Jimma University
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# Removal of Chromium from wastewater using Activated Coffee Husk Carbon

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Jimma, Ethiopia

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# Abstract

*Hexavalent chromium is well recognized as an element of environmental and public health concern. Numerous commercially available activated carbons have been used for chromium adsorption, both as-received and after chemical modifications. To ensure sound application on the mitigation of chromium, chemically activated carbon from coffee husk was utilized by considering partly the existence of substantial amount of by product coffee husks in Ethiopia. The adsorbents surface was characterized by XRD.The different physicochemical properties such as bulk density, moisture content, volatile matter, ash content, pore volume, pH and electrical conductivity were determined. The adsorption of hexavalent chromium from aqueous solution by chemically activated carbon prepared from coffee husk and its application to real wastewater was studied. The extent of adsorption was studied as a function of pH, contact time, adsorbent dose, and initial adsorbate concentration. Optimum conditions studied were found to be 60 minutes, 80 mg/l, 2, 2.5 g/100 ml and 150 rpm for contact time, concentration of adsorbate, pH, adsorbent dose and stirring speed, respectively. The adsorption efficiency of activated coffee husk was found to be 99.6% at optimal conditions. The adsorption process has best fitted pseudo-second order kinetic model than pseudo-first order kinetic model. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data, and Langmuir adsorption isotherm model was found to be best fitted to this adsorption process. The study showed that activated carbon from coffee husk is a good candidate for the removal of hexavalent chromium from contaminated water.*

**Key words**: Wastewater, *Hexavalent chromium, activated coffee husk, Low-cost Adsorbent*

# List of Abbreviations and Acronyms

| | |
|---|---|
| AAS | Atomic Absorption Spectrophotometer |
| ASTM | American Society Test Material |
| CHAC | Coffee Husk Activated Carbon |
| CH | Coffee Husk |
| CHC | Coffee Husk Carbon |
| Cr | Chromium |
| Cr (III) | Trivalent Chromium |
| Cr (VI) | Hexavalent Chromium |
| EC | Electrical conductivity |
| EGSL | Ethiopian Geological Survey Laboratory |
| RHC | Rice Husk Carbon |
| XRD | X-ray diffraction |

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# CHAPTER: ONE

# INTRODUCTION

## 1.1 Background

Chromium is a transition metal which occurs in nine different forms of oxidation states ranging from Cr (-II) up to Cr (+VI), but the two common valence states are trivalent and hexavalent chromium forms (John *et al.*, 2003); however, concerns regarding the presence of Chromium in the environment focus on the potential adverse health effects of Cr (VI)-contaminated soils, groundwater, and drinking water supplies. Hexavalent chromium is more hazardous, carcinogenic, and mutagenic and the most water soluble which easily enters to living cells. The contamination of environment by Chromium is a critical problem because of adverse effects on aquatic life and human health (Nasrabadi *et al.,* 2010; Haruna *et al.*, 2011; Mina *et al.*, 2011; Serbaji *et al.,* 2012; Manfe *et al.,* 2012).

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

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

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

Adsorption using activated carbon is one of the most economically favorable and technically feasible methods for the removal of heavy metals ions from wastewater which has received great attention over a number of years. Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume which is known for the effective removal of heavy metal ions from various industrial wastewaters (Jiang *et al.*, 2008, Gupta *et al.*, 2010).

## 1.2 Statement of the problem

Hexavalent chromium is well thought out to be a group “A” human carcinogen because of its mutagenic and carcinogenic properties .Chromium is included in the priority list of hazardous substances since it affects both; human and aquatic life .It has been also reported that excessive intake of hexavalent chromium by plants severely affects the mitotic process and reduce seed germination in extensively cultivated pulse crops (Altaf *et al.*, 2008; Mina *et al.*, 2011).

Advances in science and technology have brought remarkable improvement in many areas of development, but in the process, also contributed to degradation of environment all over the globe which increased demand for new technologies for proper treatment facilities chromium before discharge to the environment .Discharge of heavy metals which are major pollutants in marine, ground and surface waters by human activity has enormously increased since industrialization there by impacting geochemical cycle and food chain (Dhanakumar *al.*, 2007;Ramesh *et al.*, 2011;Ghaderi *et al.*, 2012).

Major industries such as leather tanning, metal plating industries use chromium compounds in attempt to improve human living standards, but the discharge of those chemicals into the environment without proper treatment reverses the intended living standard. Leather Tanning industries are ranked as the highest contributors of chromium pollution. For instance, in India 2000 – 5000 mg/l of chromium escapes into the environment annually from tannery industries, in the aqueous effluent that is much higher than the recommended permissible discharge limits of 2 mg/l as total chromium (Venkateswarlu *et.al.* 2007, Altaf *et al.*, 2008).

The predominant use of chromium in industry unfortunately introduces an environmental concern implying the primary importance of waste water treatment .The removal of chromium from wastewater using adsorbents derived from waste of plant origins has showed interesting results and generated the new concepts in pollution research.

Adsorption on activated carbon has been found to be superior compared to other conventional methods for wastewater treatment in terms of its capability for efficiently adsorbing heavy metal ions and simplicity of design .However cost is an important parameter when comparing the sorbent materials. Commercial activated carbons are very expensive due to the use of nonrenewable and relatively high-cost starting materials such as coal, which is unjustified in pollution control applications (Sourja *et al.*, 2005; Ansari *et al.*, 2009, Ali, 2010).

Coffee is one of the most popular beverages in the world in terms of consumption in which its production was 6.7 million metric tons annually in 1998-2000, and rose to 7 million metric tons annually in 2010 (Bhatnagar *et al.*,, 2010). Ethiopia, is the primary center of origin and genetic diversity of *arabica coffee* (*Coffea arabica),* which was produced up to 301, 000 tons in 2006 but this was increased to 419,000 tons by the end of 2010(Kassa H. *et al.*, 2011)**.**Clearly, this indicates that coffee husk is the main by-product generated by the coffee processing industries and disposed into land and fired. Due to the presence of polyphones which are considered as anti- nutritional and phototoxic substances such as caffeine, tannin, organic acids restricts its larger extent uses in agriculture and imposing problems on the environment.

Different researches have been conducted on the removal of hexavalent chromium using activated carbon derived from plant waste materials as written in the literature. There is no research conducted to investigate the interaction of anionic chromium compounds with activated coffee husk carbon.

In present work, experiments were performed to remove hexavalent chromium as a model heavy metal pollutant by adsorption technique using surface modified coffee husk as an adsorbent changing solution pH, adsorbent dose, contact time and initial concentration of Cr (VI) ions.

## 1.3 Significance of the study

The various investigations conducted using locally available agricultural waste materials for treatment of chromium contaminated wastewater have proven to be relatively successful although the adsorption capacity of most of the adsorbent is low and the kinetics is slow (Isa *et al.,* 2008).The application of locally available materials for adsorption requires identification, analysis, and activation to develop appropriate technique. The study investigated the physicochemical characteristics and the structural analysis of activated coffee husk carbon which tell the general adsorptive properties of the adsorbent. The study determined high adsorption capacity of activated coffee husk carbon and the fast kinetic rates of chromium. In addition to this, using coffee husk as an adsorbent is one way of waste management and recycling.

The result of the study is expected to endow with a better understanding for Environmentalists, Environmental protection Authority, Ministry of water and energy, Ministry of trade and industry to use activated coffee husk for treatment of wastewater contaminated hexavalent chromium.

# CHAPTER: TWO

# LITERATURE REVIEW

## 2.1 Over view of Chromium Chemistry

Chromium, which is the 21st most abundant element in Earth's crust, is a heavy metal with atomic number of 24 and mass number of 51.9961 which belongs to the first series of transition metals. Chromium occurs in nine different forms of oxidation states ranging from Cr (-II) up to Cr (+VI), but the two common valence states are trivalent and hexavalent chromium forms .The hexavalent species exists primarily as chromic acid ($H_2CrO_4$) and its salts, hydrogen chromate ion ($HCrO_4^-$) and chromate ion ($CrO_4^{2-}$), depending on the pH. The predominant species present, as a function of the pH, are $H_2CrO_4$ at pH less than about 1, $HCrO_4^-$ at pH between 1 and 6, and $CrO_4^{2-}$ at pH above about 6 .

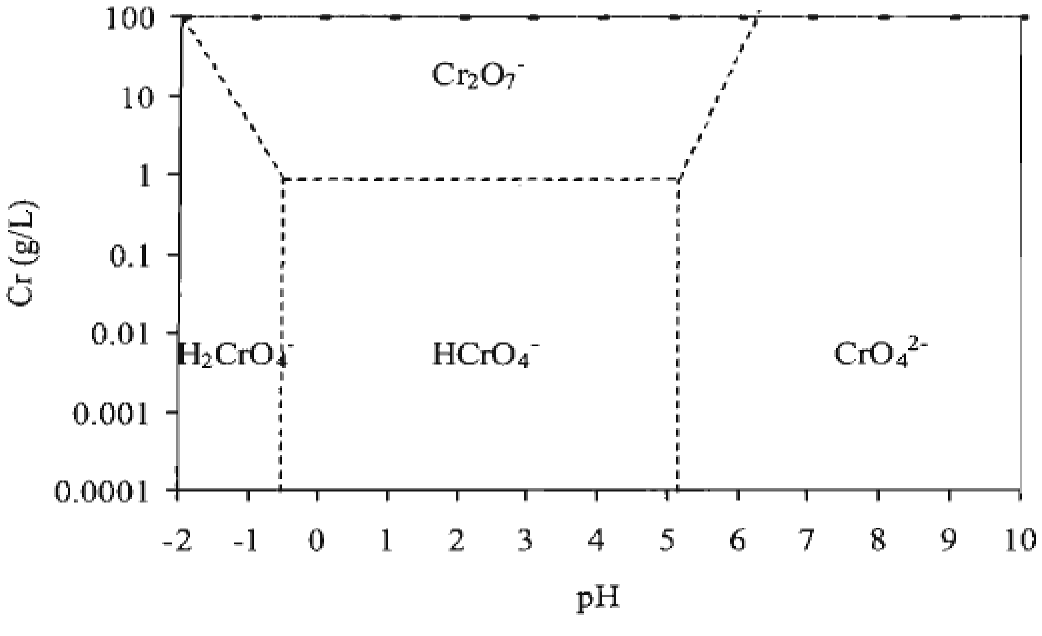

Fig.1. Relative distribution of Cr (VI) species in water as a function of pH and Cr (VI) ions concentration (Mohan *et al.*, 2007)

## 2.2 Chromium Removal Technologies

Because chromium is used either directly or indirectly in a number of manufacturing processes, treatment technologies to remove or recover chromium from industrial wastewater have been well developed.

### 2.2.1 Conventional coagulation-flocculation

Reduction and removal of chromium as Cr (III) can achieve reasonably low concentrations of chromium in treated water. However, in combination with a post treatment this could extremely be effective for controlling Cr (VI) at very low concentrations. Effective removal by hydroxide precipitation requires that the Cr (VI) first be reduced to Cr (III) using a chemical reducing agent such as ferrous sulfate, sodium bisulfate or stannous chloride.

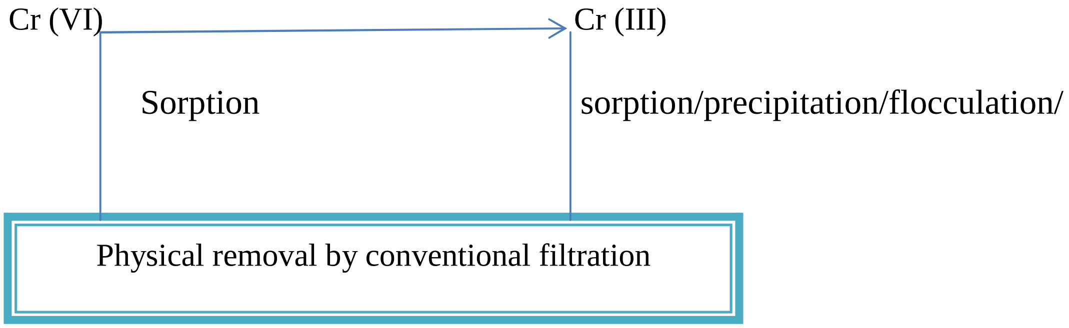

Fig.2 Chemistry of chromium in coagulation-flocculation(Besselievre,1969)

## 2.2.2 Lime Softening

Lime softening can effectively remove trivalent chromium but removal of hexavalent chromium is poor. The addition of reductant is needed to reduce Cr (VI).However; the rate and efficiency of Cr (VI) reduction are favored at low pH conditions. High pH during softening processes hinders Cr (VI) reduction reactions.In addition, even though Cr(VI) can be reduced to Cr(III) and then removed by precipitation, residual solid $Cr(OH)_3$ might be redissolved to form aqueous Cr(III).Thus, achieving chromium concentration of less 2 mg/l by using precipitative lime softening would be difficult.

## 2.2.3 Reverse osmosis

Reverse osmosis (RO) is a 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. More formally, it is the process of forcing a solvent from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. This process requires that a high pressure be exerted on the high concentration side of the membrane and it is not economical for heavy metal removal (Aljendeel H., 2011).

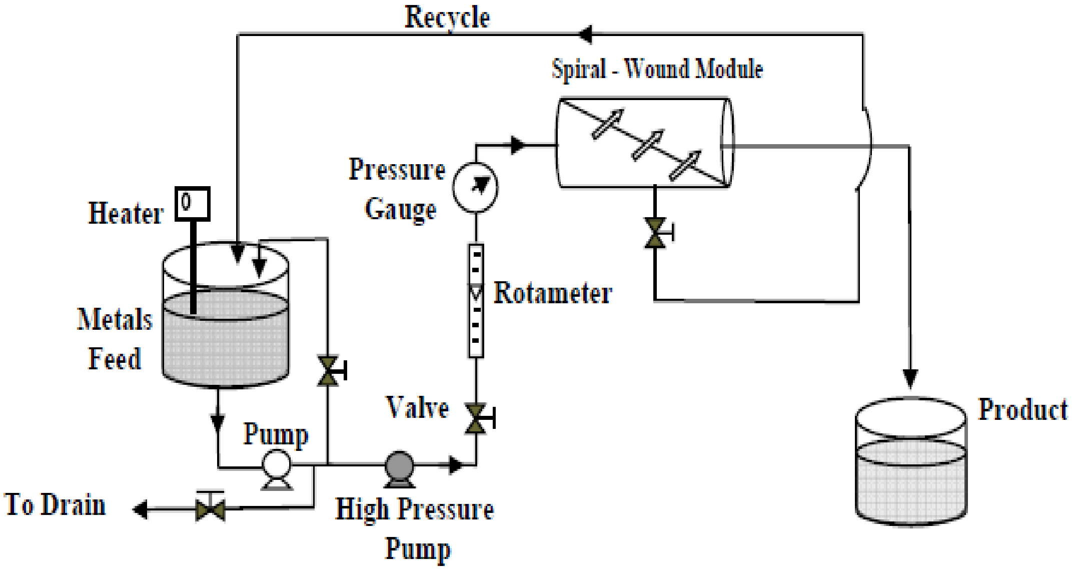

**Fig .3 Schematic Diagram of Reverse Osmosis Process**

### 2.2.4 Nanofiltration

Nanofiltration is a newer technology than reverse osmosis that often used to separate relatively small organic and inorganic compounds and (multivalent) ions from a solvent. The separation mechanism of Nanofiltration involves created electrical effects between the charged ions in the NF membrane and the co-ions in the effluent to reject the latter. High efficiency of separation at lower pressure of operation makes the Nanofiltration to be the best out of other membrane systems. For the rejection of heavy metal ions such as chromium from wastewater, Nanofiltration is a particular promising method (Religa *et al.,* 2011).

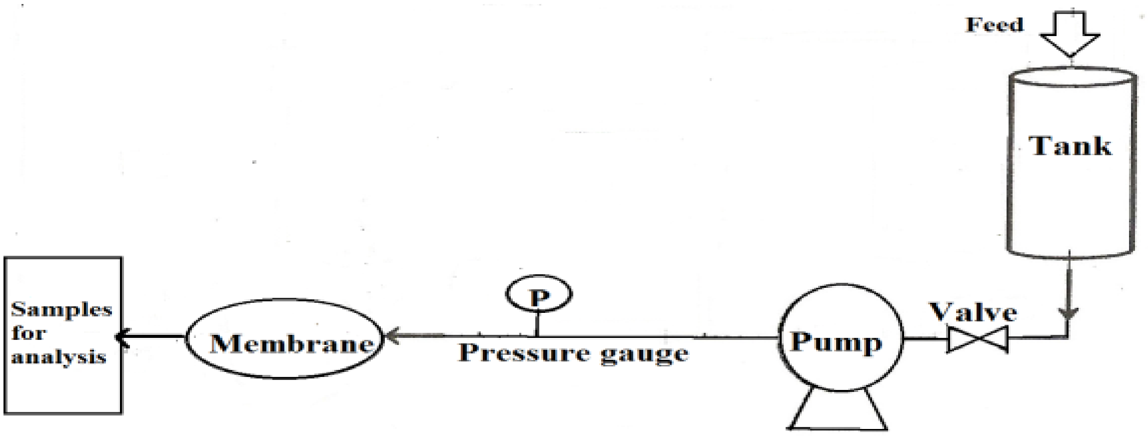

**Fig.4 Experimental set up of Nanofiltration**

## 2.5 Adsorbents used for adsorption of chromium

Kulkarni *et al.,* (2013) found; the maximum percentage removal to be 98% for 10 mg/l of adsorbate concentration, attained after 40 minutes of contact time at activated charcoal carbon dose of 0.2 g/l and the optimum pH was observed to be 2 at activated charcoal dose of 0.2 g/l. It is also observed that the rate of uptake was rapid in the early stages but gradually decreased and became constant when equilibrium was reached.

According to Ahmed *et al.,* (2012), adsorption increased from 44 to 78% when the adsorbent dose increased from 1 to 5 g/l at constant adsorbate concentration and pH 20mg/l and 2 respectively. It was also true that at initial concentration, pH and adsorbent dose as 20 mg/l, 2 and 5g/l respectively, the effect of contact time was studied  increase in contact time up to 150 min increased adsorption beyond that there was no further increase in percentage adsorption. The percentage adsorption was higher at lower pH and decreased with the increase in pH from 2 to 10 decreasing the percentage adsorption from 96 to 26.4%.When initial concentration increased from 20 mg/l to 100 mg/l, the percentage adsorption decreased from 95.2% to 45%.

Singh *et al.,* (2012) demonstrated that the adsorption of chromium (VI) was found to be maximum (93-94%) at low values of pH for the carbon dosage of 1000mg/l and nearly 100% for carbon dosage of 1200mg/l.
On the other hand, Dhanakumar *et al., (*2007) examined the correlation, $R^2$, which showed the pseudo-second order model, fits better the experimental data ($R^2$ ranges 0.994-0.997) and also the Langmuir isotherm model better fits the experimental data with $R^2$ =0.94.

According toTalokar (2011), the equilibrium data for the adsorption of chromium were analyzed in the light of Langmuir and Freundlich isotherm models and followed Langmuir adsorption isotherm. Renuga *et al., (*2010) observed that the maximum removal of Cr (VI) at pH 2 and removal was increased from 70.58% to ~100% with increasing adsorbent dosage from 50 to 200 mg. The adsorption process was found to obey Langmuir adsorption isotherm and Freundlich adsorption isotherm. Qaiser *et al.,* (2009) investigated maximum removal of chromium (VI) achieved at pH 2. The Langmuir model showed better representation of data, with correlation coefficient greater than 0.98.

Mohamed *et al.,* (2008) also investigated the effectiveness of acid treated oil palm fibre for the removal of Cr (VI) from aqueous solutions. The adsorption kinetics tested with pseudo first order and pseudo second order models yielded high $R^2$ values from 0.9254 to 0.9870 and from 0.9936 to 0.9998, respectively.

Maryam *et al.,* (2011) study showed that Almond Green Hull could be used as an efficient sorbent for the removal of Cr (VI) from aqueous solutions. The results indicated that almond green hull adsorbs over 94.14% of Cr (VI) from solutions containing 10 mg/L of Cr (VI) at sorbent amount of 4 g/l and pH 6 after 30 minutes of equilibration at room temperature. High removal efficiency of Cr (VI) observed in the first 5 minutes of sorbent contact time for concentration of 10 mg/L solution. The experimental data best fit with the Langmuir isotherm model with $R^2$ =0.9989.

.According to Isa *et al.,* (2008) Oil Palm Ash has showed the pseudo second order kinetic model better fits the experimental data ($R^2$=0.99).

Mohamed *et al.,* (2012) investigated that the removal of chromium by activated carbon was 73% at adsorbate initial concentration: 400 mg/l; pH: 2.0; adsorbents dose: 4 g/l; agitation speed: 200 rpm after 120 minutes of contact time. The correlation, $R^2$, showed that the pseudo-second order model, fits better the experimental data ($R^2$=0.990).

According to Suresh *et al., (*2012) there was an appreciable increase in percent removal of chromium up to 105 minutes and thereafter further increase in contact time the increase in removal was very small at pH 2 and 15g/l of adsorbent dose. Thus the effective contact time is taken as 105 minute. It was found that 92.2% and 91.4% removal of Cr (VI) achieved at pH2 and 3, respectively and there after the percent removal decreases with increase in pH as 4, 5, 6, and 8 at contact time of 105 minutes and 15g/l of adsorbent dose. Thus the optimum adsorption pH for Cr (VI) was taken as 2.It also showed that, as the concentration of chromium in solution increases, the percent removal of chromium decreases .The percent removal with Crotalaria burhia was found 92.2% at a Cr (VI) concentration of 40mg/l at contact time 105 minutes and 15g/l of adsorbent dose, at effective pH 2.

Veena Devi *et al., (*2012) studied the effect of adsorbent dose and found Optimum removal of chromium (about 94%) at an adsorbent dosage of 2 g. The rate of Cr (VI) binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period. After 60 minutes the adsorption reaches an optimum value of 92%. It was evident that at lower pH between 2 and 3 the maximum adsorption was after an equilibration time of 60 minutes at a stirring speed of 200 rpm adsorbent dose of 0.5g/100ml. The effect of the agitation of the sorbent/sorbate system showed the maximum of 97.77 % chromium removal at 200 rpm when 0.5 g of adsorbent and 50 ml of the solution containing 100 mg/l of chromium at pH 3 was agitated between 90 and 210 rpm. An increase in adsorption was observed from 66.66 % to 97.77 %, when the agitation speed was increased from 90 to 200 rpm.

Sekhar *et al., (*2012) studied the effect of common anions present in natural and waste waters using different plant leaves powder. Adsorption of chromium was reduced from 96% to 88%,96% to 92.2%,96% to 88.4%,96% to 84.5,96% to 92% and 96% using Bhringaraj leaves powder in the presence of $SO_4^{2-,}NO_3^{-}$,$Cl^{-}$,$PO_4^{3-}$,$F^{-}$ and $CO_3^{2-}$ but by using Aerva lanat leaves powder it was reduced from 92% to 84.3%,92% to 88.3%,92% to 88%,92% to 80%,92% to 84.5 and 92% to 88% respectively.

Singh *et al.,* (2012) determination the physicochemical characteristics such as bulk density, pore volume, moisture content, ash content and pH of the rice husk carbon to be 0.68 $g/cm^3$,0.12 ml/g,13.82%.38.02% and 6.5 respectively. On the other hand, Veena *et al.,* (2012) reported the average values of coconut shell physicochemical properties such as bulk density, volatile matter, ash content, pore volume and moisture content to be 0.262 $g/cm^3$,21.67%,1.443% and 5.21% respectively. It has been reported that carbons of pH 6-8 are useful for most applications on adsorption and good conductivity in activated carbons ranges from 51.85 μS to 70.75 μS (Khadija *et al*., 2008). On the other hand, the American Water Work Association has set a lower limit on bulk density as 0.25 $g/cm^3$ for activated carbon to be of practical use (Okieimen *et al*., 2007).

# CHAPTER: THREE

# OBJECTIVE

## 3.1 General Objective:-

The general objective of this study was to examine the potential of activated coffee husk carbon in removing chromium from waste water

## 3.2 Specific Objectives:-

- To characterize coffee husk activated carbon
- To study the effect of contact time, pH, stirring speed, initial concentration and adsorbent dose on the removal of Cr(VI) ions
- To describe the experimental data of adsorption isotherms through Langmuir and Freundlich models
- To investigate the adsorption kinetics of Cr (VI) through pseudo-first and pseudo-second order models

# CHAPTER: FOUR

# MATERIALS AND METHODS

## 4.1 Study Area and Period

The carbonization process was conducted at Jimma University Mechanical engineering department laboratory, and the presence or absence of crystalline material inside the adsorbent was analyzed at Geological Survey of Ethiopia. The Chemical activation, characterization of the activated coffee husk carbon, preparation of series of solutions and effect of different parameters were studied at Environmental Health science and Technology graduate and staff laboratory, Jimma University. Finally, the digestion of the waste water and spectroscopic analysis of the samples were conducted at department of chemistry, Jimma University, from February-June 2013.

## 4.2 Experimental

### 4.2.1 Instrumentation

The determination of amount of chromium in the effluent solutions before and after adsorption takes place was done using Flame Atomic Absorption Spectroscopy (FAAS) analytikjena novAA 300 model equipped with deuterium ark background corrector, nebulizer and hallow cathode lamp corresponding to metal of interest, in this case chromium, using air-acetylene flame.

To determine concentration of chromium in the filtrates, four series of standard chromium solutions in the range of 0.05 – 8 mg/l were prepared by diluting the stock solution of chromium with de-ionized water. A blank (de-ionized water) and standards were run in flame atomic absorption spectrometer and four point's calibration curves were established. Then, sample solutions were aspirated in to the AAS instrument and direct readings of total chromium concentrations were recorded. Three replicate determinations were carried out on each sample. The amount of chromium adsorbed was then calculated from the difference between the amount before and after adsorption.

Mass of adsorbents and mass of different chemicals whenever the stock solutions were prepared from solid chemicals was measured using analytical balance of 0.001 g accuracy (BP110S model). PH of different solutions was measured using pH meter (HQ40D multi-parameter).Series of different solutions with adsorbent by using magnetic shaker(SM 30A model). To activate and characterize the coffee husk carbon, the samples were subjected to tabular oven (D3C model.

The chrome waste was digested with concentrated Nitric acid in rectangular hood (Kottermann 730285 model). For determination of PH and conductivity CHAC the magnetic stirrer (HI 300N model) was used to mix the solution uniformly. The carbonization and characterization of coffee husk was conducted in rectangular furnace (LINDBERG 51848 model).

### 4.2.2 Preparation of the adsorbent

The coffee husk was used to activated carbon preparation as it is generated in large amount and resulting severe pollution. This husk was obtained from coffee processing unit at Gomma-2 Limmu coffee farm. The coffee husk was washed with tap water then it was sun dried for 2 days. The dried husk was crushed and ground to a sieve size of 1,000 µm.Soon after, it was impregnated with 40% $H_3PO_4$ for 2 hours. Then after, the impregnated powder was soaked with the same solution overnight followed by decantation through 212 µm sieve, air drying for 12 hours at room temperature and activation overnight at $105^oC$ in a tabular oven. Then the activated coffee husk powder was subjected to carbonization at 500°C in a tubular furnace for 1 hour. After completing the carbonization process it was cooled overnight in a tubular furnace. The produced activated coffee husk carbon was washed with distilled water and neutralized by NaOH. Then after, it was dried overnight at $105^oC$ and ground using mortar and pestle and sieved with 150 µm sieve.

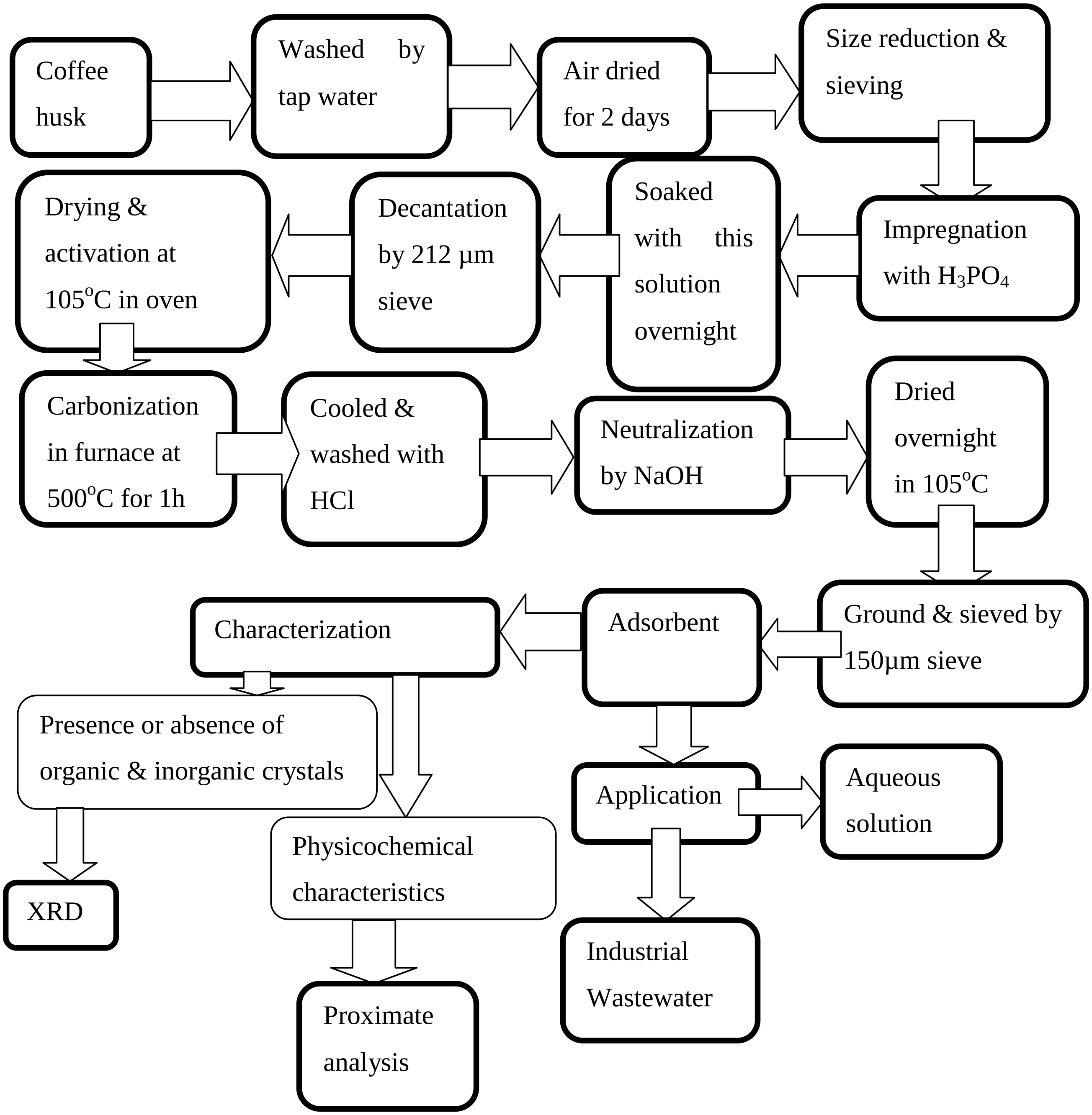

**Fig.5. Flow chart for preparation of adsorbent from coffee husk**

### 4.2.3 Preparation of adsorbate solution

The stock solution of Cr (VI) containing concentration of 1000 mg/l was prepared by dissolving 2.829 grams of potassium dichromate, $K_2Cr_2O_7$ analytical grade (99.5%), in 1000 ml of distilled water. The stock solution was further diluted with distilled water to desired concentration of test solution. The required pH of the solution was adjusted by drop wise addition of 0.1N HCl and NaOH depending on the acidity or basicity of the sample.

### 4.2.4 Applicability to industrial wastewater

The adoptability of the technique enlarged with the activated coffee husk carbon for chromium removal was undertaken with some actual effluent samples. Chrome tanning effluent was collected from Batu Tannery PLC, which is a private leather tanning industry in Addis Ababa, at discharge point. The chrome tanning liquor had pH of 3.85 and 1220.2 mg/l chromium concentration which was measured before stirring with coffee husk activated carbon. In order to study the efficiency of the coffee husk activated carbon for the actual sample, the effluent was digested with concentrated Nitric acid and then filtered through Whatmann No.41 filter paper. The resulting solution was dissolved at different time intervals, pH values including initial pH of the wastewater and at optimum conditions of coffee husk activated carbon dose, stirring speed and with actual adsorbate concentration. Finally, the solutions were subjected to atomic absorption spectroscopy for extraction of total chromium as Cr (VI).

### Experimental procedures for digestion

The chrome waste of 100 ml was transferred to a beaker and 5 ml $HNO_3$ (conc.) was added with a few boiling chips. Then this was subjected to a slow boiling and evaporated in a hood to the lowest possible volume of 20 ml before precipitation occurs. Since digestion was not complete after final volume of 20 ml, 5ml of $HNO_3$ (conc.) was added following digestion in a hood until a clear solution was observed. This was then cooled and filtered through 100 ml cylinder using Whatmann No.41 filter paper. To oxidize Cr (III), a portion of digested filtrate sample was taken into 125 ml conical flask by adding several drops of methyl orange indicator, then $NH_4OH$ (conc.) was added until solution just begins to turn yellow. Then after, 1+1 $H_2SO_4$ was added drop wise until it becomes acidic and the volume was adjusted to 40 ml followed by adding boiling chips and subjected to heat for boiling. When two drops of KMnO4 solution was added, the solution became faded then an excess of two drops of $KMnO_4$ solution was added and this gave a dark blue color. This was boiled for 5 minutes, and then 1 ml sodium azid solution was added and boiled for a minute gently. Since red color didn’t fade completely after boiling for a minute, another 1 ml sodium azid solution was added and continued boiling for 1 minute until color had faded completely and allowed to cool. The final solution was subjected to atomic absorption spectroscopy for total chromium concentration as Cr (VI) ions.

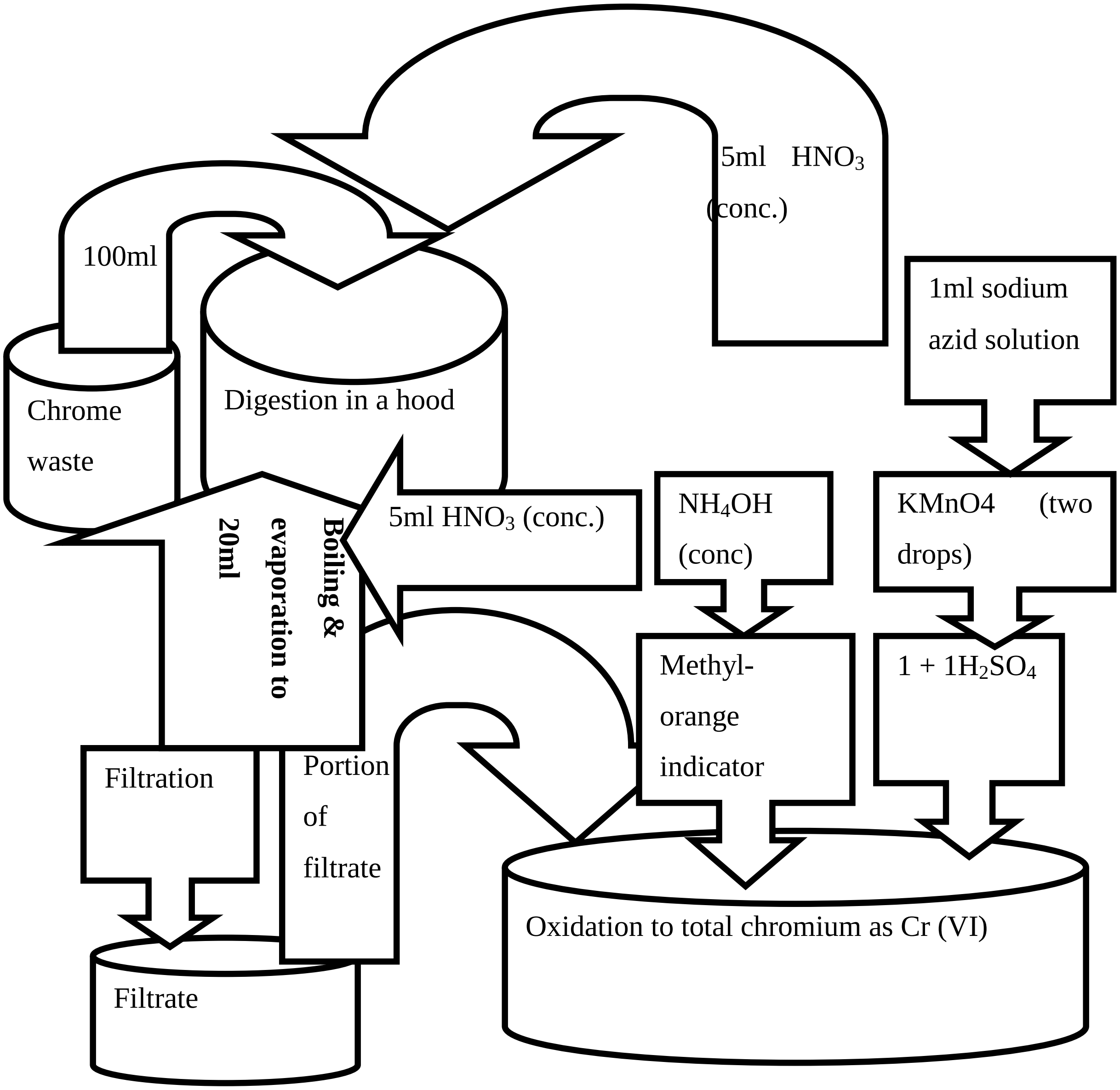

**Fig.6.Flow chart of experimental procedures for digestion and oxidation of wastewater**

## 4.2.5 Characterization of activated coffee husk carbon

### 4.2.5.1 Determination of pH and conductivity CHAC

These parameters were determined using ASTMD3838-80 of which 1.0 g of the CHAC was weighed and transferred into a 250 ml beaker and 100 ml of distilled water was added and stirred for 1 hour using magnetic stirrer. Samples were allowed to stabilize and then pH measured using an electronic pH/Conductivity meter (HQ 40D multiparameter model). The samples were further used for electrical conductivity (EC) of the CHAC and results read off in µS/cm.

### 4.2.5.2 Determination of Pore Volume

The pore volume was determined using 1.0 g CHAC sample which was immersed in water bath and boiled for 15 minutes in order to displace air from the pores. The samples were superficially dried and reweighed. The pore volume was calculated as increase in weight ($\partial$w) divided by the density of water at 25$^{o}$C.

### 4.2.5.3 Determination of Bulk Density

The bulk density was determined according to ASTM D2854-96 provided that 25 cm$^3$ density bottle was weighed and the CHAC sample was packed by repeatedly tapping the bottle so that the powder is filled up to the mark. The bottle was weighed again and the difference in the weights gave the weight of powder taken in the bottle. The bulk density of the powder was calculated by taking the ratio of weight of powder taken in the bottle to the volume of the density bottle.

### 4.2.5.4 Determination of Moisture Content

Moisture content was determined using ASTM D2867-91 method. A crucible was weighed and 1.79 g of CHAC was taken and then the crucible was placed in an electric hot air oven maintained at 105$^{o}$C for 1 hour.Thenafter, the crucible was taken out, cooled in a portable desiccator and weighed again. Heating and weighing was continued until a constant mass was obtained and the loss in weight of the powder gave percentage of the moisture content in the sample of CHAC taken used for adsorption.

Moisture content (%) $\frac{= loss\ in\ weight\ on\ drying\ (g)\ x100}{initial\ sample\ weight\ (g)}$

### 4.2.5.5 Determination of Volatile Matter

About 1.53 g of the powdered air dried CHAC was taken in previously weighed crucible. The crucible was placed in a muffle furnace maintained at about 925$^{o}$C.It was taken out exactly 7 minutes. After first cooling in air; the crucible was cooled in desiccator and weighed again. The loss in weight of the powder reported on percent basis gave volatile matter component in the sample activated coffee husk carbon.

Volatile matter (%) $=\frac{weight\ of\ volatile\ components\ (g)\ x100}{Oven\ dried\ weight\ (g)}$

### 4.2.5.6 Determination of Ash Content

Ash content determination was done according to the ASTM D2866-94 method. The residual CHAC powder from the above step was placed in a porcelain crucible and transferred into a preheated muffle furnace at a temperature of 750$^{o}$C for half an hour. After cooling in air, the crucible was cooled in a portable desiccator and weighed again. The heating, cooling and weighing cycle was repeated till constant weight was obtained, then the weight lost was reordered as the ash content of the CHAC sample(Wash).Then the %ash content (dry basis) was calculated as:

Ash (%) $=\frac{Wash}{Wo}$x100

Where $W_O$ is the dry weight of CHAC sample before ashing

### 4.2.5.7 Determination of Carbon Yield

The total carbon yield was determined after sample processing in terms of raw material mass. It was calculated by taking the ratio of carbon weight retrieved from the furnace to weight of dried carbon sample.

$Y_{ch}=\frac{Wch}{Wo}$x100,

Where $W_{ch}$=weight of carbon retrieved from the furnace, Wo =dried weight of carbon sample

### 4.2.5.8 X- ray Diffraction

The structural analysis of the activated carbon powder was determined by XRD. The XRD pattern was recorded by using Philips PW 1051 X-ray diffractometer using Cu Kα radiation (λ = 1.5405 A0) with Nickel filter.

## 4.3 Batch adsorption studies

Batch adsorption experiments were carried out by shaking 1000 mg of activated coffee husk carbon with 100 ml of potassium dichromate solution of known concentration in 250 ml Erlenmeyer flasks at room temperature on mechanical shaker. The flasks were removed after the desired contact time. A definite volume of the solution was withdrawn and quickly filtered through Whatmann No.41 filter paper. The filtrates were analyzed using Atomic absorption spectrometer (AAS) at wavelength of 357.9 nm. Cr (III) was oxidized to Cr (VI) by potassium permanganate and sodium azide. The adsorbed chromium (VI) was calculated by taking the difference of initial concentration and final chromium concentration in the filtrate.

The amount of metal ion adsorbed per unit mass of adsorbent was obtained using the equation:

$$qe = (C_o – Ce) \frac{V}{M} \quad \text{(1)}$$

where qe is the mass of adsorbate (metal ion) adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent), $C_o$ is the initial concentration (mg /L) of metal ion in solution, Ce is the final (equilibrium) concentration (mg /L) of metal ion in solution, V is the volume (L) and m is the mass of adsorbent (g) (Metcalf and Eddy 2003).

Generally, the removal efficiency of Cr (VI) was calculated as:

$$\% \text{ Removal} = [(C_o - Ce)\frac{1}{Co}] \times 100 \quad \text{(2)}$$

Where; Co and Ce are the initial and equilibrium metal ion concentrations (mg/l).

## 4.4 Adsorption isotherms

The metal uptake on the coffee husk activated carbon can be described by several mathematical relationships such as the Freundlich isotherm and Langmuir isotherm

### 4.4.1 Langmuir isotherm model

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The Langmuir-type isotherm remains to be the most widely used for practical application. The Langmuir isotherm for pure component adsorption can be obtained from Equation 1:

$$\frac{Ce}{qe} = \frac{1}{axb} + \frac{Ce}{a} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where qe= the amount of solute adsorbed per unit weight of adsorbent at equilibrium

b = The Langmuir constant related to the heat of adsorption

a = amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity when Ce/qe is plotted vs. Ce a straight line(fig.13) show the applicability of Langmuir isotherm. The values of (a) and (b) have been determined from the slop (1/a) and intercept (1/ (b * a)) for this line (Ismaeel *et al.*, 2012).

### 4.4.2 Freundlich isotherm

Freundlich isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface.

$$\ln qe = \ln Kf + \frac{1}{n}\ln Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where: the Freundlich constants *Kf* and *n*, which respectively indicate the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of *lnqe* versus *lnCe*.

The linear plots of lnqe vs $lnCe$ show that the adsorption of metal ions onto the adsorbent follows the Freundlich isotherm model.

## 4.5 Adsorption kinetics

Adsorption kinetics describe the solute uptake rate which intern control the residence time and hence the size of adsorption equipment.

Several adsorption kinetics models have been developed to understand the adsorption kinetics and rate limiting step. The Pseudo first-order and second-order kinetic models are the most popular models used to study the adsorption kinetics of heavy metals and to quantify the extent of uptake in adsorption kinetics. In order to evaluate the kinetics of chromium adsorption and potential rate controlling steps, the pseudo first and pseudo second order models were checked.

### 4.5.1 Pseudo first order model

Largergren pseudo-first order model has been expressed by the following equations:

$\frac{dq}{dt}$ = $k_1$ (qe - q)………………………………………………………………………... (5)

ln (qe - qt) = lnqe - $k_1$t…………………………………………………………………….. (6)

Where: qt and qe are the amount of Cr (VI) metal ions adsorbed per unit weight of activated coffee husk carbon (mg/g) at time t, and at equilibrium, respectively, and k1 is the adsorption rate constant or first order. The initial adsorption rate is equal to k1qe (mg/g /min$^{-1}$).

Linear plots of ln (qe -qt) versus t indicate the applicability of this model.

### 4.5.2 Pseudo second order kinetics

The pseudo second-order rate expression is:

$\frac{dq}{dt}$ = $K_2$ (qe - q)$^2$………………………………………………………………………… (7)

$\frac{t}{qt}$ = 1/$K_2$qe$^2$ + t/qe……………………………………………………….. .................. (8)

Where: qt and qe are the amount of Cr (VI) metal ions adsorbed per unit weight of activated coffee husk (mg/g) at time t, and at equilibrium, respectively, and $K_2$ is the adsorption rate constant for second order kinetics. The initial adsorption rate is equal to $k_2qe^2$ ($mgg^{-1}min^{-1}$) for second order model.

If the pseudo second-order kinetics is applicable, the plot of t/qt versus t should give a linear relationship.

## 4.6 Data quality management and Analysis

Laboratory equipments were rinsed with tap water and soaked for overnight in concentrated detergent. Then washed with tape water and soaked with 3.5 ml of $HNO_3$ added to 1000 ml of distilled water for 12 hours. Finally, they were washed with distilled water and dried in rectangular oven at $105^oC$. Duplicate experiments were carried out and the maximum difference between duplicates experiments was not more than 3%. Blank (deionized water) without adsorbent and standard chromium concentrations were run for AAS calibration, spike analysis was done. Data were carefully and honestly recorded then average values were reported. The kinetics and isotherm models were analyzed using Microsoft Excel.

## 4.7 Ethical Consideration

A formal letter was written from Jimma University, College of Public Health and Medical Sciences, Department of Environmental Health Sciences and Technology to Limmu Coffee Plantation Office, Ethiopian Geological Survey Laboratory, and Batu Leather Tanning Industry.

## 4.8 Dissemination plan

The results of the main findings will be submitted to the Department of Environmental Health sciences and Technology, College of Public Health and Medical Sciences (Jimma University), and disseminated to Ethiopian Environmental protection Authority, Ministry of water and energy, Ministry of trade and industry. Finally, the results will be presented in conferences and published in national as well as international journals.

# CHAPTER: FIVE

# RESULTS

## 5.1 Characterization of adsorbent

The result below revealed that the physico-chemical characteristics of the activated coffee husk carbon such as bulk density Pore volume, Moisture content, ash content, volatile matter, carbon yield which were carried out at laboratory. The energy dispersive X-ray diffraction (XRD) analysis was used to study the structural characteristics present in the sample.

### 5.1.1 .Proximate analysis of activated coffee husk carbon

The result of proximate analysis shows the physicochemical characteristics of activated coffee husk carbon. The magnitudes of pH, electrical conductivity, Bulk density, Pore volume, Moisture content, Ash content, Volatile matter and Carbon yield activated coffee husk carbon were determined to be 6.5,1294 µs/cm, 0.6 g/cm$^3$, 0.16 ml/g, 19%,15%,60%,68% respectively.

Table 1.Physicochemical characteristics of activated coffee husk carbon

| Characteristics | Unit | values |
|---|---|---|
| PH | --- | 6.5 |
| Electrical conductivity | µs/cm | 1294 |
| Bulk density | $g/cm^3$ | 0.6 |
| Pore volume | ml/g | 0.16 |
| Moisture content | % | 19 |
| Ash content | % | 15 |
| Volatile matter | % | 60 |
| Carbon yield | % | 68 |

### 5.1.2 X-ray Diffraction

The surface chemistry of XRD result of activated coffee husk carbon showed absence of crystalline phases inside the sample. The intensity vs. $2^{\theta}$ scale XRD profile revealed that the formation of no peak in the powdered activated coffee husk carbon sample indicating the presence of amorphous carbon structure (Fig.7).

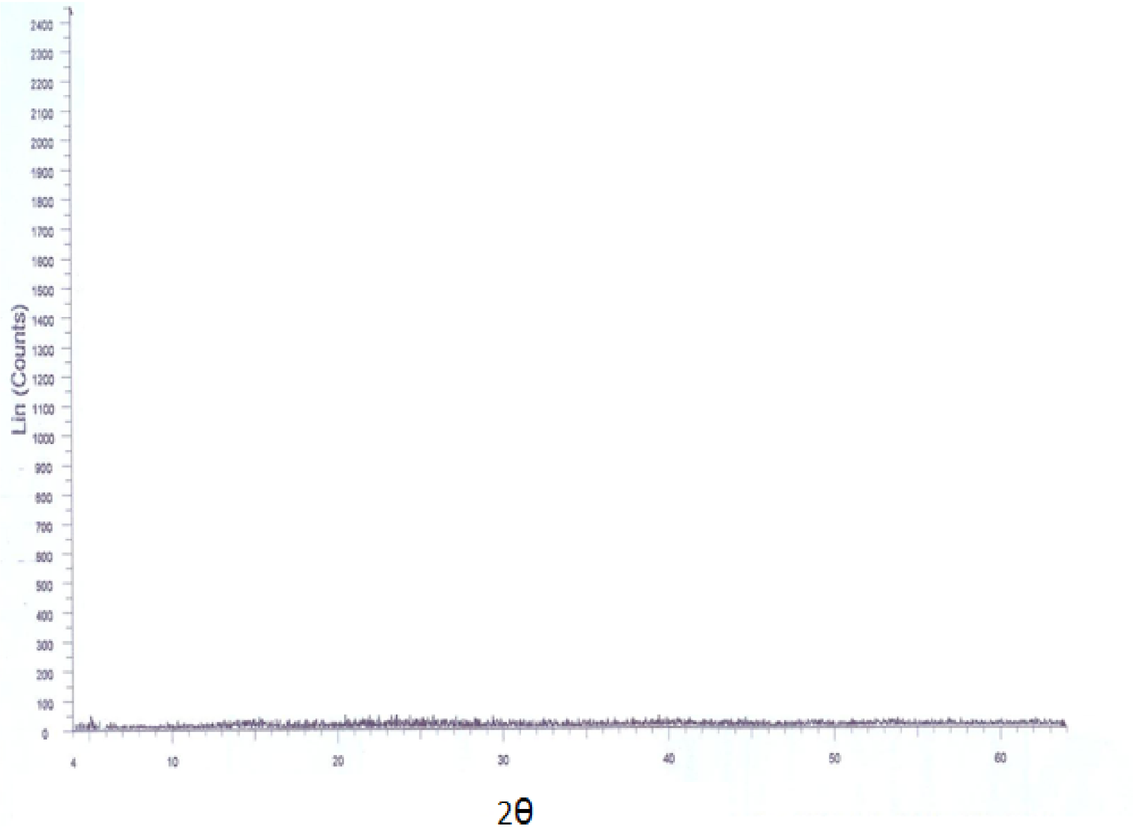

**Fig. 7. XRD profile of activated coffee husk carbon**

## 5.2 Adsorption experiments

### 5.2.1 Effect of Contact Time

As result of effect of contact time revealed the percentage adsorption of chromium on activated coffee husk carbon at contact time of 5 minutes was 70.7% this was increased to 97.8% as time passed to 150 minutes. At initial stages the rate of adsorption was high then after the rate of adsorption was decreased the removal efficiency still increased in some extent. The percentage adsorption of chromium on activated coffee husk carbon at different time intervals was 93.6%, 96.7%, 97.2%.97.4% and 97.6% as contact time passed from 30,45,60,90 and 120 minutes respectively.

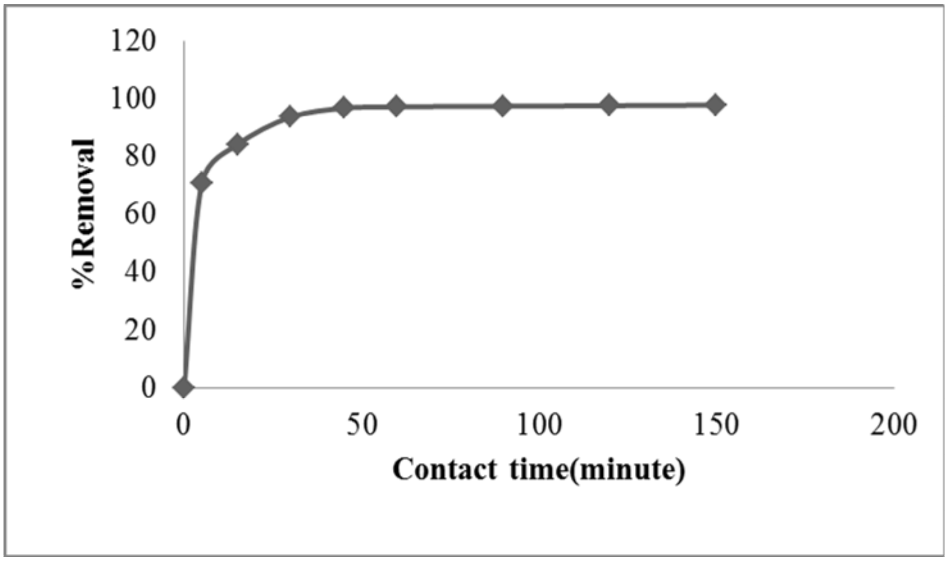

Fig.8. Effect of contact time on Cr (VI) ions removal (conditions; adsorbate initial concentration: 80 mg/l; pH: 7.0; adsorbent dose: 1 g/100 ml; agitation speed: 150 rpm)**.**

### 5.2.2 Effect of pH

The percentage removal of chromium by activated coffee husk carbon was greater than 90% up to solution pH of 5 but the maximum percentage removal was found be at solution pH of 2 and 3 which is 98.2 % and 97.2 % respectively. The chromium removal efficiency of activated coffee husk carbon was less than 90 % when the solution pH was increased above 5.It was 87.1 %,72.4 %,70 % at solution pH of 5,6,7 and 8 respectively. The decrease in chromium adsorption efficiency of activated coffee husk carbon was seen from 98.2 % -70 % when the solution pH increased from 2-8 respectively.

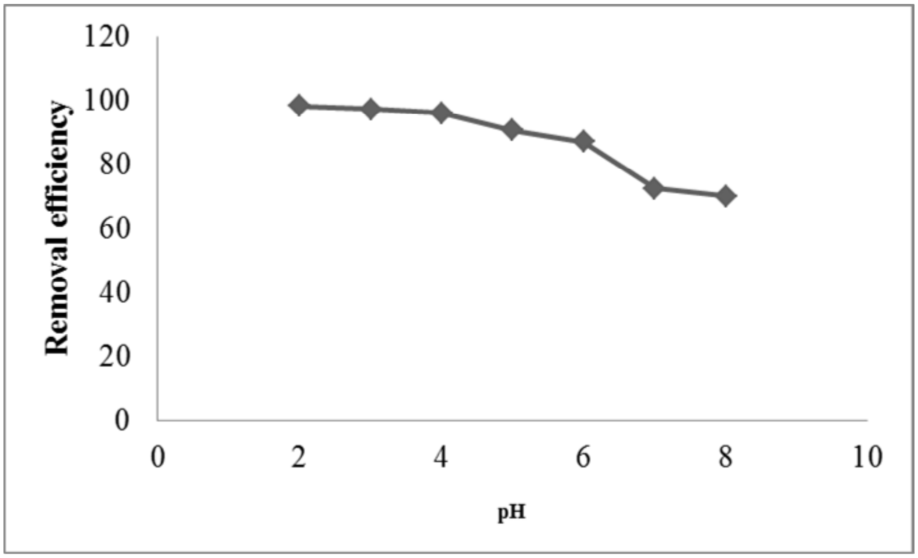

Fig.9. Effect of pH for the adsorption of Cr (VI) ions onto activated coffee husk carbon (Conditions; adsorbate initial concentration: 100 mg/l; adsorbent dose: 1g/100 ml; agitation speed: 150 rpm; contact time: 60 minutes).

### 5.2.3 Effect of stirring speed

The effect of the sorbent/sorbate system on adsorption of chromium from aqueous solution was studied at optimum conditions of contact time and pH of the solution by dissolving 1gram of activated coffee husk carbon with 100 ml chromium solution containing 100 mg/l of chromium concentration. The effect of stirring sorbent/sorbate system was monitored at low, medium and high- agitation speeds (90, 100, 120, 150, 200 rpm). The results shown that chromium adsorption of activated coffee husk carbon rapidly increased from 65.67 % to 98.6 % when the stirring speed increased from low to medium agitation speed (90 to 150 rpm). The adsorption of chromium on activated coffee husk carbon at each stirring speed was found to be 65.67 %, 75.22 %, 92.27 %, 98.6 % and 98.2%.This result indicates the percentage adsorption of chromium on this specific adsorbent decreased when the agitation speed increased above 150 rpm. As a result, the optimum stirring speed for adsorption of chromium on activated coffee husk carbon was taken as 150 rpm.

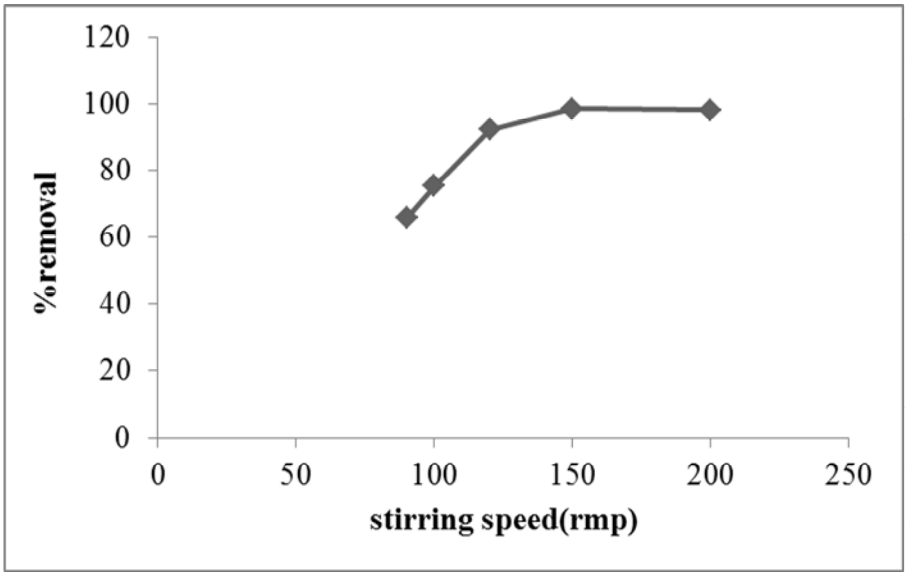

Fig.10. Effect of stirring speed on Cr (VI) ions adsorption (conditions; adsorbate initial concentration: 100 mg/l; pH: 2.0; contact time: 60 minutes; adsorbent dose: 1g/100 ml)

### 5.2.4 Effect of initial concentration

The percentage removal of Cr (VI) was studied by varying Cr (VI) ions concentration from 80 to 300 mg/l stirring with 1.0 g of activated coffee husk carbon keeping other parameters at optimum conditions. It was evident from the result that as the concentration of chromium ions in the solution increased the percent adsorption of chromium on activated coffee husk decreased rapidly from 98.91% to 57.11% when initial chromium concentration increased from 80 mg/l to 300 mg/l respectively. But the actual amount of chromium ions adsorbed per unit mass of the activated coffee husk carbon was increased with increasing in chromium ions concentration in the aqueous.

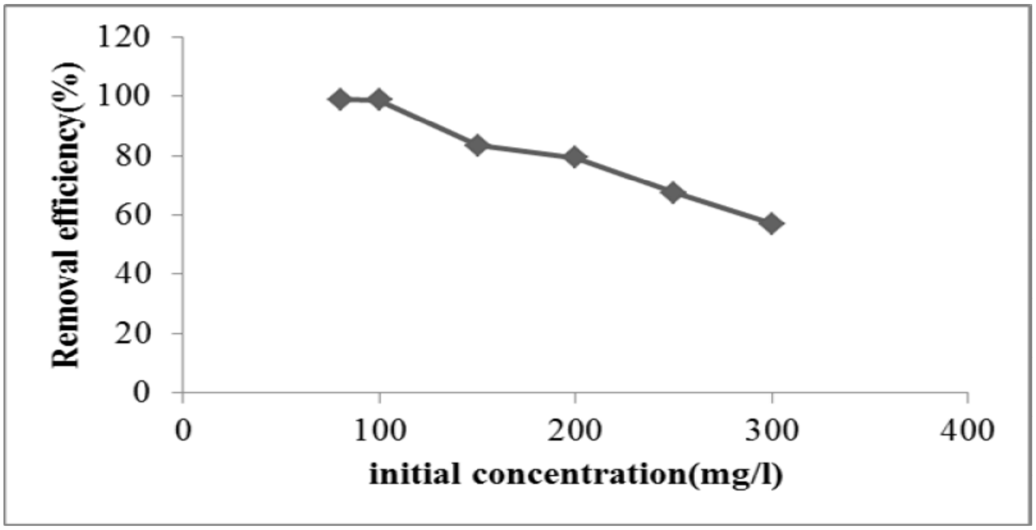

Fig.11. Effect of initial Cr (VI) ions concentration (conditions; pH: 2.0; adsorbent dose: 1g/100 ml, agitation speed: 150 rpm, contact time: 60 minutes)

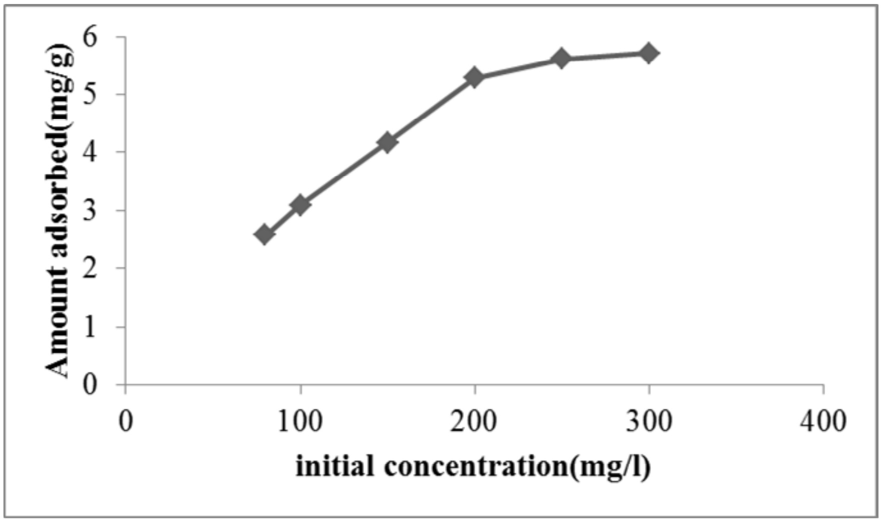

Fig.12.Effect of initial concentration (conditions; pH: 2; adsorbent dose: 1g/100 ml; agitation speed: 150 rpm; contact time: 60 minutes)

### 5.2.5 Effect of adsorbent dose

The different activated coffee husk carbon doses (0.5, 1.0, 1.5, 2.5 and 3.0 g/100 ml) were studied to see the effect on chromium adsorption keeping other parameters at optimum conditions. The results revealed that chromium removal efficiency as 85%, 97.78%.98.7%, 99%, 99.6% for activated coffee husk carbon dose of 0.5, 1.0, 1.5, 2.5 and 3 g respectively. It was evidenced that with increase in activated coffee husk carbon dose, increased the percentage adsorption of chromium. However, unit adsorption of chromium ions was decreased with increasing in activated coffee husk carbon dose (fig.14).

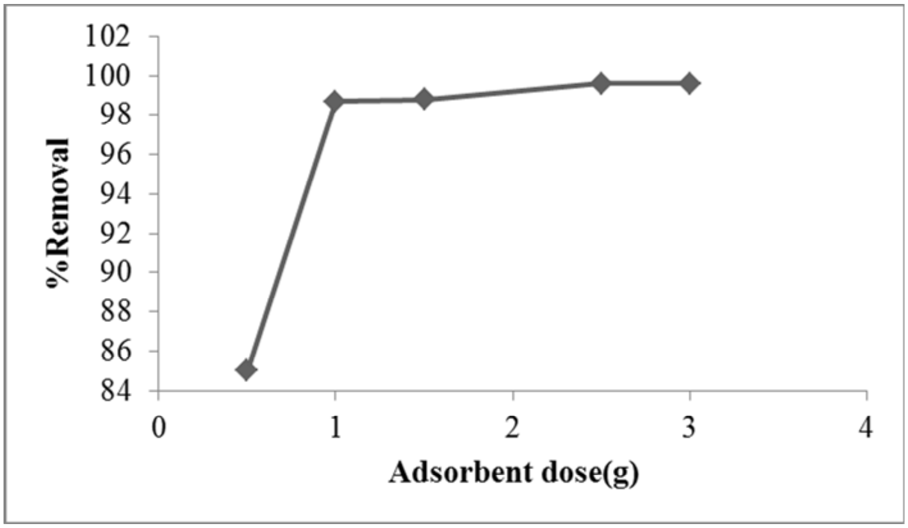

Fig.13. Effect of adsorbent dosage on adsorption of Cr (VI) ions; adsorbate initial concentration: 100 mg/l, contact time: 60 minutes; pH 2, agitation speeds: 150 rpm).

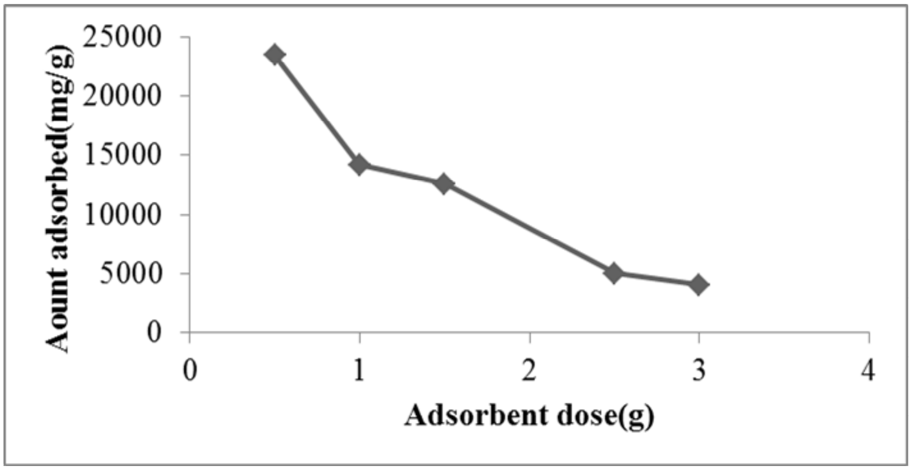

Fig.14. Effect of adsorbent dosage on adsorption of Cr (VI) ions; adsorbate initial concentration: 100 mg/l, contact time: 60 minutes; pH 2, agitation speeds: 150 rpm).

## 5.3 Adsorption Isotherm analyses

### 5.3.1 Langmuir isotherm

The results of adsorption isotherm analysis showed the values of the intercept for Langmuir isotherm found to be -6.527 while the slope was 5.997. It was also evidenced that the correlation coefficient of Langmuir isotherm was determined to be ($R^2$=0.998).

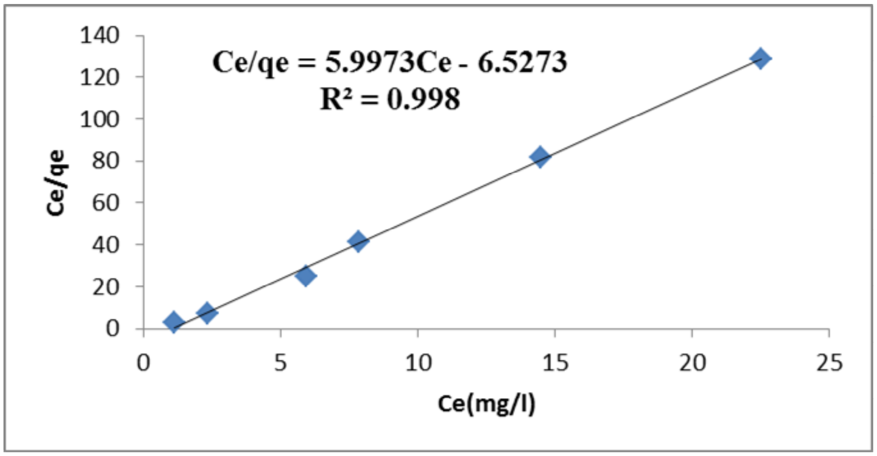

Fig.15. Langmuir adsorption isotherm for Cr (VI) ions adsorption by activated coffee husk carbon at contact time of 60 minutes

### 5.3.2 Freundlich isotherm

The value of Freundlich isotherm adsorption capacity and the adsorption intensity were calculated to be -2.884 and 4.234 respectively. It was also evidenced that the correlation coefficient of Freundlich isotherm was determined to be ($R^2$=0.968).

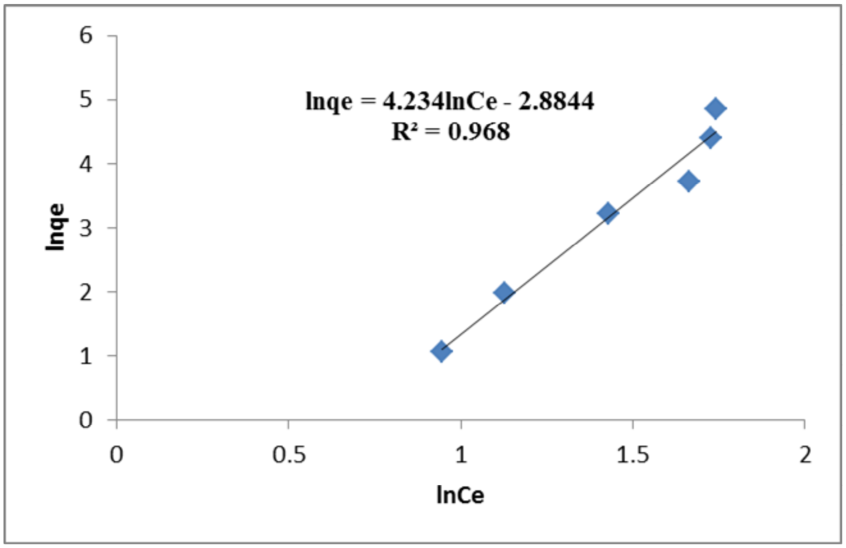

Fig.16. Freundlich Adsorption Isotherm for Cr (VI) ions Adsorption by Activated coffee husk Carbon contact time of 60 minutes.

## 5.4 Adsorption kinetics analysis

### 5.4.1 Pseudo-first order kinetics

The results of pseudo-first order kinetic plots for the adsorption of Cr (VI) ions onto activated coffee husk carbon revealed a negative relationship between the rates of Cr (VI) ions adsorption with contact time. The correlation coefficient, ($R^2$ =0.948) of pseudo-first order kinetic model was calculated from the linear plots of ln (qe-qt) vs t.

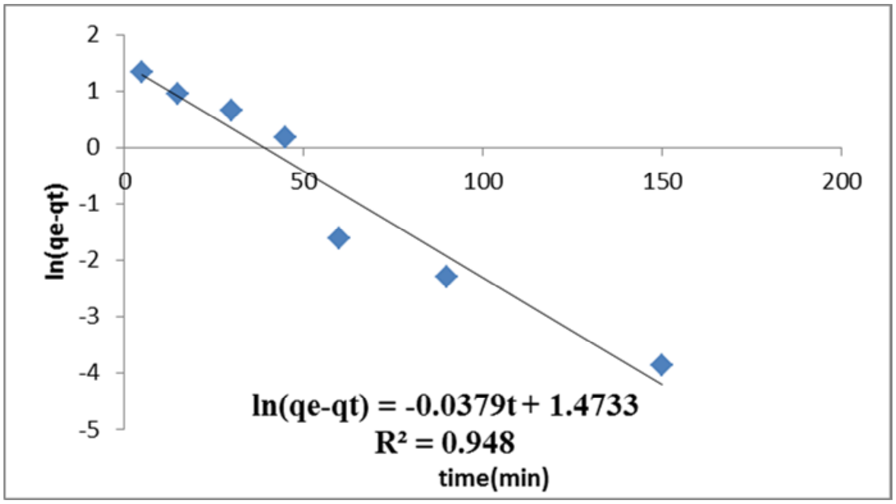

Fig.17. Pseudo-First Order Kinetic Plots for the adsorption of Cr (VI) ions onto activated coffee husk carbon

### 5.4.2 Pseudo-second order kinetic model

The results of pseudo-second order kinetic plots for the adsorption of Cr (VI) ions onto activated coffee husk carbon showed positive relationship between the rates of Cr (VI) ions adsorption with contact time. The correlation coefficient, ($R^2$ =0.998) of pseudo-second order kinetic model was calculated from the linear plots of t/qt vs t.

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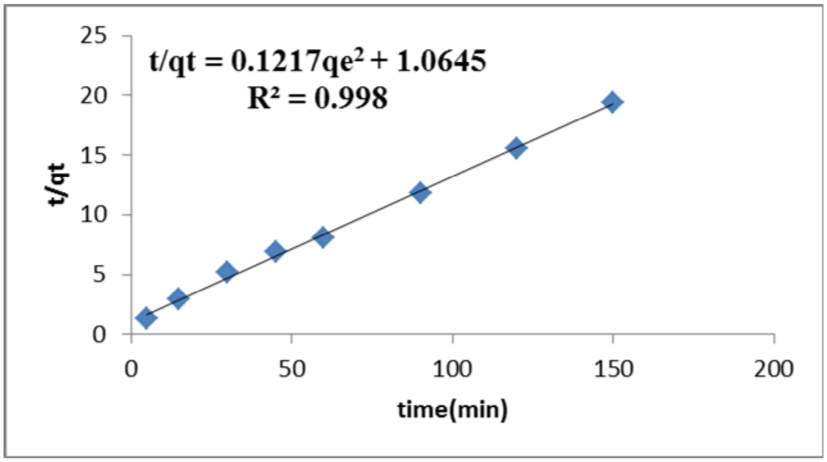

Fig.18. Pseudo-Second Order Kinetic Plots for the adsorption of Cr (VI) ions onto activated coffee husk carbon

Table 2. Langmuir and Freundlich Isotherm Constants for the Adsorption of Cr (VI) Ions onto Activated Carbon

| Adsorbent | Langmuir isotherm constants | | | Freundlich isotherm constants | | |
|---|---|---|---|---|---|---|
| ACHC | $\frac{1}{axb}$ | $\frac{1}{a}$ | $R^2$ | $\frac{1}{n}$ | Kf | $R^2$ |
| | -6.5273 | 5.997 | 0.998 | 4.234 | -2.884 | 0.968 |

Table 3.The Adsorption Kinetics Model Rate Constants for Adsorption of Cr (VI) Ions onto Activated coffee husk Carbon

| Asdsorbent | Pseudo- First Order | | | Pseudo-Second Order | | |
|---|---|---|---|---|---|---|
| | $K_1$ (min$^{-1}$) | $qe_1$ (mg/g) | $R^2$ | $K_2$ (gmg-$^{1}$min$^{-1}$) | $q_2$ (mg/g) | $R^2$ |
| ACHC | $6.238 \times 10^{-2}$ | 8.449 | 0.948 | $-1.18 \times 10^{-1}$ | 62.03 | 0.998 |

## 5.5 Applicability to industrial wastewater

It was evident that percentage adsorption of chromium from real wastewater on activated coffee husk carbon increased with contact time keeping other parameters as optimized in aqueous solution. The increase in adsorption was seen up to 88% for the contact time of 60 minutes. The maximum percentage adsorption reached to 88.9% at contact time of 150 minutes but change in percentage adsorption was negligible after 60 minutes (Fig.19).

Adsorption experiments were carried out at different pH values including pH 3.85, which is the pH of the waste effluent and at pH 2 which is the optimum pH for removal of Cr (VI) ions from aqueous solution. The percentage removal was 89%, 88.7%, 87% at pH 2, 3 and 3.85 respectively (Fig20).

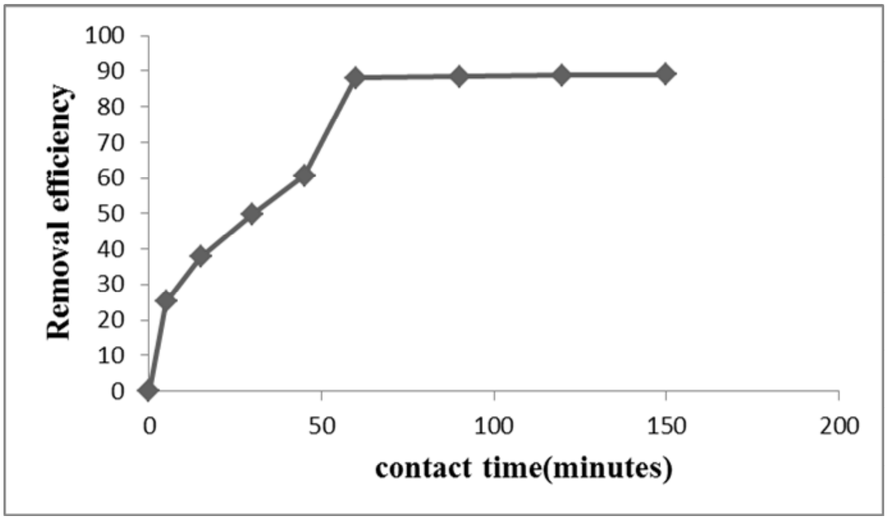

Fig.19. Effect of contact time on Cr (VI) ions adsorption from real wastewater (Optimum conditions; pH: 2.0; adsorbent dose: 3 g/100 ml, concentration: 100 mg/l, agitation speed: 150 rpm)

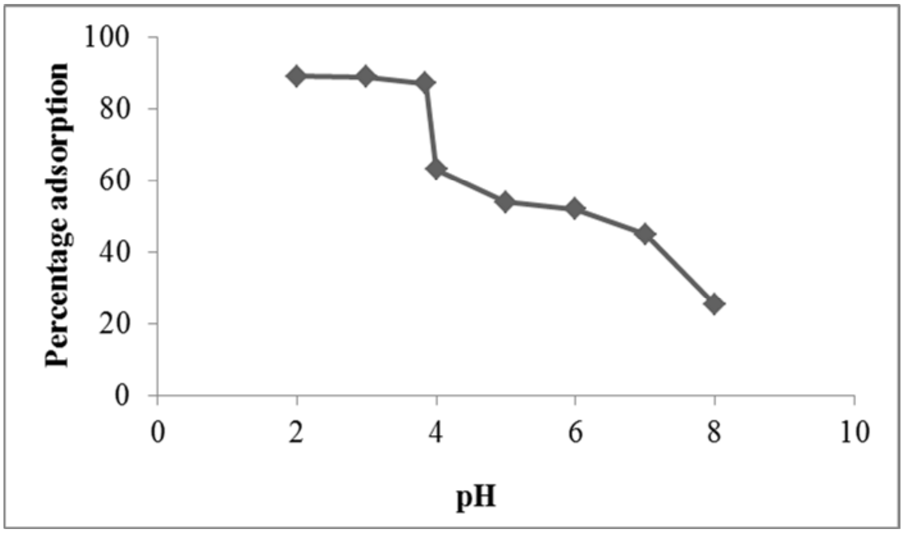

Fig.20. Effect of pH on Cr (VI) ions removal from real wastewater (Optimum conditions; adsorbent dose: 3 g/100 ml, concentration: 100 mg/l, agitation speed: 150 rpm, Contact time 60 minutes)

# CHAPTER: SIX

# DISCUSSION

The adsorption of Cr (VI) ions on activated coffee husk carbon was 70.7% at contact time of 5 minutes. It was increased to 97.2% when time passes to 60 minutes. Thereafter, further increase in contact time, the percentage removal almost remained constant (Fig.8). This result evidenced that increasing contact time after 60 minutes is simply wastage of time because the increase in adsorption efficiency after 60 minutes was insignificant.

This study is in line with the study of Veena *et al., (*2012) the maximum of 92% removal was observed at equilibration time of 60 minutes. Other similar studies have been conducted by Ahmed *et al.,* (2012) using rice husk carbon as an adsornent.This showed increase in contact time up to 150 minutes increased adsorption to 96% beyond that there was no further increase in percentage adsorption. Therefore, activated coffee husk carbon is a good candidate for the adsorption of chromium from contaminated water within short period of contact time as compared to other adsorbents compared to these literatures.

The increase on adsorption might be the availability of more adsorption sites during initial stages. The failure of adsorption with progress in contact time could be explained by the reduction of availability of adsorption sites on activated coffee husk carbon. This is because the adsorbent was progressively used up as time passes and increased the formation of adsorbate film on the active sites of activated coffee husk carbon which might be difficult to occupy due to repulsive forces between adsorbate ions on the solid and in the solution.

The influence of pH on the adsorption of Cr (VI) ions onto activated coffee husk carbon was examined in the pH range of 2 to 8.The adsorption was highly dependent on the pH of the adsorbate solution. The adsorption efficiency rapidly decreased from 98.2 % -70 % as the pH of the solution increased from 2 to 8 (Fig.9). It is in agreement with the study of Suresh *et al., (*2012) on which 92.2% and 91.4% adsorption of chromium was seen at pH of 2 and 3 respectively. The study conducted by Maryam *et al., (*2011) using Almond Green Hull showed over 94.14% adsorption at pH 6.

This could be explained by the surface chemistry of the activated coffee husk carbon in aqueous solution of chromium. Because under acidic conditions, the surface of the activated coffee husk carbon might be highly protonated. This neutralizes the negatively charged adsorbate, $Cr_2O_7^{2-}$ ions, thereby reducing hindrance to the diffusion of dichromate ions which favors adsorption of Cr (VI) in the anionic form.

The decrease in the adsorption efficiency at higher pH could be attributed to the species of chromium in the solution and surface properties of activated coffee husk carbon. With increase in pH, the degree of protonation of the surface reduces gradually and the solution becomes basic, increasing the concentration of $OH^-$ ions in the solution which hinder the diffusion of Cr (VI) ions.

At higher pH values chromate ions ($CrO_4^{2-}$) is the dominant species (Fig.9) and there might be competition between $OH^-$ and chromate ions ($CrO_4^{2-}$). The net positive surface potential of activated coffee husk carbon decreased resulting in the weakening of electrostatic forces between sorbent/ sorbate system, which ultimately favors reduction of chromium adsorption capacity. This shows that the activated coffee husk carbon is effective for the removal of chromium from aqueous solution under acidic environment up to pH 5.

The effect of stirring on sorbent/sorbate system was studied at agitation speeds of 90, 100, 120, 150, 200 rpm.When the stirring speed increased from 90 to 200 rpm,the percentage adsorption was increased up to 150 rpm and decreased at 200 rpm. The maximum removal was 98.6% at 150 rpm (Fig.6). This agreed with the research conducted by Veena Devi *et al., (*2012) using activated carbon prepared from coconut shell which showed an increase in adsorption from 66.66 % to 97.77 %, when the agitation speed increased from 90 to 200 rpm.

The possible reason for percentage reduction above 150 rpm of agitation speed might be due to physical adsorption between adsorbate and adsorbent. When agitation speed is increased the adsorbate could be returned to the bulk solution due to weak Van Dar Waals forces between sorbent/sorbate systems. Therefore, the adsorption of chromium on activated coffee husk carbon depends on agitation speed sorbent/sorbate system.

The effect of initial chromium concentration on adsorption was studied at different concentrations keeping other parameters at optimum conditions. Increasing initial concentration from 80 mg/l to 300 mg/l decreased the % removal from 98.91% to 57.11 %( Fig.11). Similar study by Ahmed *et al.,* (2012) showed the reduction in percentage adsorption on rice husk from 95.2% to 45% when the initial concentration increased from 20 mg/l to 100mg/l.

The increase in percent adsorption at lower initial concentration might be explained based on the number of moles. The ratio of the initial number of moles of chromium ions to the available surface area of activated coffee husk carbon could be larger at lower chromium concentrations and subsequently the fractional adsorption became independent of initial concentration of chromium in the solution. However, the rapid decrease in percentage adsorption at higher chromium concentrations could be explained based on available active sites on the adsorbent. The available sites of activated coffee husk carbon became fewer at higher concentrations, and hence the percentage adsorption of chromium on activated coffee husk carbon could depend upon the initial concentration of chromium in the solution.

As a result, activated coffee husk carbon is highly efficient in removing chromium from Tannery wastewater even at higher concentrations.

The adsorption of chromium was also studied at different doses (0.5, 1, 1.5, 2.5 and 3 g/100 ml) of activated coffee husk carbon. It was evident that with increase in activated coffee husk carbon dose, the percentage adsorption of chromium increased up to activated coffee husk carbon dose of 2.5 g/100 ml; thereafter the increase in activated coffee husk carbon dose fails to bring the increase in the percentage adsorption of chromium ions from the aqueous solution (fig.13). However, unit adsorption was decreased in increasing in activated coffee husk carbon dose (fig.9).

The increase in adsorption with dose might be due to increase in adsorbent surface area. The increase in adsorbent surface area could increase availability of more binding sites for adsorption. The decrease in adsorption with increase in adsorbent dose above 2.5 g/100 ml could due to decrease in the ratio of mass of adsorbent to the volume of adsorbate which reduced the mixing speed of adsorbent with adsorbate solution.

The decrease in unit adsorption with increase of dose might be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. This result shows that activated coffee husk carbon can be a good candidate for adsorption of chromium from contaminated water with minimal dose.

The applicability of the activated coffee husk carbon for the adsorption of chromium from actual industrial waste water was checked. It was evident that adsorption of chromium on activated coffee husk carbon from Tannery wastewater was 88% at contact time of 60 minutes (Fig.19).The adsorption of chromium was found to be 87% at pH 3.85 and 89% at pH 2 (Fig.20). The percentage removal of chromium using activated coffee husk carbon showed slight difference when compared with aqueous solution. The percentage removal at all optimized parameters in aqueous solution was 99.6% but reduced to 89% from real wastewater at the same optimized parameters. Sekhar *et al., (*2012) study in the literature supported that percentage reduction of chromium adsorption from 96% to 88%, 96% to 88.4%, and 96% to 84.5 in the presence of $SO_4^{2-}$ , $Cl^-$ and $PO_4^{3-}$ using Bhringaraj leaves powder. Therefore, activated coffee husk carbon can be applicable for removal of chromium from industrial waste water.

The reduction in percentage adsorption might be due to presence of other competing anions sorbed to solid surface of activated coffee husk carbon. Therefore, the presence of other anions in real wastewater interfere the active site of the adsorbent and reduce the adsorption efficiency.

To describe the experimental data of adsorption the Langmuir and Freundlich isotherm models were checked. When the correlation coefficient values compared for both isotherm models, it was seen that the Langmuir isotherm model (fig.15) with $R^2$=0.997, yields a much better fit than the Freundlich isotherm model (fig.16) with $R^2$=0.968. This study is slightly better than the study conducted by Qaiser *et al.,*and Dhanakumar *et.al,*(2009) which showed better fit of Langmuir model with correlation coefficient $R^2$= 0.98 and $R^2$ =0.94 respectively. This showed the formation of a monolayer of adsorbate on the outer surface of the activated coffee husk carbon.

The adsorption kinetic models were examined by each linear plot of ln (qe-qt) vs. t, and (t/qt) vs.t for pseudo-first order and pseudo-second order models respectively. The correlation coefficient, $R^2$, was calculated from these plots. However, the correlation coefficient, $R^2$, showed that the pseudo-second order model, fits better the experimental data with $R^2$=0.997 (Fig.18) than the pseudo-first order model with $R^2$ =0.948. The study by Mohamed *et al., (*2012) and Isa *et al.*, (2008) showed that the better fit of pseudo-second order model with $R^2$=0.990 for both studies. These results indicated that the best fit of pseudo-second order model for activated coffee husk carbon.

The experimental results for the adsorption of Cr (VI) ions onto activated coffee husk carbon showed rapid initial adsorption rate followed by a slower rate (fig.8). Initially, the adsorption sites might be open and the metal ions interact easily with the sites. As a result, higher rate of adsorption could be seen. Moreover, the concentration difference between the bulk solution and the solid-liquid interface) might be higher initially which allowed to a higher adsorption rate. The slow adsorption of chromium on activated coffee husk carbon after 30 minutes might be due to slower diffusion of solute into the interior of the activated coffee husk carbon.

# CHAPTER: SEVEN

# CONCLUSION AND RECOMMENDATION

## 7.1 Conclusion

Based on the findings the following conclusions are drawn:

Activated carbon was prepared from coffee husk by chemical activation in phosphoric acid at different activating conditions. Activated coffee husk carbon was effective for chromium adsorption in both synthetic and industrial wastewater. The optimum removal efficiency of chromium from polluted water using activated coffee husk carbon was achieved at contact time of 60 minutes. The rate of adsorption was decreased with increasing contact time beyond the equilibrium time.

The percentage removal of chromium using activated coffee husk carbon was highly pH dependent and the results showed a negative relationship with pH. The activated coffee husk carbon was very efficient in removing chromium from polluted water at lower pH values below pH 5.The maximum chromium removal efficiency of activated coffee husk carbon was found at pH of 2.

The adsorption of chromium on activated coffee husk carbon from polluted water was also dependent up on agitation speed of sorbent/ sorbate system. The study showed the increase in adsorption with increasing agitation speed of sorbent/sorbate system up to 150 rpm. The activated coffee husk carbon was effective at stirring speed of 150 rpm beyond this the removal efficiency was decreased.

The initial concentrations of chromium negatively affect adsorption of chromium on activated coffee husk carbon. The percent adsorption of chromium decreased as increase of initial concentration of chromium.

The dose of activated coffee husk carbon showed a positive relationship with chromium removal efficiency. Increase in dose of activated coffee husk carbon up to 2.5 g/100 ml was efficient in removing chromium from polluted water containing chromium concentration of 80 mg/l.The increase in adsorption of chromium on activated coffee husk carbon dose above 2.5 g/100 ml was insignificant.

The experimental data onto activated coffee husk carbon was well described by Langmuir isotherm model. The experimental data showed the formation of a monolayer of adsorbate on the outer surface of the activated coffee husk carbon.

The Kinetics of adsorption system of Cr (VI) ions activated coffee husk carbon was best described by pseudo -second order model. The adsorption of Cr (VI) ions onto activated coffee husk carbon showed rapid initial rate followed by a slower rate.

## 7.2 Recommendation

Future studies should be focused on:

- ☑ Desorption experiments and factors affecting desorption in order to recover chromium from the adsorbed surface of activated coffee husk carbon
- ☑ Investigating the regeneration of the spent activated coffee husk carbon
- ☑ Conducting column experiments even better removal efficiency will be obtained

Ministry of water being with Environmental protection authority experts should:

- ☑ Consult industrial association sectors to use coffee husk for treatment of chromium contaminated wastewaters

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# ANEX

**Geological Survey of Ethiopia**
**Geosciences Laboratory Directorate**
**Result Form**

**Case Team: - Chemical: Lab Section: - Silicate** ☐ **Gold & Base metal** ☐ **Water** ☐
**Hydrocarbon** ☐
**Case Team: - Mineralogical: Lab section: - Mineralogy** ☑ **Physical** ☐
**Client /Originator Name:** Dessalew Berihun (Jimma University)
**Client Category:- Survey** ☐ **Gov.** ☑ **Pvt.** ☐
**File name:-** 6439/13GOV **Area Ref-:-** Jimma University **No of Samples :-** 1 **Sample No.** D-27
**Sample Type:-** Powder **Lab No:-** 6439/13
**Type of Analysis:-** XRD **Preparation required:-** powder <63mic. **Date Submitted:-** 11/04/2013

**I) Identified Minerals**

None

Geological Survey of Ethiopia Central Geological Laboratory

**II) Remark note:-** (The sample is amorphous no crystalline material.)

**Described By / Analysts** **Checked by** **Date Completed** 17/04/2013

Workelul G/K

[illegible] G/Kirstos
Mineralogy & Physical Analysis
Case Team Co-ordinator

Page 1 of 1

**Fig. 11 X-ray Diffraction laboratory Profile activated coffee husk carbon**

## DECLARATION

This research is my original work; it has not been presented in this and any other university. All sources of materials used in this work have been duly acknowledged.

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…………...

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June, 2013
Jimma, Ethiopia