

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY



Thesis On

**ADSORPTIVE REMOVAL OF CHROMIUM (VI) FROM WATER
USING ACTIVATED CARBON OF *enseteventricosum midrib* LEAF AND
*erythrina abyssinica***

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Table of Contents

ACKNOWLEDGEMENT	ii
List of Tables	iv
List of Figures	v
List of Abbreviation.....	vii
ABSTRACT.....	viii
1. INTRODUCTION	1
1.2 Statement of the problem	3
1.3 Objectives of the study.....	4
1.3.1 General objective	4
1.3.2 Specific objective.....	4
1.4 Significance of the study	5
2.1. Chromium	6
2.2 Removal of Chromium	6
2.3 Adsorption and Adsorption phenomenon	7
2.5 Water treatment by adsorption.....	9
2.6Bio-adsorbents	9
2.7Low-cost adsorbents	10
2.8Types of materials for contaminant removal	10
2.11 Activated carbons (ACs).....	10
2.12 Isotherm models for adsorption	11
3.1 Description of the Study Area.....	14
3.2 Materials and Equipment	14
3.3 Chemicals and Reagents	14
3.5 Adsorbent collection and preparation	15
3.5.1 Preparation of adsorbent (tella).....	15
3.5.2 Preparation of adsorbent (Coffee).....	15
3.5.3 Preparation of adsorbent (Barley)	15
3.5.4 Preparation of adsorbent (Ash, pineapple, clay, red scoria ...).....	15
3.5.5 Screening of adsorbents	15
3.6 Physiochemical Characterization of sample	17
3.6.1 Moisture content	17

3.6.2 Volatility matter	18
3.6.3 Ash preparation and its percent.....	18
3.6.4 Fixed Carbon Content	19
3.6.5 Surface Area of the adsorbents	19
3.6.6 Point of zero charge	19
3.7 Characterization of Adsorbent samples	20
3.8 Preparation of working Cr (VI) and DPC solutions for UV–Vis’s analysis	20
3.9 Batch adsorption studies	20
3.9.1 Effect of time	21
3.9.1.1 Kinetic study for adsorption of chromium	21
3.9.1.2 Intraparticle diffusion model.....	22
3.9.2 Effect of pH.....	22
3.9.3 Effect of initial concentration	23
3.10 Adsorption isotherm models	23
3.11 Desorption process.....	24
4 RESULTS AND DISCUSSION	25
4.2. Physiochemical Characterization of sampl	26
4.3.1 Moisture content	26
4.3.2 Ash value	26
Volatility	28
4.3.4 Specific surface area determination	27
4.3.5 Point of zero charge	28
4.4.1 Fourier transforms infrared (FT-IR) spectrum analyses of EA powder.....	30
4.6 Batch adsorption studies	34
4.6.1 Effect of contact time.....	34
4.7 Kinetic study for adsorption of chromium	35
4.8 Intraparticle diffusion.....	38
4.9 Effect of pH.....	40
4.10 Effect of chromium (VI) Concentration.....	42
4.10.1 Adsorption isotherm model.....	43
4.11 Desorption of adsorbents	45
5. Conclusions and Recommendation	47
5.1 Conclusion	47

5.2 Recommendation	47
6. REFERENCES	48

List of Tables

Table: 1.0 Toxic Metal in Industrial Effluents

Table: 2.0 Hazardous effects of some heavy metals

Table: 3.0 List of Instruments used during the whole experiment

Table: 4.1. The analyses of (AC-EVML) and (AC-EA) Activated adsorbents

Table: 4.0. Screened adsorbents with their percent removal

Table: 4.2. Parameter for kinetics study

List of Figures

Figure: 1 Heavy metal density

Figure: 2: Compounds of chromium used for several purposes

Figure: 3 Adsorption monolayers

Figure: 5 Relationships between the three components of an adsorption system

Figure: 3.1 Preparation of adsorbents and pretreatments

Figure: 3.2 Activated carbons prepared from EVBL and EA

Figure: 4.0 FTIR spectra of EA-AC and the Cr (VI)-loaded EA-AC, Cr (VI)

Figure: 4.1 FTIR spectra of EVML-AC and the Cr (VI)-loaded EVML-AC, Cr (VI)

Figure: 4.3. XRD diffract grams of EA and Cr-loaded EA

Figure: 4.4. XRD diffract grams of AC-EVML and Cr-loaded AC-EVML

Figure: 4.5. Percent removal for 0.1g of AC-EVML adsorbent 5mg/L concentration of chromium

Figure: 4.6. Percent removal for AC-EA adsorbent Vs contact time

Figure: 4.7. Effect of pH for the adsorption of Cr (VI) ions onto activated AC-EVML carbon

Figure: 4.8. Effect of pH for the adsorption of Cr (VI) ions onto activated AC-EA carbon

Figure: 4.9. Effect of Initial concentration for the adsorption of Cr (VI) ions AC-EVML

Figure: 4.10. Effect of Initial concentration for the adsorption of Cr (VI) ions AC-EA

Figure: 4.11. Pseudo first order for AC-EVML adsorbent

Figure: 4.12. Pseudo second order for AC-EVML adsorbent

Figure: 4.13. Pseudo first order for AC-EA adsorbent

Figure: 4.14. Intra particle diffusion for AC-EA adsorbent

Figure: 4.15. Langmuir isotherm for AC-EVML

Figure: 4.16. Freundlich isotherm for AC-EA

Figure: 4.17. Langmuir isotherm for AC-EVML

Figure: 4.18. Freundlich isotherm for AC-EVML

Figure: 4.19. Zero Point charge of AC-EVML.

Figure: 4. 20. Zero Point charge of AC-EA

List of Abbreviation

AC	Activated carbon
Cr (III)	Chromium (III)
Cr (VI)	Chromium (VI)
DPC	Diphenyl carbazide
EA	Erythrina abyssinica
EDX	Energy dispersive X-ray
EVML	Enset ventricosum midrib of leaf
FTIR	Fourier transforms infrared
PFO	Pseudo first order
PSO	Pseudo second order
SEM	Scanning electron microscopy
IARC	International agency for research on cancer
MPL	Maximum permissible level
USEPA	United state environmental protection
WHO	World Heath organizations
XRD	X- ray diffraction
UV VIS	Ultra-violet visible spectre photomètre

ABSTRACT

Discharge of chromium containing water solution into the environment poses a serious environmental and health problem. There is need for environmentally friendly and cost-effective methods for removal of chromium containing water. The main objective of present study is to investigate the adsorptive removal of chromium (VI) from aqueous solution using activated Carbon of *Erythrinaabyssinica* (AC-EA) & *Enseteventricosummidrib leaf* (AC-EVML) because it is high removal capacity, low cost and easy accessibility. Activated Carbon EVML and EA adsorbents were prepared Sulfuric acid activation method at 100 °C. Characterization of these adsorbents such as physicochemical parameter, point of zero charge, Fourier transform infrared radiation spectroscopy, surface area and X-ray diffraction was done prior to bio sorption process. Activated adsorbents were assessed in batch mode adsorption experiment for percentage chromium removal and milligrams per gram chromium uptake as a function of contact time, pH, and initial concentration. Results showed maximum removal efficiency for Cr (VI) at 9 h and 6 h contact time, by AC-EVML and AC-EA, respectively at 0.1 g and pH 2. Percentage removal of Cr (VI) increased with increasing contact time (from 0.5 h to 12 h). Sorption kinetics of chromium adsorption by activated adsorbents was predicted reliably using a pseudo-first order, pseudo-second order and intra particle diffusion model. The kinetic adsorption data well fitted to pseudo-second order. Equilibrium uptakes were evaluated using Langmuir, Freundlich and Temkin adsorption isotherm models and the equilibrium data well fitted into Langmuir isotherm. The study demonstrated the efficiency of activated adsorbents and presents it as a viable low-cost adsorbent for bioremediation.

Key: Chromium, efficiency, capacity, adsorption isotherm, kinetic isotherm, AC-EVML, AC-EA

1. INTRODUCTION

Water pollution using heavy metals including Cr(VI) is a serious environmental concern due to their toxic effects.¹ The damages caused to the environment are due to industrial and domestic waste water and it adversely affect the human health.² The main sources of these metals are mining, tannery, battery manufacturing industries, fossil fuel, metallurgical and chemical manufacturing.³ The modern chemical industries are based largely on catalysts, many of which are metals or metal compounds; production of plastics, such as polyvinyl chloride, involves the use of metal compounds, particularly as heat stabilizers and so forth.⁴ Metals such as Cd, Cr, Co, Cu, Zn, Pd, Hg, Ni, Ag, and Sr and metalloids such as Se, As and Sb are toxic beyond the limit set at trace levels. Most of these trace elements are transition metals with variable oxidation states and coordination numbers.⁵

A marked increase in population, industrialization and urbanization in the last few decades has resulted in pollution of water via Cr (VI). This will directly or indirectly affect the environment. Chromium and its alloys have wider application in industries such as metal finishing, dyes, pigments, inks, glass, ceramics, tanning, textile, wood preserving and glues industries.⁶ Cr (VI) has been declared as a powerful carcinogenic agent by the International Agency for Research on Cancer (IARC) in 1982. The U.S. Environmental Protection Agency (USEPA) approved 0.1 mg/L as the maximum allowable concentration of Cr (VI) in drinking water. Excessive intake of chromium by human's leads to hepatic and renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation. Maximum acceptable concentration of chromium in drinking water recommended by WHO is 0.01g.⁷

A number of treatment methods for the removal of chromium ions from aqueous solutions have been reported, mainly reduction, ion exchange, electro dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, and chemical precipitation.⁸ However, all these technologies have their inherent advantages and limitations in application. Most of the methods suffer from some draw backs such as incomplete chromium removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method.⁹ In the present investigation, to estimate the amount of chromium ions present

in its aqueous solutions before and after treatment and the removal of chromium from water solution using AC-EVML and AC-EA as an adsorbents were attempted. Though many conventional adsorbents are used for the effective removal of chromium (VI), AC-EVML and AC-EA.¹⁰ The present work is also aimed at fixing the optimal conditions such as initial concentration, pH and equilibrium time (for batch mode technique) for effective removal of chromium.¹¹

1.2 Statement of the problem

Chromium compounds are reported as priority pollutants, due to their mobility in natural water ecosystems and toxicity. They are stable and persistent environmental contaminants.¹² Cr exists in many oxidation states with Chromium (III) and Chromium (VI) being the primary existing oxidation states in the environment.¹³ Chromium (VI) is highly toxic, mutagenic and potentially carcinogenic to living organisms. Accumulation of Chromium (VI) in aqueous waste streams is therefore of great concern.¹⁴ Chromium carcinogenicities to humans and other living organisms has promulgated extensive research on its treatment technologies with varying levels of success; generally, the most efficient methods come with a significantly higher cost burden. Chromium (VI) from these sources can be achieved by physicochemical treatment processes such as ion exchange, coagulation-flocculation, chemical precipitation, evaporation, membrane filtration, electrochemical treatments, and adsorption.¹⁵ Adsorption processes have received significant attention due to several reasons, especially for those chromium ions that cannot be removed efficiently by other technique. Hence, it is expedient to device or seeks alternative methods of removing chromium (VI) from aqueous solution by using locally available and cheap adsorbents. To this effect, the research examines potential of to be **AC-EVML** and **AC-EA** prepared as adsorbent to remove Chromium (VI).¹⁶

Based on the above introductory brief discussion, this study is aimed to answer the following question.

1. Do the biomass-based **AC-EVML** and **AC-EA** adsorbent has promising efficiency for removal of Cr (VI) from model solution?
2. What isothermal and kinetic model does this adsorption process fits to?

1.3 Objectives of the study

1.3.1 General objective

The main objective of the research was to investigate adsorptive removal of Cr (VI) from water by using activated AC-EVML and AC-EA in a batch system

1.3.2 Specific objective

- To screen adsorbents for the effective removal of Cr (VI)
- To prepare adsorbents, AC-EVML and AC-EA, for removal of Cr (VI)
- To characterize prepared adsorbents using FTIR and XRD
- To optimize adsorption influencing parameters
- To evaluate adsorption capacities of activated AC-EVML and AC-EA for Cr (VI) from aqueous solution.

1.4 Significance of the study

This study was performed to motivate the use of natural adsorbents such as activated EVML and EA for the removal of chromium from water. It will be shown that the bio-adsorbent can absorb anions, cations, non-ionic and polar contaminants. After completion this study, it will play a vital role for providing substantial baseline information for treatment and purification water from Cr (VI). This study also shall provide a better solution to hexavalent chromium pollution in aqueous phase by developing an efficient activated adsorbent. It will provide an ideal technology to utilize and convert natural adsorbent into valuable product i.e., activated carbon which can be commercialized for the removal of contaminants from aqueous phase.

2. LITERATURE REVIEW

The scarcity of clean drinking water in the world has been a problem for decades. Some poisonous organic and inorganic contaminants, especially heavy metal ions such as Co(II), Ni (II), Cd (II), Pb (II), Hg (II), Cr (VI) and dyes, enter the food chain via wastewater. As a result, people, animals, and aquatic organisms are adversely affected.¹⁷

2.1. Chromium

Chromium (atomic number 24) is a steel-gray, lustrous, hard crystalline metal.¹⁸ It comprises about 0.037 percent of the earth's crust and therefore ranks 21st in relative natural abundance. Chromium (Cr) was first discovered in the Siberian red lead ore (crocoite) in 1798 by the French chemist Vauquelinite. The atomic weight is 51.99 g.mol⁻¹; specific gravity 7.18 to 7.20; melting point 1857 °C and boiling point 2672 °C.¹⁹

Chromium in its hexavalent form Cr (VI) is well known due to its health-related issues in humans including carcinogenic and mutagenic risks. Also, direct exposure to Cr (VI) can lead to lungs cancer, epigastria pain, vomiting and chronic diarrhea.²⁰ However, some of the industries that discharge wastewater containing chromium include fertilizer, electroplating, mining processing, metal processing, tanning, paints, battery and domestic plumbing materials. Chromium exists in two different oxidation states, that is, hexavalent chromium Cr (VI) and trivalent chromium [Cr (III)].²¹ Due to the negative effects of chromium, World Health Organization (WHO) has set a maximum permissible concentration for chromium in drinking water to be 0.05 mg/L. Thus, there is need to properly treat industrial effluent prior to its discharge into environment.²²

2.2 Removal of Chromium

The conventional physical and chemical methods used for the chromium removal from wastewater include reduction, solvent extraction, precipitation, ion exchange, membrane filtration, reverse osmosis and adsorption.²³ Among various techniques, adsorption is the most promising technique to remove and eliminate Cr (VI) from drinking water. Application of ion exchange is an attractive method to remove heavy metal contaminations. Nowadays, chelating

resins are increasingly used in the removal of metal ions due to their high adsorption capacities, selectivity and durability.²⁴

2.3 Adsorption and Adsorption phenomenon

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film. Adsorption process can be influenced by a number of factors such as pH, adsorbate concentration, adsorbent dosage, and other factors.²⁵

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface, is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent.²⁶

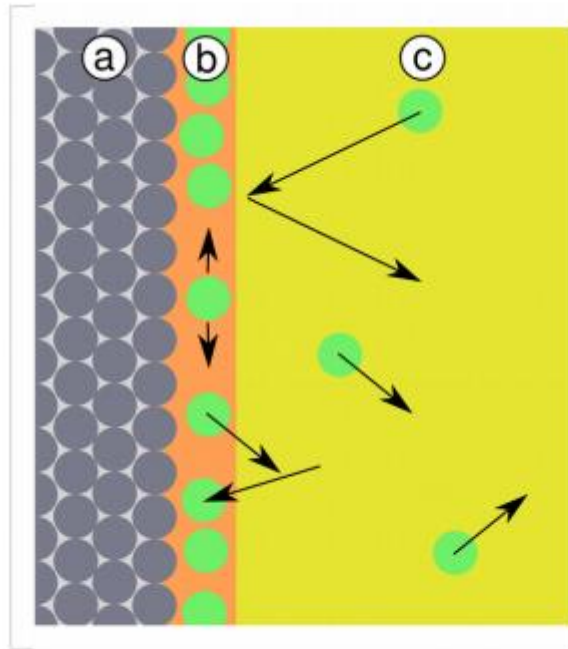


Figure 3: Adsorption monolayer

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid or liquid–solid interface. The substance being adsorbed is the *adsorbate* and the adsorbing material is termed the adsorbent.²⁷the properties of adsorbates and adsorbents are quite specific and depend upon their constituents.²⁸If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance.²⁹ On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called chemisorption. Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake.³⁰

The adsorption process is a surface phenomenon in which the adsorbate is accumulated on the adsorbent surface. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause

some of the solute molecules from the solution to be concentrated or deposited on the solid surface.³¹ In case of bulk materials, all the bonding requirements (ionic, covalent, or metallic) of the material constituent atoms are filled by other atoms in the material.³² However, the atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms, therefore they can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (an adsorbate bound to the surface by weak Vander Waals forces), chemisorption' and adsorbate tethered through covalent bonding or due to electrostatic attraction.³³

the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid for example, when a chalk stick is dipped in ink, the surface retains the color of the ink due to adsorption of colored molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside.³⁴

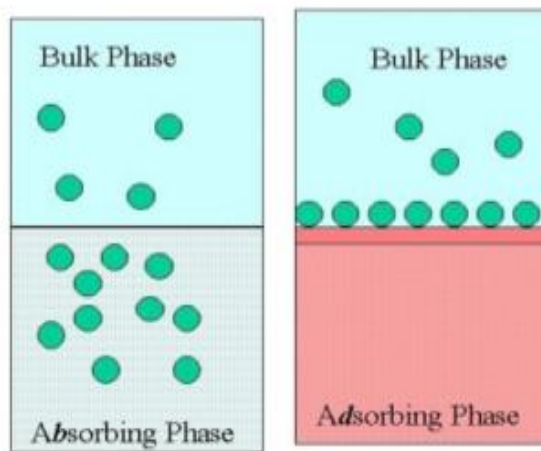


Figure 4: Absorption versus Adsorption

2.4 Water treatment by adsorption

2.4.1 Bio-adsorbents

Bio-adsorbents of chromium from aqueous solutions is relatively a new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of

chromium ions from wastewater streams.³⁵The major advantages of bio-sorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration of bio sorbent.³⁶ At low concentrations of heavy metals, the conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption are not cost-effective and suitable.³⁷ Low-cost bio sorbents are much suitable for high concentrations of metals. Various bio sorbents have been widely used for the treatment of chromium containing wastewaters.³⁸

2.4.2. Low-cost adsorbents

There are several locally existing materials that can be used for the removal of heavy metals. Low-cost adsorbents such as natural materials, agricultural wastes, modified biopolymers, or industrial by-products are found to be more encouraging in heavy metal removal due to the following considerations.³⁹ (I)They are economical, (II) they are metal selective, (III) they are regenerative, (IV) absence of toxic sludge generation (V) metal recovery and (VI) they are highly effective.⁴⁰ Recently, research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents through bio-sorption process. Moreover, biopolymers are posse a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake. The origin of the biomass must be taken into account while choosing the biomass for metal removal.⁴¹

2.5 Activated carbons (ACs) Adsorbents

ACs are adsorbents broadly applied in wastewater treatments, owing to their high surface area and high adsorption capacity.⁴² ACs prepared from algal biomass, fruit shells, agricultural wastes, sawdust, etc., may represent an accessible alternative to existing commercial products, and diverse authors have reported a considerable efficiency using them.⁴² Functional groups reported in ACs prepared from nutshells include carbonyls, phenols, lactones and carboxyl's.⁴³

2.6 Types of materials for contaminant removal

Solid materials used as adsorbents can take a broad range of chemical forms and different

geometrical surface structures. This is reflected in the range of their applications in industry, or helpfulness in laboratory practice. Adsorbents can be usually classified in five categories: ⁴⁴

- (1) Natural materials such as sawdust, wood, fuller's earth or bauxite;
- (2) Natural materials treated to develop their structures and properties such as activated carbons, activated alumina or silica gel;
- (3) Manufactured materials such as polymeric resins, zeolites or aluminosilicates;

2.7 Spectrophotometer determination Chromium from water

Spectrophotometric methods can be used for selective determination of the different chromium species using reagents to form absorbing species that present selectivity in the response. The most common method for determining Cr (VI) in aqueous solutions is based on the reaction of 1,5-diphenylcarbazide (DPC) with Cr (VI) at a pH of 2. ⁴⁵

Spectrophotometric analysis of the magenta chromogen (λ max~540 nm) which is formed by the reaction of Cr (VI) with 1,5-biphenylcarbide (DPC) in strongly acidic solution. Because of that, the development of analytical methods for speciation of Cr (III) and Cr (VI) is important compared to methods of determining these metals in total. ⁴⁶

2.8. Adsorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. In order to determine the rate limiting step during the adsorption process different kinetic models have been used to analyze the experimental data. ⁴⁷ These models include first-order, pseudo second-order and intra-particle diffusion as the most important kinetic models. Adsorption kinetics describes the rate of solute uptake, which is also responsible for the residence time needed for an adsorption study. ⁴⁸ Therefore, it is an important characteristic in defining how fast the sorption processes is carried out.

2.8.1 Pseudo first order model

First order model which is believed to be the earliest model, was developed by Langrage in 1898. To describe the kinetic process of liquid-solid phase adsorption he presented first order model as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \text{-----} 2.1$$

Where, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t and k_1 is the first-order rate constant (min^{-1}). From the plots of $\log(q_e - q_t)$ versus t , k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts.⁴⁹

Pseudo-second-order equation can be given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \text{-----} 2.2$$

2.9.2 Intraparticle diffusion model

The kinetics data were tested against the intraparticle diffusion model to identify the actual rate-controlling steps involved in the Cr (VI) sorption process. Generally, the sorption process of a sorbate by a porous sorbent can be classified as three steps as follows:⁵⁰

- (i) external mass transfer across the hydrodynamic boundary layer film surrounding the sorbent particle,
- (ii) intraparticle diffusion of the sorbate molecules within the sorbent pores either by liquid filled pores or a solid surface diffusion process, and
- (iii) Adsorption at an active site on the external or internal surface of sorbent. The third step is often considered to be extremely rapid, thus the most contribution to the rate of adsorption is film or/and pore diffusion. The intraparticle diffusion model can be represented as follows

$$q_t = k_d t^{\frac{1}{2}} + C \text{-----} 2.3$$

2. 10 Isotherm models for adsorption

There are two widely accepted and easily linearized adsorption isotherm models proposed by Langmuir and Freundlich respectively. The assumptions of the Langmuir model are: the surface consists of adsorption sites. all adsorbed species interact only with the sites and not with each other, adsorption is limited to a monolayer, adsorption energy of all sites is identical and independent of the presence of adsorbed species on the other sites.⁵¹

The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b L} \text{-----2.4}$$

Where q= uptake of species (mg/g), qmax = maximum uptake (mg/g), Ceq = equilibrium concentration in solution (mg/L), and b = constant related to energy of adsorption is the equilibrium or association constant (L/mg) and is related to the affinity between sorbent and sorbate.⁵² It is also represented as Ka. Low values of b are reflected in the steep initial slope of a sorption isotherm, indicating a desirable high affinity. Thus for “good” sorbents, a high qmax and a steep initial isotherm slope is desired. The values of qmax and KA can be found using the linear reciprocal plot of the equilibrium isotherm.

The linear form of Freundlich isotherm is given as:⁵³

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{-----2.5}$$

q where qmax is solid phase metal concentration (mg/g), k = related to adsorbent capacity, 1/n = “Heterogeneity factor” ranging from 0 to 1 and C = bulk liquid phase metal concentration.

This can be linearized by taking the natural logarithm of both sides of the equation to

3. MATERIALS AND METHODS

3.1 Description of the Study Area

The study was conducted in Jimma University located in the Oromia region of Ethiopia at a distance of around 346km south west of Addis Ababa. Different naturally available materials adsorbents were collected from Jimma city, and different chemical also collected from different laboratory such as Jimma Teachers college, Jimma technology institute and any other. Most of the research duties are done in the Jimma University Analytical Chemistry laboratory.

3.2 Materials and Equipment

The major equipment's and apparatus that were used during this thesis work includes Analytical balance (Ohaus, EP 214C Switzerland), grinder, 250 mL plastic bottles, Orbital shaker (GFL 3074 Model), Sieves (75 – 210 μm size), pH meter (model: JENWAY; 3505 pH meter), magnetic stirrer, FTIR (model: Perkin Elmer Spectrum 65), XRD, drying oven (model: Memmert, 100- 800 Germany) and Furnace (Nabertherm LHT 02/16 Germany). All glass wares (Conical flasks, Pipette, measuring cylinders, Beakers, Petri plates and Test tubes, volume metric flasks, plastic vials. UV Vis adsorption spectrophotometer (SPECORD*200 anaytikjena, GERMANY) was used to measure residual metal ion concentrations.

3.3 Chemicals and Reagents

In all experiments, distilled water was used for preparation. 2.2829 g of ($\text{K}_2\text{Cr}_2\text{O}_7$) was used for the preparation of the standard solutions for the study. Hydrochloric acid (HCl), sodium hydroxide (NaOH), and sulfuric acid H_2SO_4 and 1.5-diphenylcarbazide. The stock solution of Cr (VI) containing concentration of 1000 mg/l was prepared by dissolving 2.829 g of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ analytical grade, in 1000 mL of distilled water. The required pH of the solution was adjusted by drop wise addition of 0.1 N HCl and NaOH depending on the acidity or basicity of the sample. The desired concentrations were obtained by diluting the stock solution with distilled water to obtain concentrations ranging from 5 to 100 mg/l.⁵⁴

3.4 Adsorbent collection and preparation

3.4.1 Preparation of adsorbent (Tella)

The residual of prepared Tella which is left after drinking most of it was collected from available area left for 2 to 4 days in the sun light to dry. Then dried residue was washed to remove dirty materials. The residue again dried by sun light for next 2 to 4 days and used for adsorption study.

55

3.4.2 Preparation of adsorbent (Coffee)

Adsorbent of coffee used was prepared by normal coffee was bought from market washed to remove impurities and roasted. Then the roasted coffee was grinded to use for experimental purpose.⁵⁶

3.4.3 Preparation of adsorbent (Barley)

The stem of barley was used for this experiment. They were collected from the available area washed to remove impurities repeatedly. Then barley was grinded into piece by knife and dried by sun light for 1 day. Further, it washed for removal of dirty material and ready experimental use⁵⁷

3.4.4 Preparation of adsorbent (Ash, pineapple, clay, red scoria)

Ash was taken from home where different wood was burned to prepare food or any other purposes. Pineapples collected from available area, clay and red scoria are also obtained from their sources and washed several times to remove any dirty from them and sun dried. These materials were grinded and sieved to appropriate and used for experimental purpose⁵⁸

3.5 Screening of adsorbents

0.1g of these adsorbents: pineapple, ash, coffee, barley, tella, clay soil, pumice stones red scoria AC-EVML and AC-EA were added in to plastic vial and 40mL of 5mg/l of concentration chromium(vi) solution which was adjusted at pH 2 were mixed and shaken for 24h. Finally, the mixtures were filtered and the filtrate analyzed by UV VIS spectroscopic techniques.⁵⁹



Figure: 3.1Preparation of adsorbents and pretreatments

3.5.2 Preparation of activated carbon

The prepared adsorbents were activated chemically by sulfuric acid using a 1:1 w/w ratio. Concentrated H_2SO_4 (16% con.); 100 g of adsorbent placed in the beaker and 54.64 mL of H_2SO_4 was added to the adsorbent Then mixture was heated at 100°C on oven for 24 h. After 24 h the adsorbents were removed from the oven and cool. The activated sample were washed by distilled water until the acidity of the adsorbents removed.⁶⁰



Figure: 3.2 Activated carbons prepared from EVBL and EA

3.6 Physiochemical Characterization of sample

3.6.1 Moisture content

Moisture content: moisture content was determined using ASTM D2867-91 method. This was determined by loss on drying method. A crucible amount weighed, for each adsorbent of AC-EVML and AC-EA was taken and then the crucible was placed in an electric hot air oven maintained at 105 °C. The sample was weighed at regular intervals of 30 minutes and once the weight observed became constant, the moisture content was calculated using the equation 3.1.⁶¹

Moisture content present in the adsorbents prepared from AC-EVML and AC-EA were determined by using the gravimetric method. The water mass was determined by measuring the weight of sample origin and drying. The water weight was the difference between the weights of the wet sample and dry sample.⁶²

$$\% \text{mois ture} = \left(\frac{(W_1 - W_2) - (W_3 - W_1)}{W_2 - W_1} \right) 100 \text{-----} 3.1$$

Where W_1 = weight of the crucible, W_2 = weight of the sample and crucible before drying, W_3 = weight sample and crucible after drying

Moisture content was carried out by first washing the Petri dish material and dried on the oven at 155°C. Then Petri dish was weight and each adsorbent also weight, again the Petri dish and sample weight together. Each reading was recorded. The sample was put into oven for 2h to dry

the adsorbent then measure the sample again for the second time take a record and these can be continuous up to constant measurement is obtained. Then moisture content was calculated using the following expression.⁶³

3.6.2 Volatility matter

1g of oven-dried, powdered sample was taken in crucible. Then the crucible was kept in furnace for 10 min at the temperature of 550°C. The crucible was taken out of the furnace and allowed to cool in a desiccator. Volatility of the adsorbents prepared from AC-EVML and AC-EA were measured by heating the adsorbent on the oven at 550°C for 10min. The weight of the adsorbent before heating and after heating is measured and percent volatility of the adsorbent is measured as follow:⁶⁴

$$\% \text{ volatility} = \left(\frac{(W_2 - W_1) - (W_3 - W_1)}{W_2 - W_1} \right) 100 \text{-----} 3.2$$

Where, w1 represents weight of crucible, w2 weight of sample and crucible, w3 represents weight of crucible and sample after incineration for the given time.

3.6.3 Ash preparation and it's percent

Ash is defined as the quantity of mineral matter which remains as incombustible of testing substance. Ash content determination was done according to the ASTM D2866-94 standard procedure. A 1gram sample of adsorbents from the oven dried sample was placed in a crucible and transferred into muffle furnace at a temperature of 550°C. Then the crucible was cooled at room temperature in desiccator and its weight was recorded. The heating, cooling and weighing cycle was repeated until constant weight was obtained. Once a constant weight was observed, the % ash content (dry basis) was calculated as: The percent ash is measured as follow:⁶⁵

$$\% \text{As} = \left(\frac{(w_3 - w_1)}{w_2} \right) 100 \text{-----} 3.3$$

Where, W1 = weight of the crucible, W2 = weight of the crucible and sample before igniting, W3 = weight of crucible and sample after igniting

3.6.4 Fixed Carbon Content:

Fixed carbon was the combustible residue left after removing the moisture content, volatile matter and ash from the sample. The fixed carbon of samples was calculated by subtracting the sum of moisture content, ash content (%) and volatile matter (%) from 100.⁶⁶

$$\text{Fixed carbon (\%)} = 100 - (\text{moisture, \%} + \text{ash, \%} + \text{volatile matter, \%}) \text{ -----} 3.4$$

3.6.5 Surface Area of the adsorbents

The AC-EVML and AC-EA specific surface area was determined. 0.5 g of adsorbents was mixed with 50mL of distilled water and 30 g NaCl.

The mixture was shaken for 5min. Its final pH was adjusted to 4 with 0.1 M of NaOH and HCl. It was then titrated against 0.1M NaOH to raise the pH from 4 to 9 and the volume (mL) of 0.1M NaOH used was measured in replicate and the average value was taken for the surface area calculation by sears method. Specific surface area of adsorbent was calculated using the formula Sears method:⁶⁷

$$S = 32V - 25 \text{ -----} 3.5$$

Where, V is a volume NaOH used 32 and 25 sears' constant

3.6.6 Point of zero charge

The activated carbon point of zero charge (pHpzc) is defined as the pH of aqueous solution in which the solid exists under neutral electrical potential, and on the characterization of acidic and basic surface sites on carbon. Point of zero charge were carried out by the 0.1 g of each adsorbent were added in the plastic vial with 40 mL of 0.1M and 0.01M NaCl solution which is prepared with different pH (2-12) and shacked in to the shaker for 48 h the final pH of the solution was measured by pH meter. Changing in pH and initial pH plotted to determine point of zero charge.⁶⁸

3.7 Characterization of Adsorbent samples

Functional groups in AC-EVML and AC-EA and chromium loaded AC-EVML and AC-EA powder were examined by using the Fourier Transform Infrared (FTIR) method of analysis. The FTIR spectrophotometer was analyzed based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum 65FT-IR (Perkin Elmer) in the average range $4000\text{-}400\text{ cm}^{-1}$ using KBr pellets. The wave numbers associated to signals in the FTIR spectra from chemical functional groups were determined. XRD analysis was carried out to know the crystal phase composition of AC-EVML and AC-EA. The diffraction patterns were obtained in the 2θ range from $10\text{-}90^\circ$.⁶⁹

3.8 Preparation of working Cr (VI) and DPC solutions for UV–Vis’s analysis

A series of five working standard solutions containing 0.01, 0.1, 0.05, 1 and 2 mg/L of hexavalent chromium including a blank solution were prepared from the stock solution. A 0.25 g of DPC, which is a common complexing agent for chromium (VI), was dissolved in 50 mL acetone and shaken until complete dissolution. 2 mL 0.5M of sulfuric acid and a freshly prepared 1 mL DPC solution were then added to each sample solution and working standard, a pink color was immediately developed. The standard and sample solutions concentrations were then analyzed using the UV–Visible spectrophotometer at a wave length of 540 nm.⁷⁰

3.9 Batch adsorption studies

In all experiments, distilled water was used for preparation. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), stock solution containing chromium 1000 mg/L was prepared by dissolving 2.829 g of potassium dichromate in 1000 ml of distilled water. All experiments were carried out in batch mode.⁶⁹ The batch adsorption studies were conducted at room temperature by agitating (150 rpm) weighed quantities of the adsorbent in 40 mL of chromium water solutions at the required pH, contact time, initial concentration and dose of adsorbent. These experiments were run in the same plastic vial. In each plastic vial first determined amount of adsorbent was added. 40 mL chromium solution was added to the plastic vial which contains adsorbent.⁷¹ After shaking the sample was filtered by Whatman membrane filter paper of pore size $0.45\mu\text{m}$ using a syringe. Finally, the sample was analyzed by UV Vis for the remaining chromium in the solution. Equilibrium of this

experiment was studied using Langmuir, and Freundlich, isotherm models. The kinetics was also studied by Pseudo- first order, Pseudo-second order and intra particle diffusion models.

3.9.1 Effect of time

The effect of contact time on the adsorption efficiency and the optimum contact time for the process was studied by conducting the experiment from 0.5 to 12h with one hour time interval keeping other parameters such as pH (2), initial concentration and dose constant at 5mg/L and 0.1g of activated adsorbents. The experiment was carried out at 150 rpm incubator shaker and room temperature. After the time required for adsorption arrived the adsorbent and the solution was filtered by Whatman 0.45 filter paper. The filtrate was analyzed using UV Vis for the remaining chromium in the solution.⁷²

$$\% \text{ Removal of Cr (VI)} = \frac{C_0 - C_e}{C_0} \times 100 \text{-----} 3.5$$

The adsorption Cr (VI) capacity per unit mass of the adsorbent was calculated according to the following expression:

$$q_e = \frac{(C_0 - C_e) V}{m} \text{-----} 3.6$$

Where C_i and C_e are the initial and final chromium concentrations (mg/L), respectively, q_e is the amount of Cr (VI) adsorbed onto adsorbents (mg/g), V is the total volume of solution (L), and m is the adsorbent dosage (g).

3.9.1.1 Kinetic study for adsorption of chromium

The kinetic isotherm studies were carried out by varying the contact time from (0.5-12h) at concentration of 5mg/L at fixed volume (40mL), pH (2), optimum uptake time and room temperature. The results were analyzed by pseudo first, pseudo second order and intraparticle diffusion isotherm models.⁷³

The pseudo-first-order equation can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \text{-----} 3.7$$

Where, and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t and k_1 is the first-order rate constant (min^{-1}). From the plots of $\log(q_e - q_t)$ versus t , k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts.

Pseudo-second-order equation can be given by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \text{-----} 3.8$$

3.9.1. 2 Intraparticle diffusion model

The kinetics data were tested against the intraparticle diffusion model to identify the actual rate-controlling steps involved in the Cr (VI) sorption process. Generally, the sorption process of a sorbate by a porous sorbent can be classified as three steps as follows: ⁷⁴

- (iv) external mass transfer across the hydrodynamic boundary layer film surrounding the sorbent particle,
- (v) (ii) intraparticle diffusion of the sorbate molecules within the sorbent pores either by liquid filled pores or a solid surface diffusion process, and
- (vi) (iii) Adsorption at an active site on the external or internal surface of sorbent. The third step is often considered to be extremely rapid, thus the most contribution to the rate of adsorption is film or/and pore diffusion. The intraparticle diffusion model can be represented as follows

$$q_t = k_d t^{\frac{1}{2}} + C \text{-----} 3.9$$

3.9.2 Effect of pH

The effect of the solution pH on chromium metal ions removal using activated AC-EVML and AC-EA as an adsorbent was conducted, using a 40 mL solution of 5 mg/L of metal ion solution in the pH range of 2 to 12 at 25°C and adsorbent dosage used was 0.1 g per 40 mL solution. Flasks were shaken on an incubator shaker for 150 rpm shaking speed and 9 and 6 h contact time to make sure equilibrium is reached. After equilibrium was reached, the solutions were filtrated and analyzed to determine the metal ion concentration.⁷⁵

3.9.3 Effect of initial concentration

Another most important factor in the adsorption process was the initial concentration of chromium. Samples in the concentration range of (10-100) mg/L with 10 mg/L interval were prepared for the sake of determining the effect of initial concentration of chromium on the removal efficiency. Then it was put on the orbital shaker at 150rpm and room temperature by maintaining pH, dose and contact time constant at 0.1g and 9 and 6 h for activated AC-EVML and AC-EA adsorbents respectively. Then the residual chromium ion concentration was recorded.⁷⁶

3.9.1 Adsorption isotherm models

Isotherm studies are essential to interpret the adsorption process adequately. Several models have been used to describe experimental data for adsorption isotherms. However, among these, the Langmuir and Freundlich isotherms are the most appropriate models for this study. According to the Langmuir isotherm, adsorption occurs at homogenous sites and forms a monolayer adsorption can take place. In other words, once adsorbate is attached to a site, no further. Langmuir assumes monolayer adsorption on homogeneous surfaces with energetically equivalent adsorption sites, without interactions between the adsorbate molecules and it allows estimation of the maximum adsorption capacity of the adsorbent⁷⁷

The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \text{-----} 3.10$$

Where (mg/g) is the equilibrium concentration of hexavalent Chromium in the adsorbed phase and (mg/L) is the equilibrium concentration in the liquid phase. Langmuir constants, which are related to the adsorption capacity (q_m) and energy of adsorption (b_L), can be calculated from the slope of the linear plot of C_e/q_e versus C_e ; a straight line with slope $1/q_{max}$ and intercept of $1/q_{max}b_L$ is obtained. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as.⁷⁸

$$R_L = \frac{1}{1+b_L C_o} \text{-----} 3.11$$

Where C_0 initial concentration RL value indicates the adsorption nature to be either unfavorable if $RL > 1$, linear if $RL = 1$, favorable if $0 < RL < 1$ and irreversible if $RL = 0$.

-

In this study the equilibrium data obtained from the batch experiments were also analyzed by one of the most frequently used adsorption models, i.e., Freundlich the empirical model that describes multilayer adsorption on heterogeneous surfaces where the parameter $1/n$ is a measure of the surface heterogeneity, which becomes more heterogeneous as its value gets closer to zero. The value of $1/n < 1$ implies chemisorption's process and $1/n > 1$ indicates cooperative adsorption. At low adsorbate concentrations it is reduced to the Freundlich isotherm and at high concentrations the equation is transformed into the Langmuir isotherm, predicting monolayer adsorption.⁷⁹

The linear form of Freundlich isotherm is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{-----} 3.10$$

3.10 Desorption process

After Cr (VI) adsorption, the adsorbents were washed thoroughly with deionized water and treated with the desorption agents such as HCL and NaOH. Desorption tests were performed using HCL and NaOH. As 0.1g of saturated activated adsorbents was examined in 50mL of plastic vials and added 0.1MHCL and 0.1MNaOH of solution independently and shaken for 24h and then filtered. The filtrate was analyzed by UV Vis.⁸⁰

4 RESULTS AND DISCUSSION

This chapter provides result of laboratory analysis made for activated AC-EVML and AC-EA, characterization, effects of parameters such as pH, concentration of chromium and contact time removal capacity of the adsorbents are presented. The aqueous solution of chromium loaded with the adsorbents and performance of the adsorbents were evaluated by varying the parameters according to literature. And with amendments to optimize those factors which affect the performance of adsorbents for aqueous solution of chromium.⁸¹

4.1 Adsorbents screening

The result below shows the capabilities each adsorbent to ward removal of chromium (VI)

Table: 4.0. Screened adsorbents with their percent removal

Adsorbents	% removal
pean apple	56.12
Ash	21.25
Coffee	69.14
Barley	89.54
Tella,	94.32
EVML	99.91
EA	100.12
Charcoal	56.21
Red scoria	12.35
Pumice stone	63.25
Clay	58.47

From the above result AC-EVML and AC-EA were selected for this experiment.

4.2. Physiochemical Characterization of sample

The moisture content, Volatility content, ash content and fixed carbon content were measured and the following result were obtained

4.3.1 Moisture content

Measuring the moisture content of the adsorbent is one of the important features in order to know the adsorbent quality.⁸¹ Moisture content of activated **AC-EVML** and **AC-EA** were determined to be 12.5 and 21.75%, respectively. The moisture content of a sample refers to the percentage of water content of the sample. The lower the moisture content, the higher its adsorption efficiency since water molecules can have the potential effect in the pores of an adsorbent through filling the adsorbent binding site before it contacts with the solution.⁸²

4.3.2 Ash value

The ash content is a measure of total amount of inorganic compounds such as minerals in the activated **AC-EVML** and **AC-EA**. The **AC-EVML** and **AC-EA** were found to contain 12.32% and 18.4% ash, respectively. The higher the ash values the higher removal efficiency has been reported in literature.⁸³

4.3.3 Volatile mater and fixed carbon content of AC-EVML and AC-EA

The laboratory result of volatile matter for activated **AC-EVML** and **AC-EA** adsorbents were 16.74 and 23.26%, respectively.

4.3.3.1 Fixed carbon content

Fixed carbon is the solid combustible residue that remains after the **AC-EVML** and **AC-EA** were heated and the volatile matter was expelled. The fixed-carbon content of **AC-EVML** and **AC-EA** was determined by subtracting the percentages of moisture, volatile matter, and ash from a sample and it was obtained 59.76 and 35.84 respectively %.⁸⁴

4.3.4 Specific surface area determination

The surface area was calculated using Eq. 7 under the materials and methods section. The resulting specific surface area was 21.72 and 136.92m²/g. higher surface area of the adsorbent supports higher adsorption capacity because the surface area is one of the decisive factors in the sorption process⁸⁷. So, the larger the adsorbent surface area the greater adsorption capacity of sorbents. Activated AC-EVML has a higher surface area than activated AC-EA. Adsorbent with composition of the AC-EVML is 6.303 times than highest sorption capacity compared to AC-EA.⁸⁵

Table 4.1 Proximate analysis of adsorbents

Parameters	AC-EA adsorbent			AC-EVML adsorbent		
	Weight before dried(W ₂) (g)	Weight after dried (W ₁) (g)	% of Sample (W ₂ -W ₁)/W ₂ *100	Weight before dried (W ₂) (g)	Weight after dried (W ₁) (g)	% of Sample (W ₂ -W ₁)/W ₂ *100
Moisture	1.04	0.91	21.7	1.01	0.79	12.5
Volatility	1.0	0.7674	23.26	1.0	0.826	16.74
Ash	1.5	1.074	28.4	1.5	1.465	2.333
Carbon content	[100 – (%ash +% volatility +%moisture) = (100-64.16) = 35.84			[100 – (%ash +% volatility +%moisture) = (100-40.24) = 59.76		

4.3.5 Point of zero charge

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{pzc}) of the adsorbent because the point of zero charge is the pH value at which the surface charge of an adsorbent equals to zero. At pH value less than pH_{pzc}, the surface charge on the

adsorbent is a net positive charge, while at pH value greater than pHPzc the surface charge on the adsorbent is a net negative charge. Therefore, anion adsorption on surface of any adsorbent is favorable at pH value lower than pHPzc⁸⁸. Here, the experimental results of pHPzc (Change in pH Vs initial pH) of activated AC-EVML and AC-EA adsorbents were obtained as 3 for both adsorbents as shown in the figure below. Change in pH means pH of the solution after adsorbent is added and shaken for 24h minus initial pH of the solution before adsorbent is added.⁸⁶

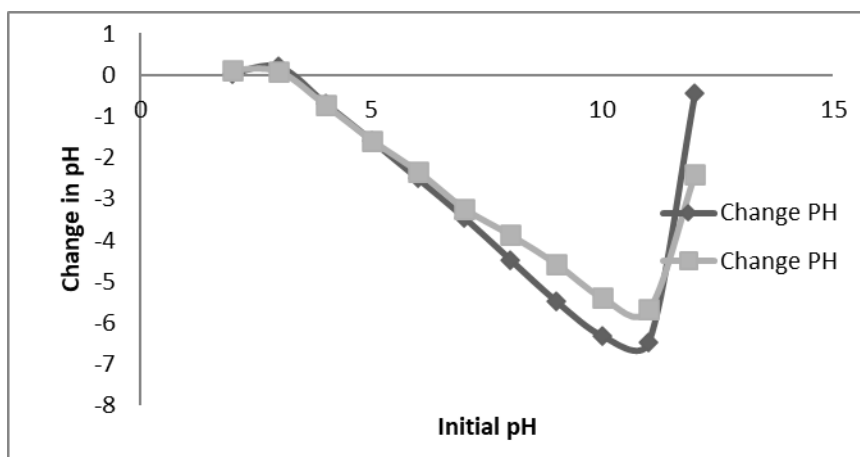


Figure: 4.1 Zero Point charge of 0.1 and 0.01M of NaCl of EVML powder

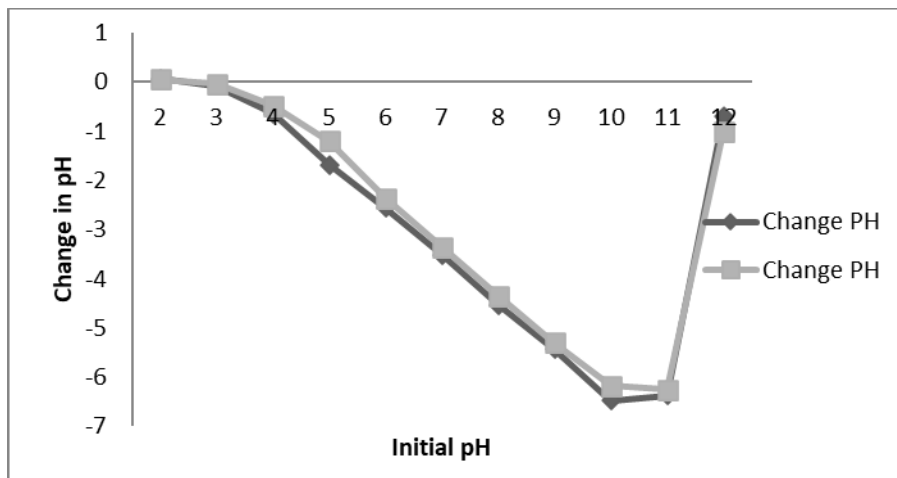


Figure: 4.2 Zero Point charge of 0.1 and 0.01M of NaCl of EA powder

4.4 Characterization of the Adsorbent

4.4.1 Fourier transforms infrared (FT-IR) spectrum analyses of EA powder

The Fourier transfer infrared spectroscopy (FTIR) analysis has been considered as a kind of direct mean for identifying the characteristic functional groups on the surface of the adsorbents which are responsible for adsorption of chromium ions.⁸⁷ The FTIR spectrum of AC-EA powder was obtain the information regarding the stretching and bending vibrations of these functional groups. Figure 4.3 illustrates the FTIR analysis for AC-EA through numerous bands from 4000 to 400 cm^{-1} .

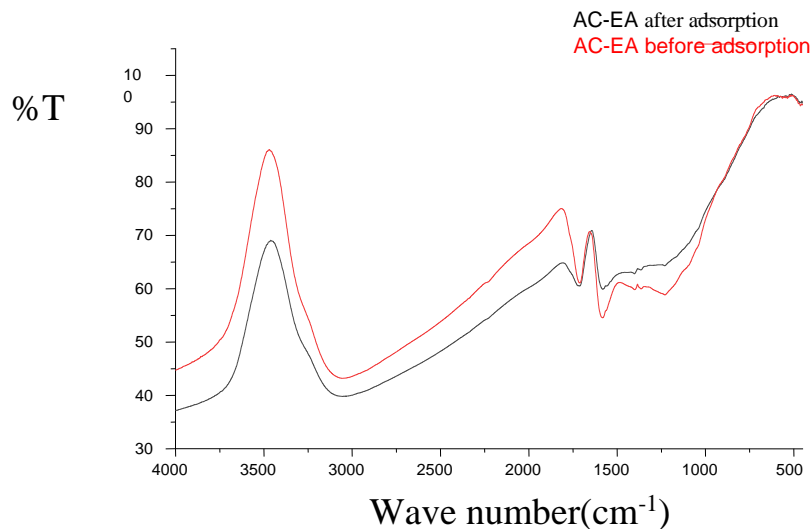


Figure: 4.3 FTIR spectra of AC-EA and the Cr (VI)-loaded, AC-EA

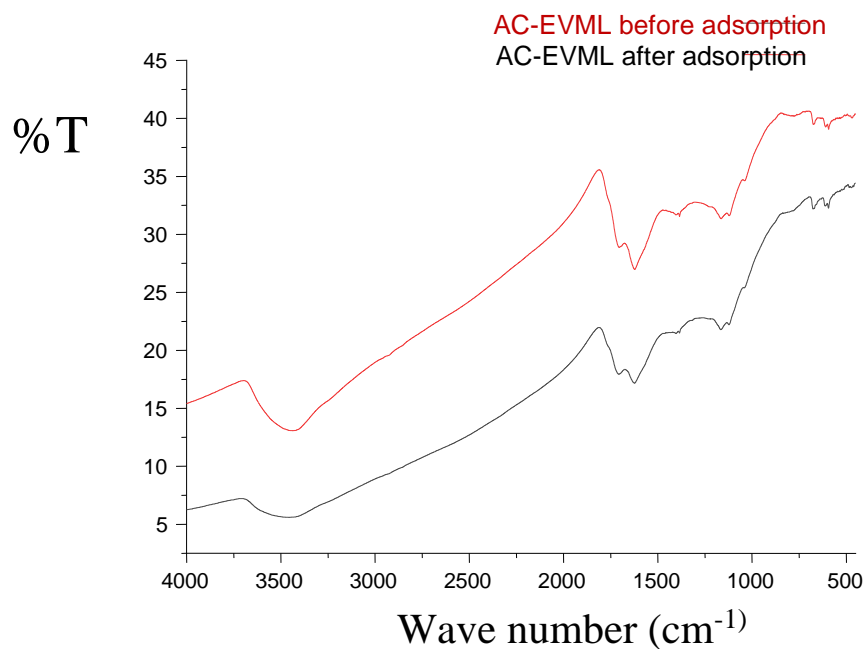


Figure: 4.4 FTIR spectra of AC-EVML and the Cr (VI)-loaded, AC-EVML Cr (VI)

The IR spectrum of AC-EVML is shown in Figure 5. The peaks are found at 1030 and 1300, 1450 and 1640 and 1540 which confirm the presence of C–O, C=O, and C=C, stretching vibrations, respectively. The band appears at 3345 cm^{-1} , which indicated the presence of water molecules (O–H stretching mode of hydroxyl groups).⁸⁹The peaks obtained.⁹⁰

4.5 X-ray diffraction analysis (XRD)

The phase of the developed adsorbent is also studied using XRD radiation. The peaks relating to the phase were detected for the AC-EA at 800°C for 2h. From figure below the narrow diffraction peaks indicated the phase composition has amorphous structure.

The XRD pattern for the adsorbents is shown in Figure 4.5. There is no peak identified in the spectrum and therefore, the particle size of developed adsorbent cannot be calculated using the Scherer formula.

The distorted pattern depicts that there is no crystalline in the adsorbents and that it purely has only the amorphous nature.⁹¹

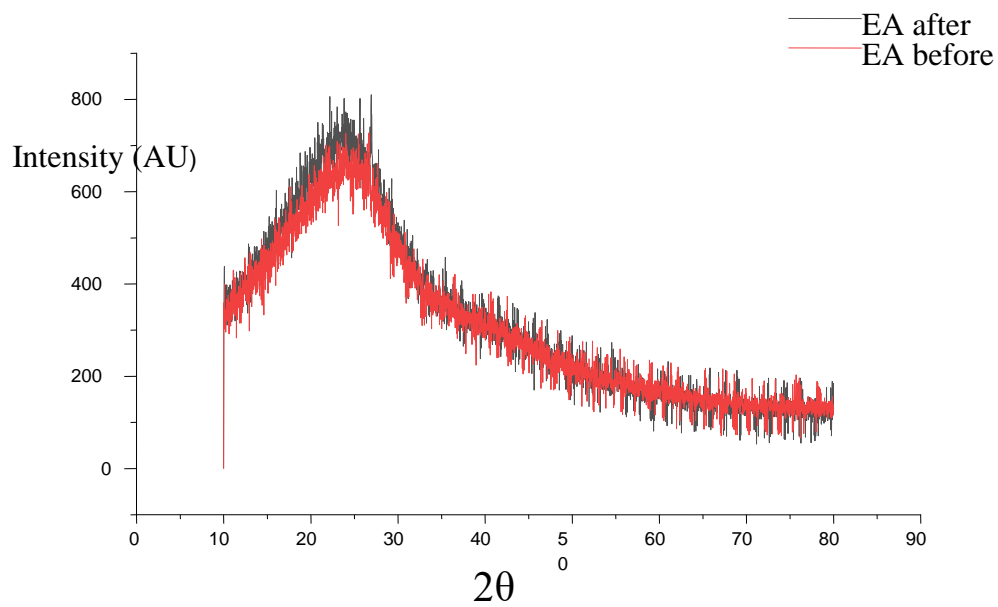


Figure: 4.5. XRD diffract grams of AC-EA and Cr-loaded AC-EA

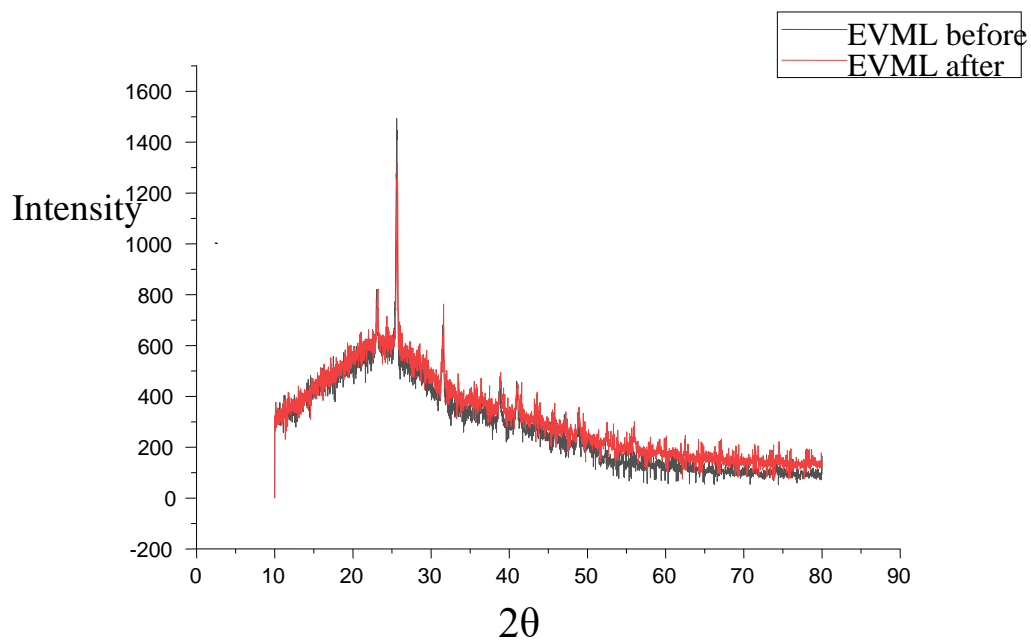


Figure: 4.6. XRD diffract grams of AC-EVML and Cr-loaded AC-EVML

The phase of the developed adsorbent is also studied using XRD radiation for adsorbent AC-EVML. The peaks relating to the phase were detected for the AC-EVML at 800°C for 2h. From figure below the narrow diffraction peaks indicates the phase composition have amorphous structure which is the same as to AC-EVML adsorbent. The wavelength considered is 1.54 Å and 2θ ranges from 10° to 90° at a step size of 0.01°.⁹²

The XRD pattern for the adsorbents is shown in Figure 4.6. There is no peak identified in the spectrum and therefore, the particle size of developed adsorbent cannot be calculated using the Scherer formula. The distorted pattern depicts that there is no crystalline in the adsorbents and that it purely has only the amorphous nature.⁹³

4.6 Batch adsorption studies

4.6.1 Effect of contact time

The effect of contact time on the adsorption of Cr (VI) ions using AC-EVML and AC-EA adsorbents investigated over time interval of 0.5h to 12 h. Figure 4.7 represents the results of the effects of contact time on the Cr (VI) adsorption. As illustrated in figure 4.7, it can be concluded that as the contact time increases, percent removal also increases until equilibrium was reached at 9 and 6 h respectively for AC-EVML and AC-EA adsorbents.⁹⁴ And it is clear that increasing the contact time beyond the 9 and 6 h for both adsorbents had not significant impact on adsorption performance. The percentage removal of the AC-EVML and AC-EA are 99.98% and 99.86% at 9 and 6 h, respectively.

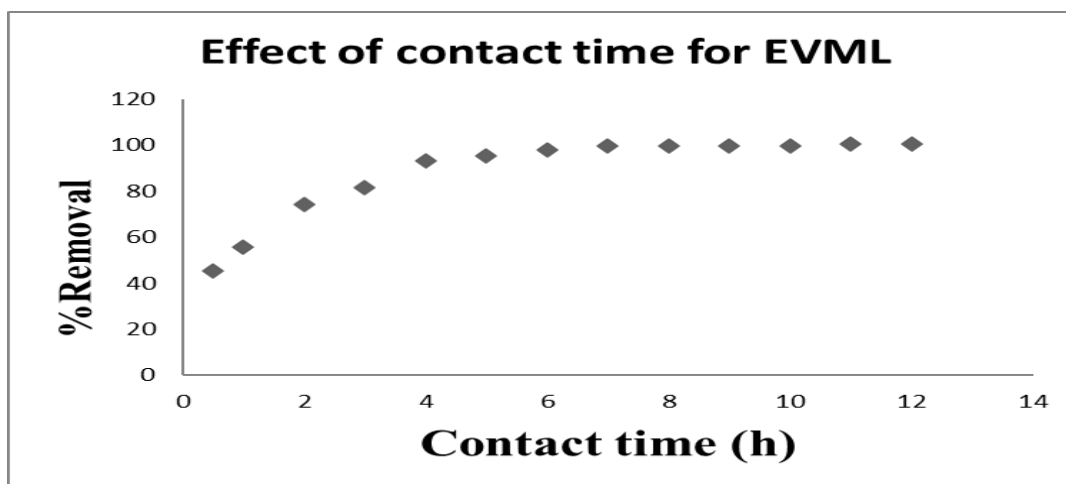


Figure: 4.7 percent removal for 0.1g of EVML adsorbent 5mg/L conctration of chromium Vs contact time

This can be explained by the fact that initially, the rate of ion uptake was faster because all sites on the adsorbent were vacant and ion concentration was high, but decrease in adsorption sites reduced the uptake rate. From experimental result the adsorption capacity increase with increase contact time which means the adsorption capacity for AC-EVML is increase from 0.9199mg/g- 2.025mg/g and decreased slightly then decrease beyond this point.⁹⁵

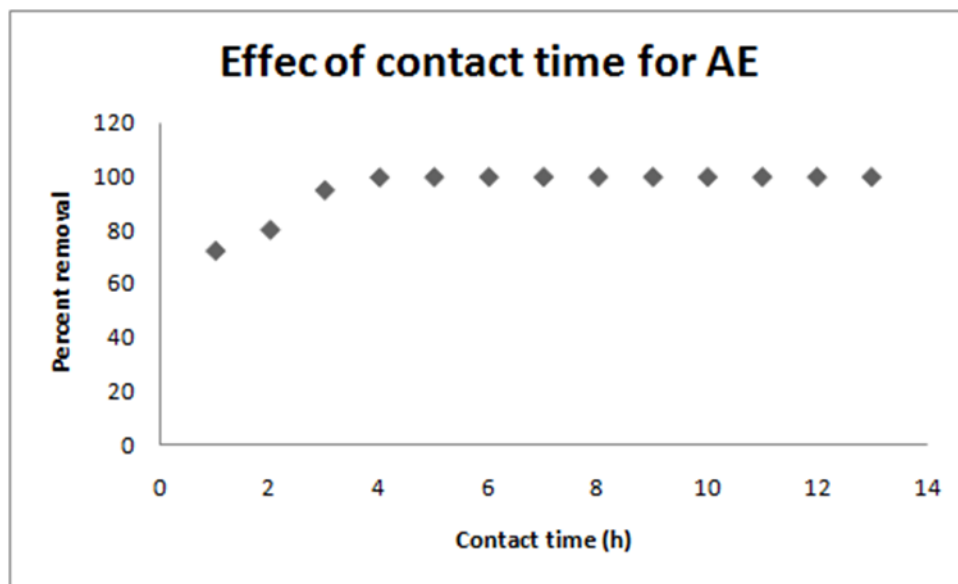


Figure: 4.8 percent removal for 0.1g of EA adsorbent 5mg/L conctration of chromium Vs contact time

From experimental result the adsorption capacity increase with increase contact time which means the adsorption capacity for AC-EA is increase from 1.458mg/g to 2.020 mg/g and constant beyond this point. This show that initially adsorption is faster gradually but decrease because of active site of the adsorbent was filled as time of adsorption increase.⁹⁶

4.7 Kinetic study for adsorption of chromium

The kinetic model's pseudo first order, pseudo-second-order and intra-particle diffusion were used to analyze the kinetic behavior of the chromium sorption process.⁹⁷ The kinetic rate constants, adsorption capacities and correlation coefficient were calculated from the slope and

intercept of their corresponding graphs for the all adsorbents.⁹⁸ The pseudo second order equation appeared to be the best fitting model than both first order for both adsorbents because it has highest R^2 which is 0.999 and 0.998 value for AC-EA and AC-EVML adsorbents respectively. This kinetic study confirmed that bio sorption of Cr ions on AC-EVML and AC-EA adsorbents were a multistep process involving adsorption Cr ions on the external surface.¹⁰⁵ Therefore, the adsorption process can be approximated more favorably by the pseudo-second order kinetic model. The pseudo-second order kinetic model is also based on the sorption capacity of the adsorbent and it assumes that adsorbents follow a second-order mechanism, so the rate of occupation of adsorption sites is proportional to the square of the number of available vacant space. The pseudo-second order kinetic model is expressed in equation 3.8. The value q_e and K_2 was calculated from the plot t/q_t vs t corresponding slope and intercept respectively.¹⁰⁶

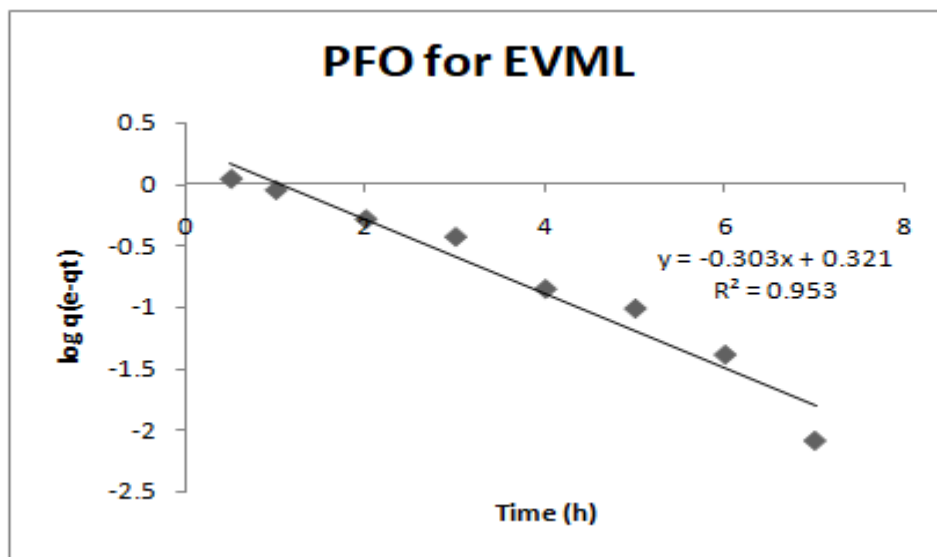


Figure: 4.9 Pseudo first order for EVML adsorbent

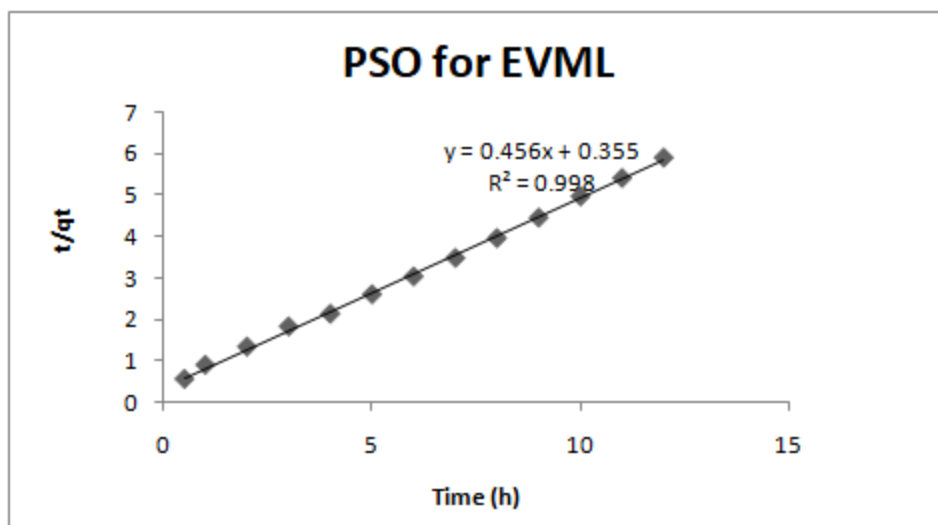


Figure: 4.10. Pseudo second order for EVML adsorbent

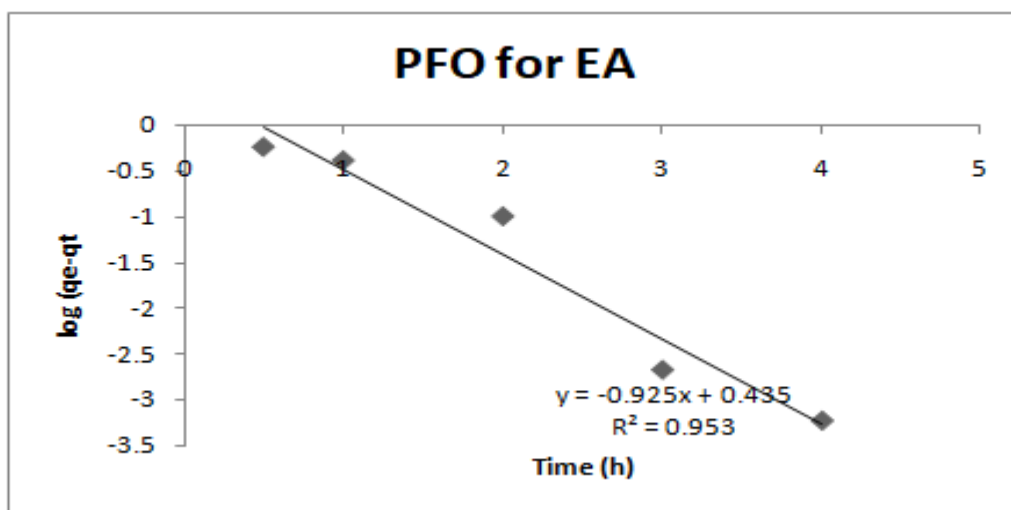


Figure: 4.12 Pseudo first order for EA adsorbent

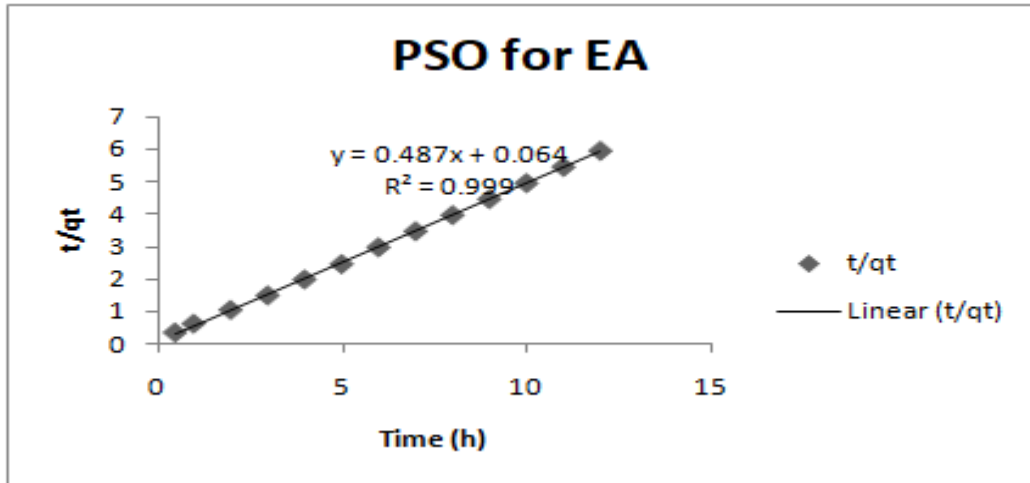


Figure: 4.11. Pseudo second order for EA adsorbent

4.8 Intraparticle diffusion

The amount of Hexavalent Chromium adsorbed per unit mass of adsorbent at time t , qt , as a function of the square root of the contact time, $t_{1/2}$, was examined using the intraparticle diffusion model. It is assumed that the larger the intercept, the greater the contribution of the surface adsorption in the rate-controlling step.⁹⁹

In the adsorption process, it might be possible that the mass-transfer rate of adsorbate molecules is controlled by the intra-particle diffusion. It is suggested that the best fit line should pass through the origin for intra-particle diffusion, which is not the case here. This confirms the fact that the intra-particle diffusion is not the only rate-controlling step during the adsorption of Cr (VI) on AC-EVML and AC-EA, and that there is also a significant contribution of the film diffusion mechanism.¹⁰⁰

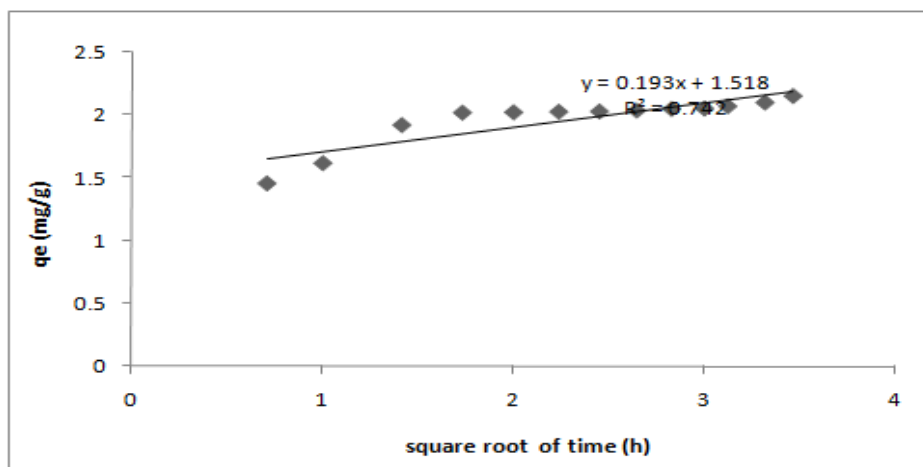


Figure : 4.12. Intra-particle diffusion for EVML adsorbent

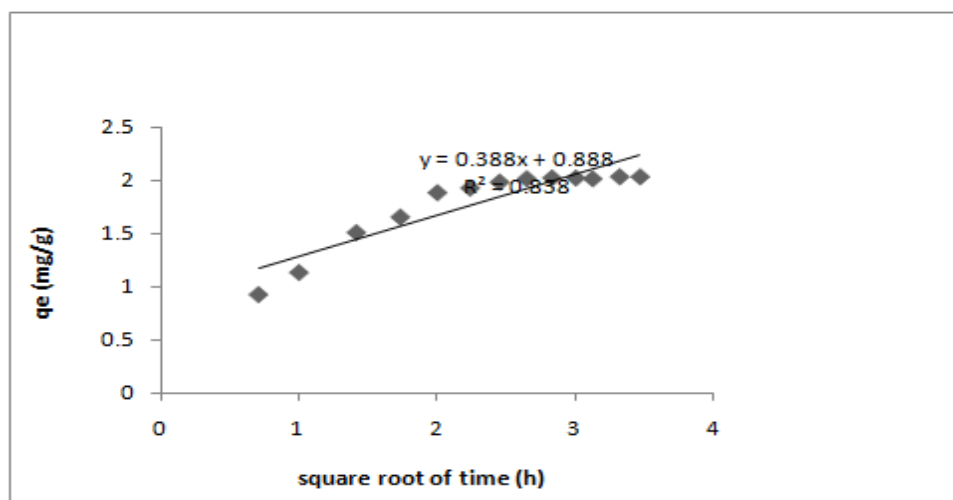


Figure: 4.13. Intraparticle diffusion for EA adsorbent

Table 4.3 Parameters of different isotherms of kinetics

Adsorbents	First order kinetic model				Pseudo Second order				Intraparticle Diffusion		
	qe mg/g (cal)	qcal mg/g (cal)	K ₁ (mg/ g min)	R ²	qe mg/ g (cal)	qcal mg/g (cal)	K ₂ (mg/g min)	R ²	Kd (mg/g min ^{0.5})	C	R ²
EVML	2.02	3.30	0.682 4	0.953	2.02	2.19	0.7029	0.998	2.573	0.888	0.838
EA	2.02	1.08	0.663	0.953	2.02	2.05	4.784	0.999	5.181	1.518	0.742

4.9 Effect of pH

The pH values affect the adsorbent surface charge, the degree of ionization, and speciation of adsorbate during adsorption. The graph in figure below showed that the percentage removal of Cr (VI) higher at lower pH. This was due to the fact that the Point of zero charge of the adsorbents were at pH = 3. The cationic adsorption is favored at pH lower than pH_{pzc}. Minimum percent removal of Cr was observed 31.31 and 19.288 for AC-EVML and AC-EA, respectively at pH higher and the maximum removal was 100.39 % and 100.19 % at pH 2 for the two adsorbents respectively.¹⁰¹

It can be seen that the maximum of Hexavalent Chromium adsorption occurs at the lowest pH value. This finding has been reported by several investigators who have found that Hexavalent Chromium removal by activated carbon is enhanced in the acidic range of pH. The favorable effect of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions (HCrO₄⁻) and their subsequent adsorption, (HCrO₄⁻) is the dominant and ionic form of hexavalent Chromium between pH 2.0 and 4.0¹⁰². This ionic form was found to be preferentially adsorbed on the surface of carbon. The negative charges could result from ox

xygenatedfunctional groups of basic character and physically adsorbed at the surface of the pores of activated

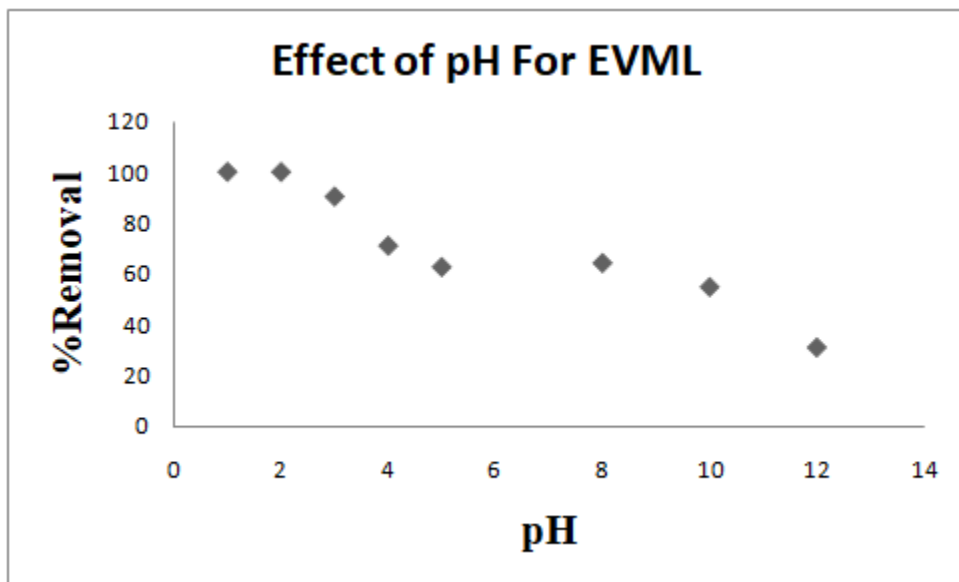


Figure: 4.14. Effect of pH for the adsorption of Cr (VI) ions onto activated EVML carbon

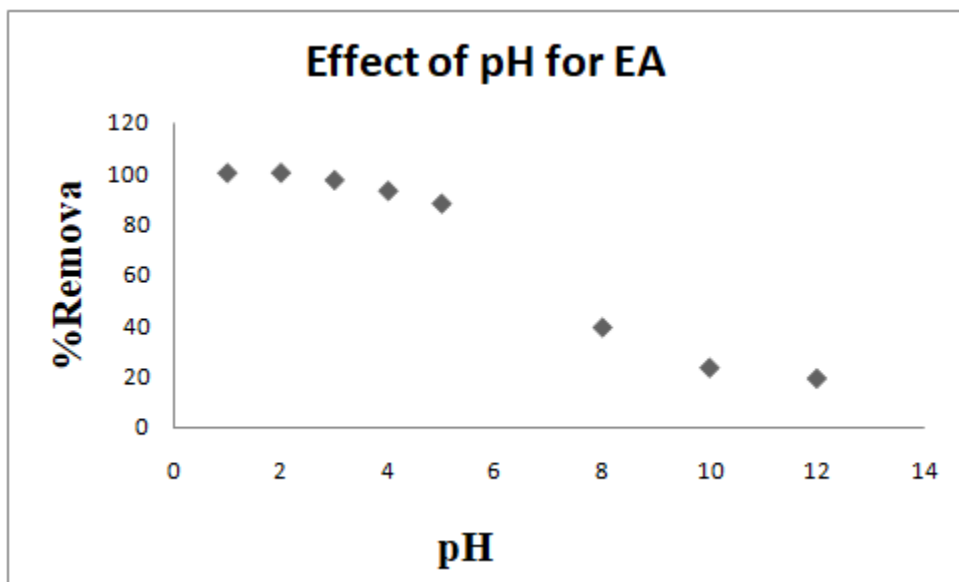


Figure: 4.15. Effect of pH for the adsorption of Cr (VI) ions onto activated EA carbon

4.10 Effect of chromium (VI) Concentration

Adsorption efficiency of adsorbents were studied from 10 mg/L– 100 mg/L Cr (VI) concentrations with 0.1g of adsorbent dose and pH 2.0, shaking to equilibrium. The best adsorption efficiency for the removal was found to be at lower concentrations whereas adsorption capacity increased as concentration increased per gram of adsorbent. Lower concentration more adsorbent active sites were available make adsorption but as concentration increase the active site of the adsorbent can be saturated with chromium.¹⁰³

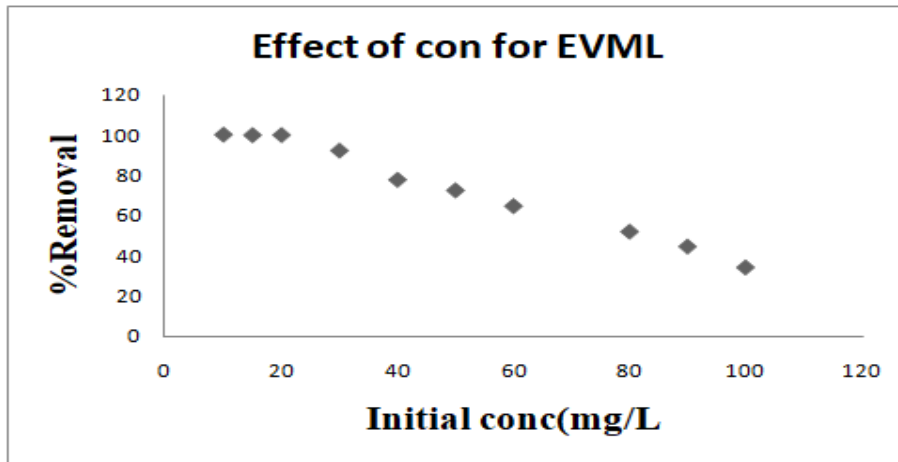


Figure: 4.16 Effect of Initial concentration for the adsorption of Cr (VI) ions onto activated EVML

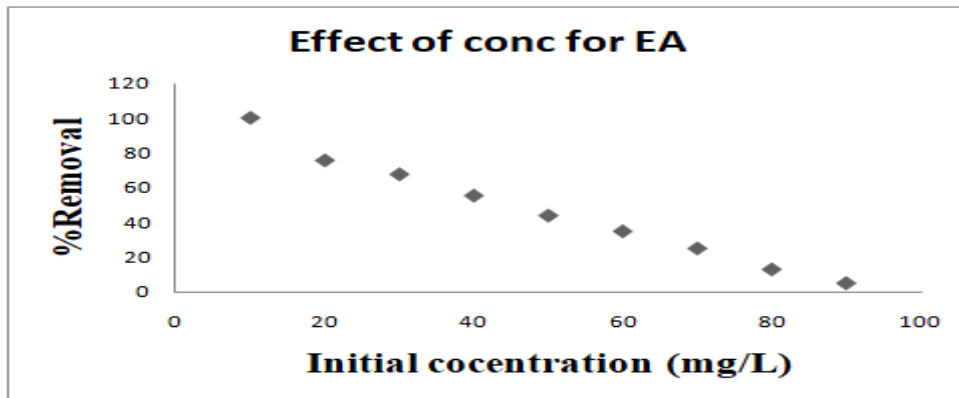


Figure: 4.17 Effect of Initial concentrations for the adsorption of Cr (VI) ions onto activated EA carbon

Maximum % removal of chromium by AC-EVML is 99.97% and by AC-EA is 100.07 at 10 mg/L. On the other hand, maximum Cr(VI) ion adsorption capacity of AC-EVML is 16.32 mg/g at initial concentration of 60 mg/L and that of AC-EA is 10.17 mg/g at initial concentration of 70 mg/L.¹⁰⁴ The increase in adsorption capacity with increasing initial concentration is due to the fact that, at fixed adsorbent dose with increasing the metal concentration, all the available active sites of the adsorbent would be fully exposed to get occupied by the metal ions that are in excess saturating and yielding a higher adsorption capacity. But from some point the adsorption capacity become decreasing this due to the decreases of the adsorbent active site as result saturation.¹⁰⁵

4.10.1 Adsorption isotherm Model

The Langmuir and Freundlich equations are commonly used for describing the adsorption equilibrium for Cr (VI) removal.¹⁰⁶ The linear forms of the Langmuir and Freundlich isotherms are used. Langmuir model fitted very well to the sorption data in the studied concentration range with a higher correlation coefficient R^2 value 0.988 and 0.994 for adsorbent AC-EA and AC-EVML respectively as shown in below. The Langmuir model assumes that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the surface of the identical (specific) adsorbent, the energy of adsorption is fixed and molecules of the adsorbent will not migrate in the surface plane. The q_m values of the Langmuir constants were calculated from C_e/q_e vs C_e plot as 15.38mg/g and 9.803mg/g for AC-EVML and AC-EA adsorbents and b value 1.711 L/mg and 6.377 L/mg for AC-EVML and AC-EA adsorbents respectively. RL a separation factor given as $\frac{1}{1+bC_0}$ also showed a result between 0 and 1 which explains a favorable adsorption.

The adsorption process can be described as unfavorable if $RL > 1$, linear if $RL = 1$, favorable if $0 < RL < 1$ and irreversible if $RL = 0$. The value of RL obtained in this study is between 0 and 1, which suggests the Langmuir isotherm model is favorable in this study.

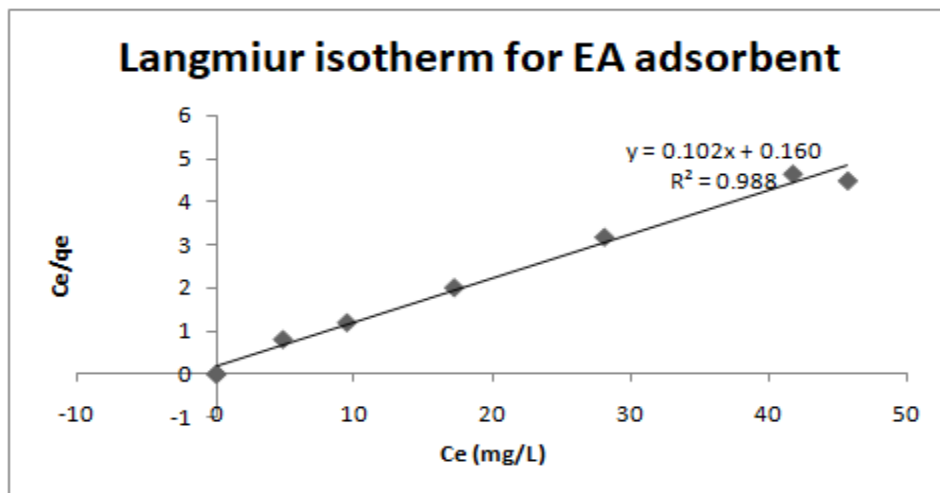


Figure: 4.18. Langmuir isotherm for EVML

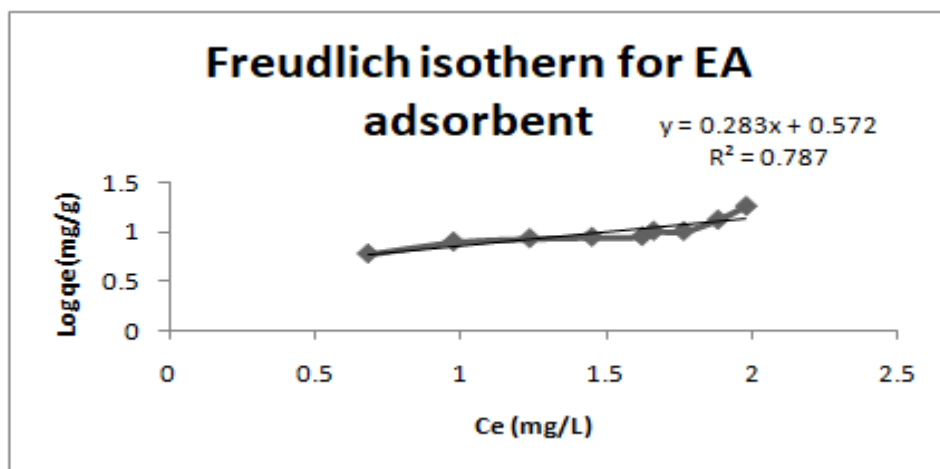


Figure: 4.19. Freundlich isotherm for EA

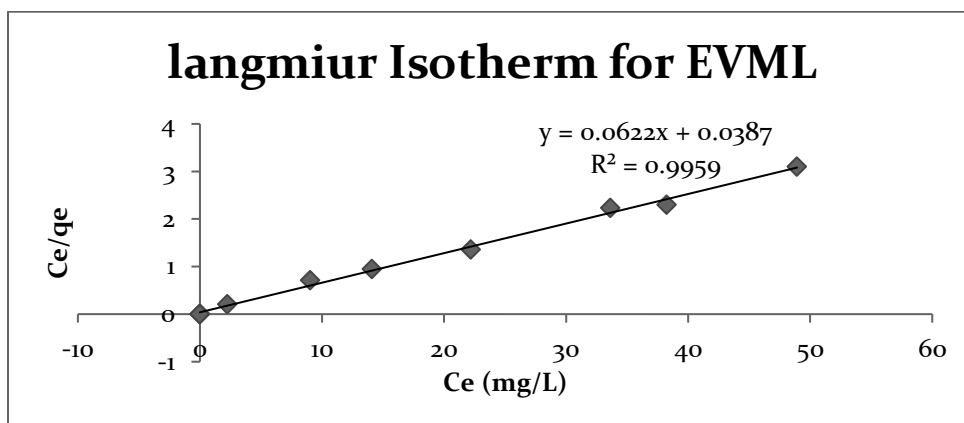


Figure: 4.20 Langmuir isotherm for EVML

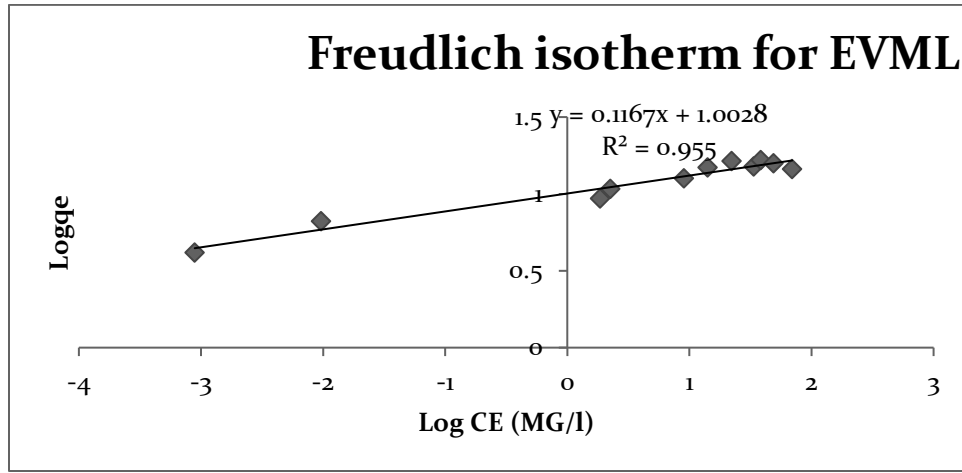


Figure: 4.21 Freundlich isotherm for EVML

Table 4.4 Parameters of different isotherms of adsorption

Adsorbent	Langmuir constants			Freundlich constants		
	Q_0	B	R^2	K_F	N	R^2
EVML	15.38	1.711	0.994	0.075	2.87	0.955
EA	9.803	6.377	0.988	0.7209	1.97	0.787

4.11 Desorption of adsorbents

The recovery of Cr (VI) from the adsorbent was performed using 0.1M NaOH solution. Adsorbent dose of 0.1 g was loaded with 40 ml of 5 mg/L of chromium solution. The Cr (VI) was absorbed by AC-EVML and AC-EA. Desorption studies attempted to recover Cr (IV) from metal ion loaded adsorbent for above-mentioned concentration. The results show that 73% of the adsorbed Cr (VI) was desorbed from AC-EVML using 0.1 M NaOH and 47% of the adsorbed Cr (VI) was desorbed from AC-EA using 0.1M NaOH. During desorption studies, the AC-EVML and AC-EA surface were completely covered by Na^+ ions. It is evident from generally, the

regeneration of adsorbents resulted in the release of Cr (VI) ions from adsorbent's surface to the solution and regenerated adsorbents can be reused for Cr (VI) removal from aqueous solution.¹¹

4.12. Comparison adsorbents capacity

TABLE 4.5 Maximum Adsorbent Capacity of Various Commercial and Low-Cost Adsorbents

S.NO.	Adsorbents	Maximum adsorbent capacity (mg/g)	Reference
1	Nano porous activated neem bark (nANB)	26.95	16
2	Coca nut shell based	20.0	85
3	Sugar beet pulp	17.2	73
4	Maize cob	13.8	81
5	Cactus	7.08	48
6	Waste tea	1.55	65
7	Soya cake	0.28	89
8	Walnut shell	1.33	97
9	Coal	6.78	42
10	Palm pressed fibers	15.0	63
11	Leaf mould	25.9	73
12	Sugarcane bagasse	13.4	73
13	AC-EVML	16.32	This work
14	AC-EA	10.17	This work

Table 4.5 shows that the maximum Adsorbent Capacity of AC-EVML and AC-EA is comparable with some of the Various Commercial and Low-Cost Adsorbents and can have promising adsorption capacity for removal Cr (VI) from water solution.

5. Conclusions and Recommendation

5.1 Conclusion

In the present study, a low-cost adsorbent of AC-EVML and AC-EA are activated using sulfuric acid and is used for the removal of Cr (VI) from aqueous solution. Adsorption capacity is found to increase with an increase in contact time and initial Cr (VI) concentration. The experimental equilibrium data are best fitted with Langmuir isotherm model, which supports the monolayer formation of Cr (VI) on adsorbents surface. The maximum adsorption capacity of the adsorbent was obtained as 16.32 mg/g and 10.17 mg/g for AC- EVML and AC-EA, which is higher than many of the adsorbents available. The kinetic data are well explained by the second-order kinetic model. The adsorption of Cr (VI) on adsorbents is more favorable at low pH values. It is found that the adsorption process of Cr (VI) removal using adsorbents, are controlled by intra-particle diffusion mechanisms. The developed second-order polynomial equation is found appropriate for expressing the adsorption capacity as a function of dependent parameters such as initial Cr (VI) concentration, contact time and initial pH of the solution. The finding of this study shows that AC- EVML and AC-EA adsorbents are promising bio-based adsorbents for removal of Cr (VI) from water solution.

5.2 Recommendation

From this study work, we understand the activated carbon of AC-EVML and AC-EA have an ability to remove chromium (VI) from aqueous solution, therefore, the following direction of work is recommended to use in real wastewater treatments. In this study, only the effect of effect of initial concentration, pH, and contact time were studied. Thus, other parameters need further study to increase the efficiency of chromium (VI) ion uptake. Optimized removal efficiency of the AC-EVML and AC-EA adsorbent can be done through continuous column experiment, and try to immobilize the adsorbent on materials to improve its removal capacity. I also recommended that during adsorption they take long time.

The FTIR IR for the AC-EA have some unclear characterization it should be characterized by other techniques.

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