowards removal of chromium from aqueous solution by adsorption method.

1.3 Objective of the Study

1.3.1 General Objectives

The general objective of the study is to investigate the removal of chromium from leather industry effluents using low cost activated carbon derived from khat stem, as an adsorbent.

1.3.2 Specific Objectives

The specific objective of this study;

- ✓ To prepare activated carbon from khat stem
- ✓ To investigate the effect of pH, concentration, contact time and dose of adsorbent towards removal of chromium from aqueous solution.
- ✓ To characterize activated carbon derived from khat.
- ✓ To investigate the efficiency of activated carbon derived from khat to removal of chromium from aqueous solution.

1.4 Significance of the Study

The significance of the proposed thesis work is the following

- ➢ Using low cost adsorbent which can be easily available and environmentally friendly for remove chromium from industrial wastewater.
- ➢ Increase purity of water by removing chromium from it.
- ➢ Reduce health problem that caused due to high chromium concentration in water.
- ➢ Using natural resource for industrial as raw material input rather than throw away to the environment.
- ➢ Reduce environmental waste or environmental conservation by using khat leftover that is simply discharged into environment and accumulates in the environment.

1.5 Scope of the Study

The thesis work was done on industrial waste water obtained from outlet of leather industry so called Houdao Chen/pelle leather production which is found around Modjo. The scope of this study is to remove chromium (VI) from industrial waste water usingactivated carbon derived from khat stem. The characterization of adsorbent was done by using X-ray Diffraction (XRD), Fourier Transform infrared Spectroscopy (FTIR), and Scanning Electron Microscope (SEM) and Point of Zero charge.

2. LITERATURE REVIEW

2.1 Water Contamination

Availability of fresh water, the nature's gift controls the major part of the world economy and it is already a limiting resource in many parts of the world. In the next century, it will become even more limiting due to increased population, climate change and urbanization thus leading to water crisis and serious consequences on the environment (Jabbar et al., 2016)

There are many source of water pollution, but the two general categories are direct and indirect sources. The direct contaminant source includes; metal plating industries, mining activities, battery manufacture, tanneries, petroleum refining, paint manufacture, pigment manufacture, printing and photographic industries(Ramesh et al., 2013). Other direct sources are wood processing industry where a chromate, copper, arsenate wood treatment produces arsenic containing wastes, inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulphide, petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium and photographic operations producing film with high concentrations of silver and Ferro cyanide.

The indirect source includes contaminant that enters to the water supply from soil ground stream system (fertilizer, pesticides and from atmosphere) via of rain water. Atmospheric contaminant is the indirect human practice contaminant such as gaseous emission from automobiles and factories.

The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing water Contamination or metal loads in the water bodies (Indhumathi et al., 2014).

2.2 Chromium

Chromium is an odourless and tasteless metallic transition element with an atomic number of 24 and atomic weight of 51.996 and in the group VI-B of the periodic table with a ground-state electronic configuration of Ar $3d^5 4s^1$ (Arun et al., 2005; Gandhi et al. 2018). It was first discovered in the Siberian red lead ore (crocoite) in 1798 by the French chemist Vauquelin. It occurs naturally as chromite ($FeCr_2O_4$) in ultramafic and serpentine rocks or

complexed with other metals like bentorite$Ca_6(Cr,Al)_2(SO_4)_3$ crocoite ($PbCrO_4$), vauquelinite ($CuPb_2CrO_4PO_4OH$), tarapacaite (K_2CrO_4), among others (Helena, 2012).

Chromium can exist in nine different oxidation states from -II to +VI, but the most stable and common forms are Cr (0), the trivalent Cr (III), and the hexavalent Cr (VI) species. Compound with chromium oxidation state of II, are strongly reducing while Chromium-VI compounds are strongly oxidizing state. Cr (0) is the metallic form, solid with high fusion point and produced in industry is a usually used for the manufacturing of steel and other alloys (Helena, 2012; Gandhi et al., 2018; Mojdeh et al., 2008)

Majority of chromium (VI) compounds are highly soluble, whereas most of the chromium (III) compounds are sparingly soluble in water. Table 1 shows some of chromium (VI) compounds which are soluble in water (Palmer Et Al. 1991).

Table 1:Chromium (VI) Compounds

Compound	Form	Solubility in Water
Calcium chromate ($CaCrO_4$)	Yellow crystal	Slightly soluble
Sodium chromate (Na_2CrO_4)	Yellow crystal	soluble
Sodium dichromate ($Na_2Cr_2O_4$)	Orange red crystal	soluble
Chromium trioxide (CrO_3)	Dark red/brown crystal	soluble
Potassium chromate (K_2CrO_4)	Yellow crystal	soluble
Potassium chromate ($K_2Cr_2O_7$)	Orange red crystal	soluble
Strontium chromate ($SrCrO_4$)	Yellow crystal	Slightly soluble

Hexavalent chromium generally exists in monomeric ($HCrO_4^-$ and (CrO_4^{2-}) or bimeric state ($Cr_2O_7^{-2}$). Presence of bimeric and monomeric species impacts orange and yellow colors to water respectively

2.2.1 Uses of Chromium

Chromium is used mainly for making alloys and steel. chromium compounds in either the chromium (VI) or chromium (III) forms are used for tanning of animal hides, chrome planting dye, pigments wood, wood preservation, plating alloying, ceramic glazes, refractory bricks, and textiles dyes and mordents (Helena, 2012; Gandhi et al. ,2018). Table 2 and 3 shows uses of chromium and Sources of hexavalent chromium (Rumpa et al., 2011)

Table 2: Uses of Chromium.

Form	Uses
Chromium (0)	Stainless steel production, alloy production, metal and alloy manufacturing
Chromium (III)	Metal and alloy manufacturing, brick lining, chrome plating, leather tanning, textiles, copy machine toner
Chromium (VI)	Chrome plating, leather tanning, textiles, copy machine toner

Table 3:Uses and Sources of hexavalent chromium

Uses	Hexavalent chromium chemicals
Pigments for paints, inks, and plastics	Lead chromate (yellow, chrome green, molybdenum orange), zinc chromate, barium chromate, calcium chromate, potassium dichromate, sodium chromate
Anti-corrosion coatings	Chromic trioxide (chromic acid), zinc chromate, barium chromate, calcium chromate, sodium chromate, strontium chromate
Stainless steel	Chromium (VI) is given off when stainless steel is cast, welded, or plasma torch cut
Textile dyes	Ammonium dichromate, potassium chromate, sodium chromate
Wood preservatives	Chromium trioxide
Leather tanning	Ammonium dichromate

2.2.2 Chromium Toxicity

Chromate is toxic to both animals and a plant due to it is a strong oxidizing agent, a potential to carcinogen and corrosive. Of the two most common oxidation states, hexavalent chromium is more toxic (Sujitha and Ravindhranath, 2018) and the mobility of hexavalent chromium is higher than trivalent chromium in the aqueous medium (Brose and James , 2013). Chromium (VI) compounds, like hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), owe their toxicity to the high solubility and diffusivity which permit them to cross the biological membrane tissues easily. Another environmentally significant chromium species is the trivalent chromium (Cr (III)) which is considered non-toxic at minute concentrations; however, at high concentration, it can be toxic (Vusumzi et al., 2019). Experiences from elsewhere example (Indhumathi et al ., 2014) show that Chromium is a trace element that is in drinking water essential for most animals, including

humans of that iron metabolism and maintenance of blood vessels. When Chromium accumulated at high levels it causes cancer in digestive tract, epigastric pain, nausea, vomiting, severe diarrhea, haemorrhage, leukaemia, stomach, genital, renal, bladder cancer, serious disorders (Khulbe et al., 2016) .

In the aqueous environment, Cr(III) may hydrolyze into several species including $Cr(OH)^{2+}$, neutral species $Cr(OH)_3^-$, $Cr(OH)_4^-$, and polynuclear species $Cr_2(OH)_2^{+4}$ and $Cr_3(OH)_4^{5+}$. These hydroxides are soluble, less mobile, and toxic to living organisms due to their tendency to form complexes with organic ligands (natural organic matter) in the environment. On the other hand, Cr (VI) hydrolyzes to $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} which are strong oxidants. The Chromium (VI) compounds are more soluble and mobile making them bioavailable. The toxicity of Chromium (VI) on humans has been primarily accredited to the chemical structural resemblance between Chromium oxyanions [CrO_4^{2-}] and sulphate ions [SO_4^{2-}] making the former able to cross the biological membranes using sulphate routes (Vusumzi et al., 2019). Chromium (VI) in the forms of dichromate ($Cr_2O_7^{2-}$),chromate (CrO_4^{2-}), and CrO_3 is considered the most toxic forms of chromium, as it presents high oxidizing potential, high solubility, and mobility across the membranes in living organisms and in the environment. Chromium (III) in the forms of hydroxides, sulphates and oxides is less toxic as it is relatively insoluble in water, mainly bound to organic matter in soil and aquatic environments and is presents lower mobility (Helena, 2012)

2.3 Removal Methods of Water Contaminants

Many treatment processes have been developed to remove contaminants from industrial wastewater using physicochemical treatment technologies such as precipitation, electrochemical processes, ion exchange,biological methods, Adsorption and membrane processes (Davoud et al., 2016; Faezeh et al., 2019; Khulbe and Matsuura, 2018)

A physical separation technique consists of mechanical screening, gravity concentration, flotation, magnetic separation, electrostatic separation, and attrition scrubbing (Sharma et al., 2016). The chemical processes include processes such as chemical precipitation, adsorption, ion exchange, and electrochemical deposition (Fenglian and Wang, 2011).

2.3.1 Chemical Precipitation

Chemical precipitation is one of the most widely used for heavy metal removal from inorganic effluent in industry due to its simple operation (Gunatilake, 2015). In the precipitation process very fine particles are generated and chemical coagulants, precipitants, and flocculation processes are used to increase their particle size to remove them as sludge. Once the metals precipitate and form solids, they can easily be removed, and low metal concentrations, can be discharged (Fu and Wang, 2011). The conceptual mechanism of heavy metal removal by chemical precipitation is presented below.

$$M^{2+} + 2(OH)^{-} \rightleftarrows M(OH)2 \downarrow$$

Where M^{2+} and OH^{-} represent the dissolved metal ions and the precipitant, respectively, while M(OH)2 is the insoluble metal hydroxide. During chemical precipitationadjustment of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal (Barakat, 2011).

2.3.2 Ion Exchange

Ion exchange can attract solution from the liquid phase to the solid phase, which is the most widely used method in water treatment industry (Tamirat and Tariku, 2019). In this process anions or cations containing special ion exchanger is used to remove metal ions in the solution. Commonly used ion exchanges are synthetic organic ion exchange resins. Ion exchange is a reversible stoichiometric chemical reaction wherein an ion from solution or electrolyte or molten salt is exchanged for a similarly charged ion attached to an immobile and insoluble solid material, maintaining the overall electro neutrality (Arshid et al., 2018).

Ion Exchange resins are water insoluble solid matter which can absorb negatively charged or positively charged ion from an electrolyte solution and after ion absorbed other ions with the same charges released into the solution in an equivalent amount. This method is highly sensitive with the pH of the aqueous phase and used at only low concentrated metal solution. The negative ions in anionic resins such as chloride and hydroxyl ions can be replaced by the negatively charged ions such as nitrate, sulphate, cyanide, dissolved organic carbon and chromate ions in the solution and positively charged ion in the resins such as sodium and hydrogen ions are exchanged with positively charged ions, such as chromium, copper, silver, nickel, cobalt, manganese lead, iron, arsenic, molybdenum, gold, zinc, tin, selenium and others (Tamirat and Tariku, 2019; Gunatilake, 2015).

2.3.3 Membrane Filtration

Membrane adsorbent technology is a membrane integration technology that was developed in the mid-1980s (Khulbe and Matsuura, 2018). Membrane separation has been increasing used recently for the treatment of inorganic effluent due to its convenient operation.

Membrane filtration capable of removing suspended solid, organic compounds and inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, Nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater (Barakat, 2011).

The membrane processes are non-polluting separation methods used in wastewater treatment. In pressure driven membrane separation processes such as microfiltration (MF), ultrafiltration (UF), Nano filtration (NF), and reverse osmosis (RO), a pressure gradient over the membrane enables the solvent (water) to permeate the membrane. Solutes existing in the feed solution are rejected to a certain extent, which depends on the membrane type. Table 4 shows properties and applications Classifications of filtration membranes (Mustapha et al., 2019).

Reverse Osmosis is separation process that uses pressure to force a solution through a membrane that retains the solute on one side and allows the pure solvent to pass to the other side. Reverse Osmosis can remove many types of molecules and ions from solution, including bacteria and is used in both industrial processes. It involves a diffusive mechanism, so that separation efficiency is dependent on solute concentration, pressure, and water flux rate(Ahmed and Yossor, 2016).

Table 4:Applications and Classifications of filtration membranes

Pore size	Retention capacity	Filtration process	Operating pressure (bar)	Application mechanism	Uses
› 0.1 µm	› 500 kDa	Micro	›2	Filtration/retention	Particles, lager bacteria
100– 2 nm	5– 500 kDa	Ultra	2-8	Filtration/retention	Macromolecules, larger virus, proteins
2–1 nm	0.1–5 kDa	Nano	6-12	Filtration/retention	Virus, divalent ions
< 1 nm	< 100 Da	Reverse osmosis	10-80	Solution/diffusion	Small organic molecules, salts

2.3.4 Biological Methods

Biological removal of heavy metals in Water involves the use of biological techniques for the elimination of pollutants from waste water. In this processes microorganisms play a role of settling solids in the solution (Faezeh et al., 2019).

The surface functional groups, such as carboxyl, hydroxyl, amino, sulfonate, and phosphate, on microbial and algal cell walls are primarily responsible for metal binding through the reaction of electrostatic interactions, ion exchange, and complexation. Extracellular polymeric substances (EPS) produced by some bacteria, fungi, and algae, such as polysaccharides, glycoprotein, lipopolysaccharides, and soluble peptides, possess anionic functional groups and have been reported to be effective in binding of heavy metal cations to the cells of these microorganisms (Tetsuro & Shuzo, 2012).

2.3.5 Adsorption Method

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by chemical and physical interactions. The heavy metal ions in the aqueous solution can be captured by the adsorbent though the physical or chemical adsorption (Khulbe and Matsuura, 2018.

Adsorption method is the relatively new process that is emerging as a potential alternative for the removal of heavy metals (Abdul, 2017). It is known to be one of the best of the technologies for the decontamination of water because it is an effective, economical and eco-friendly treatment technique. It is a process strong enough to realize water reuse obligation and high runoff standards in the industries. Adsorption is basically a mass transfer process by which the metal ion is transferred from the solution to the surface of sorbent, and becomes bound by physical and/or chemical interactions. All adsorption mechanisms are dependent on solid-liquid equilibrium and on mass transfer rates. Based on the types of intermolecular attractive forces adsorption could be divided into Physical and Chemical adsorption(Abdel and Abdul, 2017).

A. Physical adsorption

It is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction or hydrogenbonding. Physical adsorption can only be occurred in the environment of low temperature and under appropriate pH conditions.

B. Chemical adsorption

This kind of adsorption involves a strong interaction results from chemical reaction between the adsorbent and the adsorbate. This interaction creates new types of electronic bonds (Covalent, Ionic).

General mechanism of adsorption

Acording to Abdel and Abdul, 2017 thegeneral main steps involved in adsorption of pollutants on solid adsorbent are:

1. Transfer of the metal ion from bulk solution to the outer surface of the adsorbent.
2. Internal mass transfer by pore diffusion from outer surface of adsorbent to the inner surface of porous structure.
3. Adsorption of adsorbate onto the active sites of the pores of adsorbent.

2.4 Commonly Used Adsorbents

Currently, there are different kinds of adsorbents available for wastewater treatment. A number of researchers have used different types of adsorbents to examine their efficiency towards several heavy metals. Form this most commonly used once such as activated carbons, low cost materials (agricultural Waste) and others.

2.4.1 Activated Carbon

The most commonly used adsorbent is activated carbon a substance which is quite similar to common charcoal. Actually, the active carbon is much more efficient because of its high porous character. The high porous character is generated by treating carbon to steam and high temperature with or without oxygen in the presence of inorganic salts (physical method).

The carbon may be of petroleum coke, bituminous coal, lignite, wood products, coconut/peanut shells and other agro processing waste. At high temperature, parts of carbon are oxidized in CO_2 and steam. The gases are evacuated and micro fractures and pores are generated in the carbon structure. It dramatically increases the carbon surface area, making a useful material for the removal of contaminant (Yang, and Benton, 2003).In some cases, the carbonaceous matter may be treated with a chemical activating agent such as phosphoric acid, zinc chloride and the mixture carbonized at an elevated temperature, followed by the removal of activating agent by water washing (chemical method).

Active carbon uses the physical adsorption process, whereby Vander Waals attractive forces pull the solute contamination out of the solution and onto its surface. The efficiency of the

adsorption depends on the nature of the carbon particle and pore size, surface area, density and hardness as well as the nature of the contaminants (concentration, hydrophobicity, polarity and solubility of the contaminant) and contaminant attraction to the carbon.

Based on its size and shape, activated carbon is classified into four types: granular-activated carbon (GAC), powder-activated carbon (PAC), activated carbon clothe (ACC) and activated carbon fibrous (ACF). Granular and powdered are most frequently used (Tadda et al., 2016)

Due to the different sources of raw materials, the extent of chemical activation, and the physicochemical characteristics, each type of activated carbon has its specific application as well as inherent advantages and disadvantages in wastewater treatment (Mojdeh et al., 2008)

Activated carbon generation reported by many researchers were classified into four main processes which are physical and chemical activation process, pyrolysis process, carbonization and steam/thermal activation. The physical activation includes carbonization and activation step whereby steam and carbon dioxide (CO_2) are the most broadly used reagents, significantly influencing the porosity of the activated carbon (AC). The AC generation using chemical activation entails a single step whereby chemical reagents like nitric acid, phosphoric acid, zinc chloride and potassium hydroxide can simply be used at room temperature.

2.4.2 Agricultural Wastes as Adsorbent

Different agricultural wastes have been tested for their heavy metal's removal efficiency from wastewaters. Several agricultural wastes studied for the bio-sorption efficiencies in recent past include rosewood saw dust, rice husk (Jabbar et al., 2016), wheat straw (Hanan et al., 2010), coffee husk (Dessalew, 2017), maize corn cobs (Arunkumar et al., 2014), sugarcane bagasse (Mohd et al., 2018) and others.

Most important task is selection of adsorbent and its efficiency, economics and versatility of process depends on selection of adsorbent. Over the years, the focus of world has been shifted to research and development so that to discover alternatives that are cost efficient, versatile to replace commercially available less economical adsorbents, considerably waste materials (Waheed et al., 2018).

The use of locally available agricultural for removal of heavy metal from aqueous solutions at different experimental conditions is an alternative waste management or environmental conservation. Table 5 shows different type of Adsorbents and their removal efficiency toward Chromium (VI).

Table 5: Chromium (VI) removal efficiency of some Adsorbents in Literature

Adsorbent	Cr(VI) removal efficiency	pH	Type of water	Reference
Sesame Stems Dehydrated with Sulfuric Acid	97 %	2	Synthetic water	(Veyis al., 2014)
Almond green hull waste material	99.96	2	Synthetic water	(Negin et al., 2017)
Egg-Shell	60.12	2	Industrial effluent	(Sam et al ., 2017)
Fish-Scale	48.1	1.5	Industrial effluent	(Sam et al., 2017)
Active carbon Lantana camara plant	98	2	Waste water	(Sujitha et al., 2018)
Activated Carbon of Palmyra Palm Fruit Seed	89	2	Synthetic water	Kannan and Thambidurai, (2008)
Hazlenut shell	99.4	1	Synthetic water	(Mojdeh al. 2008)
Olive cake	47.1	2	Synthetic water	(Mojdeh al. 2008)
Coconut Shell	94	6	Synthetic water	(Mohanty et al.,2014)
Mango kernel activated carbon	100	2	Synthetic water	(Tadda et al., 2016)
Wheat straw and Eupatorium edenophorum	99.98	1	Waste water	(Dagang et al., 2016)
Bamboo KOH activated carbon	98.28	2	Aqueous solution	(Tamirat et al., 2014)
Teff husk activated carbon	95.57	2	Aqueous solution	(Tsegaye et al., 2020)

2.4.3Khat as an Adsorbent.

Khat (Catha edulis) is the plant that grows in certain area of east Africa and the Arab Peninsula particularly prevalent in Yemen, Djibouti, Kenya, Ethiopia, Eritrea, Somalia and Uganda (Sophie and Williams, 2013). In Ethiopia total area used for khatproduction in 2006 was 147,805 ha, with a yield of 151,724 metric tons, of which 36% was in the eastern part of the country. The soft inner part of the khat leaf is consumed by humans as a

stimulant, with the remaining leaves, twigs, and stems (leftovers) thrown away and considered as waste (Walliea et al., 2012).

Khat leaves and stem trips are chewed for their stimulating effects and depending up on the type of khat, availability on the market and nature of the person, up to 500g of fresh edible portion of the leaf can be chewed per day per individual (Melaku, 2019). On average, almost 70% of households in Yemen and 50% in Djibouti, more than 30% of Ethiopians have been reported to use khat. Ethiopia is Exporting khat to the neighbouring and the Middle East countries and in recent years the market for khat has grown to America and Europe (Minaleshewa et al., 2010). However the stems are disposed of everywhere, especially around the khat market areas, streets, dumpstersand play major contributor to the huge amount of solid waste in larger Ethiopian cities. Therefore the use of activate carbon derived from Khat stem for removal of chromium from industrial effluentat different experimental conditions is an alternative waste management or environmental conservation because khat leftover is simply discharged into environment and accumulates in the environment.The procedure how activated carbon developed from khat is described in methodology part.

2.5 Factors Influencing Adsorption Process

2.5.1 Contact Time

Every waste treatment options should be effective economically (Tangjuank et al., 2009). In order to see the rate and effectiveness of any wastewater treatment process it is very important to study the effect of time. The time of contact between the adsorbate and adsorbent is the determinant factor of the kinetics and equilibrium of the adsorption process. Therefore, studying the effect of contact time on adsorption experiment is very important for its practical applications (Iscen et al., 2007).

2.5.2pH

PH of the solution is one of the determinant environmental factors in adsorption process since it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during adsorption process. Adsorption of chromium is highly influenced by the pH of the solution according to many studies on chromium removal efficiency which decreased with an increase in pH for hexavalent chromium (Kara and Demirbel, 2010). However, the trivalent

chromium adsorption increases with an increase pH of the solution (Brose and James , 2013; Song et al., 2007).

2.5.3 Concentration

The percentage removal of Cr (VI) is studied by varying Cr (VI) ions concentration from low to high and keeping other parameters at optimum conditions. According to Dessalew (2017) as the concentration of chromium ions in the solution increases, the percent adsorption of chromium on activated carbon will be decrease rapidly when initial chromium concentration increased from low to high. But the actual amount of chromium ions adsorbed per unit mass of the activated carbon was increased with increasing in chromium ions concentration in the aqueous solution

2.5.4 Dose of Adsorbent

When the amount of adsorbent is increased more active sites will be available to which more amounts of metal pollutants can be attached (Semerjian, 2010). However, further increase in the amount of adsorbent will have a negative effect on the adsorption process. This means either the metal adsorption decreases or it becomes steady because the active site for adsorption is blocked by screening effect (Hammaini et al., 2007).

2.6 Adsorption Isotherms

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes (Omar et al., 2011). It describes how adsorbates interact with an adsorbent and is critical in optimizing the use of adsorbent. Adsorption equilibrium studies are conducted to correlate the adsorption capacity (mg/g) and residual adsorbate concentration (mg/L) in the liquid phase (Muhammad et al., 2015).

Due to the complex adsorption system in liquid phase, it was essential to apply various isotherm models, Langmuir, Freundlich, and Temkinwere selected in this study to evaluate the adsorption of Cr(VI) on activated carbon derived from khat.

2.6.1 Langmuir Adsorption Isotherm

The first isotherm applied was Langmuir because it gave information about whether adsorption is favourable or not. His assumption is based on the monolayer coverage with

fixed number of well-defined sites and all adsorption sites are equally favourable. Based up on his assumption Langmuir represents by the following Equation (Muhammad Tahir Amin et al.2015), (Davoud et al., 2016).

$$\frac{1}{qe} = \frac{1}{k_l qmax\, Ce} + \frac{1}{qmax} \quad \text{.....1}$$

Where Ce = the equilibrium concentration of chromium in the solution (mg/L) qe = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). KL is the Langmuir constant (intercept/slope), and qmax is the maximum adsorption capacity (mg/g) i.e., 1/intercept; both are calculated from the plot $\frac{1}{qe}$ vs. $\frac{1}{Ce}$. Moreover, Ce (mg/L) is the equilibrium adsorbate concentration in solution, and qe (mg/L) is the equilibrium adsorbent capacity.

In order to determine, the Adsorption process is favourable or unfavourable, a dimensionless constant separation factor or equilibrium parameter RL is defined according to the following Equation.

$$RL = \frac{1}{1+(Kl\ Co)} \quad \text{.....2}$$

Where KL (L/mg) is the Langmuir constant and C0(mg/L) is the initial Cr (VI) concentration. The RLvalue indicates adsorption process is irreversible when RL is 0; favourable when RLis between 0 and 1; linear when RLis 1; and unfavourable when RL is greater than 1(Rai et al.,2018)

2.6.2Freundlich Adsorption Isotherm

The Freundlich isotherm assumes the pollutant undergoes adsorption onto the heterogeneous adsorbent (Muhammad et al., 2015). The Freundlich model is an empirical equation which assumes that the active sites of adsorption are heterogeneous in nature and adsorption at one site affects the adsorption at the adjacent site (Rai, et al. 2018).

For solute adsorption from solution, the Freundlich isotherm is described by Equation (3).

$$qe = k_f Ce^{1/n} \quad \text{.....3}$$

Where Kf and n are the Freundlich isotherm constants and Kfindicates the adsorption capacity and n stands for the intensity of the adsorption

Equation 3 can be conveniently transformed to the following linearized form

$$log\ qe = logk_f + \frac{1}{n} logCe \quad \text{.....4}$$

Where qe is the Cr (VI) concentration on activated carbon derived from khat at equilibrium, Ce (mg/L) is the concentration of Cr (VI) in solution at equilibrium, Kf and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The higher values of kf show the greater dependency for adsorbate. The values of the 1/n between 0<1/n<1 indicates that adsorption process is favourable.

2.6.3 Temkin Adsorption Isotherm

The Temkin isotherm model contains a factor that describes the interactions between adsorbent and adsorbate (Rai et al., 2018). The derivation of the Temkin isotherm assumes that the fall in heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions (Indhumathi et al., 2014).The Temkin Adsorption isotherm is described by Equation (5 and 6).

$$qe = \frac{RT}{bt} \ln(ATCe \quad \text{.....5}$$

Temkin adsorption parameter were determined by transforming the temkin equation into linear form

$$qe = B_T \ln A_T + B_T \ln Ce \quad \text{.....6}$$

where BT= (RT)/bT, R is the universal gas constant (8.314 J/molK) and T(K) is the absolute temperature. The constant bT describes the heat of adsorption and AT explains the Temkin isotherm equilibrium binding isotherm (L/g).

2.7 Adsorption Kinetics

The kinetic models are used to study the mechanism and rate controlling step in the adsorption process. For this purpose, two kinetic models, these models include, pseudo-first-order and pseudo-second-order will be applied in this study (Davoud et al., 2016).

2.7.1 Pseudo First Order Model

First order model which is believed to be the earliest model, describe the kinetic process of liquid-solid phase adsorption and expressed by the following Equation.

$\frac{dqt}{dt} = kp1(qe - qt)$……7

Where *qe*and *q*t(mg/g) are the adsorption capacities at equilibrium and time *t*(min),respectively. Kp1 (min-1) is the pseudo first order rate constant for the kinetic model. Integration of the equation with the boundary conditions of qt=0 at t=0 and qt=qt at t=t, gives,

$ln\frac{qe}{qt} = kp1t$……..……..…..8

That can be rearranged to

$\log(qe - qt) = logqe - \frac{kp1}{2.303}t$……..……..……..9

2.7.2 Pseudo- Second Order Model

For adsorption process pseudo-second order model is used in different literatures in order to describe the adsorption isotherm. Most of the time this equation is used when the first-order model fails and the Equation for this model is written as:-

$\frac{dqt}{dt} = k2(qe - qt)^2$……...10

Integrating the equation for the boundary conditions t = 0 to t = t and qt = 0 to qt = qt, gives:

$\frac{1}{(qe-qt)} = \frac{1}{qe} + k2t$…….11

Where qe is the amount of ions sorbet at equilibrium, mg/ g; k is the equilibrium rate constant of pseudo-second order sorption, g /mg min

$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe}$ ...….....13

2.8 Thermodynamic study

In order to determine the thermodynamics feasibility,it is important to determine relevant thermodynamic parameters like the Gibbs free energy (ΔG). Change in free energy gives information whether the system is spontaneous or not and it has been evaluated by the following Equation(Rai et al. 2018).

ΔG = -RTlnKc……14

Where T is the absolute temperature (K), R is the gas constant (8.314 J/mol K) and Kc is the distribution coefficient calculated using the following equation

Kc= $\frac{qe}{ce}$ …….15

3. MATERIAL AND METHODS

3.1. Apparatus and Equipment

The apparatus and equipment that were used during this research work are:

- XRD (XRD-7000-X-RAY Diffractometer ; SHIMADZU Japan),
- UV Vis-spectrophotometer (Sm 1600 spectrophotometer; Hyderabad-500018,India),
- SEM (JEOL JCM-6000plus model instrument),
- FTIR (FT/IR-6600 FTIR Spectrometer, JASCO United States)
- pH meter (HANNA bench pH.ISE.EC meter HI-5522-02),
- Digital electronic balance (GF 6100 ,AND company Tokyo Japan),
- Universal drying Oven (SHIVKI-PID-906),
- Furnace (SX-2.5-12, China),
- Magnetic stirrer (PMC 502P United States),
- Sieve (Arm field, CEN-MKII-OOA)
- Pipettes, spatulas, Erlenmeyer flask, beaker, test tube, syringe filter, mortar and pestle, glass rod, volumetric flask, different types of beakers, and plastic bag was used.

3.2 Chemicals and Reagents

1.5 diphenylcarbohydrazide, deionized water, nitric acid, potassium dichromate, hydrochloric acid, Sodium hydroxide, was used for this study. All chemicals except deionized water (from Adama science and technology university) used in this study were analytical and were used without further purification.

3.3 Sample Collection and Preparation

3.3.1 Collection and Preparation of Contaminated Water Samples

The effluent samples were obtained from outlet of leather industry so called Houdao Chen/pelle leather production which is found around Modjo, Eastern Shoa Zone, Oromia Region, Ethiopia. Waste water was collected and composited using a 2 L plastic bottle cleaned by nitric acid and transported to ASTU Chemistry Department and stored in a refrigerator.

3.3.2 Preparation of Standard and Stock Solutions

Potassium dichromate ($K_2Cr_2O_7$) was used as the source for chromium stock solution. The standard stock solution of chromium (1000 mg/L) was prepared by dissolving 2.828 g of 99.9 % analytical grade K_2 Cr_2O_7 in 1000 mL of distilled water. Standard solutions of chromium with different concentrations were prepared from the stock solution by appropriate dilutions. 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L of chromium standard solution was prepared by diluting 10 mL, 20 mL, 30 mL, 40 mL and 50 mL of 1000 mg/L chromium stock solution with distilled water in 1000 mL volumetric flask up to the mark respectively (Dessalew Berihun, 2017).

3.4. Preparation and Characterization of Adsorbent Material

3.4.1 Preparation of Adsorbent

The stems of khat used for preparation of activated carbon were collected from East Shoa Zone AdamaKhat Tera. Then it was cut into pieces approximately 3-4 cm in size and washed with tap water several times and dried in sunlight for 7 days. The dried stem pieces were soaked in 1 N HNO_3 in the ratio 1:3 (w/w) for 24 hour and washed with deionized water, filtered and dried in an oven at 110^{o}Cfor 12 hr. After dried in an oven it was heated at 600^{o}Cfor 2 hr in a muffle furnace at controlled temperature.After Carbonization process it was cooled overnight.The produced activated carbon of Khat stem was washed with deionized water and neutralized by 1N NaOH and 1N HCL until the filtrate showed a neutral pH. Then it was dried at 110 ^{o}C for 10hr and cooled overnight and crushed. The activated carbon developed was named as active carbon derived from khat stem (ACDKS) and finally, passed through a 150-250 µm sieve (using an Arm field,CEN-MKII-OOA sieve in Adama science and technology university chemical engineering laboratory) and sealed in a polyethylene bag and stored for further characterization(Jemal et al., 2019).

3.4.2 Characterization of Activated Carbon Derived from Khat Stem.

The characteristics of ACDKS were tested for basic physical parameters such as pH, moisture content, volatile matter and ash content (Jemal et al., 2019). The crystallographic and functional group studies of ACDKS were made by X-ray diffraction (XRD) and Fourier Transform infrared spectroscopy (FTIR) respectively. The surface studies before and after adsorptions were determined by using scanning electron micro-scope (SEM).

3.4.2.1 pH

pH of active carbon derived from khat stem was measured by adding 1.0 g ACDKS to 100 mL distilled water in a 250 mL beaker volume then the beaker was covered with a watch glass and boiled on the hot plate for 5 min and sample was allowed to stabilize and then pH was measured using an electronic pH meter.

3.4.2.2 Moisture content

The moisture content was determined by loss on drying method According to ASTM 2867-99.1g of equally grinded ACDKS was accurately weighed and placed into a clean evaporating dish of a known weight. Then the dish containing a known weight of the ACDKS was incubated at 105^{o} C in an oven. After an hour, the weight of the ACDKS and the evaporating dish was weighed and finally, moisture content was calculated using the Equation 16.

$$Mc\ (\%) = \frac{Ww - Wd}{Ww} * 100 \quad \text{.....16}$$

Where Mc is the moisture content of the ACDKS in percentage, Ww is weight of the sample before drying and Wd is weight of the sample after drying.

3.4.2.3 Ash Content (Ac)

The ash content of the ACDKS was determined by weighing 1 g of ACDKS and placed in dried crucible. The crucible containing the sample was put in to amuffle furnace at temperature of 550^{o}C for 4 hours. Finally the crucibles removed from the furnace and ACDKS sample was weighed and the percent of ash content calculated bytest method (ASTM D2866 –94)usingEquation 17(Jemal et al.,2019; Awugchew, 2015).

$$Ac = \frac{W1}{W2} * 100 \quad \text{.....17}$$

Where Ac is ash content in percent, W2 is weight of the ACDKS sample before heating and W1 is weight of the sample after heating.

3.4.2.4 Volatile Mater (Vm)

1.0 g of the ACDKS sample was taken and placed in a pre-dried crucible and heated in a muffle furnace adjusted at 950 °C for 7 min. then the crucible was cooled in desiccators and weighed. Finally, the volatile matter of the ACDKS was calculated by the standard method (ASTM D5832 – 98) using Equation 18(Jemal et al.,2019; Awugchew, 2015).

$$Vm = \frac{W2 - W1}{W2} * 100 \ldots\ldots 18$$

Where Vm volatile mater of the ACDKS in percentage, W2 is weight of the ACDKS sample before heating and W1 is weight of the sample after heating.

3.4.2.5 Fixed Carbon Content (FCC)

Fixed carbon content was determined from moisture, volatile, and ash content percentage by using theEqueation 19 (Tsegaye Adane et al., 2020; Jemal Fito et al.,2019).

Fixed Carbon Content (%) = 100 %−(MC%+VC%+Ash %)…………………………..19

3.4.2.6 Particle size

The particle size of adsorbent material is one the determinant factors in the adsorption process. Therefore, to determine the particle size of grinded ACDKS was sieved using different pore size sieves

3.4.2.7Point of zero charge (pHpzc)

The point of zero charge (pHpzc) of the activated carbon is a function of pH and it is pH at which the charge of the solid surface is zero. The point of zero charge (pHpzc) of the activated carbon was determined by the solid addition method described by (Duran, 2012). For this purpose 0.1 M of 10NaCl solutions having the initial pH values ranging from 2 to 11with one increment was prepared in duplicate using 0.1 MHCl and 0.1 M NaOH. The pH of the solution was then accurately noted and in each duplicated 0.5g of a mixture of ACDKS was added, which were securely capped immediately and manually shaken for 24 hr. Then the solutions were filtered off and the adsorbent was separated. The final pH values of all solution were measured and ΔpH was made by subtracting the initial pH values from final pH values. The graph was plotted by using the final pH values against ΔpH. From the graph plotted a point of intersection of the resulting curve with the x-axis gave the pHpzc.

3.4.2.8 X-Ray Diffraction (XRD) Analysis

The activated carbon prepared was characterized by x- ray diffraction (XRD-7000-X-RAY Diffractometer) at Adama Science and Technology University material science department. A one gram of fine powder ACDKS was packed with standard sample holder and analysis was carried out on sample.XRD spectrum was recorded from 10^0- 80^0 with 2θ angles using Cu kα radiation (λ=1.54 Å) source operating at voltage 40kv and current 30 within scanning speed of 4 (deg/min).

3.4.2.9 Fourier Transform infrared spectroscopy (FTIR)

The ACDKS characterized by using Fourier Transform infrared spectroscopy (FTIR). Pellets were prepared by adding 1 mg of sample with about 300 mg of KBr in an agate mortar, and then the mixture is pressed at a pressure of 12 Pa for about 3 min and the pellet adsorbent sample was scanned over the range 500-4,000 cm^{-1} to determine the availability of the functional groups on the surface of ACDKS (Sujitha and Ravindhranath, 2018).

3.4.2.10 SEM

The surface morphology of ACDKS was investigated using a scanning Electron Microscope JEOL (JCM-6000plus model instrument) to study the surface texture and the SEM images were noted from different areas of adsorbent at 10.0KV at varying resolution from 500 x to 10,000x.

3.5 Determination Concentration of Chromium by UV Spectrophotometer

UV spectrophotometer used to determine concentration of chromium before and after addition of ACDKS. The instrument was calibrated between 10mg/L - 50mg/L and data from UV/Visible spectrophotometry experimental result shows the optimized parameters wave length is 543 nm (ʎ maxi is 543). The wave length was in close agreement with other studies (Tayone, 2015). The Cr (VI) Concentration was determined according to diphenyl carbazide method. In this method 250mg 1,5diphenylcarbazide was dissolved in 50mL acetone solution. 50mL sample was taken and 2mL of 3M H_2SO_4 and 1mL of diphenyl carbazide were added (Sujitha and Ravindhranath, 2018). Chromium (VI) concentrations were estimated by the intensity of the red brownish colour complex formed, was measured using UV spectrophotometer at 543nm.

3.6 Determination of Adsorption Efficiency

Adsorption measurement was made by batch techniques at room temperature because of its simplicity and reliability. The batch adsorption studies were carried out at desired pH value, contact time and adsorbent dose. The pH of solution was monitored by adding 1 N of HCl and 1N NaOH as per required value using pH meter. The 1g of ACDKS were added to 100mL of potassium dichromate solution in beaker and stirred for desired time with 150 rpm at room temperature. The time required for reaching equilibrium condition was estimated by drawing graph at regular interval of time. The concentrations of chromium

were determined after filtration through syringe filter. The amount of chromium adsorbed on ACDKS was known after comparing concentration of chromium before and after treatment. Adsorption efficiency in percent and milligram of Cr adsorbed per gram of adsorbent were calculated using the Equations 20 and 21 respectively (Naba and Sambrita, 2019). Finally, average of the triplicate results were used to plot the result.

$$\% R = \frac{CO - Cf}{Co} * 100 \quad \ldots\ldots 20$$

Where %R is percent removal, Co is initial concentration and C*f* concentration after adsorption

$$qe = \frac{v(co - cf}{m} \quad \ldots\ldots 21$$

Where qe is metal removal in mg/g, co is initial concentration, cf concentration after adsorption, m is adsorbent mass in gram and v is volume of solution used during the experiment.

3.7 Batch Adsorption Experimental Optimization

The experimental optimization test was carried out to make some parameters function at their best and keeping other parameters constant. For batch experiment 100mL of known chromium (VI)with known adsorbent dose (1g to 3.5 g) were placed in a 500ml beaker. The desired pH (1-8) was adjusted by adding 0.1 HCl and NaOH then beaker was placed on magnetic stirrer at room temperature and stirred at 150rpm for determined time period (30 min – 210 min). The adsorbate was separated from the adsorbent using syringe filter and final Cr (VI) Concentration was determined.

3.8 Effect of adsorption parameters

3.8.1 Effect of pH

To study the effect of solution pH on chromium (VI) ion removal, test solution containing 50 mg/L of chromium (VI) ion were prepared to pH values of2 – 8 adjusted by adding 0.1 HCl and NaOH. Then 1g of adsorbent was added to each test solution containing 50mg/L of chromium (VI) ions and stirred for 180 min to reach equilibrium(Dessalew, 2017).

3.8.2 Effect of Dose

To investigate the effect of ACDKS dose, experiments were conducted at various adsorbent dose (1g, 1.5g, 2g, 2.5g, 3g, 3.5 g)keeping pH =2,with 50 mg/L chromium (VI) ion concentration and 180 min contact time at room temperature (Rai et al. (2016).

3.8.3 Effect of Concentration

The effect of concentration was determined by adding 1g of ACDKS intoeachtest solution containing 10mg/L, 20mg/L, 30mg/L, 40mg/L and 50 mg/L of chromium (VI) ionat pH = 2 and stirred for 3hrs(Dessalew, 2017).

3.8.4 Effect of Contact Time

The effect of contact time was investigate by varying time (0.5, 1, 1.5, 2, 2.5, 3 and 3.5 hrs) at the optimized concentration, pH and ACDKS dose at room temperature (Dessalew, 2017).

3.9Adsorption Isotherm

To study the adsorption isotherms the optimum conditions which were found from previous optimization experiments was applied only by varying adsorbent dose. These experiments were carried out using adsorbent dose in the range of 1g-3.5g with 0.5 g difference. For each adsorbent dosage 100mL of sample was taken at optimum agitation, room temperature for 180 min. The data from the experiment were fitted into Langmuir, Freundlichand Temkinadsorption isotherm models (Indhumathi et al., 2014).

3.10Kinetics Study

It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process was evaluated. These experiments were conducted for the optimum contact time by setting chromium concentration, pH, adsorbent dosage and agitation speed constant. Then sample was withdrawn in every 30 minute interval for determination of residual chromium (VI) concentration in the solution. Then data from the experiment was introduced into pseudo-first order model and second order models (Indhumathi et al., 2014).

3.11Data Analysis

The Microsoft word and excelwasused for writing, calculating, making charts, making table, making graphs and recording all data from experimental processes. Origin 2018 software was used for analysis and graphing of FT-IR, XRD and experiments data. SPSS software was usedto evaluate whether the overall F ratio for the ANOVA is significant and to evaluate whether different between any two pairs of mean for the Tukey tests are significant.

4. RESULTS AND DISCUSSION

4.1 Characterization of Adsorbent.

4.1.1 Proximate Analysis of activated carbon.

The proximate analysis of the activated carbon derived from Khatstem was done in order to know moisture content, volatile matter, ash content and fixed carbon content of activated carbon produced. The proximate analysis was carried out using oven and muffle furnace found in Chemical Engineering Department. The proximate analysis was done based on ASTM (ASTM D2867-09 for moisture content, ASTM D5832-98 for volatile matter content, ASTM D2866-94 for ash content and the result obtained shown in the Table 6. The detail calculation part was included under appendix 7.1

Table 6: Proximate analysis of ACDKS after treated with nitric acid

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Proximate Analysis	Mass in % after proximate analysis
Particle size	150-25 µm
pH	4.74 ± 0.02
Moisture	4.5 ± 0.14
Volatile mater	24 ± 0.26
Ash content	19.499 ± 0.71
Fixed carbon	52 ± 0.83

Nwabanne and Igbokwe (2012) studied application of response surface methodology for preparation of activated carbon from Palmyra palm nut and obtained % of moisture content 4.1 and also in other studies activated carbon obtained from Plantain (Musa paradisiaca) fruit stem 7.33±1.5 % of moisture content reported (Ekpete et al., 2017).Moisture content of ACDKS recorded was 4.5 ± 0.141 which is low and indicates that the developed activated carbon was good quality. As moisture content is lower the adsorption efficiency of the adsorbent is become higher. This is due to water molecule can have the potential effect in

the pores of an adsorbent by filling the adsorbent binding site before it contact with the solution, thus reducing the efficiency of the activated carbon(Anisuzzaman et al.,2015). So that activated carbon developed was stored in air tight bag if not it might absorb moisture content from surrounding since the surface heterogeneity play an important role in adsorption process.

The volatile mater of the ACDKS was 24 ± 0.263 whereas the ash content was 19.499 ± 0.707 which are suggested that ACDKS has relatively lower inorganic content value. In other studies activated carbon obtained from Plantain (Musa paradisiaca) fruit stem 31±6.08 % of ash content and 32.33± 1.15 % volatile mater reported (Ekpete et al., 2017). The volatile mater and ash content values made ACDKS preferable for adsorption. Ash content reduces the efficiency of reactivation and overall activity of activated carbon. The lower the ash value the better the activated carbon for use as adsorbent (Ekpete et al., 2017). The value of resulting fixed carbon content of ACDKS recorded was 52 ± 0.829.

4.1.2 Point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) is defined as the pH of the mixtures at which surface charge density on the material is zero (the surface of material has net electrical neutrality) and its value was determined by the solid addition method (Nurgul and Adife, 2016). pH_{pzc} values for activated carbon (ACDKS) produce at optimized operational parameter is around 4.2. This observation reconfirms that lower pH_{pzc} values around 4.2 indicated that carbonized ACDKS surface had acid functional groups on it and values of pH_{pzc}<4.2 show dominancy of acidic groups over basic groups.

A positive charge of ACDKS surface can be obtained at pH below the pH_{pzc} and negative charge of surface can obtained at pH levels beyond the pH_{pzc}. A positive charge of ACDKS surface preferring the uptake of negative charge (anionic) species on the other hand negative charge of ACDKS surface preferring the uptake of positive charge (cationic) species. Having knowledge of this value helps to decide at which pH value one should work during adsorption studies. Hence the adsorbent percent removal capacity increases below pH pzc value. Similar results are reported by other work (Ramlah et al., 2018). Figure 1 Show the point of zero charge (pH_{pzc}) of the activated Carbon derived from Khat Stem were around 4.2 and at this point the surface of ACDKS is neutral but below this point the surface of ACDKS is positively charged which attracts the negatively charged chromate ion and this results in the increase of adsorption.

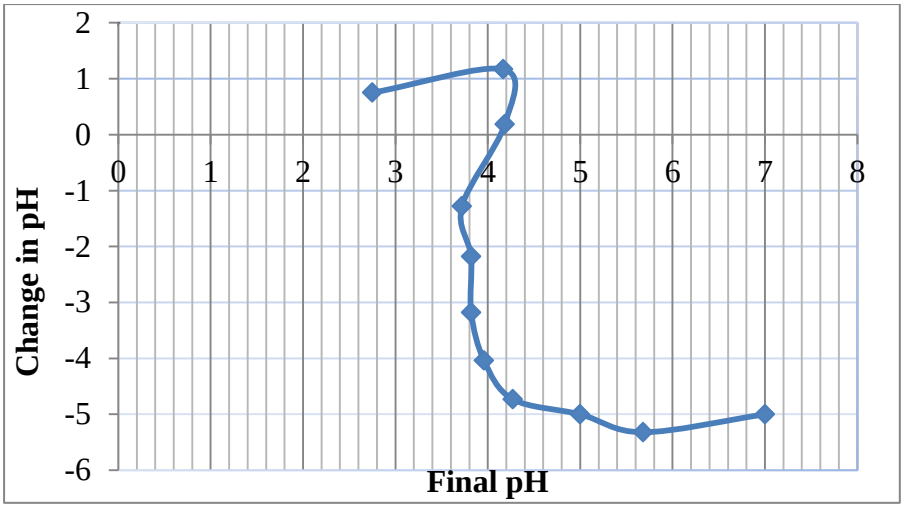

Figure 1: Point of zero charge (pH_{pzc}) of the activated Carbon derived from Khat Stem

4.1.3 FT-IR Analysis

Figure 2 Shows the FT-IR spectra of the activated Carbon derived from Khat Stem. The spectra of activated Carbon derived from Khat Stem before and after Cr (VI) sorption were used to detect changes in the vibration frequencies of the functional groups. The spectra of adsorbent were measured between wave numberranges 400-4000 cm^{-1}. The functional groups such as carboxyl (COOH), amid ($-NH_2$), phosphate (PO_4^{-3}) and hydroxyl (-OH) have the main role in absorbing heavy metals especially hydroxyl, amino, C═O and C─O groups are the main effective on adsorption of Cr (VI) ion(Marandi, 2011).

The broad band in the region around 3437 Cm^{-1} is corresponded to the surface hydroxyl of bonded carboxylic acid and (-NH) groups(Samson and Adedibu, 2016;Marandi, 2011). The O–H stretching vibrations present within a broad range of frequencies indicating; the presence of bonded O–H bands of carboxylic acid and free hydroxyl groups on the surface of ACDKS (Samson and Adedibu, 2016; Bin Wu et al., 2018). The C–H stretching of surface methyl groups observed at bands around 2918 cm^{-1}(Samson et al., 2016; Ruofei et al., 2017) and peaks at 2378 $cm^{-1}$are associated with existence of C≡C or C≡N (Sujitha and Ravindhranath, 2018).

The peaks at about 1629 cm^{-1} might be due to C=O stretching of carbonyl group, which suggests ketone, carboxylic acid, and ester (Bin Wu et al., 2018; Attia et al., 2010). This feature may also be due to C=C stretching of the aromatic rings formed by decomposition of C–H bonds to form a more stable aromatic C=C bonds at the higher activation temperatures

(Sumrit et al., 2015). The peak at about 1085 and 1090 cm^{-1} corresponds to the stretching vibration of C–O or C–H group in carboxylic and alcohol (Samson et al., 2016; Sumrit et al., 2015). The ionization of both the hydroxyl and carboxylic acid functional groups present in the structure of the adsorbent can be achieved by deprotonation making it to interact with metals easily and therefore may be the major sorption sites for the removal of hexavalent chromium ions from solutions (Samson and Adedibu, 2016). The additional peaks at 619 cm-1 can be assigned to bending modes of aromatic compounds (Attia et al., 2010). The FT-IR spectrum of the activated Carbon derived from Khat Stem obtained after adsorption of chromium (VI) ions is shown in Figure2. The FT-IR spectrum of ACDKS before and after adsorption showed shift in wave number and intensity. The wave number at 3437,2926,1624,1090, and 490cm^{-1} before adsorption of chromium (VI) ion was shifted to 3442, 2921, 1629, 1085 and 479 cm^{-1} after chromium (VI) ion respectively. These shift in wave number show that the hydroxyl or amine, aldehyde, carbonyl and carboxylic or alcohol group involved in the adsorption of chromium (VI) ions.

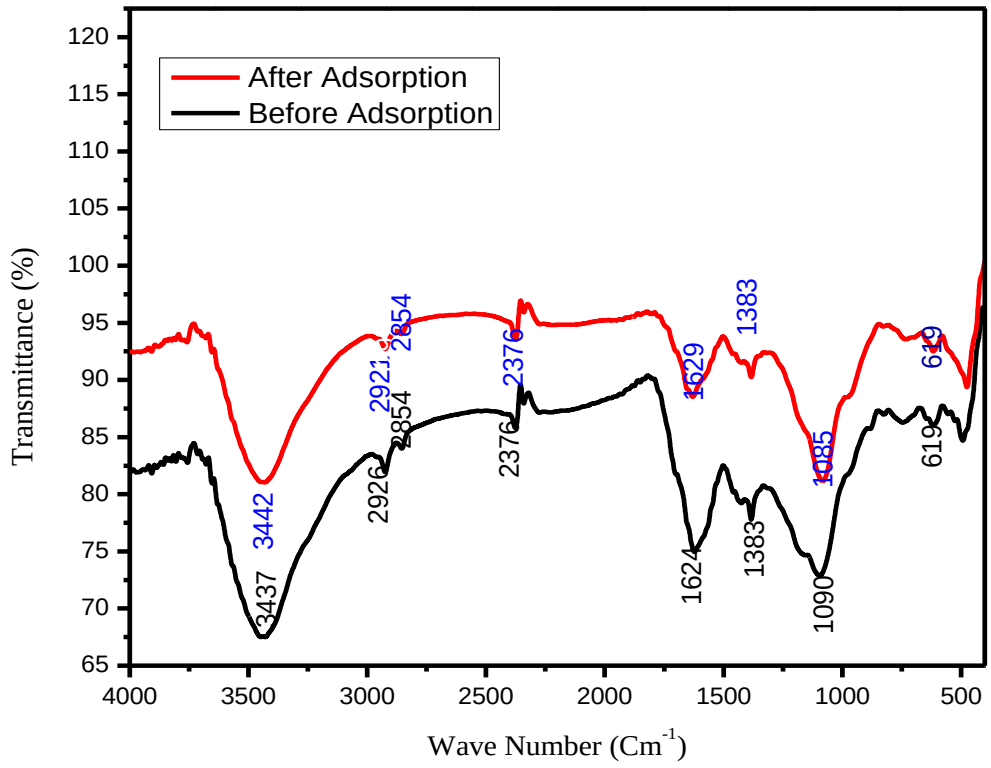

Figure 2 :FTIRanalysis of ACDKS before and after adsorption of Cr (VI) ions.

4.1.4 SEM Analysis

Differences in SEM images were observed between surface topography of activated Carbon derived from Khat Stem before and after adsorption .The Scanning Electron Microscope (SEM) technique was used to observe the surface physical morphology of activated carbon derived from Khat Stem. The micrographs before and after adsorption of Cr metal ions on the surface of the adsorbent material are given in Figure 3. The SEM image of the adsorbent before adsorption shows unoccupied pore of various sizes and shapes on the adsorbent shown in Figure 3 A. These features favour the easy penetration of the adsorbate onto the surface of the adsorbent but after adsorption there is an emphatic change such as reduction in the size of some pores, disappearance of some pores, disappearance of corners or edges. As seen in Figure 3 B the outer pores are covered by adsorbates and the pores are no longer visible. These reveal that the adsorption of chromate on the surface of the activated carbon derived from Khat Stem.

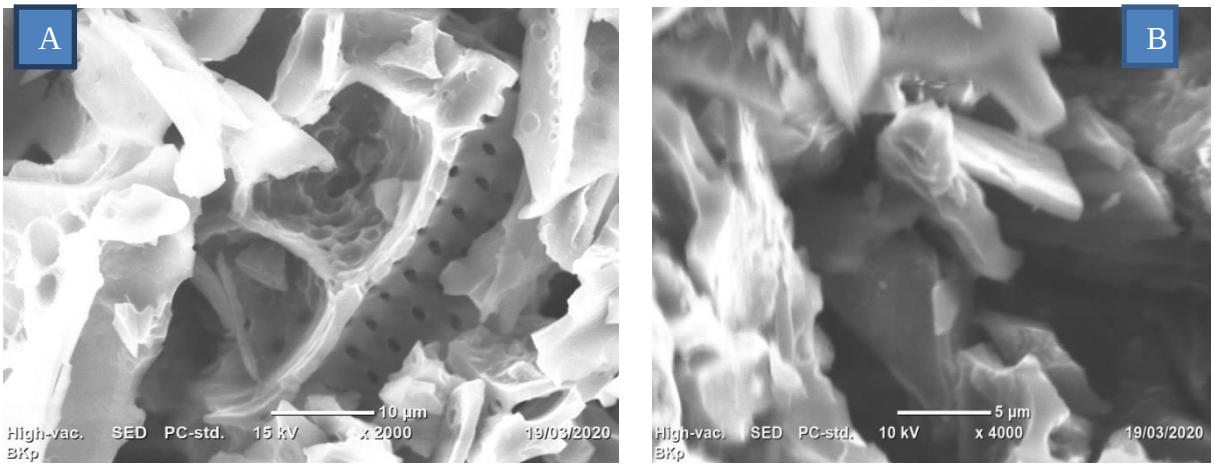

Figure3:SEM analysis of ACDKS before (A) and after (B) adsorption of Cr (VI) ions

4.1.5XRD Analysis

X-ray diffractograms for the activated carbon derived from Khat Stem before and after adsorption of Cr (VI) ions are shown in Figures 4. There was two broad diffraction peak was noticed at $2\theta = 23.53^{o}$ and $2\theta=44^{o}$ for both the samples (before and after adsorption). This indicates the existence of graphite crystallinity in both the samples. But as the peak is not sharp crystalline nature is less and amorphous nature is more. This finding is similar to the characterization and properties of activated carbon prepared from Tamarind Seeds by KOH Activation for Fe (III) adsorption from aqueous solution (Sumritet al., 2015).

There is close relationship between average crystal domain diameter (D) and degree of graphitization. Sujitha and Ravindhranath(2018) reported the smaller values of D the higher degree of graphitization. The D value of ACDKS is 0.756 nm is less than the D value of commercial activated carbon (3.7914) and activated carbon derived from lantana Camara plant (1.6445) reported by (Sujitha and Ravindhranath, 2018) .

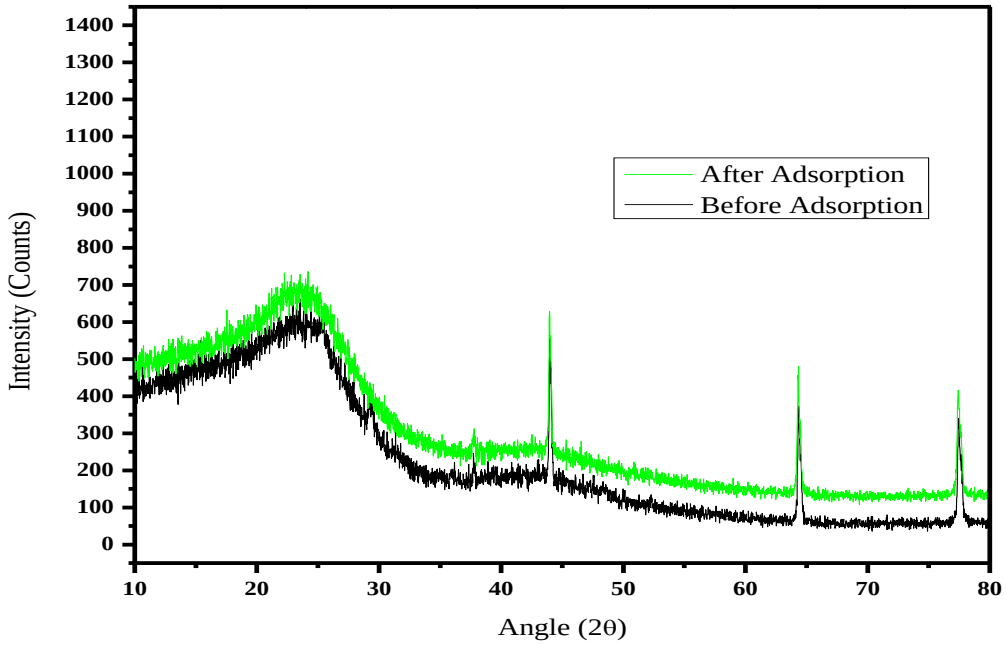

Figure4: XRD analysis of ACDKS before and after adsorption of Cr (VI) ions

The broad diffraction peaks of ACDKS before and after adsorption located at 2θ = 23.53 and 44 which revealed an amorphous structure that was irregularly stacked by carbon rings and useful for generating an adsorbed gap (Andi and Paulus, 2018).

4.2 Effect of Adsorption Parameters

4.2.1 Effect of pH

The effect of pH on the adsorption of chromium (VI) ions on the ACDKS was carried out over the pH range of 1-8 keeping all parameters With a 1 g adsorbent dose, contact time of 180 minutes and chromium concentration of 50 mg/L. Figure 5 and 6shows percentage removal efficiency Vs pH and milligram of adsorbate per gram of adsorbent Vs different pH respectively.

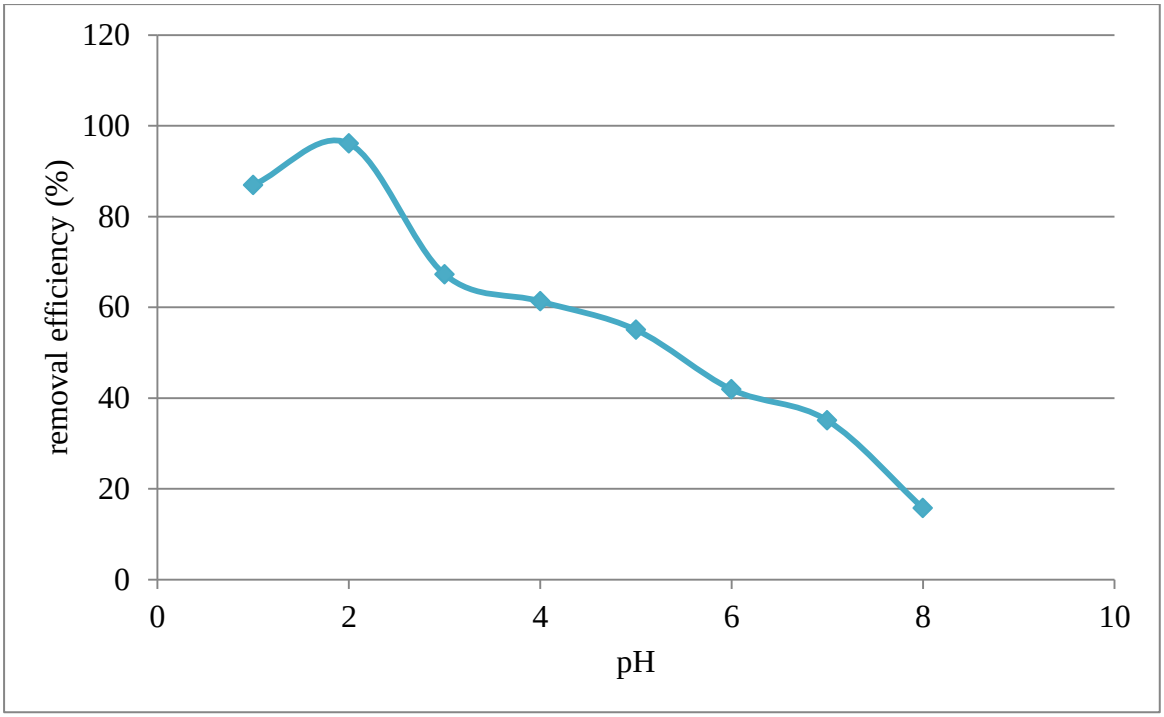

Figure 5: Effect of pH on chromium (VI) removal by ACDKS chromium concentration = 50 mg/L, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and time = 3 hr

The removal efficiency is higher at pH 2 and after pH 2 the removal efficiency was decreased and at pH of 8 minimum removals efficiency of ACDKS was recorded. The removal efficiency of ACDKS was less than 70 at the pH greater than 4andsharp decline from 96.121 % to 15.736 % when solution pH increased from 2-8 respectively. The reason behind to this is at low pH values adsorbent can easily protonate and generate positive net charge. the presence of large number of H^+ ion at this pH values on the adsorbent surface that results in significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions (Attia et al. 2010). As the pH increase dual competition of both the anions (OH^- and CrO_4^{2-}) to be adsorbed on the surface of adsorbent of which OH^- is predominant (Attia et al. 2010). This indicates that ACDKS is applicable for removal of chromium (VI) from aqueous solution under acidic condition.

At acidic pH or pH range 1.0 – 6.0 chromium ion co-exists in different forms such as hydrogen chromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$),trichromate $Cr_3O_{10}^{2-}$, tetrachromate ($Cr_4O_{13}^{2-}$)of which $HCrO_4^-$ is predominant (Rai et al., 2018; Attia et al., 2010). These result clearly revealed that the active form of chromium (VI) that can be observed by activated carbon derived from khat stem was $HCrO_4^-$.

As the pH values of solution increases concentration of the $HCrO_4^-$ shifts to other forms $Cr_2O_7^{2-}$ and chromate (CrO_4^{2-}). Finally as the pH is increased above 7.0, CrO_4^{2-} is dominant form of chromium (VI) (Dagang et al., 2016; Rai et al., 2018). $Cr_2O_7^{2-}$ or $HCrO_4^-$ ions need only one active site, where as CrO_4^{2-} ions needs two active sites because of its two negative charges. Due to more $HCrO_4^-$ ions at low pH values needs single site for adsorption an increase in the adsorption capacity of chromium (VI) was observed (Rai et al., 2018). Removal of chromium (VI) at different pH was also calculated in milligram of Cr adsorbed per gram of adsorbent using Equation 21. As it is observed in Figure 6 higher adsorption was observed at pH 2 which is 4.8 mg/g and minimum adsorption was observed at pH 8 which is 0.785 mg/g. Analysis of variance (ANOVA) demonstrated that pH had significantly effecton the adsorption efficiency of ACDKS,$F(7, 16)=1271.515$, $P=9.5*10^{-21}<0.05$, also the Tukey Post hoc tests showedthat all the mean were significantly different $P<0.05$ (see appendixes Table A 9)

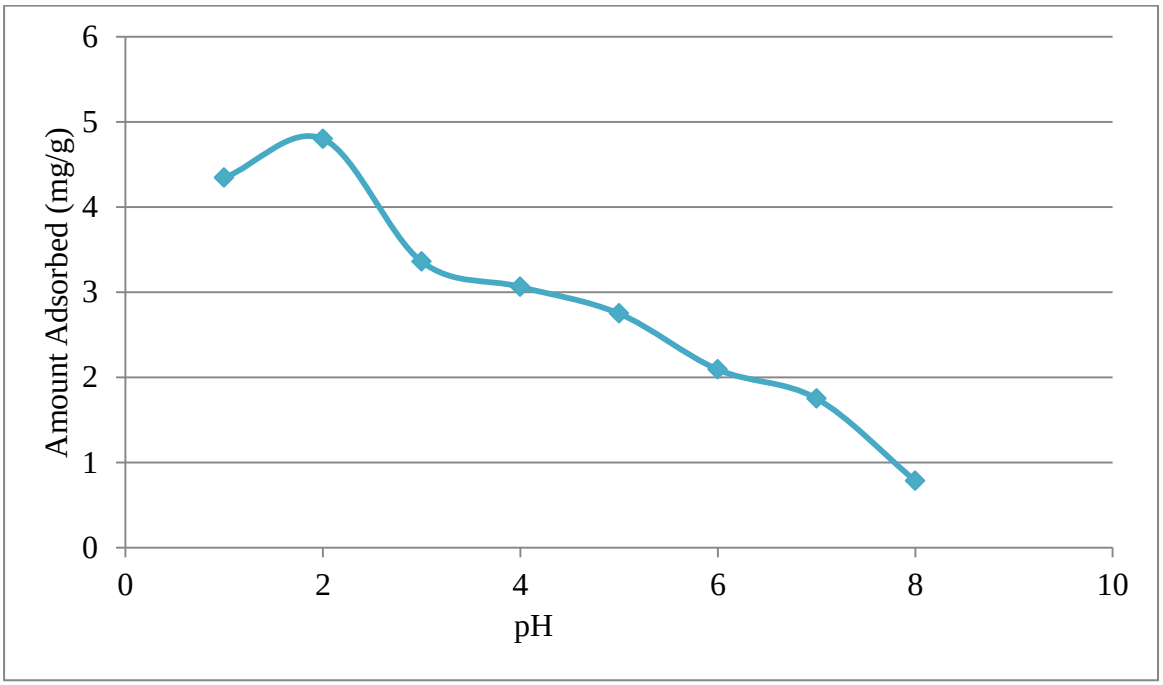

Figure 6: Effect of pH on chromium (VI) uptake by ACDKS chromium concentration = 50 mg/L, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and time = 3 hr.

4.2.2 Effect Initial Concentration

The Adsorption of chromium (VI) ion on ACDKS as a function of initial was studied by varying initial concentration of chromium (VI) ion from 10mg/L to 50mg/L by keeping all parameters constant and the result are represented in Figure 7 and 8.It is noted that, with an increase in the initial concentration of chromium (VI) ion from 10mg/l to 50mg/l, the percentage of removal efficiency of chromium (VI) ion was decreased from 100% to 96.121 %. As it is observed in Figure 8the amount of chromium (VI) ion adsorbed on to the adsorbent increased from 0.987 mg/g to 4.8 mg/g with an increase in the initial concentration of chromium (VI) ions from 10mg/l to 50 mg/l.

At low concentration, the active sites of the adsorbent are more in comparison with the needed sites and due to sufficiently available sites, the adsorption of chromium (VI) ions is independent of the initial concentration of chromium (VI) ions (Sujitha and Ravindhranath, 2018). As concentration increase the active site of adsorbent to the chromium (VI) ion concentration is less and active sorption sites are not sufficiently available for this reason all the active sites on the adsorbent surface gate occupied (Rai et al. 2016).

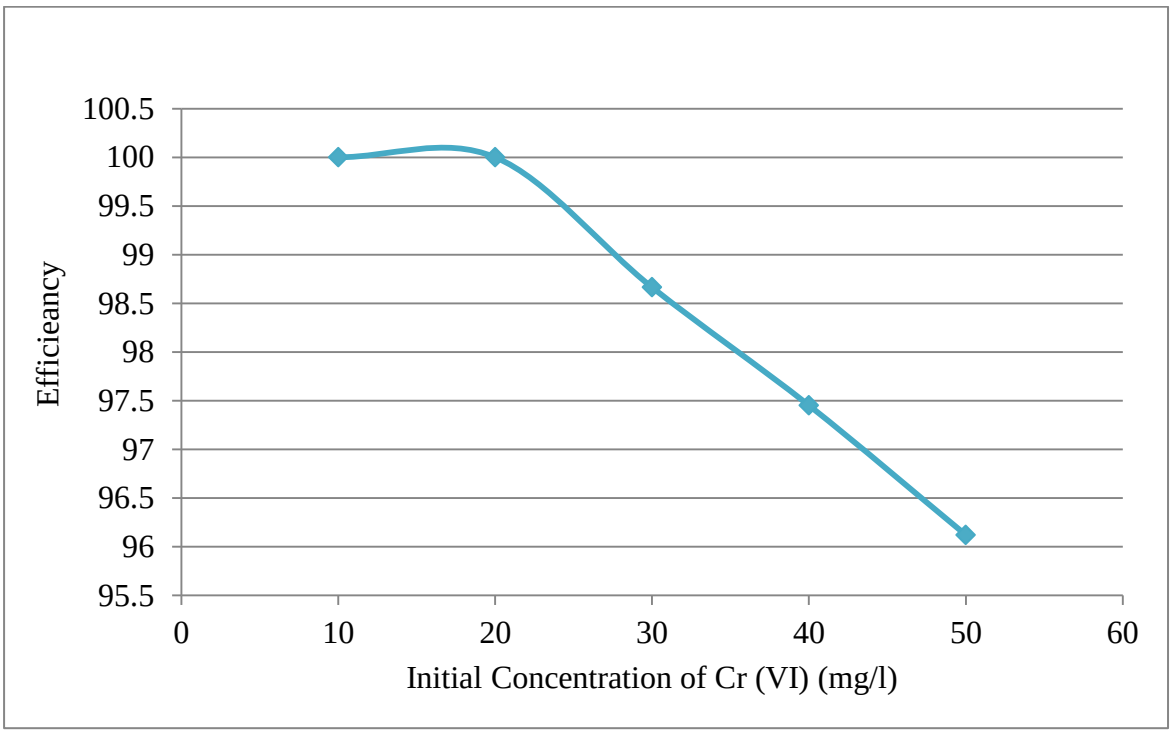

Figure 7:Effect of initial concentration on chromium (VI) removal by ACDKS by ACDKS pH = 2, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and time = 3 hr.

Rai et al. (2018) reported that the percentage removal of chromium (VI) ion decreased as concentration of chromium (VI) ion in solution is increased. This is due to less active sites being available for chromium (VI) ions because their sites saturate above a certain concentration. Therefore, at higher concentration of chromium (VI) ion, the percentage of removal efficiency was dependent on initial Cr (VI) concentration.Analysis of variance (ANOVA) demonstrated that concentration had significantly effect on the adsorption efficiency of ACDKS, $F(4, 6) = 473.103$, $P = 2.4*10^{-11} < 0.05$, also the Tukey Post hoc tests showed that all the mean were significantly different $P < 0.05$ except concentration 9.86 and 20.014 which $P > 0.05$ revealed that not significant different between the two groups (see appendixes Table A 8).

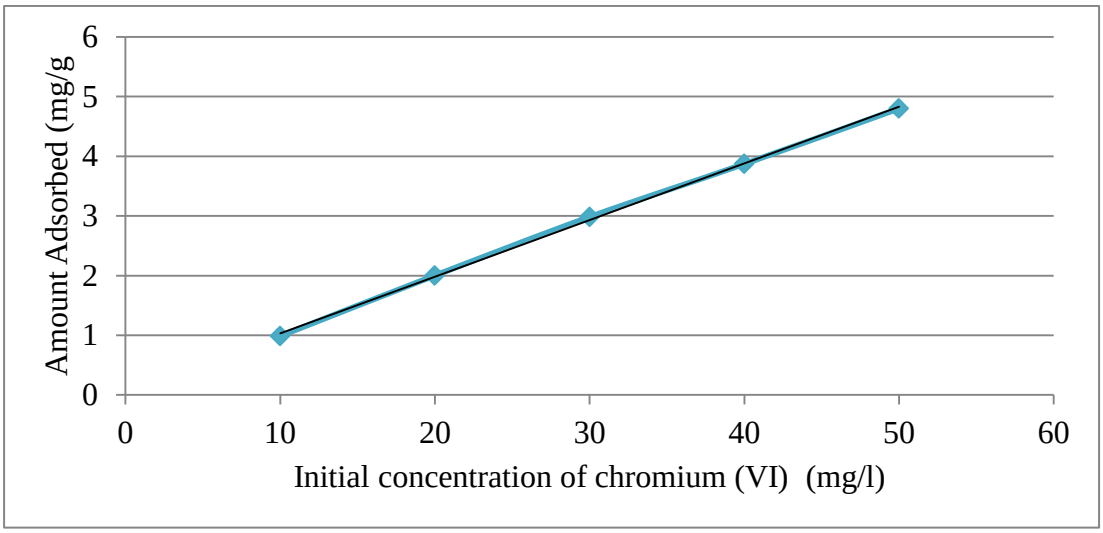

Figure 8: Effect of initial concentration on chromium (VI) uptake by ACDKS at pH = 2, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and time = 3 hr.

4.2.3 Effect of Dose.

The effect of adsorbent dosage on the removal efficiency of chromium (VI) ion was examined over the range of adsorbent dose 1g - 3 g keeping all the parameters constant with an optimum pH 2, contact time 180 min and 50 mg/L of chromium concentration.

The result which is presented in the Figure 9indicate that an increase in adsorbent dose show increase in percentage of removal efficiency in agreement with Dessalew (2017);Rai et al. (2016) and Attia et al. (2010) however, as shown in figure 10 unit adsorption of chromium (VI) was decreased from 4.80 mg/g to 1.653 mg/g with increasing does from 1g - 3 g.

Analysis of variance (ANOVA) demonstrated that dose had significantly effect on the adsorption efficiency of ACDKS, F (5, 12) = 264.113, P = $7.73*10^{-12}$ < 0.05, also the Tukey Post hoc tests showed that all the mean were significantly different P < 0.05 except dose 2.5g group and 3g, 3.5g group and also 3g group and 3.5 g group;which P > 0.05 show that there is no significant different between the thesegroups (see appendixes Table A 6).

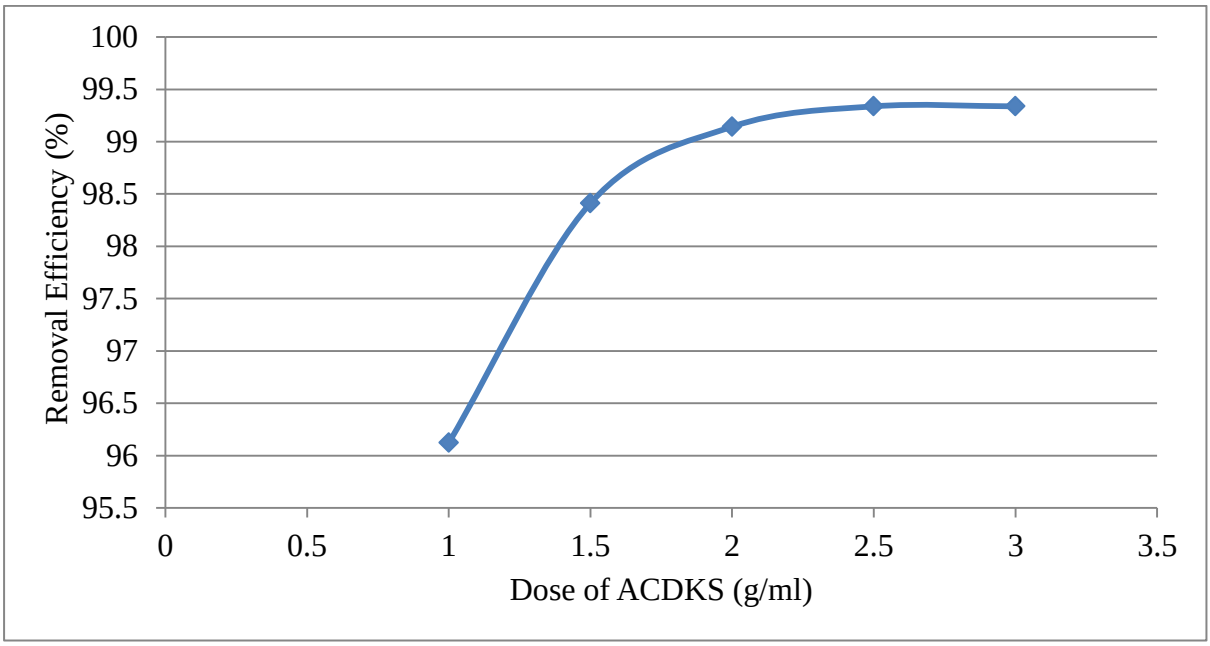

Figure 9: Effect of adsorbent dose on chromium (VI) removal efficiency by ACDKS at pH = 2, steering speed = 150 rpm and time = 3 hr and chromium concentration = 50 mg/L.

From Figure 9it is clear that percentage removal efficiency of ACDKS increase from 96.121 % - 99.33 % as the adsorbent dose increase from 1 to 2.5 g/100mL and at the dosage of 3g the percentage of removal efficiency reached at adsorption equilibrium and there was no further increase in the adsorption of chromium (VI) observed with further increase ACDKS dosage. This is attributed to the increase in surface area of the adsorbent and the availability of more adsorption active sites as the sorbent dosage is increased (Sujitha and Ravindhranath, 2018).

From the above investigation it is concluded that percent of removal efficiency increase with increase in adsorbent dose and metal up take in mg/g was decrease with increase in adsorbent dose. Similar finding have also been reported on in earlier studies (Dagang et al., 2016)

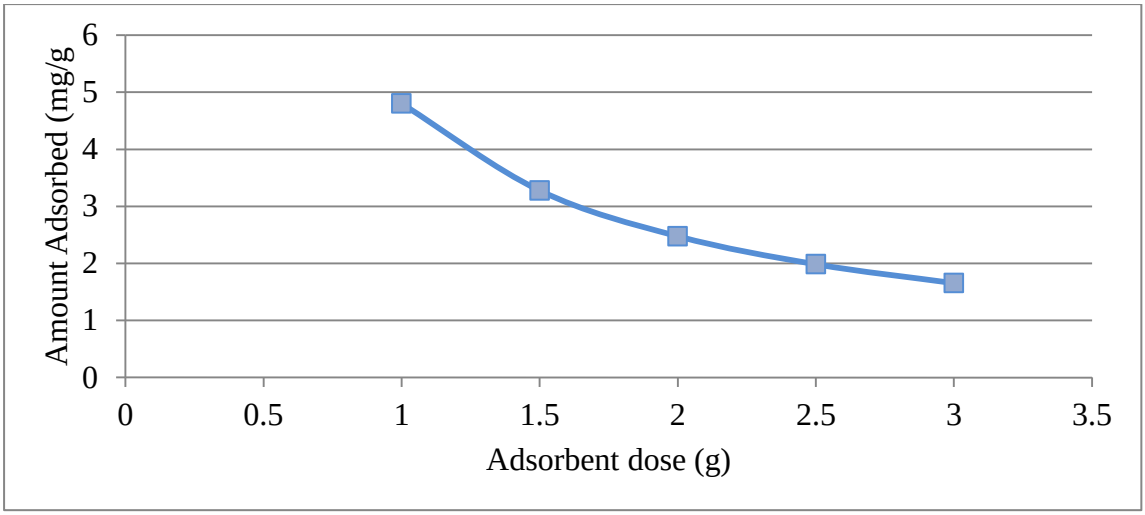

Figure 10: Effect of adsorbent dose on chromium (VI) uptake by ACDKS at pH = 2, steering speed = 150 rpm and time = 3 hr and chromium concentration = 50 mg/L.

4.2.4 Effect of Contact Time

The influence of contact time on removal efficiency of chromium (VI) ion was investigated within the time range of 30 min to 210min. It was shown in (Figure 11) that the adsorption efficiency of chromium (VI) ions increased with increasing contact time up to 180 min and later, it was remain constant.

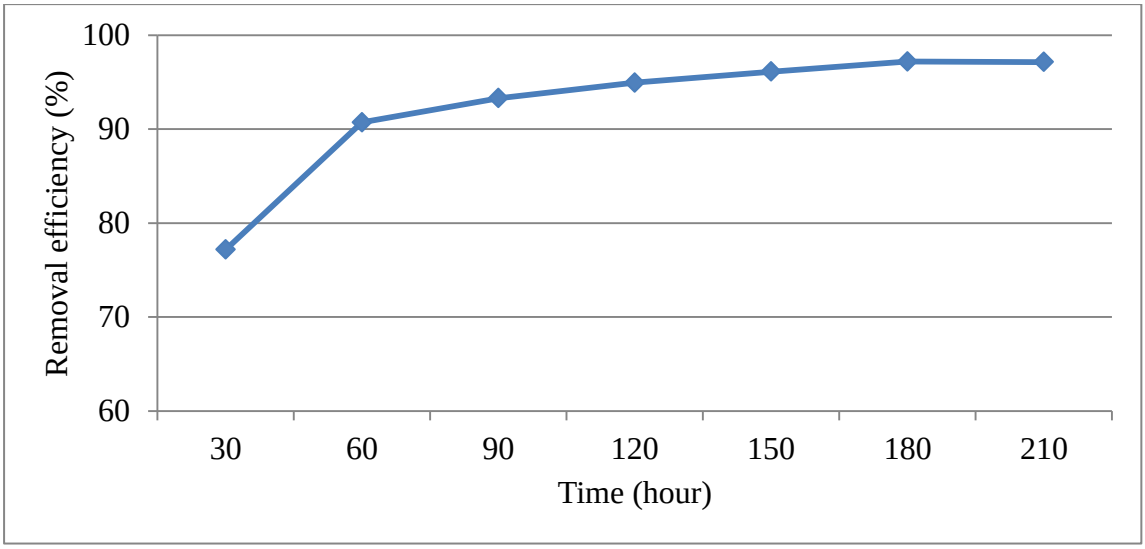

Figure 11: Effect of contact time on chromium (VI) removal efficiency by ACDKS at pH = 2, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and chromium concentration = 50 mg/L.

The maximum percent, which is 97.145 % of chromium (VI) ion, are removed at 180 min and at a time of 30 min the minimum present 77.17 % of removal are observed.At the initial stages the high removal efficiency is probably due to the availability of large number of adsorption site and chromium (VI) is bound quickly on adsorbent surface at a quick adsorption rate which saturated with time.The result showed that with increase in contact time, unit adsorption of chromium (VI) ion was increased as shown in Figure 12.

The uptake of chromium (VI) from aqueous solution at different time interval was 3.85, 4.53, 4.65, 4.74, 4.78, 4.80, 4.80 mg/g as contact time pass from 30, 60, 90, 120, 150, 180, 210 min respectively. After 120 min there is no significant increase in uptake of chromium (VI) or percentage of chromium (VI) removal. Hence an equilibrium time of 180 min was optimised for further studies.Analysis of variance (ANOVA) demonstrated that contact time had significantly effect on the adsorption efficiency of ACDKS, $F(6, 14) = 376.3436$, $P = 1.2*10^{-14} < 0.05$, also the Tukey Post hoc tests showed that all the mean were significantly different $P < 0.05$ except 120 min time group with150 min time group, 180 min time group and 210 min time group and also 150 min time group with 180 min time group and 210 min time groupadditionally 180 min time group and 210 min time group which is $P > 0.05$ revealed that not significant different between these groups (see appendixes Table A 7).

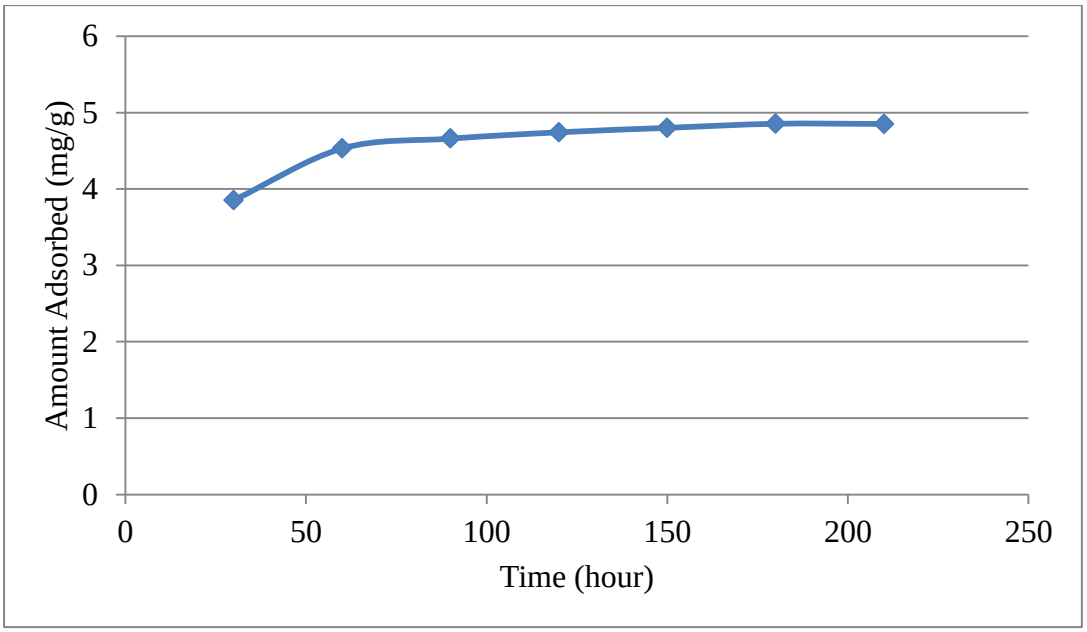

Figure 12: Effect of contact time on chromium (VI) uptake by ACDKS at pH = 2, adsorbent dose = 1 g/100mL, steering speed = 150 rpm and chromium concentration = 50 mg/L.

4.3 Applicability to Real Sample

The effluent samples were collected from outlet of leather industry so called Houdao Chen/pelle leather productions which were found around Modjo, Eastern Shoa Zone, Oromia Region, Ethiopia.The concentrations of Chromium (VI) in the water samples collected was higher than the permissible level as shown in Table 8.

Chromium (VI) removal efficiency of the ACDKS has been tasted on real sample water at two different pH values; pH 2 which is at optimum pH for chromium (VI) removal from aqueous solution and pH 7.5, which is the pH of the real sample collected from Houdao Chen/pelle leather production industry keeping all parameters constant with an optimum contact time 3hr and ACDKS dose 1g.

The concentration of chromium (VI) in the real sample was 16.36 ± 0.22mg/l and this concentration was reduced to1.47 ± 0.01 and 11.28 ± 0.04after adsorption at pH 2 and 7.5 respectively as shown in Table 7.Relatedamount of chromium (VI) concentration 19.78 mg/l was also reported byTsegaye and Awrajaw, (2020)samples taken from Bahir Dar Tannery SC, Ethiopia.The maximum percentage removal efficiency 91% at pH 2 and the removal efficiency decreased when compared to aqueous solution prepared in laboratory. This is due to interfering ions such as co-anions namely SO_4^{2-},CO_3^{2-},NO_3^-,$Cl^-$and $PO_4^{3-}$and co-cations, namely Ca^{2+},Mg^{2+},Zn^{2+},$Cu^{2+}$and Fe^{2+}(Sujitha Ravulapalli and Ravindhranath Kunta, 2018).

Table 7:Removal of Chromium (VI) from real waterby using ACDKS at optimized condition

Type of Sample	Initial concentration of Cr(VI) in the sample (mg/L) before treatment ± SD (n=3)	Initial concentration of Cr(VI) in the sample (mg/L) after treatment + SD (n=3)		Removal efficiency (%)		Adsorption capacity (mg/g)	
Tannery industry effluents		pH=2	pH=7.5	pH=2	pH=7.5	pH=2	pH=7.5
	16.36 ± 0.22	1.47 ± 0.01	11.28 ± 0.04	91	31.07	1.6	0.51

Table 8: Physicochemical property ofHoudao Chen/pelle tannery

pH	7.53
Colour	Dark blue
Odour	Un pleasant
Conductivity	14,650 µ s/cm
Cr (VI) concentration	16.363 ± 0.2175 mg/l

4.4 Thermodynamic Study

It is important to determine the thermodynamic parameters like the change in free energy, in order to describe the thermodynamic nature of removal of chromium (VI) ions on activated carbon derived from khat stem and equation14 and 15were used to calculate thermodynamic parameters. The value of thermodynamic parameters is given in Table 9 below. The negative value of ΔG is indicating that the adsorption of chromium (VI) ions on activated carbon derived from khat stem is spontaneous.

Table 9: Thermodynamic parameters

Kc	3.128
ΔG	-2.825 KJ/mol

4.5 Adsorption Isotherm.

It is important to investigate the adsorption isotherm for the description of capacity of adsorption. An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes (Omar et al.,2011).

4 .5.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm assumes that qualitatively the formation of monolayer adsorbate on the outer surface of the adsorbent, then after no further adsorption is takes place. According to this model stated uniform energy of adsorption on the surface and there is no transmigration of adsorbate on the plane of surface. As it was presented in Figure 13below the graph of Ce/qe Vs Ce was plotted. KL is the Langmuir constant, and qmax is the maximum adsorption capacity ($mg \cdot g^{-1}$) and calculated from intercept and slope.

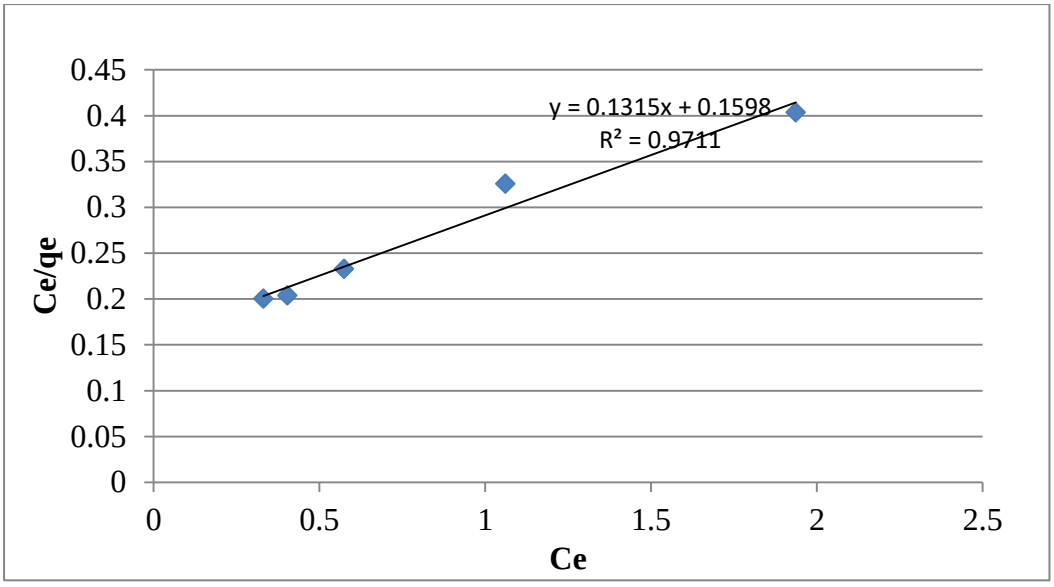

Figure 13: Langmuir adsorption isotherm model

Table 10: Langmuir adsorption isotherm parameters

Q_{max}	7.605 mg/g
K_L	0.8939 L/mg
R^2	0.9711
R_L	0.0214
Equation	1/qe= 0.1598(1/ce) +0.1315

The RL (the separation factor) value lies between 0 and 1 which confirm that the adsorption process of chromium (VI) ion is favourable on activated carbon (ACDKS). The maximum adsorption capacity (q_{max})by ACDKS determined was 7.605 mg/g which means 7.605 mg of chromium is absorbed by one gram of ACDKS. The value of R_L is 0.0214which is indicate that adsorption of chromium on ACDKS is favorable adsorption. R^2 is 0.9571 which is less than R^2 value of Freundlich Adsorption Isotherm for this reason Langmuir adsorption isotherm parameters model does fail to describe the experimental finding.

4 .5.2Freundlich Adsorption Isotherm

To determine whether Freundlich adsorption isotherm model fit to the experimental value or not the graph of log qe as a y-axis and log Ce as x-axis was plotted. From linear equation the value of Kf (adsorption capacity) and 1/nwas calculated and the Freundlich adsorption isotherm equation was developed.

The smaller 1/n becomes, the greater the expected heterogeneity is and if n is between one and ten or 1/n was less than one,it indicates a favorable sorption process (Somchintana and Varong, 2016).As the data in Table 11, showsthe value of 1/n is 0.5768 while n is 1.734 confirm that the sorption of chromium (VI) ion on ACDKS is favorable and R^2 is 0.9926 indicate that the sorption data is fitted well to Freundlich adsorption isotherm model.

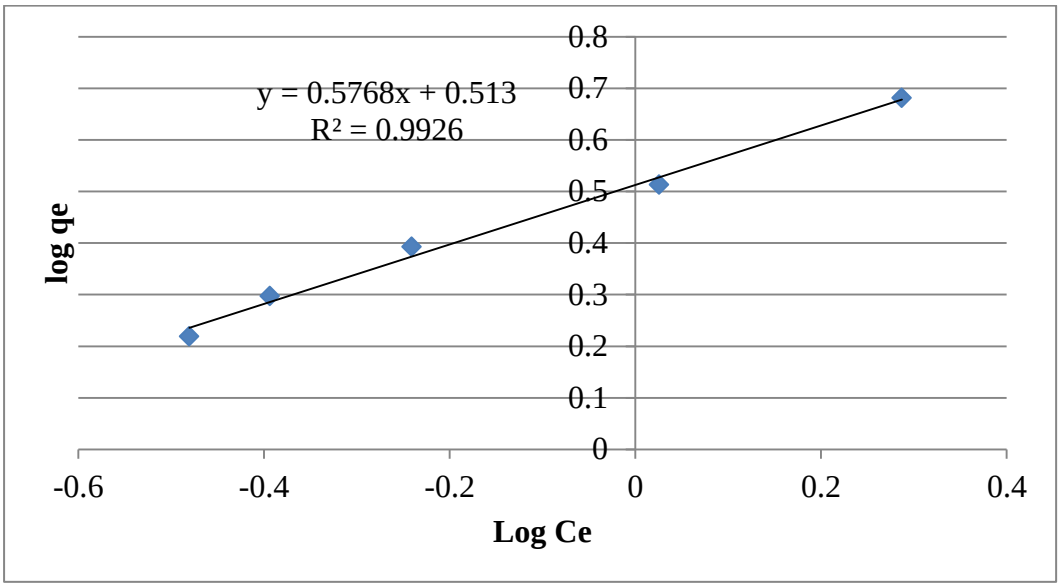

Figure 14: Freundlich Adsorption Isotherm

Table 11: Freundlich Adsorption Isotherm parameters

n	1.734 mg/g
1/n	0.5768
R^2	0.9926
Kf	3.258
Equation	Log qe= 0.5768 +0.513 log Ce

4.5.3Temkin Adsorption Isotherm

To determine whether Temkin adsorption isotherm model fit to the experimental value or not the graph of qe VS Ce was plotted and its linearity was determined from correlation coefficient (R^2).The parameters for the Temkin adsorption isotherm were calculated by using Temkin adsorption isotherm equation from the experimental data as shown in Figure 15 and the value of parameters are given in Table 12.Slope and intercept were used to determine theTemkin isotherm constant.

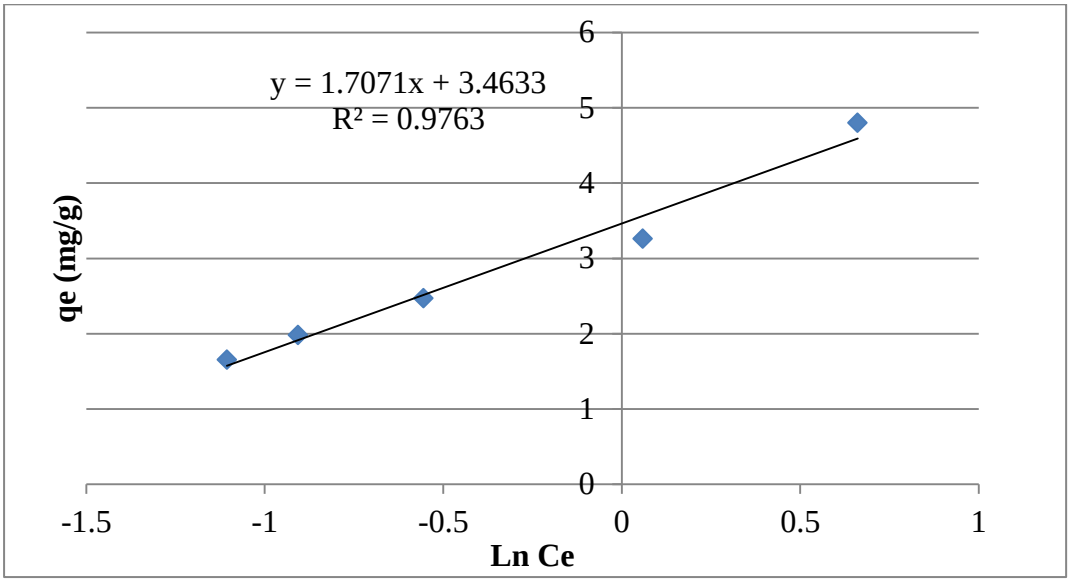

Figure 15: Temkin adsorption isotherm

Table 12: Temkin Adsorption Isotherm parameters

B	1.7071j/mol
At	7.604 L/g
R^2	0.9763
Equation	Log qe= 3.4633 +1.7071 ln Ce

From the Temkin isotherm plot in Figure 15,the value of At=7.604 l/g, B=1.7071 J/mol which indicate that the adsorption of chromium (VI) ion on ACDKS is physical adsorption and R^2 =0.9763. Based on correlation coefficient of determination (R^2=0.9763) shown in Figure 15,it is concluded that Temkin adsorption isothermmodel does not fit well to the equilibrium data compared to Freundlich isotherm model.

4.6 Adsorption Kinetics

Various sorption kinetics models have been used to describe the removal of metals from solution. For this purpose, two kinetics models, i.e. pseudo first- order and pseudo- second order were used in this study. The linear pseudo first and second order kinetics were tested in order to investigate the kinetics model of chromium (VI) ion adsorption on ACDKS and to find which adsorption kinetics fit the experimental data.

4.6.1 Pseudo First Order Kinetics Model

To determine whether adsorption mechanism is determined by pseudo first order or not the graph of log (qe-qt) vs. t was plotted as stated in Equation (7) and its linearity was observed by considering correlation coefficient value. The values of k1 and qe were calculated from slope and intercept of the plot of log (qe-qt) Vs t respectively and Table 13 summarize the value of the kinetics parameters. The pseudo first orderplots of chromium (VI) adsorption on ACDKS for three different concentrations (10, 30, 50 mg/L) are shown in Figure 16. The value of R^2 for the pseudo first- order was low as compared to R^2 value of pseudo- second order. The lower R^2 value obtained indicate that adsorption of chromium (VI) ion on ACDKS does not follow pseudo first order kinetics.

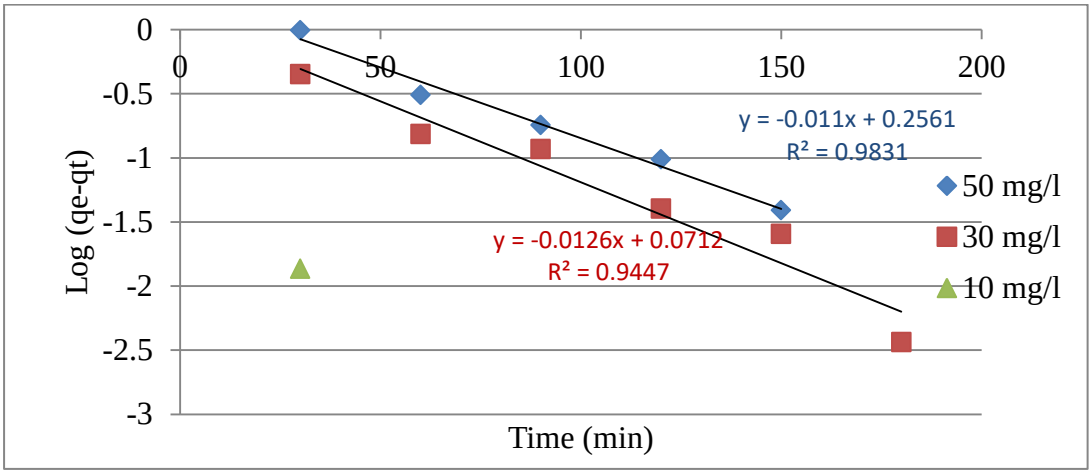

Figure 16: Pseudo first order kinetic curve

4.6.2 Pseudo Second Order Kinetics Model

To determine whether adsorption mechanism is determined by pseudo second order or not the graph of t/qt vs. t was plotted using Equation (8) and its linearity was observed by considering correlation coefficient value. The values of qe and K_2 were calculated from slope and intercept of the plot of t/qt vs. t respectively and Table 13 summarize the value of

the kinetics parameters. The pseudo second order plots of chromium (VI) adsorption on ACDKS for three different concentrations (10, 30, 50 mg/L) are shown in Figure 17. The value of R^2 for the pseudo second- order was higher as compared to R^2 value of pseudofirst-order.Therefore pseudo second- order adsorption model is more favourable to describe the adsorption kinetics of chromium (VI) ion on activated carbon derived from Khat stem, which indicate that chemisorption is the rate limiting step.Rai et al.(2018) reached similar conclusions in the case of adsorption of hexavalent chromium from aqueous solution by activated carbon prepared from almond shell. The calculated and experimental adsorption capacities are very close;this indicates that the validation and application of pseudo second-order in the description of adsorption data.

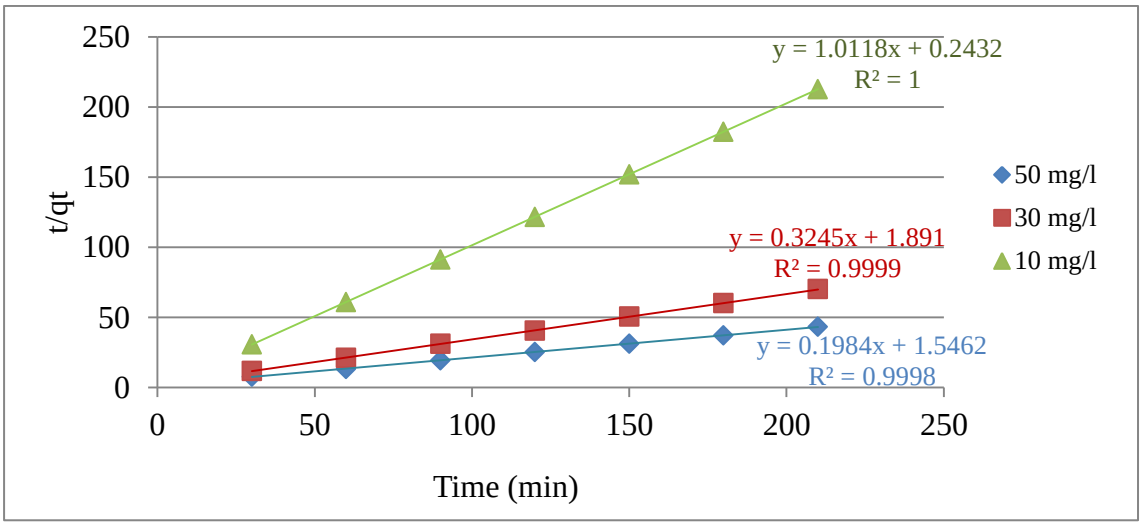

Figure 17: Pseudo second order kinetics curve

Table 13: Adsorption Kinetics parameters

Adsorbent	**Concentration**	**Pseudo-first order**			
		K1(min^{-1})	Qe (cal)	Qe (exp)	R^2
	10mg/l	-	-	0.986	-
	30 mg/l	$-2.9x10^{-2}$	1.178	2.99	0.9447
	50 mg/l	$-2.5x10^{-2}$	1.803	4.839	0.9831
ACDKS		**Pseudo-second order**			
		K2($gmg^{-1}min^{-1}$)	Qe (cal) mg/g	Qe(exp) mg/g	R^2
	10mg/l	4.2094	0.988	0.986	1
	30 mg/l	5.57x10-2	3.081	2.99	0.999
	50 mg/l	2.84x10-2	4.987	4.80	0.999

4.7 Comparison with other Adsorbents

The adsorption capacities of activated carbon derived from khat stem have been compared with other adsorbent reported in the literature for the removal of chromium (VI). These have been listed in Table 14given below. Results from Table 14 shows that this study is revealed that ACDKS has similar adsorption capacity with other adsorbents.

Table 14: Langmuir based maximum adsorption capacity of different adsorbents for the adsorption of Hexavalent Chromium

Adsorbents	Adsorption capacity (mg/g)	Reference
Activated carbon derived from Lantana camara.	26.25	(Sujitha and Ravindhranath, 2018)
Human Hair	9.852	(Naba and Sambrita, 2019)
Coffee husk activated carbon	7	(Waleska . et al., 2008)
Bamboo waste activated carbon	59.23	(Tamirat et al., 2014)
Olive stone activated carbon	71	(Attia et al., 2010)
Mango kernel activated carbon	7.42	(Rai et al .2016)
Teff husk activated carbon	7.485	(Tsegaye et al. 2020)
Coffee husk activated carbon	5.7113	(Dessalew, 2017)
Activated carbon derived from khat stem	7.604	This work

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Activated carbon derived from Khat stems (ACDKS) was prepared and characterized. The study was employed with 150 µm - 250µm particle size and batch method was used to investigate efficiency of adsorbent for different parameters such as pH, initial concentration, adsorbent dose and contact time have been studied at room temperature. The adsorption of chromium (VI) by ACDKS was highly pH sensitive.Optimum parameters pH 2, dose 1g, concentration 50(mg/L) and contact time 180min were obtained. Isotherm model of the process were fitted well by the Freundlich adsorption isotherm and kinetics of adsorption is well defined by the pseudo-second-order model.

Maximum adsorption 100 % was obtained at 180 minutes, 10 mg/L of chromium (VI) solution and 1g of ACDKS dose at room temperature with 150 rpm. Keeping all parameters constant and increase the initial concentration of chromium (VI) ion in synthetic water from 10mg/l to 50mg/l, the percentage of removal efficiency of chromium (VI) ion was decreased from 100% to 96.121 %. The maximum percentage removal efficiency of real sample was 91.004 % at pH 2 and the removal efficiency decreased when compared to aqueous solution prepared in laboratory. The maximum adsorption capacity (q_{max}) determined from Langmuir adsorption isotherm was 7.605 mg/g. Thermodynamic study predicted that the adsorption is feasible, spontaneous at room temperature.

5.2 Recommendations

Activated carbon prepared from khat stems had been shown to have the potential in removing chromium (VI) ions from aqueous solution. To investigate effectiveness of ACDKS further the following studies could be recommending to other researchers.

- ✓ Itis bettertoperformtheBETinordertoinvestigatethesurfacearea.
- ✓ Real sample or industrial effluents may contain many an interfering ions such as co-anions that compete with chromium for adsorption such as SO_4^{2-}, CO_3^{2-}, NO_3^-, Cl^- and PO_4^{3-}. Therefore the effect of interfering ions should be investigated.
- ✓ Investigation the reusability of the adsorbent.
- ✓ Conduct column adsorption in order to investigate the efficiency of ACDKS at pilot-plant scale-up.

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7. APPENDIXES

7.1 Proximate Analysis of ACDKS

- ✓ **Moisture content calculation**

% Moisture Content = $\frac{W1-W2}{W1-W3}$ x100

Where, W1 Crucible weight + sample before drying= 34.32

W2 Crucible weight + sample after drying=34.274

W3 crucible weight =33.32

Crucible 1

% M C =$\frac{34.32-34.274}{34.32-33.32}$x100 = 4.6

Crucible 2

W1 Crucible weight + sample before drying= 28.120

W2 Crucible weight + sample after drying=28.076

W3 crucible weight =27.120

% M C =$\frac{28.120-28.076}{28.120-27.120}$x100 =4.4

Average Moisture Content =4.5

- ✓ **Ash content**

% Ash content = $\frac{\boldsymbol{W1-W2}}{\boldsymbol{W1-W3}}$ X100

Crucible 1

W1 Crucible weight + sample before drying= 26.62

W2 Crucible weight + sample after drying=26.423

W3 crucible weight =25.6

% A C =$\frac{26.62-26.423}{26.62-25.6}$x100 = 19.313

Crucible 2

W1 Crucible weight + sample before drying= 26.62

W2 Crucible weight + sample after drying=26.4192

W3 crucible weight =25.6

% AC =$\frac{26.62-26.4192}{26.62-25.6}$ x100 =19.686

W1 Crucible weight + sample before drying= 26.62

W2 Crucible weight + sample after drying=26.423

W3 crucible weight =25.6

Average ash content =19.5

- ✓ **Volatile mater**

% VM = $\frac{\boldsymbol{W1-W2}}{\boldsymbol{W1-W3}}$ X100

Crucible 1

W1 Crucible weight + sample before drying= 26.6

W2 Crucible weight + sample after drying=26.365

W3 crucible weight =25.6

% VM =$\frac{26.6-26.365}{26.62-25.6}$x100 = 23.5

Crucible 2

W1 Crucible weight + sample before drying= 26.6

W2 Crucible weight + sample after drying=26.355

W3 crucible weight =25.6

% VM =$\frac{26.6-26.355}{26.6-25.6}$x100 =24.5

Average Volatile mater=24

- ✓ **Fixed carbon content**

Fixed carbon content = 100-(%MC+%VM+%AC)

100-(4.5 % + 19.499+ 24%) = 52.0005%

7.2 **Point Of Zero Charge of ACDKS**

Table A 1 Point of Zero charge of ACDKS

Initial pH	Final pH	Δ pH
2	2.751	0.751
3	4.168	1.168
4	4.183	0.183
5	3.72	-1.28
6	3.819	-2.181
7	3.82	-3.18
8	3.96	-4.04
9	4.27	-4.73
10	5	-5
11	5.68	-5.32
12	6.9	-5.1

7.2: Tables for Effect of Adsorption

Table A 2:Effect of pH on chromium (VI) removal by ACDKS, chromium concentration = 50 mg/l, adsorbent dose = 1 g/100ml, steering speed = 150 rpm and time = 3 hr

pH	Co	Ce1	Ce2	Ce3	Ce Av.	% Removal of chromium (VI)	Removal capacity (mg/g)
1		6.875	6.145	6.948	6.656	86.67	4.343
2		2.058	1.912	1.839	1.936	96.121	4.8
3		16.219	16.437	16.364	16.341	67.281	3.360
4	50	19.285	20.088	18.555	19.309	61.337	3.063
5		21.474	23.664	22.204	22.447	55.052	2.749
6		28.045	29.503	29.503	29.017	41.898	2.092
7		31.693	33.153	32.423	32.423	35.077	1.751
8		41.912	42.277	42.058	42.083	15.736	0.785

Table A 3: Effect of initial concentration on chromium (VI) removal by ACDKS pH = 2, adsorbent dose = 1 g/100ml,steering speed = 150 rpm and time = 3 hr

Initial concentration (mg/l)	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Average Ce (mg/l)	% Removal of chromium (VI)	Removal capacity (mg/g)
10	0	0	0	0	100	0.986
20	0	0	0	0	100	2.001
30	0.452	0.379	0.379	0.403	98.613	2.982
40	0.963	1.109	0.963	1.011	97.41	3.869
50	2.058	1.912	1.839	1.936	96.128	4.800

Table A 4: Effect of adsorbent dose on chromium (VI) removal efficiency by ACDKS at pH = 2, chromium concentration = 50 mg/l, steering speed = 150 rpm and time = 3 hr

Dose (g)	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Average Ce (mg/l)	% Removal of chromium (VI)	Removal capacity (mg/g)
1	2.058	1.912	1.839	1.936	96.122	4.800
1.5	1.036	1.036	1.109	1.060	97.8759	3.258
2	0.598	0.452	0.671	0.574	98.8502	2.468
2.5	0.379	0.306	0.379	0.354	99.1913	1.981
3	0.306	0.379	0.306	0.330	99.3374	1.653
3.5	0.306	0.306	0.379	0.330	99.3374	1.653

Table A 5: Effect of contact time on chromium (VI) removal efficiency by ACDKS at pH = 2, adsorbent dose = 1 g/100ml, steering speed = 150 rpm and chromium concentration = 50 mg/l.

Time	Ce1 (mg/l)	Ce2 (mg/l)	Ce3 (mg/l)	Average Ce (mg/l)	% Removal of chromium (VI)	Removal capacity (mg/g)
30	10.525	11.985	11.693	11.401	77.170	3.854
60	4.686	4.540	4.686	4.637	90.714	4.530
90	3.445	3.299	3.518	3.420	93.150	4.652
120	2.496	2.423	2.642	2.520	94.952	4.742
150	2.058	2.131	2.204	2.131	95.732	4.781
180	2.058	1.839	1.912	1.936	96.122	4.800
210	1.985	1.912	1.912	1.936	96.122	4.800

7.3 ANOVA and Tukey Test Result

Table A 6: ANOVA and TUKEY test result of dose effect

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.2553578	5	1.25107	264.113	7.72929E-12	3.1058752
Within Groups	0.0568427	12	0.00474			
Total	6.3122005	17				

Multiple Comparisons

Dependent Variable: concentration

Tukey HSD

(I) Doseeffect	(J) Doseeffect	Mean Difference (I-J)	Std. Error	Sig.		
					Lower Bound	Upper Bound
1.000	1.500	.876000*	.056195	.000	.68724	1.06476
	2.000	1.362667*	.056195	.000	1.17391	1.55142
	2.500	1.581667*	.056195	.000	1.39291	1.77042
	3.000	1.630333*	.056195	.000	1.44158	1.81909
	3.500	1.630333*	.056195	.000	1.44158	1.81909
1.500	1.000	-.876000*	.056195	.000	-1.06476	-.68724
	2.000	.486667*	.056195	.000	.29791	.67542
	2.500	.705667*	.056195	.000	.51691	.89442
	3.000	.754333*	.056195	.000	.56558	.94309
	3.500	.754333*	.056195	.000	.56558	.94309
2.000	1.000	-1.362667*	.056195	.000	-1.55142	-1.17391
	1.500	-.486667*	.056195	.000	-.67542	-.29791
	2.500	.219000*	.056195	.020	.03024	.40776
	3.000	.267667*	.056195	.005	.07891	.45642
	3.500	.267667*	.056195	.005	.07891	.45642
2.500	1.000	-1.581667*	.056195	.000	-1.77042	-1.39291
	1.500	-.705667*	.056195	.000	-.89442	-.51691
	2.000	-.219000*	.056195	.020	-.40776	-.03024
	3.000	.048667	.056195	.948	-.14009	.23742
	3.500	.048667	.056195	.948	-.14009	.23742
3.000	1.000	-1.630333*	.056195	.000	-1.81909	-1.44158
	1.500	-.754333*	.056195	.000	-.94309	-.56558

	2.000	-.267667*	.056195	.005	-.45642	-.07891
	2.500	-.048667	.056195	.948	-.23742	.14009
	3.500	.000000	.056195	1.000	-.18876	.18876
3.500	1.000	-1.630333*	.056195	.000	-1.81909	-1.44158
	1.500	-.754333*	.056195	.000	-.94309	-.56558
	2.000	-.267667*	.056195	.005	-.45642	-.07891
	2.500	-.048667	.056195	.948	-.23742	.14009
	3.000	.000000	.056195	1.000	-.18876	.18876

*. The mean difference is significant at the 0.05 level.

Table A 7: ANOVA and TUKEY test result of time effect

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	209.14979	6	34.8583	376.346	1.20101E-14	2.847726
Within Groups	1.2967233	14	0.09262			
Total	210.44651	20				

Multiple Comparisons

Dependent Variable: Concentration

Tukey HSD

		Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
(I) Time	(J) Time					
30.000	60.000	6.763667*	.248493	.000	5.91517	7.61217
	90.000	7.980333*	.248493	.000	7.13183	8.82883
	120.000	8.880667*	.248493	.000	8.03217	9.72917
	150.000	9.270000*	.248493	.000	8.42150	10.11850
	180.000	9.464667*	.248493	.000	8.61617	10.31317
	210.000	9.464667*	.248493	.000	8.61617	10.31317
60.000	30.000	-6.763667*	.248493	.000	-7.61217	-5.91517
	90.000	1.216667*	.248493	.003	.36817	2.06517
	120.000	2.117000*	.248493	.000	1.26850	2.96550
	150.000	2.506333*	.248493	.000	1.65783	3.35483
	180.000	2.701000*	.248493	.000	1.85250	3.54950
	210.000	2.701000*	.248493	.000	1.85250	3.54950

90.000	30.000	-7.980333*	.248493	.000	-8.82883	-7.13183
	60.000	-1.216667*	.248493	.003	-2.06517	-.36817
	120.000	.900333*	.248493	.034	.05183	1.74883
	150.000	1.289667*	.248493	.002	.44117	2.13817
	180.000	1.484333*	.248493	.001	.63583	2.33283
	210.000	1.484333*	.248493	.001	.63583	2.33283
120.000	30.000	-8.880667*	.248493	.000	-9.72917	-8.03217
	60.000	-2.117000*	.248493	.000	-2.96550	-1.26850
	90.000	-.900333*	.248493	.034	-1.74883	-.05183
	150.000	.389333	.248493	.704	-.45917	1.23783
	180.000	.584000	.248493	.287	-.26450	1.43250
	210.000	.584000	.248493	.287	-.26450	1.43250
150.000	30.000	-9.270000*	.248493	.000	-10.11850	-8.42150
	60.000	-2.506333*	.248493	.000	-3.35483	-1.65783
	90.000	-1.289667*	.248493	.002	-2.13817	-.44117
	120.000	-.389333	.248493	.704	-1.23783	.45917
	180.000	.194667	.248493	.983	-.65383	1.04317
	210.000	.194667	.248493	.983	-.65383	1.04317
180.000	30.000	-9.464667*	.248493	.000	-10.31317	-8.61617
	60.000	-2.701000*	.248493	.000	-3.54950	-1.85250
	90.000	-1.484333*	.248493	.001	-2.33283	-.63583
	120.000	-.584000	.248493	.287	-1.43250	.26450
	150.000	-.194667	.248493	.983	-1.04317	.65383
	210.000	.000000	.248493	1.000	-.84850	.84850
210.000	30.000	-9.464667*	.248493	.000	-10.31317	-8.61617
	60.000	-2.701000*	.248493	.000	-3.54950	-1.85250
	90.000	-1.484333*	.248493	.001	-2.33283	-.63583
	120.000	-.584000	.248493	.287	-1.43250	.26450
	150.000	-.194667	.248493	.983	-1.04317	.65383
	180.000	.000000	.248493	1.000	-.84850	.84850

*. The mean difference is significant at the 0.05 level.

Table A8: ANOVA and TUKEY test result of Concentration effect

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	8.06774	4	2.01694	473.104	2.39728E-11	3.47805
Within Groups	0.04263	10	0.00426			
Total	8.11037	14				

Multiple Comparisons

Dependent Variable: concentration

Tukey HSD

(I) Initialconcentration	(J) Initialconcentration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
10.000	20.000	.000000	.053312	1.000	-.17545	.17545
	30.000	-.403333*	.053312	.000	-.57879	-.22788
	40.000	-1.011667*	.053312	.000	-1.18712	-.83621
	50.000	-1.936333*	.053312	.000	-2.11179	-1.76088
20.000	10.000	.000000	.053312	1.000	-.17545	.17545
	30.000	-.403333*	.053312	.000	-.57879	-.22788
	40.000	-1.011667*	.053312	.000	-1.18712	-.83621
	50.000	-1.936333*	.053312	.000	-2.11179	-1.76088
30.000	10.000	.403333*	.053312	.000	.22788	.57879
	20.000	.403333*	.053312	.000	.22788	.57879
	40.000	-.608333*	.053312	.000	-.78379	-.43288
	50.000	-1.533000*	.053312	.000	-1.70845	-1.35755
40.000	10.000	1.011667*	.053312	.000	.83621	1.18712
	20.000	1.011667*	.053312	.000	.83621	1.18712
	30.000	.608333*	.053312	.000	.43288	.78379
	50.000	-.924667*	.053312	.000	-1.10012	-.74921
50.000	10.000	1.936333*	.053312	.000	1.76088	2.11179
	20.000	1.936333*	.053312	.000	1.76088	2.11179
	30.000	1.533000*	.053312	.000	1.35755	1.70845
	40.000	.924667*	.053312	.000	.74921	1.10012

*. The mean difference is significant at the 0.05 level.

Table A 9: ANOVA and TUKEY test result of pH effect

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3703.2719	7	529.039	1271.51	9.50737E-21	2.6571966
Within Groups	6.6571167	16	0.41607			
Total	3709.929	23				

Multiple Comparisons

Dependent Variable: Concentration

Tukey HSD

(I) pHeffect	(J) pHeffect	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1.000	2.000	4.719667*	.526669	.000	2.89626	6.54307
	3.000	-9.684000*	.526669	.000	-11.50741	-7.86059
	4.000	-12.653333*	.526669	.000	-14.47674	-10.82993
	5.000	-15.791333*	.526669	.000	-17.61474	-13.96793
	6.000	-22.361000*	.526669	.000	-24.18441	-20.53759
	7.000	-25.767000*	.526669	.000	-27.59041	-23.94359
	8.000	-35.426333*	.526669	.000	-37.24974	-33.60293
2.000	1.000	-4.719667*	.526669	.000	-6.54307	-2.89626
	3.000	-14.403667*	.526669	.000	-16.22707	-12.58026
	4.000	-17.373000*	.526669	.000	-19.19641	-15.54959
	5.000	-20.511000*	.526669	.000	-22.33441	-18.68759
	6.000	-27.080667*	.526669	.000	-28.90407	-25.25726
	7.000	-30.486667*	.526669	.000	-32.31007	-28.66326
	8.000	-40.146000*	.526669	.000	-41.96941	-38.32259
3.000	1.000	9.684000*	.526669	.000	7.86059	11.50741
	2.000	14.403667*	.526669	.000	12.58026	16.22707
	4.000	-2.969333*	.526669	.001	-4.79274	-1.14593
	5.000	-6.107333*	.526669	.000	-7.93074	-4.28393
	6.000	-12.677000*	.526669	.000	-14.50041	-10.85359
	7.000	-16.083000*	.526669	.000	-17.90641	-14.25959
	8.000	-25.742333*	.526669	.000	-27.56574	-23.91893
4.000	1.000	12.653333*	.526669	.000	10.82993	14.47674
	2.000	17.373000*	.526669	.000	15.54959	19.19641
	3.000	2.969333*	.526669	.001	1.14593	4.79274
	5.000	-3.138000*	.526669	.000	-4.96141	-1.31459

	6.000	-9.707667*	.526669	.000	-11.53107	-7.88426
	7.000	-13.113667*	.526669	.000	-14.93707	-11.29026
	8.000	-22.773000*	.526669	.000	-24.59641	-20.94959
5.000	1.000	15.791333*	.526669	.000	13.96793	17.61474
	2.000	20.511000*	.526669	.000	18.68759	22.33441
	3.000	6.107333*	.526669	.000	4.28393	7.93074
	4.000	3.138000*	.526669	.000	1.31459	4.96141
	6.000	-6.569667*	.526669	.000	-8.39307	-4.74626
	7.000	-9.975667*	.526669	.000	-11.79907	-8.15226
	8.000	-19.635000*	.526669	.000	-21.45841	-17.81159
6.000	1.000	22.361000*	.526669	.000	20.53759	24.18441
	2.000	27.080667*	.526669	.000	25.25726	28.90407
	3.000	12.677000*	.526669	.000	10.85359	14.50041
	4.000	9.707667*	.526669	.000	7.88426	11.53107
	5.000	6.569667*	.526669	.000	4.74626	8.39307
	7.000	-3.406000*	.526669	.000	-5.22941	-1.58259
	8.000	-13.065333*	.526669	.000	-14.88874	-11.24193
7.000	1.000	25.767000*	.526669	.000	23.94359	27.59041
	2.000	30.486667*	.526669	.000	28.66326	32.31007
	3.000	16.083000*	.526669	.000	14.25959	17.90641
	4.000	13.113667*	.526669	.000	11.29026	14.93707
	5.000	9.975667*	.526669	.000	8.15226	11.79907
	6.000	3.406000*	.526669	.000	1.58259	5.22941
	8.000	-9.659333*	.526669	.000	-11.48274	-7.83593
8.000	1.000	35.426333*	.526669	.000	33.60293	37.24974
	2.000	40.146000*	.526669	.000	38.32259	41.96941
	3.000	25.742333*	.526669	.000	23.91893	27.56574
	4.000	22.773000*	.526669	.000	20.94959	24.59641
	5.000	19.635000*	.526669	.000	17.81159	21.45841
	6.000	13.065333*	.526669	.000	11.24193	14.88874
	7.000	9.659333*	.526669	.000	7.83593	11.48274

*. The mean difference is significant at the 0.05 level.

7.4 Some selected figure during laboratory work

Figure A 2:Innovative Technology Center for Sustainable Development (iTCSD) Laboratory

Figure A 1: Collection of filtered sample before 1, 5diphenyl carbazide

Figure A 4: Sample ready for measurement after 1, 5diphenyl carbazide added Laboratory

Figure A 3:Houdaochen Tannery; Place where real sample collected (Modgo).

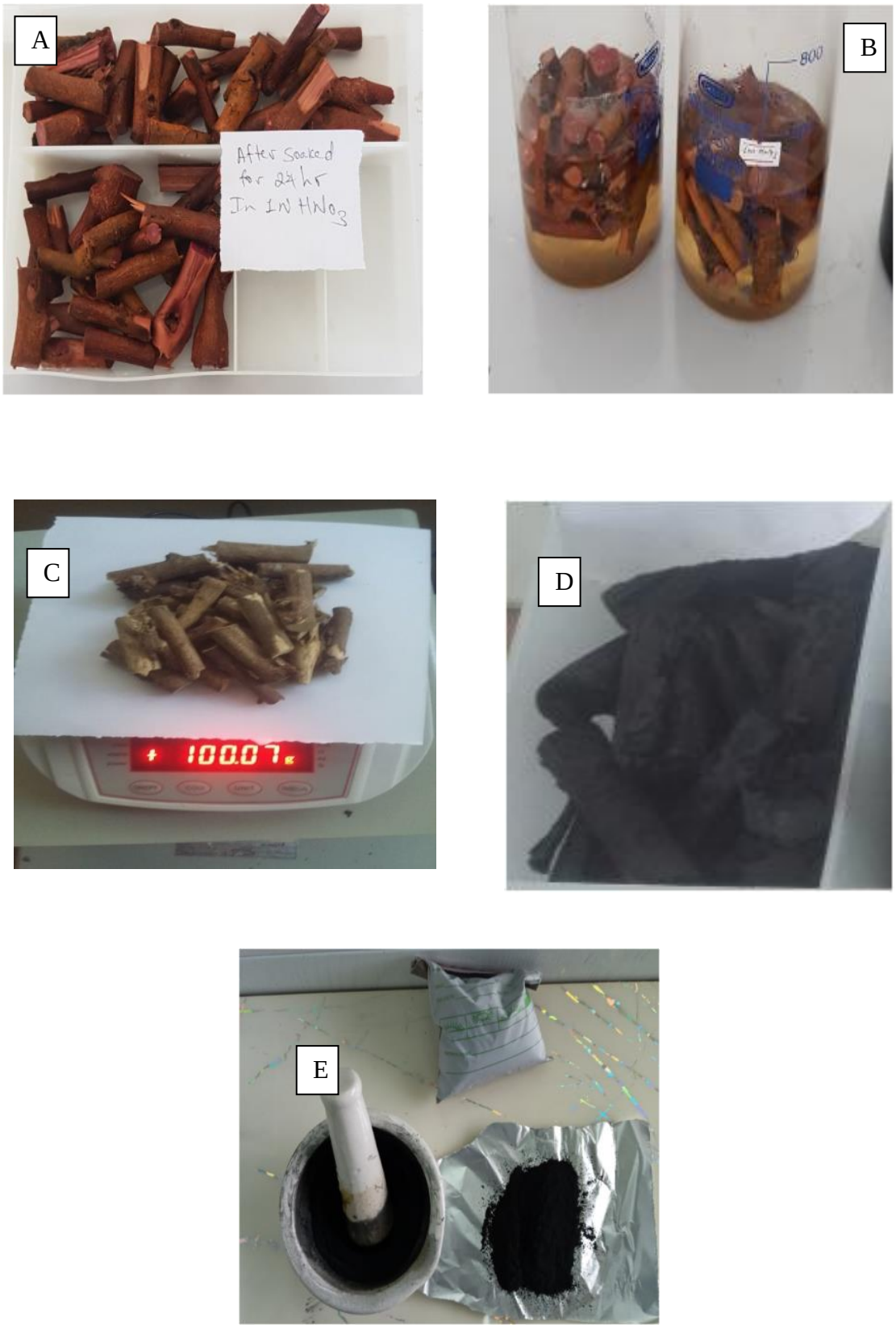

Figure A 5: Preparation of Adsorbent A, Weighing of raw B, Soaking with 1NHNO3 C, after soaked with 1NHNO3 for 24 hr D, activated carbon developed E, Grinded activated carbon

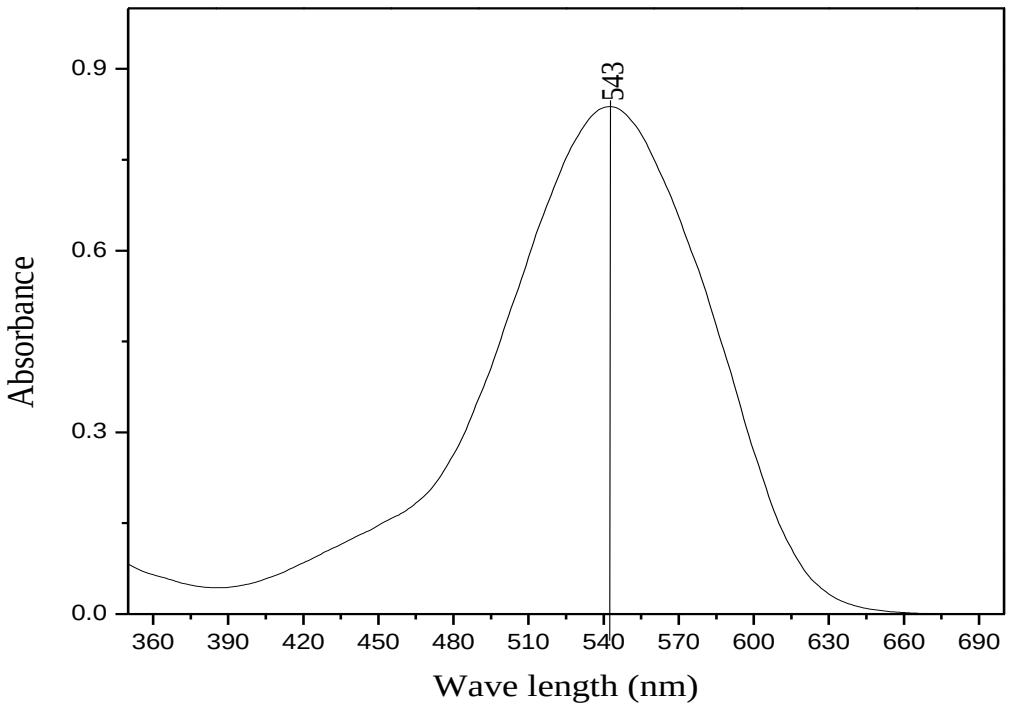

Figure A 6 :UV-Visible ʎ maximum absorption of Chromium (VI)

Figure A 7: Chromium containing solution before and after treatment