ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABAB INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIOENGINEERING

Removal of chromium hexavalent (Cr(VI) from aqueous solution using activated carbon prepared from *Prosopis Juliflora Plant* and find the optimal operating condition for adsorption process.

A thesis submitted to the school of Chemical and Bio-Engineering presented in partial fulfillment of the requirements of the Degree of Masters of Science in Chemical and Bio- Engineering (environmental engineering stream)

BY

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Addis Ababa, Ethiopia

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This is to certify that the thesis prepared by Molalign Emirie, entitled**:** ***Removal of chromium hexavalent (Cr(VI) from aqueous solution using activated carbon prepared from Prosopis Juliflora Plant and find the optimal operating condition for adsorption process.*** and submitted in partial fulfillment of the requirements for the Degree of Master of Science in Chemical and Bio-Engineering (Under Environmental Engineering stream) complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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Abstract

In the present study adsorption of chromium (VI) ions from aqueous solution by activated carbon prepared from Prosopis Juliflora plant was investigated under batch mode. The removal of hexavalent chromium was optimized by using response surface methodology. The influence of various process parameters such as initial chromium (VI) concentration, solution pH, sorbent dose and contact time on the removal process were investigated. A total of 30 sorption experimental runs were carried out employing the detailed conditions designed by response surface methodology based on the Central Composite Design. The analysis of variance (ANOVA) depicted that the quadratic model was suitable for the responses. Contour and response surface plots were used to determine the interaction effects of main factors and optimum conditions of process, respectively. From the experimental result, maximum chromium (VI) removal of 99.23 % was obtained at the optimum condition of initial chromium (VI) concentration (80 mg/L), pH (1.5), adsorbent dose (10g/L) and contact time (106.79 min). The experimental removal efficiency (99.23 %) agreed very well with the predicted one (99.27 %), indicating the suitability of the model employed and the success of response surface methodology in optimizing the conditions of the removal of chromium (VI) ions from aqueous solution.

Keywords: *Response surface methodology; Prosopis Juliflora; adsorption; ANOVA; Contour*

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List of abbreviation

AC	Activated Carbon
DOE	Design of Experiment
CCD	Central Composite Design
FTIR	Fourier Transform Infrared Spectroscopy
Ce	Equilibrium concentration in mg/L
C_o	The initial concentration (mg/l)
q_m	Freundlich constant
K_L	Langmuir constant
q	Adsorption capacity in mg/g
q_{max}	Maximum adsorption capacity in mg/g
q_e	Equilibrium adsorption capacity in mg/g
q_t	Adsorption capacity at time t in mg/g
K_1	Pseudo first order kinetics constant (min^-)
K_2	Pseudo second order kinetics constant (min^-)
K_f	Freundlich constant
RSM	Response surface methodology
ANOVA	Analysis of variance
PZC	Point of zero charge
PJF	Prosopis Juliflora

1. Introduction

1.1 Background

Waste water discharges from leather industries, chromate mining activities and electroplating industries are often contaminated with high concentrations of hexavalent chromium which has negative effect on the water environment. Hexavalent chromium compounds are toxic, carcinogenic (having the potential to cause cancer), and mutagenic and even cause lung cancer [1, 2].

Chromium compounds are widely used in leather tanning, electroplating, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile and steel fabrication industries. Effluents from these industries contain large quantities of hexavalent chromium. The undesirable effects of Cr (VI) can be avoided by treating the effluents prior to discharge into water streams. Various techniques have been employed for the removal of heavy metals including precipitation, adsorption, ion-exchange, membrane separation and reverse osmosis [3].

Activated carbons because of their high surface area, micro-porous character and the chemical nature of their surface have been considered as potential adsorbents for the removal of heavy metals from industrial effluents [4]. The adsorption efficiency of activated carbon depends on surface area and pore volume and these principle characteristics made activated carbon ideal for adsorption. However, for the removal of dissolved metal ions, the surface properties also play an important role [5]. Carbon adsorption is not as effective at removing metals as it is in removing organic compounds. Therefore surface modification techniques by activation (physical or chemical) were used to boost up the adsorption capacity and to add selectivity to adsorbent. The characteristics of the adsorbent greatly influence the removal efficiency of activated carbon. In general, the properties of the activated carbon vary depending on the nature of the raw material, activating agent and the conditions of activation process [5].

Activated carbon demand has been benefitted from a continuing intensification of the global environmental movement as well as rapid industrialization. In most developing and developed countries, use of AC in pharmaceutical sector offers the strongest growth prospect [6]. Additionally, an environmental concern in developing regions has been spurred new growth in

water treatment applications, which is already the largest single market in developed countries. Besides the necessity of clean drinking water, government environmental regulations that vary by region also impact the demand for AC in this sector significantly. Recently, carbon has been one of the magnificent elements which have revolutionized field of material and other sciences. From carbon one can obtain activated carbon which is best porous absorber with excellent properties. Activated Carbon (AC) is the common term used for a group of absorbing substances of carbon form, with a highly developed internal surface area and porosity that make the carbon more absorbent [6]. The fascinating properties of activated carbon are obtained when a carbonaceous raw material impregnated with dehydrating agents is subjected to carbonization, or when a char is subjected to controlled gasification by oxidizing gases [4].

AC concern industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining and mineral processing, nuclear, automobile and vacuum manufacturing, because of its adsorptive properties. It has also wide application in drinking water purification and wastewater treatment. Adsorption of Chromium using carbonaceous materials is the most economical and effective method for removal of Chrome as a remedy to clean the water prior to release to the environment [3-5]. Hence, owing to its vast applications, the demand for activated carbon in world market is increasing as more and more countries are becoming industrialized. Ethiopia's domestic market for activated carbon is also fast expanding with rapid growth of several end user industries and country's strategic plan to comply with green development strategy. The majority of activated carbon used throughout the world is produced by steam activation (physical activation). In this process, the carbonized product is reacted with steam over 900^{o}C. Another procedure used in the production of activated carbon involves the use of chemical activating agents before the carbonization step. The most commonly used activating agents are phosphoric acid, zinc chloride and salts of sodium and magnesium. Chemical agents act as dehydration agents and they may restrict the formation of tar during carbonization. Chemical activation is usually carried out at lower temperatures than the simple pyrolysis and the activation process with steam or carbon dioxide. The production at lower temperatures promotes the development of a porous structure, because under these conditions elementary crystallites of smaller dimensions are formed [7].

In this research, a local forestry wood, *Prosopis Juliflora*, was used to produce an activated carbon. The activated carbon was produced via chemical activation using phosphoric acid as activating agents and was characterized by several techniques. Prepared activated carbon was employed for removal of Cr (VI) from aqueous solutions.

Also the interaction effects of the four parameters on adsorption process were also in the present investigation, optimization of the process parameters affecting the adsorption process make by a five-level, four factors, and central composite experimental design with Design Expert software.

Central composite design technique was used to reduce the number of experiments, time, overall process cost and to obtain better response and many authors applied central composite designs for the development of adsorption process in various applications.

In Ethiopia especially in Afar region, *Prosopis Juliflora* is a plant, largely used as a local charcoal production. Hence the burnt carbon can be utilized for wastewater treatment at a cheaper cost easily operation. The purification process is simply an adsorption process and does not involve any chemical reactions. Wood or carbonaceous product on burning gets activated; the activation is simply the process of increasing the surface area of the carbon atom and inducing a positively charged atom [8].

1.2 Statement of the problem

Along with the economic growth, increasing number of population and increasing use of industrial product, untreated wastewater produced industrially also increased. With discharging of wastewater into the water body like leather tanning, textile and electroplating industry lot of chromium heaxavalent used. As a result, rivers and lakes pollution, water bloom happened and results in problem for water supply and reservoirs.

Due to untreated water effluents are discharged into the river from these. These industry areas are also flood-prone, resulting in further contamination of the water bodies. Approximately 70 % of the surface water and 60 % of the drinking water contains hexavalent chromium at more than double national and international standards (0.05 mg/L) [9, 71, and 7]. Therefore, the industries employee low cost and alternative activated carbon methods to remove the toxic Cr (VI) and protect the environment.

Although there are several physico-chemical methods, like chemical precipitation, electrolysis, ion-exchange, ultra-filtration, reverse osmosis etc, which are commonly employed for removal of toxic heavy metals from wastewaters, these methods have major disadvantage such as incomplete metal removal. utilization of expensive equipment and monitoring system requirements, high reagent or energy requirements and generation of toxic sludge or other waste products that require disposal. Therefore, it is a great necessary for developing inexpensive and efficient adsorbent material that easily available in large quantity and economically feasible to treat the wastes effluent from different industries using *Prosopis Juliflora* as adsorption material.

Due to severe (harsh) environmental degradation in the area the ecosystem has lost its natural immunity to react against invasive (all-encompassing) species. Thus, *Prosopis Juliflora* has become a problematic species expanding at an alarming rate in the Afar region, Dire Dewa and Methehara areas. It is fast growing, drought resistant, and with a remarkable coppicing power. Such unique adaptive traits of the species have got negative impact for local biodiversity and ecosystems. The most negative impact of *Prosopis Juliflora* is:

- The thorn of *Prosopis* on penetrating the eye or skin of human and animals causes more inflammation than expected from the physical injury.
- According to reports by local Afar pastoralists, the ingestion of the pod (seed) over long periods of time will result in death of cattle's.
- *Prosopis* replaced the local biodiversity in several spots in Afar region, mainly rangeland and dry riversides. By doing so, it will eventually evict or push out the local Afar pastoralists (cattle farmer) from their home and pasture fields aggravating(make worse) food and feed shortage in the region.

Therefore, the main focus of this study is to evaluate the adsorption performance of activated carbon prepared from *Prosopis Juliflora* for Cr (VI) (found mostly in leather industry waste water). Hence, change the problematic species (*Prosopis Juliflora*) into economic resource in the Ethiopia and so that it is substitute product for activated carbon to use for water and wastewater treatment.

1.3 Objectives of the Research

1.3.1 General objective

The overall objective of this work is to remove of chromium hexavalent (Cr (VI) from aqueous solution using activated carbon prepared from Prosopis Juliflora Plant and find the optimal operating condition for adsorption process.

1.3.2. Specific objectives

The specific objectives of this study are:

- to prepare activated carbon from *Prosopis Juliflora (invasive tree found in Rift valley region)* via chemical activation method using H_3PO_4.
- to examine the characteristic of raw material and activated carbon produced
- to evaluate the adsorptive capacity of prepared activated carbon for Chromium hexavalent in aqueous solution.
- to find optimal adsorption parameters (pH, adsorbent dose, initial Cr (VI) concentration, and contact time)for efficient removal of Cr (VI).
- to develop a model for the Cr (VI) adsorption process on prepared activated carbon by Design of Experiments (DOE) using Central Composite Design (CCD).
- to develop Kinetic and Isotherm models during adsorption of Cr(VI) on prepared activated carbon
- to compare the adsorption performance of prepared AC against carbonized charcoal and commercially available activated carbon.

1.4. Significance of the Research

The significance of this study can be seen from three different angles. The first significance is the production of activated carbon has growth of economy, especially in the increasing of industry, our country will able to fulfill its demand of activated carbon and also it will be in position of expert the product from the neighboring countries. As a result, the country gaining foreign currency and create job opportunity for community.

The second significance of the study is on the environment especially for Afar region. Since the activated carbon is going to produce from *Prosopis Juliflora*, the study will be considered as reducing the spread of species in the region. Hence, health problem of the animals such as cattle's camels, etc will be reduced and the ecosystem of the region will stable for living especially for pastoralists. Therefore, the immigration of the Afar people will be reducing because of spread of grasslands rather than *Prosopis Juliflora* species.

The third significance of the research is changed the plant (*Prosopis Juliflora)* to economic resource and to use for the removal of heavy metals discharging from different industries, so that the country addresses the environmental friendly and human health problems.

2. Literature Review

2.1. Chromium and its Impact on Environment and Health

2.1.1 Overview

Chromium is the 21st most abundant element in earth crust and its valance state ranges from -2 to +6, but it is generally found as trivalent [Cr (III)] and hexavalent chromium [Cr (VI)] in natural environments. Trivalent chromium occurs naturally in many vegetables, fruits, meat, grains and is often added to vitamins as a dietary supplement, whereas hexavalent chromium, most often produced by industrial processes and mining of chromium ore, is an indicator of environmental contamination. It occurs in combination with other elements as chromium salts, some of which are soluble in water.

Chromium is an extremely versatile element and finds a wide variety of uses. About 80% of the mined chromium is used for metallurgical applications, of which most is used in the stainless steel industry. It is used to manufacture ferrous and non-ferrous alloys, in chemical industry for pigment production, electroplating, leather tanning, and as a catalyst in the synthesis of many organic chemicals [38].

2.1.2. Chemistry and Behavior

Elemental chromium is a transition group metal and the most commonly occurring states in chromium compounds are +2, +3, and +6 with the +2 being unstable and readily oxidizes to +3. Cr (III) compounds are most stable and the presence of Cr (VI) can generally be attributed to the industrial activity. Most of the Cr (III) compounds are sparingly soluble in water, whereas the majority of Cr (VI) compounds are highly soluble. Table 2.3shows some of Cr (VI) compounds which are soluble in water.

Table 2.1 Hexavalent chromium compounds [38].

Compound	**Form**	**Solubility in water**
Sodium Chromate (Na_2CrO_4)	Yellow Crystal	Soluble
Calcium Chromate ($CaCrO_4$)	Yellow Crystal	Slightly soluble
Sodium Dichromate ($Na_2Cr_2O_7$)	Orange red crystal	Soluble
Potassium Chromate (K_2CrO_4)	Yellow Crystal	Soluble
Chromium Trioxide (CrO_3)	Dark red/brown crystal	Soluble
Potassium Dichromate (K2Cr2O7)	Orange red crystal	Soluble
Strontium Chromate ($SrCrO_4$)	Yellow Crystal	Slightly soluble

Chromium (VI) generally exists in monomeric ($HCrO_4$ - and CrO4 -2) or bimeric state (Cr2O7 -2). Presence of monomeric and bimeric species imparts yellow and orange colors to water, respectively [38].

2.1.3. Environmental Occurrence

Almost all the sources of chromium in the earth's crust are in the trivalent state. The most important mineral deposit for chromium is in the form of chromite ($FeCr_2O_4$). Acid mine drainage can make the chromium available to the environment. Hexavalent chromium compounds are used in metal finishing and chrome plating, in stainless steel production, in the manufacture of pigments, as corrosion inhibitors, and wood preservation. As the living matter does not produce energy required for the oxidation of Cr (III) to Cr (VI) in the organism, all the hexavalent chromium present in the environment is due to the human or industrial activities.

Hexavalent chromium is a strong oxidizing agent particularly in acidic media and tends to associate with oxygen, thereby forming chromate and dichromate [39]. The mineral form of Cr(VI) rarely occurs naturally in the environment as the crocoite (PbCrO4) and only a small amount of hexavalent chromium is formed by natural oxidation of Cr(III) in the soil, the rest is mostly introduced anthropogenically into the environment as a result of industrial processes [39].

2.1.4. Toxicology

Occupational exposure to hexavalent chromium generally occurs by inhalation and by skin (dermal) contact. Workers may be exposed by inhalation to fumes and mists containing Cr (VI)

when hot-cutting or welding stainless steel, or other chromium-containing metal alloys. However, when a substance is inhaled, a small amount is inevitably ingested. The general public may be exposed to Cr (VI) by drinking water from contaminated sites. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05 mg/l [9].

2.1.4.1. Effects of Short-term Exposure

Soluble trivalent chromium substances cause irritation to the eyes and skin, but this effect is usually related to their acidic nature. Chromium compounds can cause skin rashes in some people who are 'chromium-sensitive'. By contrast, hexavalent chromium is hazardous by all exposure routes:

- Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma).
- Ingestion may affect kidney and liver functions.
- Skin contact may result in systemic poisoning, damage or even severe burns.

2.1.4.2. Effects of Long-term Exposure

Exposure to hexavalent chromium, if prolonged or repeated, may lead to perforation of the nasal septum. The oral exposure of Cr (VI) can cause vomiting, oral ulcers, abdominal pain, indigestion, and diarrhea. Hematological effects such as leucicytosis and immature neutrophils were also noted. Both soluble and insoluble Cr (VI) compounds are able to cause structural damage to DNA, leading to genotoxicity. Studies indicate that Cr (VI) induced DNA damage may result in clastogenesis, altered gene expression, and the inhibition of DNA replication and transcription.

Chromium (VI) exists as highly soluble dichromate or chromate anions and is known to be toxic to all living organisms. It is proved to have a well-established carcinogen effect on human beings by the inhalation and oral route of exposure. The main concern about Cr (VI) compounds is associated with their mobility, which can easily lead to the contamination of both surface and ground waters [9]. Cr (VI) can be toxic for biological system, and water-soluble Cr (VI) is extremely irritating and toxic to human body tissue owing to its oxidizing potential and easy permeating of biological membranes. It leads to liver damage, pulmonary congestion, edema, and skin irritation resulting in ulcer formation. Chromium (VI) is toxic to numerous plants, animals,

bacteria and as a confirmed human carcinogen, poses a great threat to human health and environment. Trivalent chromium on the other hand, present mainly as relatively insoluble, immobile and non-toxic hydroxides and oxides. The toxicity of trivalent chromium is 500 to 1000 times less to a living cell than hexavalent chromium. Hexavalent chromium has been recognized as more toxic among heavy metals and hence it receives much more attention [9].

2.2 Chrome Tanning and Waste water Treatment

Currently, chrome tanning is the most widely used technique for leather tanning, as it offers a product with the best performance at a reasonable price. By this technique, around 8% of the leather weight is added as chromium salt. However, a significant share of the pollution resulting from tannery wastewater comes from this stage, due to the chrome that is not fixed to leather amounting 15% of the total chrome added to the tanning bath [74]. Tannery wastewater is usually homogenized with the rest of industrial effluents and chrome precipitates as chromium hydroxide, thus being retained in the sludge of the water treatment plants. Another environmental impact, which cannot be easily corrected in tannery wastewater, is salinity, reaching conductivity values on the order of 10.000-12.000 μs/cm [71, 19, and 15]. The main contribution to the effluent salinity is derived from the salt used for the preservation of the skins after flaying, followed by the high salinity of the pickling baths (preparation of skins with salts and acids prior to the addition of the tanning agent) and the tanning stage. Therefore, 30% of the chlorides contained in the effluent come from the pickling bath, and 60% of the sulphates come from the tanning bath [74].

The characteristics of the wastewater vary considerably from tannery to tannery depending upon the size of the tannery, chemicals used for the specific process, amount of water used, type of final product produced by a tannery and technology advancement. According to [71], a composite tannery wastewater has BOD5 (1900 - 4800 mg/L), COD (7900 - 15200 mg/l), sulfide (325 - 930 mg/l) and total chromium (30 - 150 mg/l).

Another study in Pakistan also indicated BOD5 (840 - 18620 mg/L), COD (1320 – 5400 mg/L), TN (236 - 350 m/L), sulfate (800 - 6480 mg/L), sulfide (800 - 6480 mg/L) and chromium (41-133 mg/L) [73].

The use of chromium (Cr) in chrome tanning, plating, paints, corrosion inhibitors, reinforced steel, textiles, and fungicides contribute to Cr discharge in the environment. However, the tanning industry is one of the major contributors of Cr pollution in many water resources [72]

2.3. Activated Carbon

Activated carbon (AC) is a non-graphitic, non-graphitizable carbon with a highly disordered microstructure. It is well known for high adsorption capacity due to its high surface area and porosity [9].

2.3.1. Historical Background

In ancient times (1500B.C), activated carbon (AC) has been used for medical purpose. There after the adsorptive powers of AC were discovered in 1773 when Scheele [21] conducted experiments with gases. However in 19^{th} century, the industrial production of activated carbon was well established and gradually it replaced bone chare in sugar refining processes [21].

2.3.2 Raw Materials

Although activated carbon can be produced from almost any raw material, it is most cost effective and environmentally conscious to produce activated carbon from waste materials. Activated carbons produced from coconut shells have been shown to have high volumes of micropores, making them the most commonly used raw material for applications where high adsorption capacity is needed. *Prosopis Juliflora* and other woody scrap materials also contain strongly developed microporous structures which are good for adsorption. Producing activated carbon from olive, plum, apricot, and peach stones yields highly homogenous adsorbents with significant hardness, resistance to abrasion and high micropore volume.

The quality of the resulting activated carbon is considerably influenced by the raw material. Although the activation procedure employed mainly determines the chemical nature of the surface oxides and the surface area of the resultant product, the structure of the pores and the pore size distributions are largely predetermined by the nature of the starting material. Any cheap substance with a high carbon and low ash content can be used as a raw material. Raw materials for the production of activated carbon include number of carbonaceous materials, especially wood, peat, brown coal, bituminous coal, lignite, coconut shells, almond shells, pits from peaches and other fruit, petroleum-based residues and pulp mill residues [18].

The selection of raw material for preparation of porous carbon, several factors are taken into consideration. The factors are:

- High carbon content

- Low in inorganic content (i.e. low ash)
- High density and sufficient volatile content
- The stability of supply in the countries
- Potential extent of activation
- Potential extent of activation
- Low degradation upon storage

Lignocelluloses materials constitute the more commonly used precursor and account for around 45% of the total raw materials used for the manufacture of activated carbon. Low content in organic materials is important to produce activated carbon with low ash content, but relatively high volatile content is also needed for the control of the manufacturing process.

Since the manufacturing process involves the removal of volatile matter, the economic relationship between price, availability and quality of raw materials on one side and volatile content on the other side, is an important one.

2.4 Prosopis Juliflora

The genus *Prosopis* consists of more than 70 species distributed in southwest Asia, Arica, and from western North America to Patagonia [10]. This genus has been selected for a forestation and massive restoration areas in arid and semi-arid lands in India, Iran and various countries in Africa. In Africa and Asia, as it is fast growing, hardy and drought-resistant tree with remarkable coppicing power turned to an invasive plant [10]. Prosopis Juliflora Called in Ethiopia, 'Weyane/Dergi-Hara' (Afar), 'Biscuit' (Dire-Dawa), elsewhere; mesquite, algarrobo,. They came originally from the Americas, there are many species, often confused, but work by the Ethiopian Agricultural Research Organisation (EARO) and the Henry Doubleday Research Association (HDRA) has confirmed that *Prosopis Juliflora* is the one commonly found in the above regions of Ethiopia [11]. Its first introduction is believed to have been in the late 1970s at Goro nursery, Dire-Dawa, possibly from India. In Afar, it may have been introduced possibly from Dire-Dawa or independently from Kenya or Sudan by foreigners working in the Middle Awash irrigation project in the late 1970s and early 1980s. Prosopis was planted over large areas until 1982, continued by the Food for Work Programme from 1986 to 1988. Some planting still continues, with *Prosopis* seedlings being grown for living fences and shade trees.

Prosopis Juliflora was widely distributed in Ethiopia as a biological soil and water conservation agent during the late 70s. Now it is considered a major threat because of its invasive nature. *Prosopis Juliflora* has an aggressive invasive character invading pastureland, irrigated cultivated lands and irrigation canals causing an irreversible displacement of natural pasture grasses as well as native tree species [12].

In terms of coverage, the areas most adversely affected nationally include the Afar and Somali Regions in the east and southeast of the country and the area around Dire Dawa City. There are also moderately affected areas in Amhara, Oromia, Southern Nations Nationalities and Peoples (SNNP) and Tigray Regions – that is, in the mainly dry lands of Central, East and North Ethiopia [13].

There is a potential to control the spread of *Prosopis Juliflora* to farmlands and key pasturelands by promoting utilization which proved economic incentive to local people to be involved in the management if planned and regulated carefully. Farm-Africa had been supporting local communities through provision of hand tools and organizing mass campaigns to clear *Prosopis Juliflora* from pasturelands and cultivable areas. However the approach couldn't get wider acceptance as there was no immediate benefit to the people. The idea of control through utilization such as charcoal production and pod crushing was raised with the principle of providing incentive for local people to be engaged on the control initiatives [14]. Cooperatives set up by Farm Africa were able to clear *Prosopis Juliflora* from over 396 hectares of land, in one year, and availed pasture as well as cultivable land to local communities depending on the potential of the land [15]. Because *Prosopis Juliflora* expands in Afar its area faster than the area that is brought under productive use, research from Farm Africa shows that not much can be done to eradicate *Prosopis Juliflora*, if external support in terms of community mobilization, technology transfer, private sector participation and supply of resources is not taking place.

2.4.1. Chemical composition of Prosopis Juliflora

The constituents of woody biomass can be divided into cellulose, hemi-cellulose, lignin, extractives, ash and water. The levels of chemical constituents in *P. Juliflora* have been estimated as 25%-30% hemi-cellulose, 40%-45% cellulose, 11%-28% lignin and 3%-15% extractives [16]. Extractive chemicals from woody biomass include sugar, resins, volatile oils,

fatty acids, tannins, alcohols and phenols with a tannin content of up to 9% of the woody material.

Table 2.2 physical and chemical properties of *Prosopis Juliflora and other precursors [16, 17]*.

Properties	Coconut shell	Bale fruit shell	*Prosopis Juliflora*
Chemical composition			
Cellulose	19.82	24.35	43.06
Lignin	30.11	19.90	27.41
Hemicelluloses +others	50.07	55.75	45.89
Proximate analysis			
Moisture	10.46	8.27	10.5
Volatile mater	67.67	72.12	70. 46
Fixed carbon	18.29	16.72	17.08
Ash	3.58	2.89	2.12

Bushes of Prosopis Juliflora along the road in Afar, Ethiopia

Prosopis eradication; cutting Prosopis eradication; burning

Figures 2.1 Prosopis Juliflora and its management mechanisms

2.5. Preparation of Activated Carbon

Generally activated carbon can be prepared from various raw materials including agricultural and forestry residues. Generally most of the precursors used for the preparation of activated carbon are rich in carbon [22]. Production of AC was achieved typically through two routes, physical activation and chemical activation [22].

2.5.1 Physical Activation

Physical activation is a two-step process. It involves carbonization of raw material followed by activation at elevated temperatures in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures. Carbonization temperature ranges between 400 C^o to 800 C^o, and activation temperature ranges between 800 C^o to 1100 C^o. Physical activation of various raw materials. Generally, CO_2 is used as activation gas, since it is clean, easy to handle, and it facilitates control of the activation process due to the slow reaction rate at high temperatures [22]

2.5.2. Chemical Activation

Preparation of activated carbon by chemical activation is a single step process in which carbonization and activation is carried out simultaneously. Initially the precursor is mixed with chemical activating agent, which acts as dehydrating agent and oxidant. Chemical activation offers several advantages over physical activation which mainly include (i) lower activation temperature (< 500 C^o) compared to the physical activation temperature (500 – 900 C^o) [18], (ii) single activation step, (iii) higher yields, (iv) better porous characteristics, and (v) shorter activation times [23] The most commonly used chemical activating agents are H_3PO_4, $ZnCl_2$, and KOH.

2.6. Structure of Activated Carbon

The adsorption capacity of activated carbon highly depends on the structure of activated carbon, such as porous structure, Crystalline Structure and Chemical Structure [9].

2.6.1 Porous Structure

The high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume, and pore size distribution. All activated carbons have a porous structure, containing up to 15 % of mineral matter in the form of ash content [22]. The porous

structure of AC formed during the carbonization process and was developed further during activation, when the spaces between the elementary crystallites are cleared of tar and other carbonaceous material. The structure of pores and pore size distribution largely depends on the nature of the raw material and activation process route.

The activation process removes disorganized carbon by exposing the crystallites to the action of activating agent which leads to the development of porous structure. The pore systems of activated carbon are of different kinds and the individual pores may vary greatly both in size and shape. Active carbons are associated with pores starting from less than a nanometer to several thousand nanometers. A conventional classification of pores according to their average width (w), which represents the distance between the walls of slit shaped pore or the radius of a cylindrical pore, [24] and officially adopted by the International Union of Pure and Applied Chemistry [25] is summarized in Table 2.2

Table 2.3. Classification of pores according to their width [25]

Type of pores	Width (w)
Micro pores	< 2 nm (20 A^o)
Mesopores	2 – 50 nm (20 – 500 A^o)
Macro pores	> 50 nm (> 500 A^o)

The effective radii being less than 2 nm, the adsorption in micropores occurs through volume filling and there is no capillary condensation. Generally micropores have a pore volume of 0.15 to 0.70 cm3/g, and constitute about 95% of the total surface area of the AC. Brunauer (1970) and Dubinin (1979) further classified that the micropores can be subdivided into two overlapping microporous regions such as ultra-micropores (with effective pore radii less than 0.7 nm), and super-micropores (having radii of 0.7 to 2 nm). Generally the microporous structure of an adsorbent is characterized by adsorption of gases and vapors and, to a small extent, by smallangle x-ray technique [24] Mesopores, also termed as transitional pores, ranges from 2 to 50 nm of width. The surface area of mesopores does not constitute more than 5% of total surface area and their volume varies in between 0.1 and 0.2cm3/g. However, by using special methods, it is possible to enhance mesopores attaining a volume of 0.2 to 0.65 cm3/g and surface area of 200 m2/g. Capillary condensation and adsorption desorption hysteresis are the characteristic features of mesopores [26]. Beside their contribution to the adsorption of adsorbate, mesopores act as

conduits which lead the adsorbate molecule to the micropore network. Pores having effective radii larger than 50 nm are considered as macropores, frequently in the range 500 to 2000 nm. Hence, in adsorption process macropores are not of considerable importance but they act as transport channels for the adsorbate into the mesopores and micropores. Macropores can be characterized by mercury porosimetry and by electron microscopy [27].

2.6.2. Crystalline Structure

Microcrystalline structure of activated carbons starts to develop during the carbonization process. The Crystalline structure of activated carbons differed from the graphite with respect to the interlayer spacing. The interlayer spacing ranges between 0.34 and 0.35 in active carbons, which is 0.335 in case graphite. The basic structural unit of activated carbon is closely approximated by the structure of graphite.

Much of the literature suggests a modified graphite structure for activated carbon. During the carbonization process free valences were created due to the regular bonding disruption of micro-crystallites. In addition, process conditions and presence of impurities influence the formation of vacancies (pores) in microcrystalline structure [28].

Based on the graphitizing ability, active carbons are classified into two types, graphitizing and non-graphitizing carbons. Graphitizing carbon had a large number of graphite layers oriented parallel to each other. The carbon obtained was delicate due to the weak cross linking between the neighbor micro-crystallites and had a less-developed porous structure. The non-graphitizing carbons are hard due to strong cross-linking between crystallites and show a well developed microporous structure [29, 30]. The formation of non-graphitizing structure with strong cross-links is promoted by the presence of associated oxygen or by an insufficiency of hydrogen in the original raw material.

2.6.3. Chemical Structure

Besides the porous and crystalline structure, an active carbon surface has a chemical structure as well. Though the adsorption capacity of activated carbon is determined by its porous structure but is strongly influenced by a relatively small amount of chemically bonded heteroatoms (mainly oxygen and hydrogen) [22]. The variation in the arrangement of electron clouds in the

carbon skeleton results in the creation of unpaired electrons and incompletely saturated valences which influences the adsorption properties of active carbons, mainly for polar compounds.

Activated carbons are invariably associated with significant amounts of oxygen, hydrogen [31] and other heteroatoms like sulfur, nitrogen and halogens [31]. Much of the literature show that the heteroatoms are bonded to carbon atoms of the edges and corners of the aromatic sheets or to the carbon atoms at defect positions to form carbon-oxygen, carbon-hydrogen, carbon-sulfur, carbonnitrogen, and carbon-halogen surface compounds, known as surface groups or surface complexes [31].

2.7. Classification of Activated Carbon

Activated carbons are complex products and the classification is difficult based on their preparation methods, physical properties, and surface characteristics. However, the general classification of activated carbons based on particle size divides them into Powered Activated Carbon (PAC), Granular Activated Carbon (GAC), and Activated Carbon Fibres (ACF) [22].

2.7.1 Powered Activated Carbon

Powered Activated Carbon (PAC), has a typical particle size of less than 0.1 mm and the common size of the particle ranges from 0.015 to 0.025 mm. Typical applications of PAC are industrial and municipal waste water treatments, sugar decolorization, in food industry, pharmaceutical, and mercury and dioxin removal from a flue gas stream [32].

2.7.2. Granular Activated Carbon

Granular Activated Carbon (GAC) has mean particle size between 0.6 to 4 mm. It is usually used in continuous processes of both liquid and gas phase applications. GAC has an advantage over PAC, of offering a lower pressure drop along with the fact that it can be regenerated and therefore reused more than once. In addition to the proper micropore size distribution, its high apparent density, high hardness, and a low abrasion index made GAC more suitable over PAC for various applications [32].

2.7.3 Activated Carbon Fibers

Activated carbon Fibers (ACFs) are carbonized carbons which are subsequently heat treated in an oxidizing atmosphere. ACF began to be developed in 1970 using the precursor viscose rayon

which mainly consists of cellulose. Later the rmoset polymer materials like saran and phenolic resins were used as precursors to produce ACF [33]. A good ACF precursor must be non-graphitic and non graphitizable carbon fibre which was isotropic in nature. From the end of 1980s, interest is still centered on the production of ACFs from various inexpensive precursors [34].

2.8. Activated Carbon Applications

Activated carbon is an excellent and versatile adsorbent and its main applications include the adsorptive removal of color, odor, taste, and other undesirable organic and inorganic impurities from drinking waters; in the treatment of industrial waste water; air purification in food processing and chemical industries; in the purification of many chemical, food and pharmaceutical products; in respirators for work in hostile environments; and in a variety of other gas-phase applications. Nearly 80% of the total activated carbon is consumed for liquid phase applications where, both granular and powdered activated carbons can be used [35]. For gas-phase applications, granular activated carbon is usually the choice.

The aqueous phase adsorption for the removal of both organic and inorganic compounds has been a very important application of activated carbon and researchers have reported potential applications of GAC to liquid phase. By using activated carbon, satisfactory results were obtained in the removal of organic chemicals from water [36] and the adsorptive removal of organic compounds was compared with the inorganic ones [35].

Heavy metal ions stand out among the inorganic aquatic pollutants due to their persistence and toxicity. The heavy metal flux into groundwater and surface water has been increased randomly due to the unrestrained usage in industrial processes. Natural waters have been found to be contaminated with several heavy metals arising mostly from mining wastes and industrial discharges [37]. According to World Health Organization [9] the most toxic heavy metals include cadmium, chromium, copper, lead, mercury, and nickel.

2.9. Chromium (VI) Removal by Activated Carbons.

As discussed, the toxicity caused by hexavalent chromium is high and therefore priority is given to regulate this pollutant at the discharge level. Currently there are several methods available for the removal of Cr(VI) from industrial effluents. Chemical precipitation,

coagulation, ion exchange, solvent extraction, and membrane filtration produce large amounts of sludge and waste that need to be disposed of and can consequently cause a lot of problems to the environment due to the presence of high content of chromium. Other techniques such as ultra-filtration, nano-filtration, and reverse osmosis are associated with high capital and operational costs[42].

Table2.4 various techniques used for Cr (VI) removal and their drawbacks [42].

Technique	Disadvantages
Distillation	• Takes time for purification • Uses electricity all the time the unit is operating • Some contaminants can be carried into the condensate • Requires careful maintenance to ensure purity
Ion exchange	• Resin fouling • Heating is required to maximize efficiency • Does not effectively remove particles, pyrogens or bacteria • High operating costs over long-term
Filtration	• Low chemical and thermal stability • Membrane fouling • High capital cost • Requires tight operation and Maintenance
Reverse osmosis	• Limited flow rates • Requires high pressure inflow • Damaged membranes are not easily detected
Ultraviolet (UV) radiation	• Not suitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter • Not effective against non-living contaminant, lead, asbestos, many organic chemicals, chlorine, etc • Requires electricity to operate

One of the technologies that can overcome these disadvantages is the adsorptive removal of hexavalent chromium by various adsorbents. In recent years, scientists focused on the preparation of adsorbents from various waste materials for the removal of contaminants from the

environment as this technology not only solves the problem of waste disposal and also converts a potential waste to a valuable product. Adsorption by activated carbons for the removal of contaminants has various advantages over other processes. Activated carbons are very effective adsorbents due to their very high surface area and pore volume. Rate of adsorption by AC is very high and faster adsorption kinetics. High quality effluents can be obtained after treatment [43].

Among the numerous adsorbents available, activated carbon has been undoubtedly the most popular and widely used for the removal of hexavalent chromium from aqueous phase. Activated carbon can be prepared from various precursors through different methods and operating conditions. The adsorption capacity of the prepared activated carbon depends mainly on the type of precursor used and method of preparation.

2.10. Effect of Process Parameters

The effect of different process parameters such as pH, Initial metal concentration, contact time, adsorbent dose, and initial Cr (VI) concentration were strongly studied and the optimum conditions determined in various studies [9-16].

2.10.1. Effect of pH

The pH of the solution is an important factor for the removal of Cr (VI) by activated carbons. Tested coconut shell based activated carbons for the removal of Cr (VI) at different pH values ranges from 2.0 to 8.0. They observed that the adsorption of Cr (VI) continuously decreased with the increase in pH and the maximum adsorption was observed at pH 2.0.

Chromium exists in different oxidation states and the stability of these forms depends on the pH of the system [44] and the equilibrium between different ionic species of chromium as follows:

$$H_2Cr_2 \leftrightarrow H^+ + HCro_4^-$$

$$HCro_4^- \leftrightarrow H^+ + Cro_4^-$$

$$2HCro_4^- \leftrightarrow Cr_2o_7^{2-} + H_2o$$

The rapid decrease in the removal of Cr(VI) with the increase of pH may be due to that low pH leads to an increase in H+ ions on the carbon surface, which results in significantly strong electrostatic attraction between /0123 and positively charged carbon surface [101]. Also found that the sorption capacity of AC prepared from almond shells was higher in acidic pH (<5) due to the negatively charged chromium species bind through electrostatic attraction to positively charged

functional groups of the adsorbent surface. At pH >5, the decrease in sorption capacity is due to the increase of the negative charge on the adsorbent surface, thus the electrostatic force of attraction between the adsorbent surface and adsorbate ion decreased.

Based on the equilibrium constants of hydrolysis for Cr (VI), the two major species in the solution are $HCro_4^-$ (dominant in pH range of 1.0 to 6.0), and Cro_4^- (dominant in pH range of 6.0 to 8.0). And they explained the adsorption of Cr (VI) on activated carbon by the following reactions and they observed the pH of the final solution decrease due to the release of protons [45].

$AC\text{-}\ OH_2^- + HCro_4^- \leftrightarrow AC\text{-}\ OH_2Cro_4^- + H^+$

$AC\text{-}\ OH_2^- + Cro_4^{2-} \leftrightarrow AC\text{-}\ OHCro_4^{2-} + H^+$

Proposed totally different mechanism that the removal of Cr (VI) at low pH is governed by the active reduction reaction given by the following equations and they noticed the increase in pH of the final solution [101].

At low PH

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

At moderate PH

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

The effect of pH on the adsorption of Cr (VI) is attributed to the interactions between ions in solution and complexes formed at the adsorbent surface. The Cr(VI) can form different species at different pHs in aqueous solutions and the maximum adsorption of Cr(VI) on the various adsorbents was found at pH 2.0 and negligible at pH values over 8.0 [46].

2.10.2. Effect of Contact Time and Initial Chromium (VI) Concentration

Activated carbons prepared using different precursors such as cornelian cherry, apricot stone, and almond shells were applied for the removal of Cr (VI) from aqueous solution [47]. The removal of Cr (VI) for all the types of AC was shown to increase with time and initial Cr (VI) concentration. The amount adsorbed increased from 10.60 mg/g to 59.40 mg/g with the increase in initial Cr (VI) concentration from 20 to 300 mg/l in 72 h of contact time.

The adsorption of Cr (VI) on tamarind wood activated carbon was rapid initially within 20 min and with further increase of time the adsorption kinetics decreased, and finally reached equilibrium within 40 min. The adsorption capacities increased from 44 to 99% with the decrease of initial Cr (VI) concentration from 50 to 10 mg/l [48].

Much slower rate of adsorption was reported for the removal of Cr (VI) by various commercially available ACs and the equilibrium was reached in about 5 days [50], whereas Cr (VI) removal by Hevea Brasilinesis sawdust activated carbon increases with time and attains equilibrium value at a time of about 300 min. The amount adsorbed was found to be dependent on the initial Cr (VI) concentration, and it increases with the increase in metal concentration. At low concentration of Cr (VI), the available surface for adsorption is very large, so that the removal becomes independent of the initial Cr (VI) concentration. However, at high concentrations this ratio is low concluding that the percentage removal depends on the initial concentration of Cr (VI) [49].

2.10.3. Effect of Adsorbent Dose

The Cr (VI) removal efficiency was found to increase with the increase of adsorbent dose in various studies and after reaching the optimum value, further increase in adsorbent dose does not shows any significant change [50, 51]. The trend of increase in removal capacity is due to the fact that the availability of more adsorption sites for the metal ions [51].

2.11. Previous Studies

- **Saw dust**

Saw dust was investigated as a low cost adsorbent for removal of Cr (VI) from synthetically prepared industrial effluent electroplating and tannery industries [54]. The experimental results demonstrate that the sawdust adsorbent has a significant capacity for adsorption of Cr (VI) from wastewater streams. The maximum adsorption of Cr (VI) on sawdust was obtained at pH 1. The equilibrium time obtained was 105 min for Cr (VI) adsorption on sawdust. The equilibrium data for the adsorption of Cr (VI) on sawdust was tested with various adsorptions isotherm models such as Langmuir, Freundlich, Redlich-Peterson, Dubinin-Radushevich and Generalized equation. The Langmuir isotherm model was found to be most suitable for the Cr (VI) adsorption using sawdust. The maximum adsorption capacity obtained using the Langmuir isotherm model was 41.5 mg g^{-1} at pH 1. Various kinetic models such as pseudo first- order, second-order and

Elovich model were used to evaluate the mechanism of adsorption of Cr (VI) on sawdust. The adsorption process follows second order kinetics and the corresponding rate constants, for initial Cr (VI) concentration ranging from 100 was found to 3.39x10-3g mg^{-1} min^{-1}.

- **Wheat shell**

The use of wheat shell was examined as a potential adsorbent for Cr (VI) removal from aqueous solution [54]. The experimental results showed that the adsorption process is pH dependent and have maximum removal at pH less than 3 at 35^{o}c. They also reported that the experimental data fitted best to both Langmuir's isotherm (R^2 =0.9998) and Freundlich isotherm (R^2= 0.9998) with q_{max} = 0.1574mg/g and K_f = 1.9288 mg/g respectively at initial metal concentration of 5g/L, adsorbent dose 20g/L and temperature of 35^{o}c.

- **Commercial coffee waste**

Commercial coffee waste was investigated for the removal of Cr (VI) and Cu (II) metal from aqueous solution [55]. The experimental results revealed that for the formaldehyde treated commercial coffee waste at pH 2, the percentage Cr (VI) removal was 5% and for untreated commercial coffee waste it was 4%. However, increasing the pH from pH 2 to 5 increased the adsorption capacity to 62% for the formaldehyde treated waste. After pH 5 the percent removal stays constant. The kinetics study showed that a very fast increase in adsorption rate of Cr (VI) ions by treated coffee waste occurred at the first 20 minutes and equilibrium was reached after 3 hours. The experimental kinetics data fitted well to pseudo- second order (R^2 =0.993) and pseudo-third order (R^2=0.872). The experimental data on the isotherm fitted well to Langmuir's (R^2 = 0.996) and Freundlich's model (R^2= 0.94) with q_{max}=43.75mg/g and K_f=12.505mg/g.

- **Algal biomass**

Green micro algal isolate, Chlorella Miniata was used for biosorption and bioreduction of Cr (VI) from aqueous solutions [56]. The experimental results showed that, at initial pH of 1.0 and biomass dose of 2g/L, nearly 100% Cr(VI) was removed within 58 hours while increase the pH to 4 resulted in decrease of the removal capacity to 10%. However, at pH 2 with 1g/L ,2g/L and 5g/L of biomass dose, the Cr (VI) removal percentages obtained were 60%, 85% and 1000%respectively with respective equilibrium time of 240, 215 and 150 hours. The

experimental results also showed that the equilibrium time for 100mg/L, 60 mg/L and 200mg/L was 105, 72 and 30 hours. The results also showed that Cr(III) appeared gradually in the solution with the removal of Cr (VI) indicating the Cr (VI) adsorbed on the algal biomass was reduced to Cr (III) . The experimental results on the adsorptions kinetics showed that the data fitted well to the pseudo first order kinetics model with reaction rate constant of $0.0215h^{-1}$, R^2= 0.973 for initial metal concentration of 20mg/L.

Non living biomass of Sorgassum sea weed (marine algal) was used to remove Cr (VI) from aqueous solution [57]. It was found that at temperature of 22^oc, biomass dose of 2.5g/L and initial metal concentration of 100mg/L, maximum Cr (VI) removal of 60 mg/g was obtained within 60 minutes. The experimental data fitted well to the Lagmuir isothermal model with q_{max}= 114mg/L with R^2 =0.99.

3. Materials and Methods

3.1 Materials

3.1.1 Chemicals and Reagent

All the reagents used for the current investigation were of analytical grade from. Distilled water was used throughout the study. Glass ware and plastic ware were cleaned by soaking in 10 %(v/v) nitric acid and rinsed with distilled water prior to use.

- Standard Cr (VI) solution (1000mg/L): prepared by dissolving 2.829 gram of overnight deride $K_2Cr_2O_7$(s) in 1000ml of distilled water.
- Calibration standards: Lower concentration standards were prepared from the stock solution.
- Working Cr (VI) solutions: working solutions at different concentrations were prepared daily from the stock solution.
- pH adjustment: (1M) NaOH RANKEM, India) and 1M HCl (RANKEM, India) were used.
- Adsorbent activation: 98%H_3PO_4 (RANKEM, Indian) was used for *Prosopis Juliflora* activated carbon.
- Spectrophotometric analysis: 1.5-Diphenylcarbized (Merck, Germany), Acetone 99% (sigma Aldrich, USA) and 3M H2SO4 (RANKEM, India) were used for the Spectrophotometric analysis of Cr (VI) ions.
- Point of zero charge: 0.1MKNO3 (BDH, England) was used.

3.1.2 Equipments and apparatus

The instrument and apparatus used throughout the experiment are listed below in table 3.1.

Table 3:1 List of equipments and instruments used for in this study

Instrument or apparatus	**Manufacturer and model**	**Use**
Cross beater mill	Retsch (Germany)	Size reduction of adsorbent
Analytical sieves with shaker	Retsch, AS200 (Germany)	Sampling sieving
Drying Oven	Memmert, 100-800 (Germany)	Sample drying
Analytical balance	Ohaus, EP214C (Switzerland)	Sample weight
Vacuum Pump	KNF laboport	Vacuum filtration
Spectrophotometer	Jenway6300 (England)	Cr (IV) analysis
Tubular furnace		Sample pyrolysis
Furnace	Nabertherm LHT 02/16 (Germany)	To Convert sample to ash
pH meter with glass electrode	Jenway 3505 (England)	pH measurement
Temperature controlled water bath shaker	Stuart SBS 40 (England)	Shaking Samples
Micro Pipette (different volume)	Socorex Acura835 (Switzerland)	Volume measurement
Magnetic stirrer		Mixing samples for pH measurement
FTIR	Perkin Elmer spectrum65	Surface functional groups detrmination

3.2 Experimental Methods

3.2.1 Raw material collection and pre treatment

All the experiments were carried out with *Prosopis Juliflora* species. The raw material used for this thesis, the wood of *Prosopis Juliflora*, was collected from Gewane district located in Afar Regional state which is one of the famous Prosopis Juliflora Cultivation areas in the country. The wood was carefully collected from only one plant species (*Prosopis Juliflora* species) in order to avoid contaminations. It was then crushed using crushing machine and sieved mechanically to get a uniform size distribution between 10 to 18 mesh (or 1- 2mm). The sample was then dried in an oven at 110^{o}c to reduce its moisture content (6-10%). The dried sample was then stored in air tight plastic bags and stored in clean space for further experiment.

The carbonization setup

The carbonization process for all samples was done using a horizontal tubular furnace (Carbolite). Nitrogen gas (99.6% purity) is continuously ejected to the tubular furnace in order to create inert atmosphere by discharging atmospheric gases and also to remove the volatile component from the tube. Nitrogen gas was also used for cooling the reactor when carbonization is completed. The samples were packed inside the tubular stainless tube using fiber glass. The fiber glass was in order to keep the sample in a specific position (high heating regions of the reactor). The hot discharge gases (smoke), nitrogen gas from the reactor and the volatile matter passing out from the reactor is directed to a cold water bath and finally released to the atmosphere through a rubber tubes.

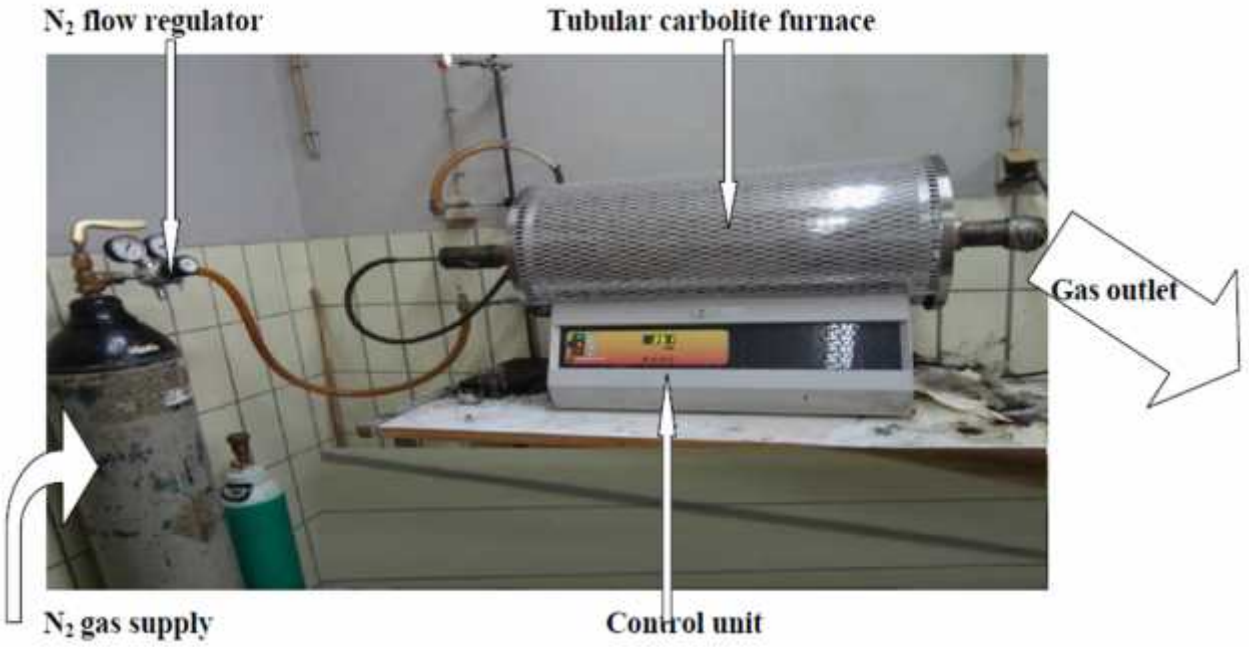


Figure 3.1 Carbonization process equipment setup

3.2.2 Preparation of Charcoal (Control) via Carbonization

A 100 gram of pretreated sample was placed in a horizontal stainless steel tubular reactor equipped with tubular furnace, temperature controller, and N_2 gas inlet. The carbonization was performed at optimum conditions 500^0C, with heating rates 10 and 12^0C/min and the carbonization time 60, minutes referee from the literature [58]. Direct Carbonization of the P*rosopis Juliflora* without activation was done in order to investigate the effect of carbonization

temperature and carbonization time on the yield of product and on the adsorption capacity of charcoal for Cr (VI) in aqueous solution. The product yield was calculated by:

$$Yield\ (\%) = \frac{M1}{Mo} * 100$$

Where:

M_0: mass of raw material used (dry basis)

M_1: mass of product obtained (dry basis)

3.2.3 Preparation of activated carbon via chemical activation (H_3PO_4)

A 100 gram of pretreated sample (1-2mm size) was soaked into the 300ml aqueous solution containing desired amount of activating agent for 12 hrs. The impregnation ratio between sample (dry basis) and activating agent was maintained at 1:1 (wt/v). The samples were then dried in oven for overnight at 105^0C to remove water. The impregnated sample was then placed in a horizontal stainless steel tubular reactor equipped with horizontal tubular furnace (Carbolite), temperature controller, and N_2 gas inlet. The carbonization was performed at activation temperatures, heating rates and activation time (450^0C, 10^0C/min, and 60 min) respectively.

The product is temporary stored in a dissector for some time and then the activated carbon was washed several times using distilled water in order to remove the H_3PO_4 and attain a neutral pH. After washing, the product was dried in oven overnight and stored in air tight plastic bags until it is needed.

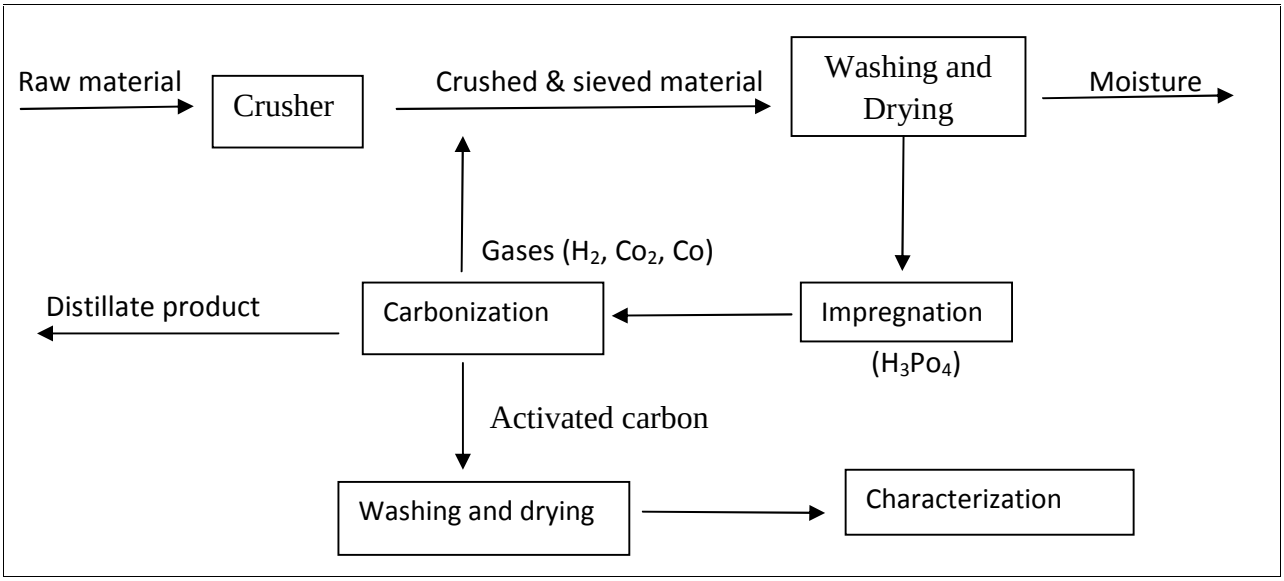


Figure 3.2 Schematic diagrams for preparation of activated carbon

3.2.4 Characterization of the adsorbent

3.2.4.1 Proximate Analysis on Laboratory prepared adsorbent

- ***Determination of % Moisture content***

To determine the % moisture contents of the laboratory prepared adsorbent material, 0.5g sample was taken in a clean and dry crucible (W_1) and kept in an oven at 105^{o}C for 2hrs. The sample was then kept in desiccators to cool and weight, again it was kept in an oven until constant weight after drying was obtained (W_2) and % moisture was determined by the following formula.

$$\text{Moisture}\ (\%) = \frac{(W1)-(W2)}{(W1)} x100$$

Where:

W_1 = weight of sample and crucible before drying (in gram)

W_2 = weight of oven dried sample and crucible (in gram)

Volatile matter:

The sample was measured (1 gram) and placed in a dry and clean crucible (W1). The crucible was then closed to protect it from air contact while inside the furnace. It was then heated up to 900 ^{0}C for exactly 7 min in a furnace. The crucible was then cooled in desiccators and weighed (W2) and the volatile matter content was determined by following the formula:

$$\%\ \text{volatile mater} = \frac{W1-W2}{W1} X100$$

Where:

W1 = weight of sample and crucible before heating (gram).

W2 = weight of sample and crucible after heating (gram).

- **Determination of % Ash content ASTM 1102-84 (Reapproved 2001) (69)**

An empty crucible and cover was ignited in the muffle at 600^{o}C for 1hr and cooled in a desiccators and weight to the nearest 0.1mg. A certain amount gram of sample air-dried laboratory prepared adsorbent was placed in the crucible, the weight of crucible plus specimen was noted. The crucible and contents was placed in the muffle furnace and ignited until all the carbon was eliminated. The temperature of final ignition was set at 600^{o}C; the sample was kept for 3hrs. After the 3hr, the crucible with its contents was removed and placed in desiccators to cool to 30^{o}C. The crucible with its contents was weighted accurately. The following formula was used to obtain ash content in the adsorbent.

$$\text{Ash content}(\%) = \frac{W1}{W2} x100$$

Where:

W1= weight of ash (in gram)

W2 = weight of sample oven- dried sample (in gram)

- ***Fixed Carbon Content***

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture content, ash content, and volatile matter content subtracted from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)

3.2.4.2 pH of zero charge determination

The point of zero charge (pH_{pzc}) of the solid biomass is a function of pH. The pH at which the charge of the solid surface is zero is referred to as the point of zero charge (pH_{pzc}). The point of zero charge (pH_{pzc}) of the biomass was determined by the solid addition method. For this purpose a series of 100ml of Erlenmeyer flasks 45ml of standard solution of 0.1 $MKNO_3$ was transferred. The initial pH_s of solution (pH_i) were approximately adjusted from 1.0 to 8.0 by adding either 0.1 MHCl or NaOH. The total volume of the solution in each flask was made exactly to 50ml by adding the 0.1$MKNO_3$ solution of the same strength. The pHi of the solution was then accurately noted, and 0.1g of adsorbent was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48hr with intermittent manual shaking. The final pH values of the supernatant liquid (pH_f) were noted. The difference between the initial and final pH (ΔpH) values in y-axis was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x-axis gave the pHpzc.

3.2.4.3 FTIR analysis

The FTIR analyses were conducted using Perkin Elmer spectrum 65 FTIR Spectrometer in average wave number from 4000 to 400cm-1. The laboratory prepared activated carbon samples for the analysis were first milled in a ceramic pestle and mortal to powdery conditions. The powder was then mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1mm, required for FTIR analysis.

3.2.5 Batch adsorption experiment

Batch experiment were carried out at room temperature by adding the specified gram of samples powder and shaking with 100ml of Cr(VI) solution in a 250ml conical flask, the samples were agitated at a rate of 200rpm for specified times. After agitation, the powder was removed by filtration using what man number 1 filter paper. The concentration of Cr (VI) in the filtrate was determined using Jenway UV-VIS spectrophotometer with 1, 5-diphenyl carbonized in acidic conditions. All samples were carried out in duplicate under the same conditions and the average results were taken.

The percentage removal of Cr (VI) was calculated by using following equation:

$$\% \text{ Removal} = \left(\frac{C_o - C_t}{C_o}\right) x100$$

Where; C_o and C_t are the Cr (VI) concentrations in milligrams per liter initially and at a given time t respectively. The adsorption capacities of adsorbents used in this study were determined by using the equation:

$$q = \frac{(C_o - C_e)V}{(W)}$$

Where V is the volume of the solution (L), C_o is the initial concentration (mg/l), C_e is the equilibrium concentration (mg/l), and W is the weight of the adsorbent (g).

The effects of pH of solution, initial Cr concentration, adsorbent dose and adsorption time on the adsorption performance of prepared activated carbon were thoroughly investigated using central composite design to find optimal adsorption conditions.

3.2.5.1 Effect of pH of solution

The effect adsorption of Cr (VI) was studied for solution pH ranging from 1 to 4. 0.5g of adsorbent was contacted with 100ml of 60mg/l of Cr (VI) solution. HCl or NaOH solutions (0.1N) were used to adjust pH values. All pH measurements were taken using a laboratory pH meter.

3.2.5.2 Effect of Initial Concentration

The initial concentration of Cr (VI) was varied from 40 to 200mg L^{-1}. 0.5g of adsorbent was contacted with 100ml of different concentration of Cr (VI). Samples were shaken at 200rpm for two hours at 20^{o}C.

3.2.5.3 Effect of adsorbent dose (amount in gram)

The amount of the adsorbent was varied from 0.25 to 2g. Each sample was contacted with 100ml of 60ml/L of Cr (VI) solution for two hours and shaken at 200rpm at 20^{o}C.

3.2.5.4 Effect of contact time on Chromium (VI) adsorption

2g of the adsorbent was contacted with one liter of Cr (VI) 60 mg/L for different period of time. The solution was mixed using a laboratory rotary shaker at rate 200rpm. 5ml of samples was taken in frequent intervals using a micro pipette, and filtered through No 1 whatman filter paper. The samples were collected, and analyzed for up to 3hours. Samples were collected at a 15 minutes interval.

3.2.5.5 Analysis of Chromium (VI) ions

The concentration of the residual Cr (VI) ions in the solution was determined by UV-spectrophotometer at 540nm. A.25% w/v solution of diphenyl carbazide was prepared in 100ml acetone. 5ml each of the sample solutions, containing various concentration of Cr (VI) (0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1mg/L) were pipette out into 50ml standard volumetric flasks. To this 2ml of $3MH_2SO_4$ was added following by 2ml of diphenyl carbazide and the total volume was made up to 50ml using distilled water. The solutions were allowed to stand 10 minutes before measurement. Chromium concentration estimated by the intensity of the color complex formed was measured using a UV- visible spectrophotometer. The absorbance was measured against a reagent blank at wavelength of 540nm. A linear plot was obtained indicating adherence to the Beer Lambert's law in the concentration range studied.

3.2.6. Statistical analysis and optimization of adsorption process parameters

The experimental design for optimization of Cr (VI) adsorption onto activated carbon prepared from *Prosopis Juliflora* was done by applying Response Surface Methodology (RSM) through five levels Central Composite Design (CCD). Design Expert (Stat-Ease, Inc., version 7.1.1, Minneapolis, USA) software was used for statistical data analysis. In order to investigate the effect of various independent process parameters such as initial concentration (A), pH (B), adsorbent dose (C) and contact time (D) on % removal of Cr (VI), batch experiments were conducted based on the central composite design (CCD). A CCD with 30 experiments was used for the

optimization of process parameters. The coded values of the independent variables were determined by the following equation.

$N = 2^k + 2k + n_o = 24 + 2(4) + 6 = 30$

Where N is the total number of experiments required and K is the number of factors. Five different levels for each experiment in coded form +α,-1, 0, +1, and -α, the value of α depends on the number of points in the factorial portion of the design [63]. The value was fixed at 2 as shown below.

$$\alpha = \alpha^{k}/_{4} = 2^{4}/_{4} = 2$$

The relationship between the coded and uncoded form of the variables is given by;

Coded value = $(z_i) = (\frac{xi - xi^*}{\Delta xi})$

Where $z_i$is the coded value of i^{th} test variable, xi the uncoded value of the i^{th} variable, xi* is the uncoded value of the i^{th} variable at center point and Δxi is the step change. Design expert software version 7 was used for optimization of the four adsorption process parameters. The range and levels of individual variables are given in table 3.3.

Table 3.2 Experimental factor levels used in central composite design

Independent Variables	Coded factor	Coded levels		
		-1	0	+1
Initial metal Concentration (mg/L)	A	80	120	160
PH meter	B	1.5	2.75	4
Adsorbent dose (g)	C	0.5	0.75	1
Contact time (min)	D	60	90	120

The maximum and minimum values set based on the concentration of the effluent from leather tanning industry and from literature used for this study

3.3. Modeling of Cr (VI) Adsorption

Modeling of the adsorption of Cr(VI) on prepared ACs was carried out by using Central Composite Design (CCD) by Designing of Experiments (DoE) using the software Design Expert – 7.1.1 (Stat-Ease, Inc). The central composite design is employed to reduce the total number of experiments in order to achieve the best overall optimization conditions of the process. Effect of various factors such as pH, Cr (VI) concentration, adsorbent dose and contact time on the

percentage removal of Cr (VI) by AC was studied. The effect of main factors as well as the effect of their interactions on the response was determined. In the present study, a five-level and four-factor central composite design (30 runs) was used for the modeling of adsorption process. The general mathematical model developed by using central composite design is as follow.

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_i x_i^2 + \sum_{i,j=1\ (i \neq j)}^{4} \beta_{ij} x_i\ x_j + \varepsilon \quad ------3.10$$

Where; Y is the response variable, β_0, β_i, β_{ij} and β_{ii} are the regression coefficients for intercept, linear effect, double interaction and quadratic effects respectively, x_i, x_j are the independent variables and Ɛ is error.

3.3.1 Adsorption Kinetic models

The study of adsorption dynamics describes the solute uptake rate, and this rate controls the habitation time of adsorbent uptake at the solid-solution interface. Chemical kinetics gives information about reaction pathways and times to reach equilibrium. Adsorption kinetics shows a large dependence on the physical and/or chemical characteristics of the adsorbent material. Different models have been used to investigate the mechanism of adsorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of Cr (VI) adsorption.

3.2.6.1 Pseudo first order kinetic model

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of Cr (VI) adsorption onto activated carbon powder. The pseudo-first-order rate equation, this model is also known as Largergren model, proposed in 1898, which assumes a first order adsorption kinetics and can be represented by the equation [59].

$$\frac{d_q}{d_t} = K_1(q_e - q_t)$$

Where: q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg/g), k1 is the rate constant of pseudo first order adsorption (1/min). After integration and applying boundary conditions t=0 to t=t and qt=0 to qt=qe, the integrated form becomes:

$$\log(q - q_t) = \log(q) - \frac{K_t}{2.303}t$$

The values of log (qe – qt) were linearly correlated with t. The plot of log (qe – qt) versus t should give a linear relationship from which k_1 and qe can be determined from the slop and intercept of the plot, respectively [59]. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter $\mathbf{K_1}$ $(q_e - q_t)$ does not represent the number of available sites and the parameter log (qe) is an adjustable parameter and often found not equal to the intercept of the plot log (qe – qt) versus t, whereas in true first order, log (qe) should be equal to the intercept [59].

3.2.6.2 Pseudo-second-order kinetic model

The pseudo second-order adsorption kinetic rate equation is expressed as [59].

$$\frac{dq_t}{dt} = K_2(q - q_t)^2 \quad \text{----------3.1}$$

Where: k_2 is the rate constant of the pseudo second order adsorption (g/mg.min). For the boundary conditions t=0 to t=t and qt=0 to qt=qe, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{1}{q - q_t} = \frac{1}{q} + K_2 t \quad \text{----------3.2}$$

Equation (3.2) can be rearranged to the linear form as below (Equation 3.3):

$$\frac{t}{q_t} = \frac{1}{K_2 q_t^2} + \frac{1}{q}t \quad \text{----------3.3}$$

If the initial adsorption rate, h (mg/g.min) is:

$$h = K_2(qe) \quad \text{----------3.4}$$

Then equation (3.2) becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q}t \quad \text{----------3.5}$$

3.3.2 Adsorption Isotherm Models

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species [60]. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate Cr (VI) uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce.

3.2.7.1 Langmuir Isotherm

The Langmuir model [61] is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q = \frac{q_m K_L C}{1 + K_L C} \quad \text{----------3.6}$$

The constants in the Langmuir isotherm can be determined by plotting (1/qe) versus (1/ Ce) and making use of above equation rewritten as:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{q_m K_L} X \frac{1}{C} \quad \text{----------3.7}$$

Where q_m and KL are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of q_m and KL will be determined from the graph of 1/Ce Vs 1/qe.

3.2.7.2 Freundlich Isotherm

The Freundlich isotherm model [62] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of Cr (VI) adsorbed per unit mass of adsorbent, qe, and the concentration of Cr (VI) at equilibrium, Ce.

$$qe = K_f Ce^{\frac{1}{n}} \quad ----------3.8$$

The logarithmic form of the equation becomes,

$$\log q = \log K_f + \frac{1}{n}\log C \quad ----------3.9$$

Where: K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log Ce Vs log qe was employed to generate the intercept value of K_f and the slope of n. The magnitudes of K_f and n show easy separation of adsorbate ions from the aqueous solution and indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity.

4. Results and Discussions

4.1. Proximate analysis of raw material (PJF)

The proximate analysis (composition) of the *Prosopis Juliflora* was done, before activation process or soaking, in order to know the moisture content, volatile matter, ash content and most importantly the fixed carbon content of the *Prosopis Juliflora*. The proximate analysis was carried out using Box-type furnace found in our school. The proximate analysis was done using (ASTM; D1762-84 (Reapproved 2001)) and the result obtained is shown in table below. The detailed calculation part is also included under appendix A.

Table 4.1: Raw material (PJF) proximate analysis

Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)
11.5 %	2.215 %	71 %	15.285 %

The above result shows that, the ash content of the raw material (PJF) is found to be very low (2.215%) as compared to other precursors in the literature. This makes PJF one of the best raw materials for activated carbon production. The volatile matter of PJF is high and this has a negative effect on the amount of activated carbon produced. Therefore, the amount of volatile organic components (VOC) which will be released out to the atmosphere will be much higher. Hence, a mechanism was developed for trapping the VOCs from polluting the environment. For this case, there was an attempt to trap the VOCs using mechanisms such as, using a chiller with a glass condenser for trapping the gases before they escape to the environment and also it has been tried to direct the VOCs into a water bath. The first aim of directing the gases into a water bath is to trap the harmful gases (especially CO and CO_2) from escaping to the atmosphere and also to convert the CO_2 gas into carbonic acid, which is a harmless substance. The condensed gas from the glass condenser and tars can be also used as bio-oil or as a binder for producing shaped activated carbons.

4.2 Characterization of produced Activated Carbon

4.2.1 Ash content

The results of ash content analysis for the adsorbent produced by phosphoric acid activation are shown below. The ash content for the phosphoric acid treated activated carbon shows a slight decrement as compared to the ash content of raw material (PJF). Also, the ash content for the Carbonized charcoal carbon showed a large increase as compared to the phosphoric acid treated activated carbon. As discussed in literature review high ash content results in a decreased efficiency on the adsorptive capacity of the Carbon, this could be another reason for obtaining very low percentage adsorption from the acid treated AC. The calculation is the same way as raw material proximate analysis.

Table 4.2 Ash content for AC

Materials	Moisture (%)	Ash content (%)	Volatile Matter (%)	Fixed Carbon (%)
Acid treated AC	6.21	1.03	75.06	17.70
Carbonized charcoal	9.25	2.05	74.02	14.68

4.2.2 Point of Zero Charge Determination

The adsorption of the charged chromium hexavalent group onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution pH.

The pH_{pzc} is defined as the pH of the suspension at which the surface acidic or basic functional groups of the adsorbent no longer contribute to the pH value of the solution [64]. The pHpzc of each adsorbent, i.e., carbonized charcoal and phosphoric acid treated *Prosopis Juliflora* activated carbon were assessed from the figure of the difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the initial pH value (pH_i) as displayed in figure 4.1and figure 4.2 respectively.

From the graph, it can be seen that each adsorbent was positively charged at pH less than six. However, above pH six there was a charge reversal. The pH_{pzc} of adsorbent were found to be 5.8 and 4.3 for carbonized charcoal and acid treated *Prosopis Juliflora* activated carbon respectively. It has been reported by earlier researches that the pH_{pzc} of an adsorbent decreases with increase in acidic groups on the surface of the adsorbents. From the results, it can be conclude that acid

treated of the adsorbent gave a positive (acidic) surface charge for the adsorbent since pH_{pzc} for the acid treated was found to be lower than that of the untreated surface. The relationship between pH_{pzc} and adsorbent capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the pH_{pzc} while anions adsorption will be favorable at pH values lower than the pH_{pzc} [64]. The reduction in the value of the pH_{pzc} for the phosphoric acid treated adsorbent may be caused by removal of acid soluble material from the Prosopis Juliflora biomass and protonation of surface functional groups like the carboxylic group.

The pH_{pzc} value for the carbonized charcoal was obtained to be 5.8(Fig 4.1). At pH values below PZC, the activated carbon had a net positive charge, since the electrostatic attraction between positively charged adsorption sites and positively charged chromium hexavalent causes a decrease in the chromium hexavalent removal. Moreover, with a decreasing pH value, the fraction of neutral chromium hexavalent species increases, leading to a decreased adsorption. However, at pH values above PZC, the negative charged carbon surface is favorable for the adsorption of chromium hexavalent especially at basic pH values.

The PH_{PZC} values for the two products are shown in the subsequent graphs below.

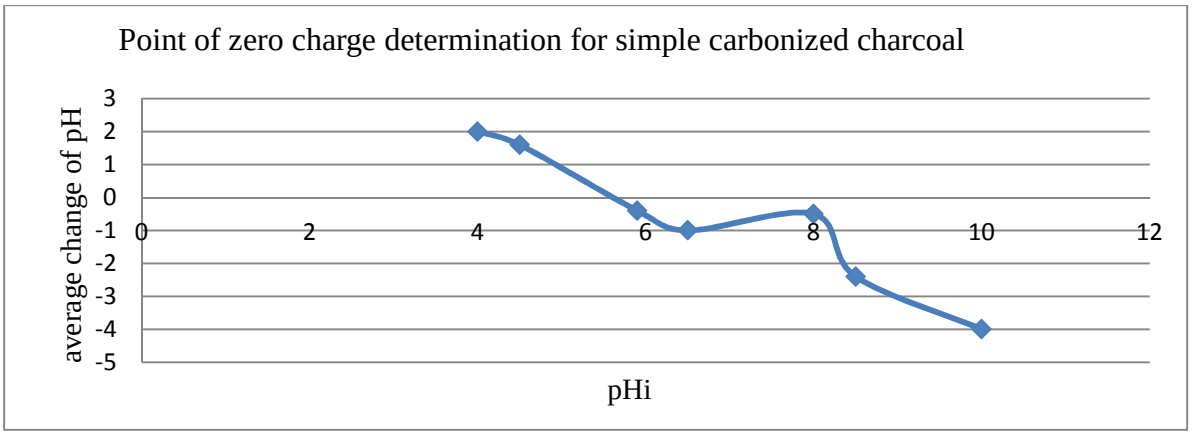


Figure 4.1 pH_{pzc} for simple carbonized charcoal

This graph shows that anion adsorption is enhanced at pH less than 5.8, while pH of greater than 5.8 is preferable for cationic adsorptions. Hence, the adsorption result obtained from the carbonized charcoal was found to be good since the pH of the initial chromium hexavalent is at 6.20 which are a basic (cationic) chromium hexavalent.

Point of Zero Charge Determination for phosphoric acid Treated AC

From the curve below (figure 4.2) it is shown that a point of zero charge is found around pH of 4.3. The activated carbon works best for cationic molecules at acidic pH. This indicates that anion adsorption is enhanced at PH less than 4.3, while PH of greater than 4.3 is preferable for cationic adsorptions. Hence, the adsorption result obtained for Cr (VI) removal (which is anionic solution and having a PH of 6.54 at 80ppm) using acid treated AC was found to be the best of the product. The graph shows as that, anionic solution are best adsorbed at pH>pHzpc (i.e pH>4.3) and pH =6.54 was the initial pH of chromium hexavalent solution. Hence acid treated AC effectively works at the given pH of the chromium hexavalent solution.

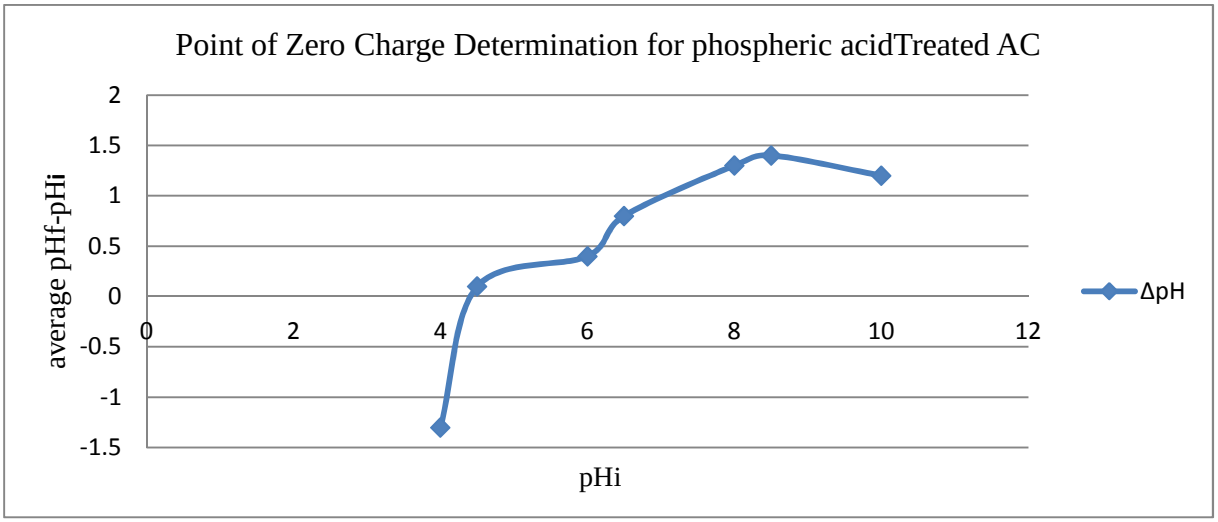


Figure 4.2 pH_{pzc} phosphoric acid treated activated carbon.

4.2.3 Fourier Transformer Infrared (FTIR) Spectroscopy Analysis.

FTIR spectra is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band and can obtain structural and bond information on a complex to study compounds. According to Krishnani [65], the pattern of adsorption of metals onto adsorbents is attributable to the active groups and bonds present on the adsorbent.

Therefore, in this study, FTIR spectroscopy was done for quantitative analysis of major functional groups responsible for chromium adsorption process onto adsorbent prepared from *Prosopis Juliflora* plant. The FTIR spectra of Cr (VI) ions loaded and unloaded adsorbent in simple carbonized charcoal and activated carbon treated by phosphoric acid were recorded in the range of

4000cm^{-1} to 400cm^{-1}. Figures bellow shows the recorded spectra of all three forms of adsorption before and after adsorption.

The spectrum obtained for a particular biomass is always a characteristic feature of that biomass. Quantitative and qualitative analysis (shift or an increase or decrease in the sharpness of the peaks) of that characteristic spectrum and its comparison with any other corresponding spectrum reveals the extent of variation in the specific peaks. These variations finally help in predicating the extent of involvement of that particularly ascribed functional group, in the adsorption process. All the IR spectra obtained in present study were analyzed separately.

4.2.3.1 FTIR result for simple carbonized charcoal.

For the carbonized charcoal the peak near the wave number 3400 to 3500cm^{-1} represents O-H stretching groups and the stretching –NH groups [75]. The peak in the range of 2400 to 3200cm^{-1} represents N-H of ammonium ions. The peak in the range of 1550 to 1610cm^{-1} represents C=O of carboxylic acid group. And the band in the range of 1220 to 1260cm^{-1} represents C-O of ethers aromatic functional group. All these mentioned peaks were shown in the unloaded carbonized charcoal adsorption in figure4.3.

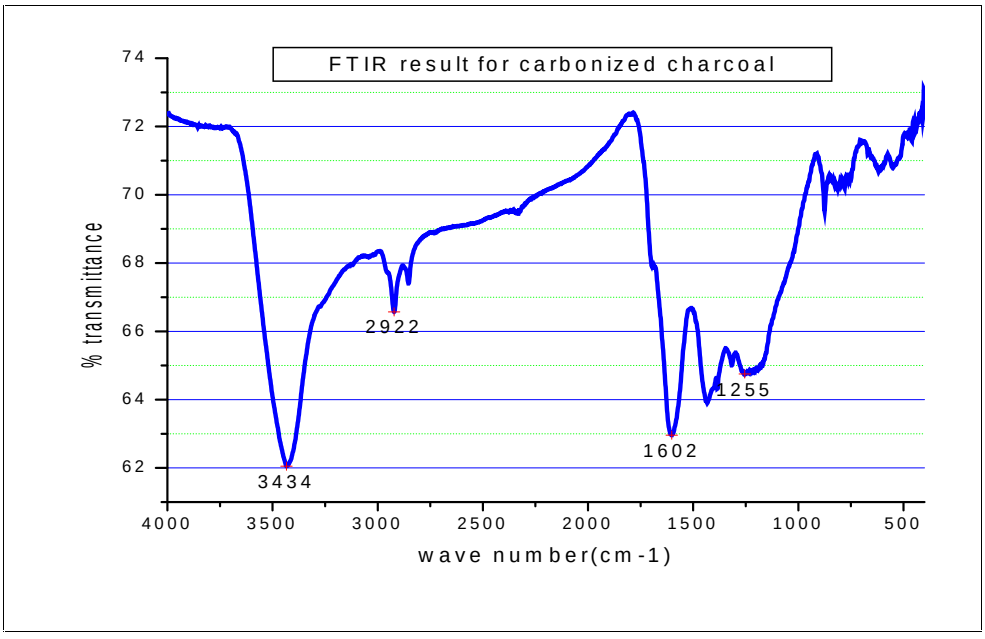


Figure 4.3 FTIR result for simple carbonized charcoal

4.2.3.2 FTIR result for phosphoric acid treated AC before adsorption.

From figure 4.4, below it can be said that, the most dominant peaks we have are located at wave number of 3400 to 3500 cm^{-1}, 2400 to 3200 cm^{-1}, 1550 to 1610 cm^{-1} and 1150 to 1200 cm^{-1}. The functional groups associated with these wave numbers are, -OH stretching group and –NH groups, C=O carboxylic groups and C-O stretches of alcohols respectively [75]. The acid treated result in the shifting of the wave number from 3434 to 3429cm^{-1}, 2922 to 2921cm^{-1}, 1602 to 1567cm^{-1} and 1255 to 1157cm^{-1} in the simple charcoal and acid treated activated carbon respectively.

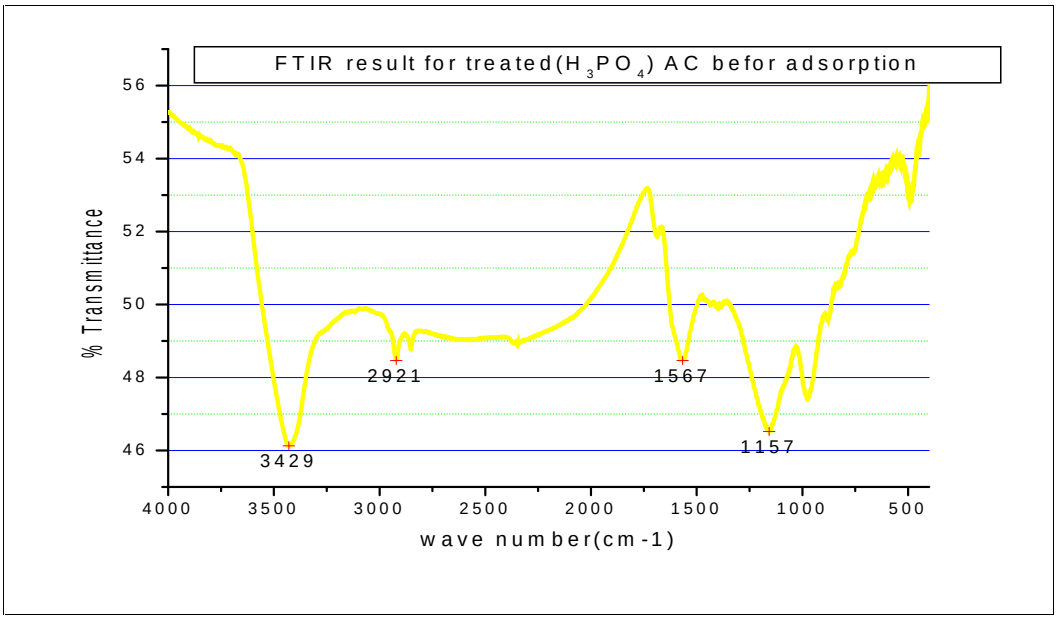


Figure 4.4 FTIR result for phosphoric acid treated AC before adsorption

4.2.3.3 FTIR result for phosphoric acid treated AC afore adsorption.

From figure 4.5, below it can be said that, the most dominant peaks we have are located at wave number of 3400 to 3500 cm^{-1}, 2400 to 3200 cm^{-1}, 1550 to 1610 cm^{-1} and 1150 to 1200 cm^{-1}. The functional groups associated with these wave numbers are, -OH stretching group and –NH groups, C=O carboxylic groups and C-O stretches of alcohols respectively [75]. The acid treated result after adsorption in the shifting of the wave number from 3429 to 3424cm^{-1}, 2921 to 2922cm^{-1}, and 1157 to 1173cm^{-1} in the acid treated activated carbon before adsorption and acid treated activated carbon after adsorption respectively. The FTIR spectrum of the acid treated before adsorption and after adsorption *Prosopis Juliflora* activated carbon loaded with 80mg/L of Cr (VI) ions showed

either a redaction or shift in wave number and intensity of peaks. For instance the vibration wave number at 3429cm^{-1} unloaded Cr (VI) ions form was shifted to 3424cm^{-1}, 2921cm^{-1} unloaded form was form shifted to 2922cm^{-1} and 1157cm^{-1} unloaded form was shifted to1173cm^{-1} loaded Cr (VI) ions respectively. These shift wave numbers indicate that the hydroxide, amine and alcohol groups were involved in the adsorption of Cr (VI) ions but not carboxylic groups because of the fixed wave number.

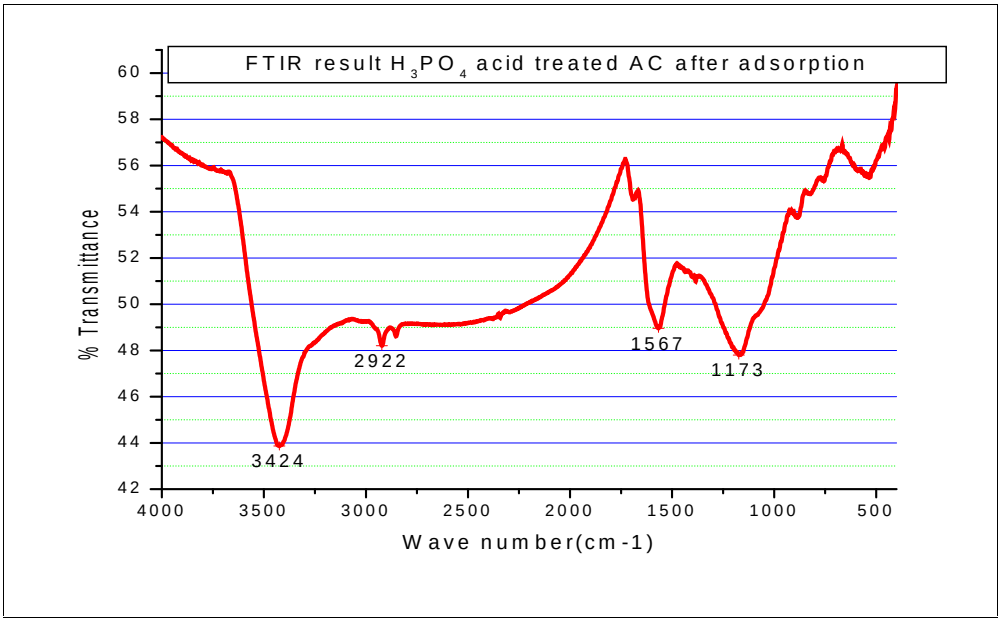


Figure 4.5 FTIR result for phosphoric acid treated AC after adsorption

4.3 Batch Adsorption studies

4.3.1 Effect of solution pH

pH of the aqueous solution is an important parameter for adsorption of metals on the adsorbents. pH dependence of metal uptake is related to both surface functional groups on the surface of the adsorbent and the metal chemistry of the solution (hydrolysis, complexation by organic and/or inorganic ligands, redox reaction). This in turn influences the metal uptake behavior. For that purpose the pH values of Cr (VI) solutions were adjusted to a range of 1, 2, 3 and 4, keeping all other process parameters constant prior to the experiments. Parallel experiments were carried out for all two adsorbents, under the similar experimental conditions. The results obtained are discussed below.

4.3.1.1 Simple carbonized charcoal

The variation in Cr (VI) ions percentage removal and adsorption capacity of simple carbonized charcoal with respect to solution pH is shown in figure (4.6A). The results obtained showed that with increase in solution pH, both the Cr (VI) percentage removal and the adsorption capacity decreased. The maximum removal and adsorption capacity were observed to be 98.81% and 11.86% mg/g respectively at solution pH 1.

4.3.1.2 Acid treated activated carbon

Figure showed the Cr (VI) ions removal and adsorption capacity of acid treated activated carbon at variable solution pH values. From the figure it is evident that the solution pH affects the adsorption process. The increase in solution pH from 1to 4 resulted in sharp decrease in both percentage removal and adsorption capacity. The maximum of 99.61 percent of Cr (VI) removal was achieved with adsorption capacity of 11.95 mg/g at solution pH one.

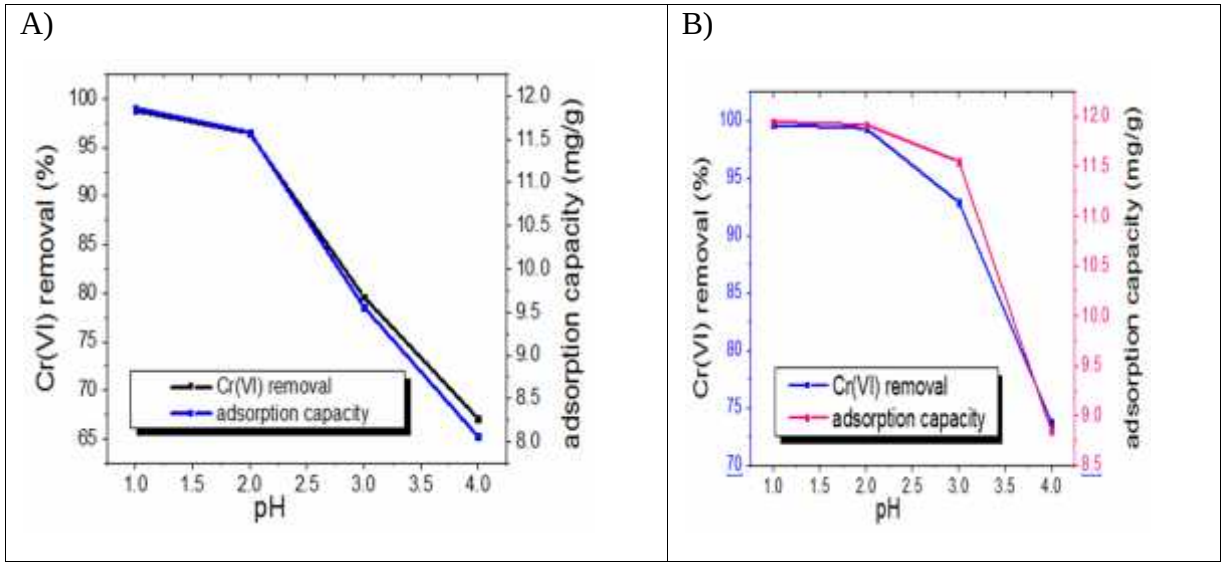


Figure 4.6 Effect of solution pH on adsorption of Cr (VI) ions of (A) charcoal and (B) activated carbon

The results obtained can be explained by the fact that the solution pH is directly related to the large availability of positively charged active sites on the surface of the adsorbent to bind with the metal ions. As solution pH decreased, the surface of the adsorbents exhibits increasing positively charged active sited. Hence the toxic metal to be removed is negatively charged Cr (VI) ions like $HCrO_4^-$, CrO_7^{2-}, and CrO_4^{2-} the adsorption is favored at lower solution pH values. Therefore,

electrostatic attraction probably plays an important role in adsorption of negatively charged chromium ions at low solution pH. Additionally, the dominant form of Cr (VI) at pH 1 is the acid chromate ion species ($HCrO_4^-$) which would shift to other forms CrO_7^{2-}, and CrO_4^{2-} with increase in pH. Since there is an increase in sorption of Cr (VI) as pH decrease to 1.0, it may be suggested that $HCrO_4^-$ is the active form of Cr (VI) which is being absorbed by the activated carbon.

4.3.2 Effect of initial metal concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of chromium (VI) ions between the aqueous and solid phases. The adsorption of Cr (VI) ions was carried out at different initial metal concentration ranging from 80-200mg/L at pH 1. Under the given experimental conditions, the relationship between initial Cr (VI) ion concentrations, the Cr (VI) percentage removal and the adsorption capacity have been investigated. The results obtained from the study are given below.

4.3.2.1 Simple carbonized charcoal

The graph of Cr (VI) percentage removal and the adsorption capacity of simple carbonized charcoal at different Cr (VI) ion concentration are presented in figure (4.7A). As evident from the graph, the maximum parentage removal of 98.92% was obtained at initial Cr (VI) concentration of 80mg/L. The increase in the Cr (VI) concentration from 80-200mg/L resulted in decrease of the percentage removal from 98.92 to 86.26. The investigation on the adsorption capacity revealed that the increase in Cr (VI) concentration resulted in the increase of the adsorption capacity. The maximum adsorption capacity of 17.25mg/g was achieved at initial Cr (VI) concentration of 200mg/L.

4.3.2.2 Acid treated activated carbon

The adsorption yield (%) and the adsorption capacity mg/g of the acid treated activated carbon at different initial concentration of Cr (VI) are shown in figure (4.7B). The percentage removal showed negative slope while the adsorption capacity showed positive slop with increase in Cr (VI) concentration. The maximum Cr (VI) removal of 99.41% and maximum adsorption capacity of 17.65 mg/g was achieved at initial at Cr (VI) concentration of 200mg/L.

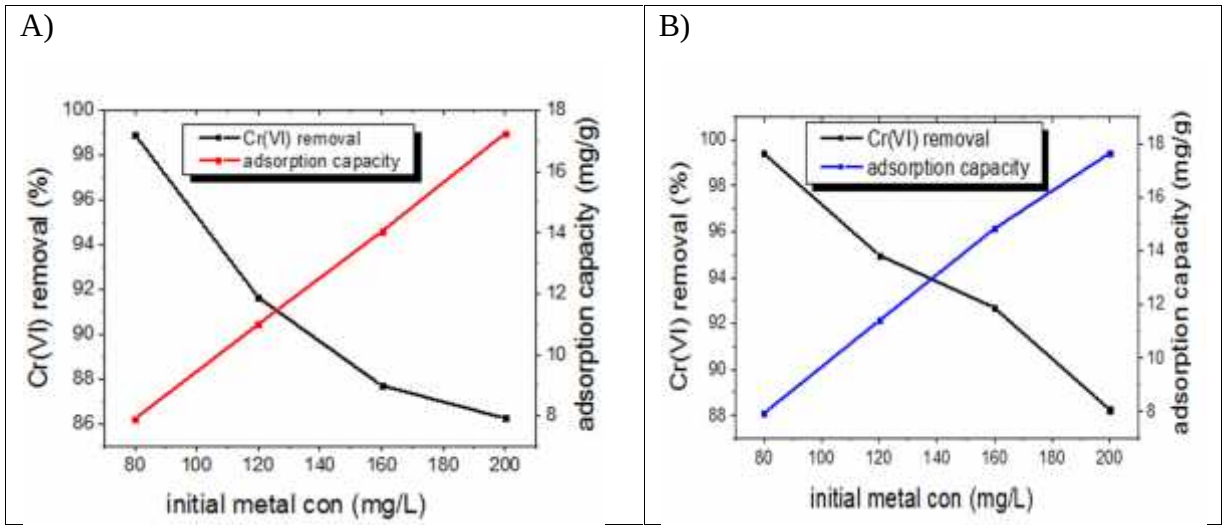


Figure 4.7 Effect of initial Cr (VI) concentration on adsorption efficiency of (A) charcoal (B) activated carbon.

From the above discussed results that, the Cr (VI) ions percentage removal and the adsorption capacity are directly affected by the variation in the initial Cr (VI) ion concentration. The results obtained can be attributed to the fact that the adsorbent dose being constant (5g/L) the number of available binding sited at the surface remains the same with the number of chromium ions increased with increase in the metal concentration. This in turn will result in the increase of ratio of metal ions to that of the available binding sites resulting in the decrease in the Cr (VI) ions removed. However, the increase in the adsorption capacity with increase in the initial Cr (VI) concentration may be explained as, at fixed adsorption dose and increasing the metal concentration, all the available active sites of the adsorbent would be fully exposed to get occupied by the Cr (VI) ions that are in excess saturating and yielding a higher adsorption capacity [66]. Similar pattern in the adsorption capacity and percentage removal were reported by different researchers [64, 65, and, 9].

4.3.3. Effect of adsorbent dose

The adsorbent dose strongly influences the extent of adsorption. It determines the sorbante-sorbent equilibrium of the system [47]. The adsorption of Cr (VI) ions from the test solutions were analyzed in terms of percentage removal and adsorption capacity of the simple carbonized charcoal and acid treated activated carbon. The data obtained are discussed as follow.

4.3.3.1 Simple carbonized charcoal

The percentage removal and adsorption capacity at different adsorbent dose in 100ml of 80mg/L Cr (VI) solution at pH 1is shown in figure (4.8A). The gradual increase in the adsorbent dose from 0.25mg/L to 10 mg/L, the percentage removal of Cr (VI) increased from 90.46% to 99.36% while the adsorption capacity (mg/g) decreased from 28.93% to 7.93% with the same increment in adsorbent dose.

4.3.3.2 Acid treated activated carbon

The variation in the percentage removal and the adsorption capacity of acid treated activated carbon with variation adsorbent dose in presented in figure (4.8B). The respective results obtained for the Cr (VI) percentage removal was 99.51% at adsorbent dose of 10g/L and 29.6% at adsorbent dose of 2.5g/L.

It is clear from the experimental results obtained that, the increase in the adsorbent dose increased the percentage removal with decreasing the adsorption capacity. These results can be justified by the fact that the total metal removed depends on the number of the available binding sites, where as the specific metal uptake was the ratio of the amount of the metal ion removed per unit weight of the adsorbent.

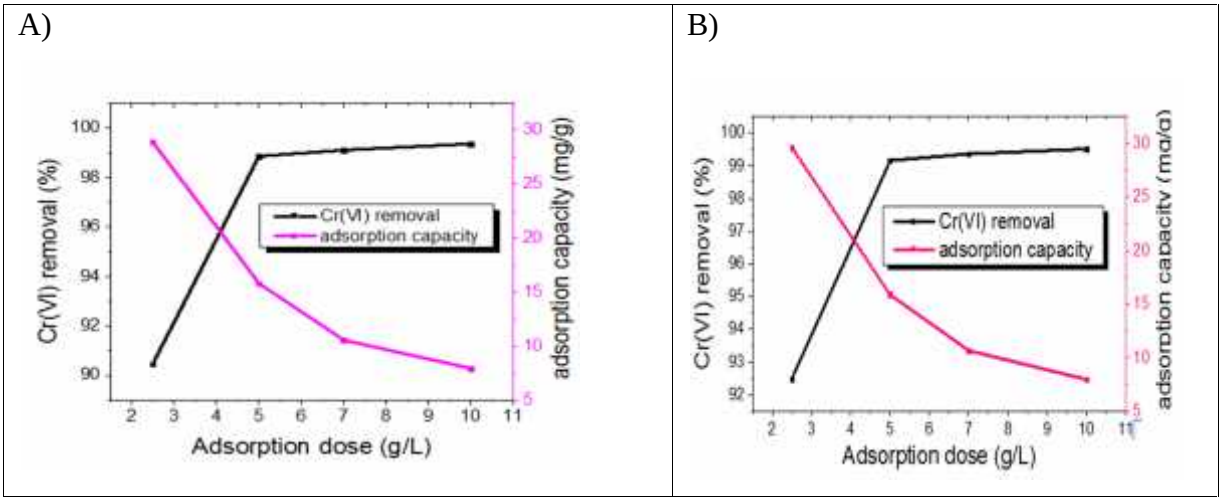


Figure 4.8 Effect of adsorbent dose on adsorption of Cr (VI) ions, (A) charcoal and (B) activated carbon.

An increase in the adsorbent dose generally increases the metal ion removed due to the increase surface area of the adsorbent which in turn increase the number of binding sites available for the adsorption process. On the other hand, the quantity of adsorbent metal ion per unit weight of the adsorbent decreases with increase in the adsorbent dose which may be due to the complex interaction of several factors. One important factor at high adsorbent concentration is that the available metal to be sorbet is insufficient to completely cover the available exchangeable sites which in turn results in low adsorption capacity [48]. Similar graph patterns in the adsorption capacity and percentage removal were reported for adsorption of Cr (VI) using sawdust [53], papaya seed powder [53], wheat shell and sugar cane bagasse [68]

4.3.4. Effect of contact time

Generally, the adsorption capacity and the removal efficiency of metal ions by adsorbents will increase with increase in contact time. However, in practice it is necessary to optimize the contact time, considering the adsorption process. The effect of contact time on the adsorption of Cr (VI) ions using adsorbents prepared from *Prosopis Juliflora* wood investigated over time interval of 15 to 165 minute. The results obtained are summarized as follows.

4.3.4.1 Acid treated activated carbon

The pattern of variation of Cr (VI) percentage removal and the adsorption capacity of the adsorbent treated with phosphoric acid with respect to contact time is presented in appendix (A.6). Both the Cr (VI) removal and the adsorption capacity showed increase with increasing time up to 105 minutes then proceeds slow increase until both reached the maximum at 150 minutes with 99.46% removal of Cr (VI) ions and 7.957mg/g adsorption capacity. After 150 minutes there were no change in the adsorption capacity and the percentage removal.

The higher rate of adsorption in the initial stage of the adsorption process could be due to the electrostatic interaction between the Cr (VI) ions and the surface functional groups such as the hydroxyl and carboxylic present on the surface of the adsorbent. These functional groups present on the adsorbent surface will start binding the chromium ions as soon as they come in contact with each other. The mechanism of the solute transfer to the solid during the adsorption process includes diffusion through the fluid film around the adsorption particle and diffusion through the pores to the internal adsorption sites. The fast dynamic behavior of chromium removal by the

adsorbent suggests that average contact time for the adsorption process based on the experimental conditions.

As time progress, the number of available binding sites decreased thus decreasing the rate of adsorption. This phenomenon indicates adsorption of Cr (VI) took place in two stages, the first one the rapid surface adsorption followed by the slow pore diffusion to the internal binding sites [49].

Data on the adsorption of Cr (VI) ions using different adsorbents have shown wide range of adsorption time. For example; the equilibrium contact time required for Cr (VI) removal using saw dust and pine leaves were 60 and 70 minutes [50]. While for avocado shell (57) the adsorption equilibrium was achieved within 120 minutes at pH 2 and 1g/L adsorbent dose. When orange peel (57) was used for removal of Cr (VI) and Zn (II), the equilibrium was achieved within 30 minutes with initial metals concentration of 100mg/L and solution pH 3. For brown marine algal biomass with species *Padina Boergesenil* for chromium adsorption from electroplating wastewater equilibrium was reached within 180 minutes [67].

It should be noted that there are several parameters which affect the equilibrium adsorption time. Some of these parameters are the string rate, the physicochemical properties of the adsorbents (for example, surface charge density, protein and carbohydrate composition of the adsorbents surface area, etc), adsorbent dose, initial metal concentration, presence of the competitive ions and the properties of the metal under study.

4.4 Adsorption Kinetics Models

Kinetic models can be helpful in better understanding of the mechanisms of heavy metal adsorption and in evaluating the performance of the adsorbents for heavy metal removal [68]. The kinetics also describes the solute uptake, which in turn controls the residence time of the adsorbent at the solid solution interface [69].

In order to examine the controlling mechanism of the adsorption process, various kinetics models were used to test the experimental data. To obtain the rat constants and the order of adsorption reactions, pseudo first order, and pseudo second order kinetic models were applied to kinetic data obtained at 20^{o}C, solution pH 1.5, initial metal concentration of 80mg/L, contact time 106.79 min and adsorbent dose of 10g/L at 200rpm string rate.

4.4.1 Pseudo first order kinetics model

$$\log(q - q_t) = \log(q) - \frac{K_t}{2.303}(t) \quad ----------4.1$$

The values of log (qe – qt) were linearly correlated with t. The plot of log (qe – qt) versus t should give a linear relationship from which k_1 and qe can be determined from the slop and intercept of the plot, respectively. The kinetics model for pseudo first order adsorption is given for the acid treated activated carbons prepared

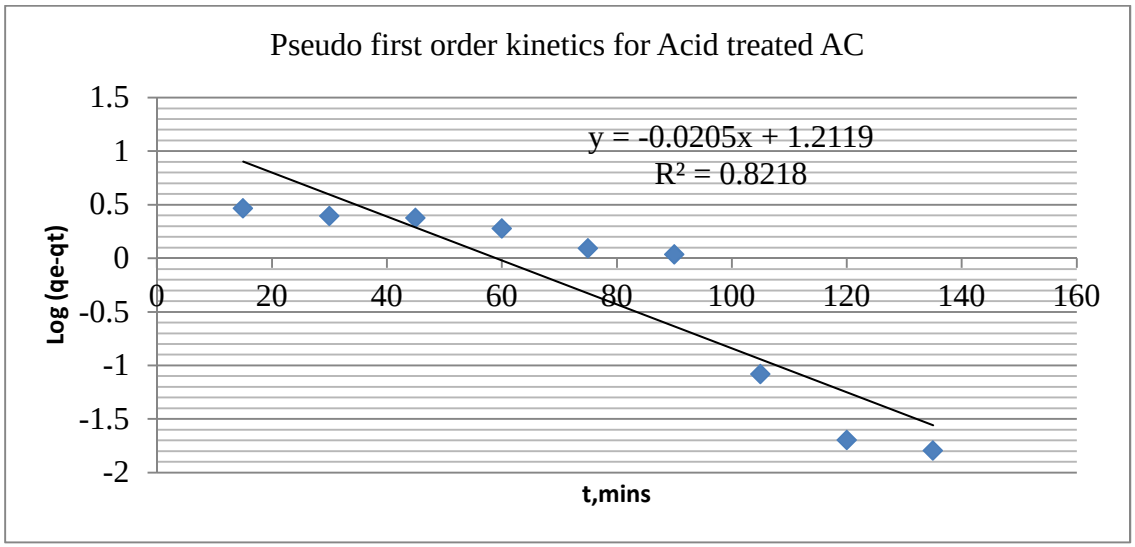


Figure 4.9 pseudo first kinetics order plot for carbonized charcoal.

4.4.2 Pseudo second order Kinetics

The pseudo second-order adsorption kinetic rate equation is expressed as [59];

$$\frac{dqt}{dt} = K_2(qe - qt)^2 \quad ----------4.2$$

Where: k_2 is the rate constant of the pseudo second order adsorption (g/mg.min). For the boundary conditions t=0 to t=t and qt=0 to qt=qe, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}(t) \quad ----------4.3$$

From figure the correlation coefficient (R^2) is found to be 0.821, and 0.986 for the phosphoric acid treated for the pseudo first –order and pseudo-second order reaction respectively. From the given graphs shown the best kinetic model that fits to the experimental data for adsorption process is obtained to be pseudo second order kinetics model. Therefore, this model is selected to be the best model for the products used. Hence, taking pseudo second- order as best kinetics

model, the parameters such as adsorption capacity and chromium (VI) ion removal 7.957 and 99.46% at equilibrium concentration respectively and its rate of adsorption (k_2) value is found to be 0.110.

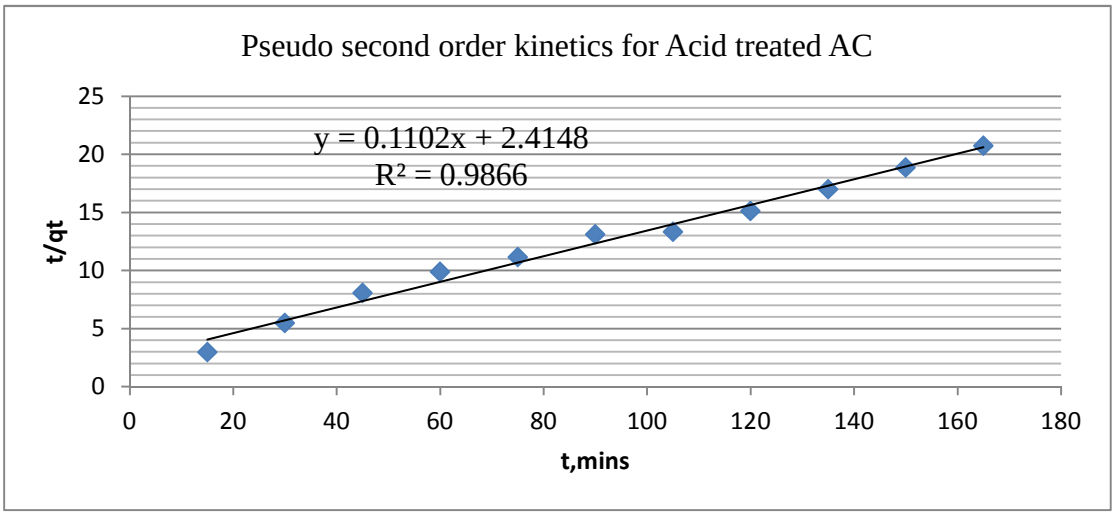


Figure 4.10 pseudo second order kinetics plot for acid treated activated carbon

4.5 Adsorption Isotherm models

Data was obtained from effect of initial metal ion concentration which was simulated using the two most commonly used model isotherms, Langmuir and Freundlich.

Based on the data processed in accordance with the Langmuir isotherm equation, the Langmuir constants and the theoretical maximum adsorption capacity is obtained from the plot with highest R^2

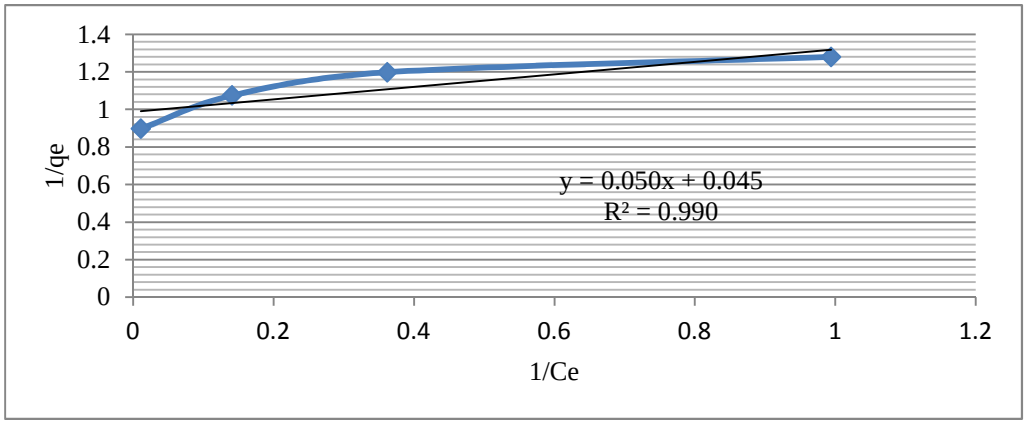


Figure 4.11 Langmuir isotherms for Cr (VI) removal at optimum point.

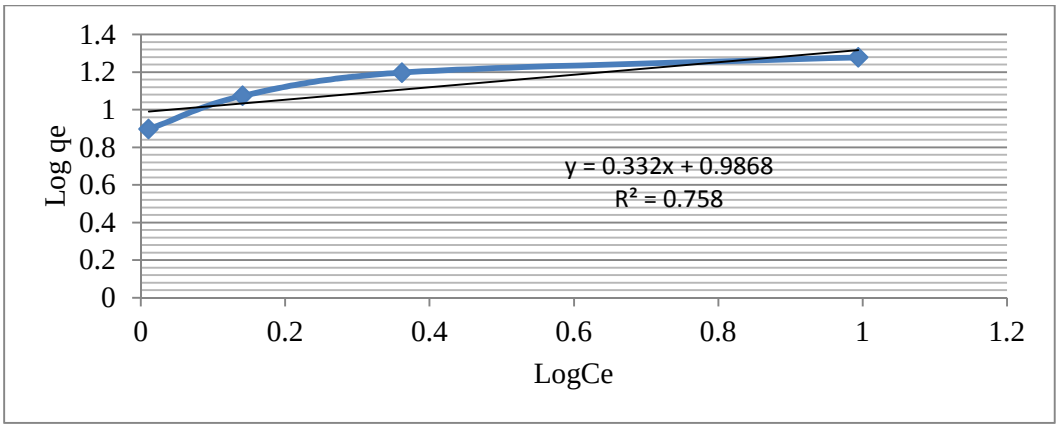


Figure 4.12 Freundlich isotherms for Cr (VI) removal at optimum point.

It is indicated from the graph above that equilibrium data are well represented by Langmuir isotherm equation when compared to the Freundlich equation. Where, the Langmuir fitting was mostly closed to the experimental data than the freundich equation fitting. The best fit of equilibrium data in the Langmuir isotherm expression confirms the adsorption onto the adsorbent surface is homogeneous in nature where once the heavy metal occupies the site no further adsorption takes place. According to Langmuir, the adsorption of solute from aqueous solution onto the adsorbents surface occurred as monolayer adsorption on the homogeneous number of exchanging sites. This phenomenon describes the uniform adsorption energy on the absorbent surface [61, 62]. It also describes short term and mono component adsorption of heavy metal.

4.6 Statistical Analysis of adsorption process

The statistical analysis of Cr (VI) adsorption experiments conducted using acid treated *Prosopis Juliflora* activated carbon was carried out using the response surface methodology (RSM). The percentage removal of Cr (VI) was entered as a response in the selected design lay out. The major statistical analysis of the adsorption process was model generation; model fitness test and ANOVA analysis are presented and discussed as follows.

4.6.1 Chromium (VI) adsorption modeling and model analysis

Adsorption experiments were carried out using the phosphoric acid treated Prosopis Juliflora wood activated carbon adsorbent according to (CCD) of the response surface methodology. The results (percent Cr (VI) removal) from the wastewater aqueous solution on the interaction of four

process factors initial metal concentration (A), pH (B), adsorbent dose (C) and contact time (D) were used for the model generation. From the output of different model summary statistics in the table below focus on the model maximizing the Adjusted R-Squared and the Predicted R-Squared values large therefor ,the quadratic model is sugested.

Tabel 4.3 Model Summary Statistics

Source	Std. Dev.	R. squared	Adjusted R. squared	Predicted R. squared
Linear	9.97	0.8577	0.8350	0.7887
2FI	10.06	0.8900	0.8321	0.8217
Qaudratic	0.61	0.9997	0.9994	0.9983
Qubic	0.47	0.9999	0.9996	0.9918

A second order quadratic regression was performed to estimate the response function as a second order polynomial after the examination of the model fit summery revealed that quadratic model was statistically significant for the response percent chromium (VI) removal. To examine the combined effect of four different independent process parameters on percentage removal of Cr (VI) 30 experiments were performed. The experimental design is given in Table4.4, along with experimental data and predicted responses.

Table 4.4 CCD matrixes for the experimental design and predicted responses for Cr (VI) removal

Run order	Coded Value				Cr (VI) removal (%)	
	A	B	C	D	Observed	Predicted
1	160	1.50	0.50	60	83.12	82.55
2	200	2.75	0.75	90	72.93	72.74
3	40	2.75	0.75	90	94.45	94.08
4	80	4.00	1.00	60	58.25	58.73
5	120	2.75	0.75	30	46.99	46.64
6	120	2.75	1.25	90	91.25	90.44
7	120	2.75	0.75	90	78.32	78.54
8	160	1.50	1.00	60	86.25	86.49
9	120	0.25	0.75	90	96.89	97.47
10	120	2.75	0.25	90	68.45	68.69
11	120	2.75	0.75	150	72.21	71.99
12	160	4.00	0.50	60	18.59	19.19
13	160	4.00	1.00	60	38.21	38.49
14	160	1.50	0.50	120	95.98	95.72
15	120	2.75	0.75	90	78.25	78.54
16	120	2.75	0.75	90	78.45	78.54
17	160	4.00	1.00	120	50.89	51.16
18	80	1.50	1.00	120	99.65	99.27
19	80	1.50	0.50	60	84.21	84.15
20	120	2.75	0.75	90	78.34	78.54
21	80	4.00	1.00	120	69.98	70.91
22	80	1.50	1.00	60	88.76	88.92
23	120	5.25	0.75	90	6.89	5.74
24	120	2.75	0.75	90	79.08	78.54
25	160	4.00	0.50	120	33.99	34.18
26	80	4.00	0.50	120	53.12	53.09
27	80	4.00	0.50	60	38.45	38.49
28	160	1.50	1.00	120	97.12	97.33
29	80	1.50	0.50	120	96.76	96.82
30	120	2.75	0.75	90	78.82	78.54

Regression analysis was performed to fit the response functions, i.e. percentage removal of Cr (VI). The second order polynomial equation developed represent responses as functions of initial metal concentration (A), pH (B), adsorbent dose (C) and contact time (D). An empirical relationship between the response and the input test variables in coded units can be expressed by the following equation:

$$\%R\ Cr(VI) = 78.54 - 5.34\ A - 22.93\ B + 5.44\ C + 6.34D - 4.45\ AB - 0.21AC + 0.12\ AD + 3.84BC + 0.46\ BD - 0.58\ CD + 1.22\ A^2 - 6.73B^2 + 0.26\ C^2 - 4.81\ D^2 \quad \text{----------4.4}$$

The above equation describes how Cr(VI) adsorption onto *Prosopis Juliflora* wood activated carbon was affected by the individual variables (linear and quadratic) or double interaction. Negative coefficient values indicate that individual or double interactions factors negatively affect Cr(VI) adsorption while positive coefficient values represents that factors increase Cr(VI) removal percentage. For instance, among all linear factors initial concentration and pH had a negative effect but adsorbent dose and contact time had a positive effect on Cr(VI) removal.

Table 4.5 Analysis of variance (ANOVA) for the quadratic model

Sourec	Sum of sqares	df	Mean square	F value	p-value prop>F	
model	17454.97	14	1246.78	3348.04	< 0.0001	significant
A	*683.20*	1	683.20	1834.63	< 0.0001	
B	*12620.21*	1	12620.21	33889.62	< 0.0001	
C	*709.70*	1	709.70	1905.80	< 0.0001	
D	*963.55*	1	963.55	2587.47	< 0.0001	
AB	*317.11*	1	317.11	851.54	< 0.0001	
AC	*0.69*	1	0.69	1.86	0.0477	
AD	*0.25*	1	0.25	0.66	0.2923	
BC	*236.01*	1	236.01	633.76	< 0.0001	
BD	*3.36*	1	3.36	9.02	0.0089	
CD	*5.39*	1	5.39	14.48	0.0017	
A^2	*40.54*	1	40.54	108.86	< 0.0001	
B^2	*1243.90*	1	1243.90	3340.29	< 0.0001	
C^2	*1.79*	1	1.79	4.82	0.0443	
D^4	*633.74*	1	633.74	1701.81	< 0.0001	
Residual	5.59	15	0.37			
Lack of fit	*5.04*	10	0.50	4.57	0.1815	*not significant*
Pure error	*0.55*	5	0.11			
Cor total	17460.56	29				
R^2 = 0.9997 R^2 Adjusted = 0.9994 R^2 Predicted = 0.9983 Adeq Precision =216.738						

The adequacy and significance of the quadratic model was justified by the analysis of variance (ANOVA). The ANOVA summary is given in Table 4.5 the analysis was done by means of Fisher's 'F'-test. The model F-value observed was 3348.04 enlightening that the model was significant. The parameters having an F-statistics probability value less than 0.05 are said to be significant [60]. In this present study the probability of model F statistics value was <0.0001 indicating that the model suggested by the software was highly significant. In this case A, B, C, D, AB, AC, BC, BD, CD, A^2, B^2, C^2 and D^2 are statistically significant ($P<0.05$) model terms at the 95 % confidence level. The non-significant value of lack of fit (F-value of 4.57) for the model showed that the developed model is valid [60]. Furthermore the fitting of the experimental data to the regression model was checked and suitably explained by the value of the adjusted determination coefficient (R^2Adj= 0.9994). This result means that 99.94 % of the total variation on Cr (VI) adsorption data can be explained by the selected model. The adequate precision ratio of 216.738 indicates an appropriated signal to noise ratio. The ratio determined was greater than 4, representing that the quadratic model can be used to navigate the design space and to find the optimal conditions of this process. Furthermore, the relationship between actual values and predicted values (Fig.4.13) showed that the actual values are distributed relatively near to the straight line, indicating good fitness of the model. Again in Fig4.14, the plot of studentized residuals versus run order was tested and the residuals were scattered randomly around ±3.00. This was an indication of better fitment of the model with the experimental data.

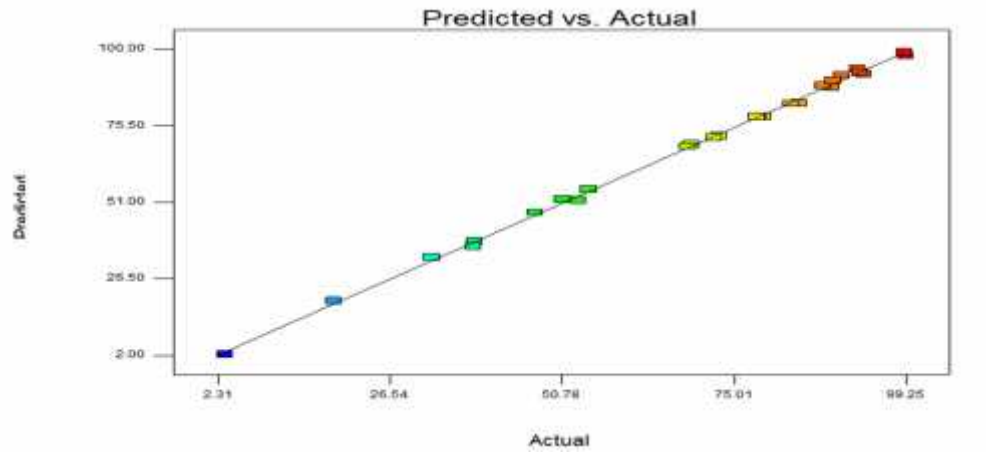


Figure 4.13 Comparison between the actual values and the predicted values of RSM model for adsorption of Cr (VI).

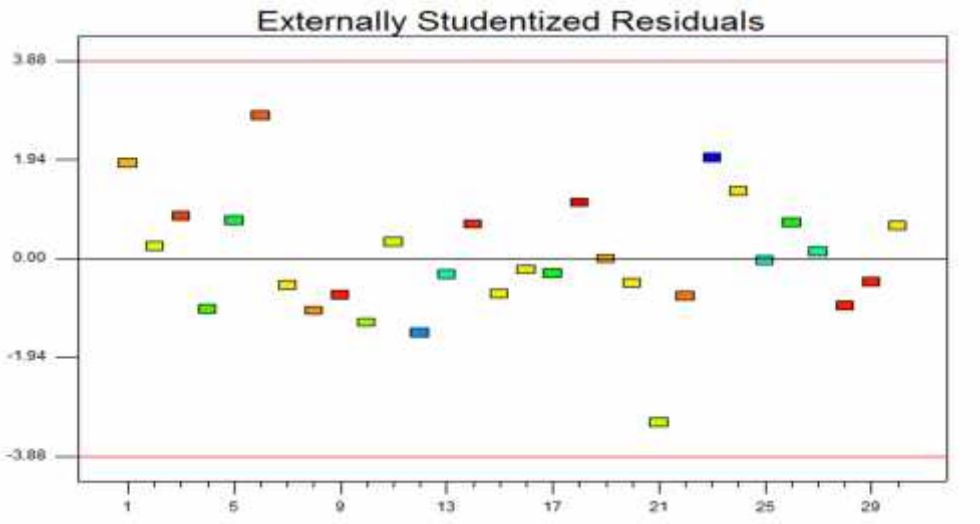


Figure 4.14 Plot of Studentized residuals versus experimental run number

4.6.2 Estimation of quantitative effects of the factors

As discussed in the previous section, the ultimate objective of CCD method used in this study was to find out the significant effects of the process parameters viz., initial concentration, pH, adsorbent dose and contact time on the removal efficiency of Cr (VI). 3D response surface and contour plots were used to investigate the effect of all the factors on the responses.

4.6.2.1 The combined effect of solution pH and initial Cr (VI) concentration

The combined effect of pH and initial concentration on removal efficiency of Cr (VI) at constant adsorbent dosage (1g/100ml) and contact time (106.79 min) is depicted in Figure 4.15 The percentage removal of Cr (VI) ion increased with decreasing the initial concentration of Cr (VI) ions as well solution pH. This can be explained by the fact that all adsorbents have a limited number of active binding sites and at a certain concentration the active sites become saturated [60]. It is also clear from Fig4.15 that the removal efficiency decreases with increase in pH from 1.5 to 4.0. It is noted that the maximum removal at all the studied concentrations takes place at pH 1.5. The maximum removal efficiency of 91.79 % was observed at constant adsorbent dosage (1g/100ml) and contact time (120 min) meaning that two factors were constant.

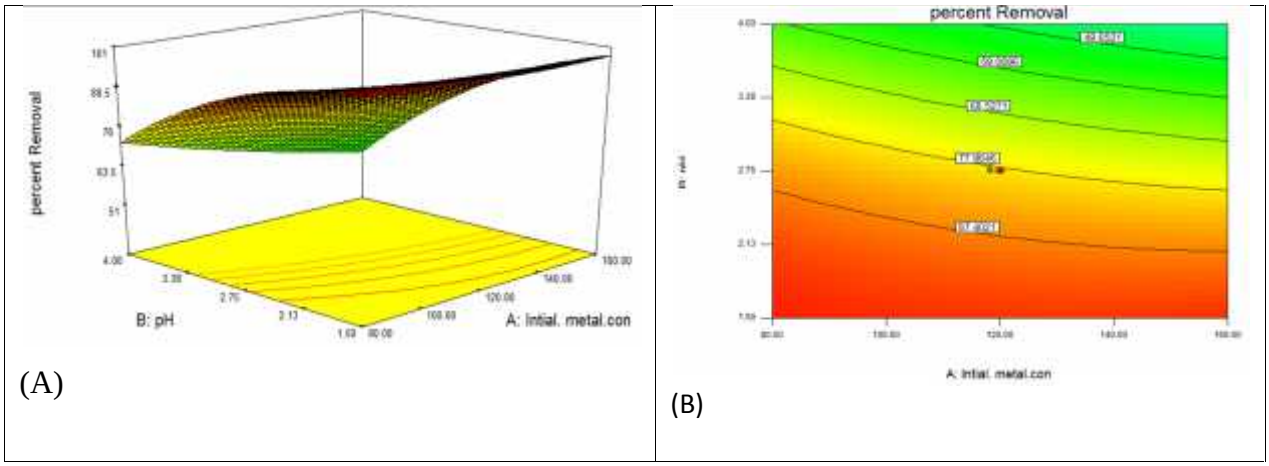


Fig 4.15 Effect of the interaction between pH and initial concentration on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.2.2 The combined effect of adsorbent dose and initial Cr (VI) concentration

The combined effect of initial Cr (VI) of initial Cr (VI) concentration and adsorbent dose on the percentage removal of chromium (VI) is shown in figure 4:16 From the plot it can be seen that, the increase in both initial Cr (VI) concentration and adsorbent dose resulted in reduction in percent removal of chromium (VI), while the decrease in adsorbent dose and initial Cr (VI) increased the % removal of Cr (VI). The plot also showed that at lower pH value, the variation in contact time has more effect on the % removal of Cr (VI) than initial metal concentration.

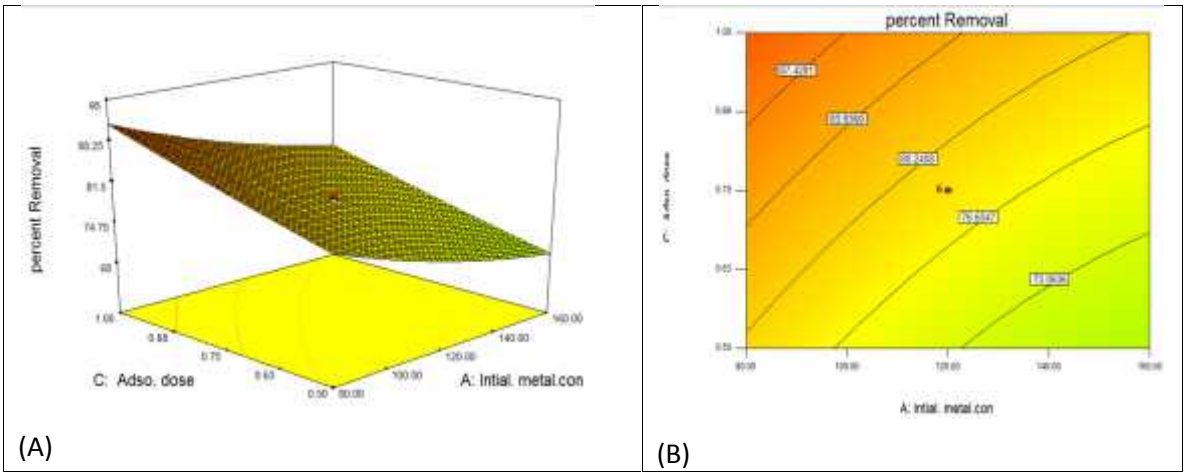
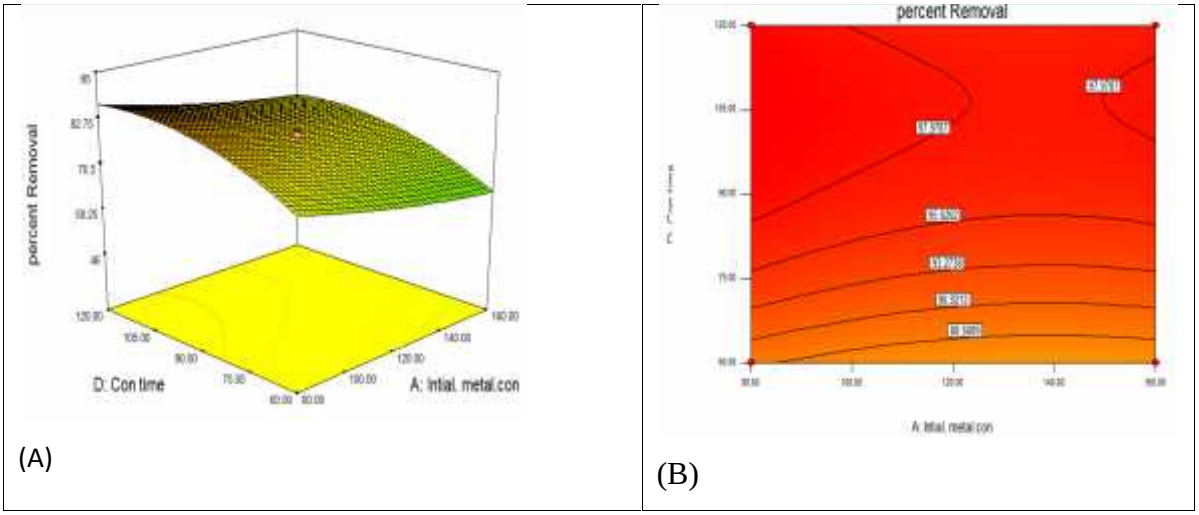


Fig 4.16 Effect of the interaction between adsorbent dose and initial concentration on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.2.3 The combined effect of initial Cr (VI) concentration and contact time

The interaction effect of contact time and initial Cr (VI) concentration on the percent removal of Cr (VI) is shown in figure 4. From the 3D figure it can be seen that at solution pH of 1.5 and adsorbent dose 1g/100ml, the contact time from 60 to 120 minute and initial Cr (VI) concentration from 80 to 160 mg/L resulted in smaller increment in % removal of chromium (VI). The result indicated that, the interaction of contact time and initial metal Cr (VI) concentration at lower pH and higher adsorbent dose have no significant effect on the % removal of Cr (VI). This is because at lower pH value there will be maximum percent Cr (VI) removal due to the protonation of surface functional groups. This result also supported by the ANOVA analysis which showed that the interaction of contact time and initial metal Cr (VI) concentration have no significant effect on the % removal since the calculated value of "prob>F" was 0.2923 , which is greater than 0.05. therefor the intraction between contact time and initial metal Cr (VI) concentration has no significant effect on the % removal of Cr (VI).



(A) (B)

Fig 4.17 Effect of the interaction between contact time and initial concentration on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.2.3 The combined effect of solution pH and adsorbent dose

The interaction between pH and adsorbent dose on Cr (VI) removal is presented in Fig. 4.18 It was observed that a sharp decrease in the Cr (VI) ion removal occurred when the pH value of the solutions changed from 1.5 to 4.0. The maximum adsorption of Cr (VI) ions are obtained at pH 1.5. The decrease in Cr(VI) ion removal efficiency at higher pH might be due to the competition between OH^- and chromate ions (CrO_4^{2-}), where the former being the dominant species wins the race.

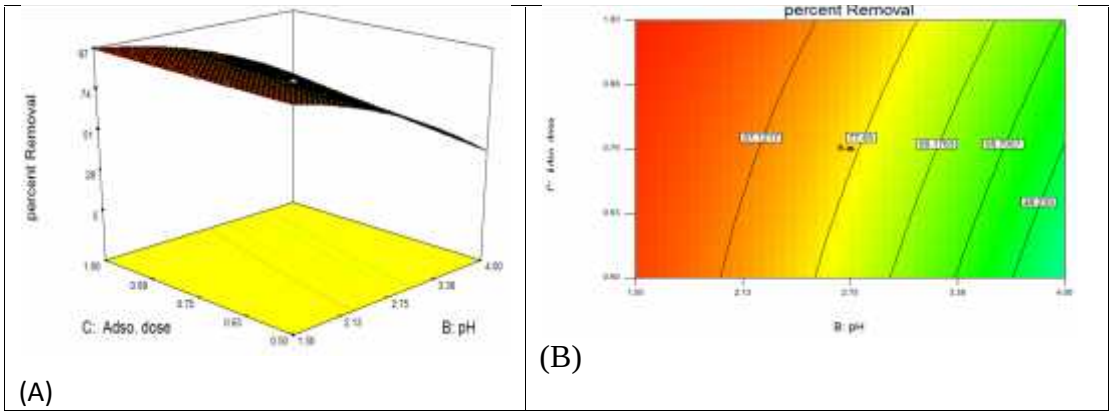


Fig 4.18 Effect of the interaction between pH and adsorbent dose on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.2.4 The combined effect of solution pH and contact time

Figure 4,19 showed the effect of solution pH and adsorption contact time on the percentage removal of Cr (VI) ions by the phosphoric acid *Prosopis Juliflora* activated carbon. From the contour plot it can be seen that, with increase in contact time and solution pH, the percentage removal of Cr (VI) decreased significantly. This result indicates that both adsorption factors have significant effect on the % removal of Cr (VI). Also the ANOVA analysis showed the combined effect of solution pH and contact time have "prob.>F" value of 0.0089, which indicates the significance of the factors on the percent removal of chromium (VI).

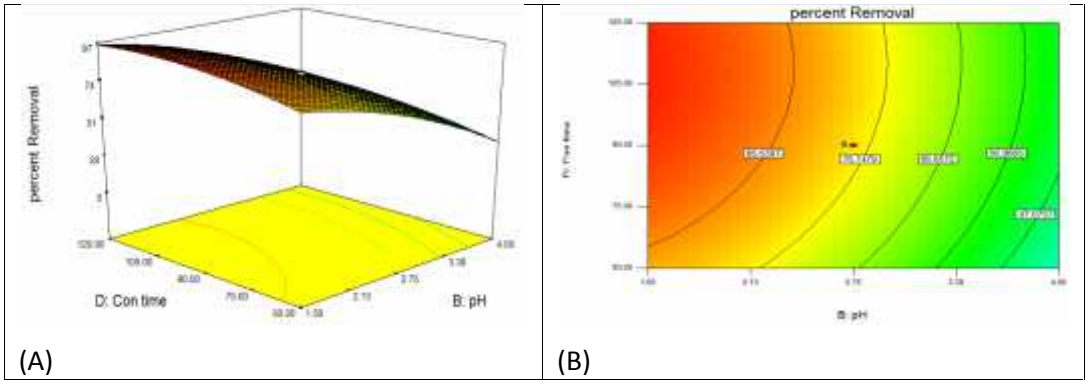


Fig 4.19 Effect of the interaction between pH and contact time on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.2.5 The combined effect of adsorbent dose and contact time

Figure 4.20 presented the interaction effect of adsorbent dose and contact time on the percent removal of Cr (VI). From the plot it can be seen that, increasing in both adsorbent dose and

contact time resulted in increased percent removal of Cr (VI). The result also indicated that as lower solution pH (pH=1.5), both terms have significant effect on the % removal Cr (VI).

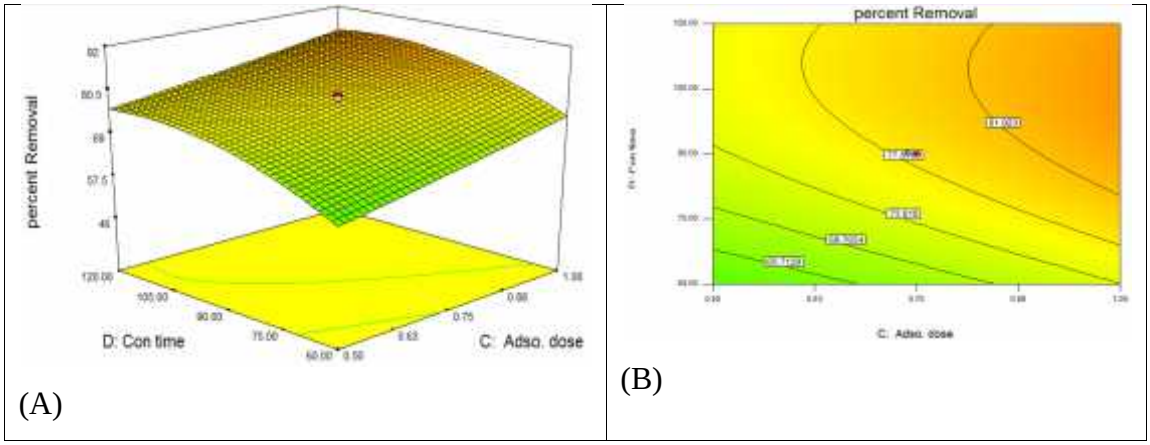


Fig 4.20 Effect of the interaction between adsorbent dose and contact time on Cr (VI) removal (a) Response surface plot (b) Contour plot

4.6.3 Optimum condition for Cr (VI) removal

Optimization was carried out after observing all the interaction effects between the adsorption variables. The proficiency of 'point optimization' was used for all the variables. Table 4:3 shows the optimum working conditions (ultimate goals, high and low limits) of the response (percent removal of Cr (VI)) and factors (solution pH, adsorbent dose, and initial Cr (VI) concentration and contact time) employed during the optimization analysis. In view of the increasingly stringent effluent discharge limits, the targeted criterion was maximized for % removal of Cr (VI) while the factors values were set in the range studied.

A set of solutions were generated by the Design-Expert 7.1.1 version software, to determine the optimum conditions of the process which would select the values have high composite desirability and removal efficiency. The software searched for a combination of factors that simultaneously satisfied the requirements placed on the ultimate goals of response and each of the factors.

Table 4.4 presents the optimum conditions in uncoded units (solution pH, adsorbent dose, Initial Cr (VI) concentration and contact time) which give the highest composite desirability (0.998) from the Design expert software. The predicted (%) and experimental (%) values of % removal

of Cr (VI) under the optimum conditions are also presented. The very small deviation, i.e., (%), between the predicted and experimental values of % removal of Cr (VI) indicates that the model (eq 4.1) is suitable and sufficient to predict the Cr (VI) adsorption process using the phosphoric acid treated activated carbon in the range of variables studied.

Table 4.6 working conditions of response and factors for optimization.

Variables	Ultimate goal	Experimental range	
		Lower limit	Upper limit
pH	In the range	1.5	4
Adsorbent dose (g/100ml	In the range	0.5	1
Initial Cr (VI) concentration (mg/L)	In the range	80	160
Time (min.)	In the range	60	120
% removal of Cr (VI)	Maximize	6.89	99.65

4.6.4 Validation Experiments

In order to verify the optimization results, an experiment was performed under predicted conditions by the developed model. The model predicted 99.27 % removal of Cr (VI) at pH – 1.5, concentration – 80 mg/L, adsorbent dose – 10 g/L and contact time–106.79 min. The experimental value obtained at these conditions is 99.23 % and is closely in agreement with the result obtained from the model and hence validated the findings of the optimization.

Table 4.7 Optimum conditions and model validation

Variables	Optimum results
pH	1.5
Adsorbent dose (g/100ml)	1
Initial Cr (VI) concentration (mg/L)	80
Time (min.)	106.79
% removal of Cr (VI)	99.27
Desirability	0.998
Experimental % removal of Cr (VI)	99.23
Deviation in percent	2.8

4.6.5 Comparison of Prepared AC against commercial Activated carbon

The produced activated carbon (phosphoric acid treated activated carbon) and a commercially produced activated carbon are used to compare on the optimum adsorption process parameters such as initial Cr (VI) 80mg/L; solution pH 1.5, adsorbent dose 1g/100mL and contact time 106.79min on the adsorption efficiency of the chromium (VI) ion removal. The result shown on the adsorption efficiency of the commercial activated carbon to remove chromium (VI) ions at optimum condition is 89.02%, this indicated that the adsorption efficiency of commercial activated carbon less than the adsorption efficiency of *Prosopis Juliflora* activated carbon produced in this finding ,see from the figurer below. The reason may be comes from the variation between the adsorption efficiency of commercial activated carbon and the activated carbon produced in lab. Due to the raw material, chemical activation agent and the production process parameters such as time and temperature as well the commercial activated carbon isn't the specific type of which would applied for Cr (VI) solution.

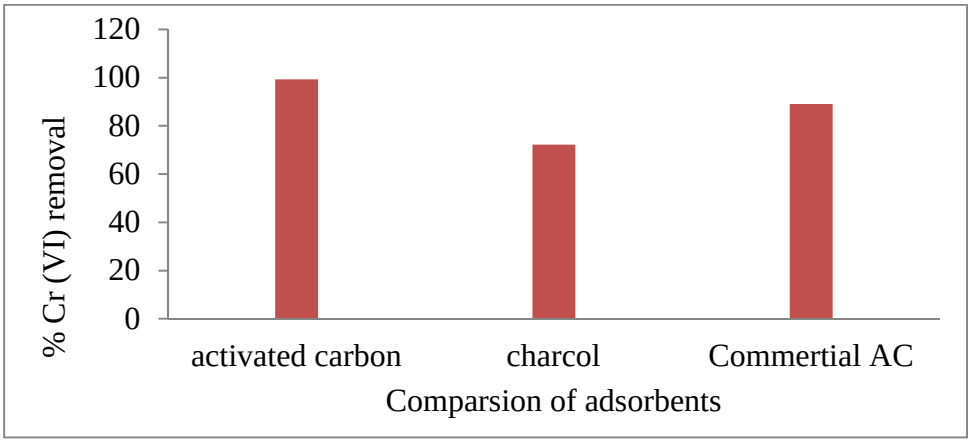


Figure 4.21 Comparisons of different activated carbons on Cr (VI) removal

5 Conclusions and Recommendation

5.1 Conclusion

The study presented in this thesis aimed at developing an inexpensive and effective adsorbent for Cr (VI) removal from aqueous solution. For this reason, a *Prosopis Juliflora* used as adsorbent. The adsorbent (*Prosopis Juliflora* wood) was activated with locally available chemical (phosphoric acid) in order to enhance the percentage removal of Cr (VI) ions. Then the Cr (VI) removal performances of the adsorbent under different experimental conditions were investigated. The physic-chemical composition of adsorbent was investigated, such as ash content, volatile mater, fixed carbon, surface charge (point of zero charge), and available surface functional groups on the surface of the adsorbent were investigated. The adsorption data were then used to investigate the adsorption isotherm models and adsorption kinetics models. Finally, the acid treated activated carbon produced from Prosopis Juliflora plant was used for the adsorption model generation and the investigation and optimization of the interaction of adsorption process parameters on the percentage removal of Cr (VI) using Design expert software.

- Chemical composition analysis results indicated that the adsorbent was very well raw material to produce activated carbon, since it has high fixed carbon content.
- The acid treated decreased the point of zero charge of the adsorbent indicating the protonation of the adsorbent surface, while the carbonized charcoal increased the point of zero charge indicating no protonation on the adsorbent surface.
- The FTIR analysis revealed the presence of the carbonyl group, carboxylic group, amino group and hydroxyl group among other functional groups on the surface of the adsorbent.
- The FTIR analysis also indicated the involvement of the hydroxyl group, amine group and carbonyl group but not carboxylic group because they have fixed wave number.
- The results from the batch adsorption experiments indicated that the adsorption of Cr (VI) ions by Prosopis Juliflora wood activated carbon was affected by the solution pH, adsorbent dose, initial Cr (VI) concentration, contact time and chemical activation. The percentage removal of Cr (VI) ions increased with increasing contact time and adsorbent dose and decreasing solution pH and Cr (VI) concentration.
- The kinetic results obtained from this study fitted well with the pseudo second order kinetic model and the equilibrium adsorption capacity calculated based on the pseudo second order

kinetic model showed good agreement with the adsorption capacity obtained from experimental results.

- The adsorption equilibrium isothermal data conformed well to the Langmuir isothermal model for acid treated activated carbon (R^2=) indicating the adsorption of Cr (VI) ions by the Prosopis Juliflora plat wood followed a monolayer pattern.
- The results from the statistical analysis of the adsorption process using the response surface methodology revealed that the adsorption process using acid treated Prosopis Juliflora plant activated carbon can be represented by a quadratic regression model based on the highest value of determination coefficient of R^2 =0.9997 and predicted determination coefficient of R^2= 0.9983.
- The ANOVA analysis showed that the removal of Cr (VI) ions is highly affected by the solution pH, adsorbent dose, initial Cr (VI) concentration, contact time and the interaction between the solution pH with other factors also the interaction between adsorption dose and contact time.

This study was focused on the adsorption of Cr (VI) ions onto *Prosopis Juliflora* pant activated carbon from aqueous solution. Response surface methodology was used to determine the optimum reaction conditions. According to the ANOVA analysis, except the initial Cr (VI) concentration, adsorbent dose and contact time and the interaction terms are statistically significant. The present findings in this research demonstrate the feasibility of utilizing *Prosopis Juliflora plat* as a sorbent for Cr (VI) removal and to change the dangerous spices (Prosopis Juliflora plant) to economic resource and address environmental friendly.

5.2 Recommendations

Adsorbent prepared from *Prosopis Juliflora* had been shown to have the potential in removing Cr (VI) ions from aqueous solution. Thus in order to further investigate it's effectiveness the following studies could be carried out.

- Investigation on the application of the adsorbent to remove other heavy metal ions from synthetic and actual waste water in a single metal and multiple metal systems.
- The detail investigation of the morphological characteristics of the adsorbent and the reusability of the adsorbent.
- Determination of the effectiveness of the adsorbent for the removal of inorganic and organic chemicals such as dyes and pesticides.
- Conduct column studies and explore the possibilities of developing a pilot or even an industrial process unit for the effective removal of heavy metals from aqueous solutions using *Prosopis Juliflora* plat activated carbon.

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Appendix A **(**Raw material (PJF) proximate analysis**)**

- **Moisture content**

Crucible 1	**Crucible 2**
(B) Crucible weight = 24.60gm	(B) crucible weight = 25.80gm
(C) Crucible with sample weight = 25.60gm	(C) crucible with sample weight = 26.80gm
Result after Cooling	Result after Cooling
(D) Crucible with sample weight = 25.49gm	(D) crucible with sample weight = 26.68gm %

%Moisture content (crucible 1) $= \frac{(C-D)}{(C-B)} * 100\%$

$= \frac{0.11}{1} * 100\% = 11\%$

% Moisture content (crucible 2) $= \frac{(C-D)}{(C-B)} * 100\%$

$= \frac{0.12}{1} * 100\% = 12\%$

Average moisture content = 11.5%

Ash content determination

Crucible 1	**Crucible 2**
(B) Crucible weight = **20.7955**gm	(B) crucible weight = **20.7955**gm
(C) Crucible with sample weight = 21.7955gm	(C) crucible with sample weight = 21.7955gm
Result after Cooling	Result after Cooling
(D) Crucible with sample weight = 21.7735gm	(D) crucible with sample weight = 21.7732gm

% Ash content (crucible 1) $= \frac{(C-D)}{(C-B)} * 100\%$

$= \frac{0.022}{1} * 100\% = 2.2\%$

% Ash content (crucible 2) $= \frac{(C-D)}{(C-B)} * 100\%$

$= \frac{0.0223}{1} * 100\% = 2.23\%$

Average Ash content = 2.215%

Volatile matter determination

Crucible 1	**Crucible 2**

(B) Crucible weight = 24.60gm (B) crucible weight = 25.80gm

(C) Crucible with sample weight = 25.60gm (C) crucible with sample weight = 26.81gm

Result after Cooling Result after Cooling

(D) Crucible with sample weight = 24.78gm (D) crucible with sample weight = 25.98gm

*(Y): is moisture content in percent as calculated in the above

% Volatile matter content (crucible 1) $= \frac{(C-D)}{(C-B)} * 100\% - Y$

$= \{\frac{0.82}{1} * 100\%\} - 11.5 = 70.5\%$

% Volatile matter content (crucible 2) $= \frac{(C-D)}{(C-B)} * 100\% - Y$

$= \frac{083}{1} * 100\%\} - 11.5 = 71.5\%$

Average Volatile matter content (%) = <u>71%</u>

***Prosopis Juliflora* Plant Composition**

Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)
11.5 %	2.215 %	71 %	15.285%

Appendix B: Experimental data.

Table B -1: Data for calibration of the spectrophotometer

Known Concentration	Absorbance		Average
	Trial 1	Trial 2	
0	0	0	0
0.05	0.020	0.022	0.021
0.1	0.064	0.066	0.065
0.2	0.131	0.132	0.132
0.4	0.201	0.202	0.201
0.6	0.362	0.362	0.362
0.8	0.491	0.493	0.492
1.0	0.630	0.634	0.632

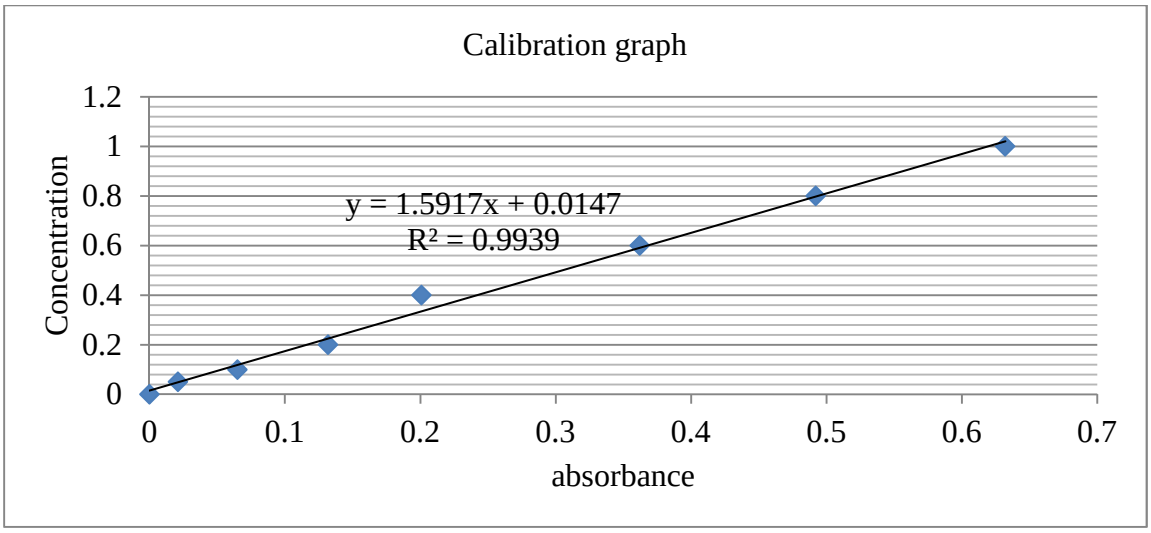


Figure B.1 Calibration graph for determination of Cr (VI) concentration.

Table B-2: Effect of solution pH on the adsorption of Cr (VI) for carbonized PJC.

Solution pH	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
1	0.027	0.026	0.027	1.42	11.86	98.81
2	0.098	0.097	0.098	4.25	11.58	96.46
3	0.605	0.606	0.606	24.45	9.56	79.62
4	0.982	0.984	0.983	39.45	8.06	67.12

Table B-3: Effect of solution pH on the adsorption of Cr (VI) for activated PJC.

Solution pH	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
1	0.002	0.003	0.003	0.47	11.95	99.61
2	0.012	0.012	0.012	0.83	11.92	99.31
3	0.205	0.206	0.206	4.46	11.55	92.88
4	0.782	0.784	0.783	31.49	8.85	73.76

Table B-4: Effect of initial Cr (VI) concentration on the adsorption of Cr (VI) onto Carbonized charcoal

Initial Cr(VI) conc.	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
80	0.012	0.013	0.013	0.87	7.91	98.92
120	0.142	0.243	0.243	10.02	11.00	91.65
160	0.285	0.485	0.485	19.64	14.04	87.72
200	0.482	0.681	0.682	27.48	17.25	86.26

Table B-5: Data for the effect of initial Cr (VI) concentration on the adsorption of Cr (VI) onto activated PJC.

Initial Cr (VI) conc. (mg/l)	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
80	0.002	0.003	0.003	0.47	7.95	99.41
120	0.142	0.143	0.143	6.04	11.40	94.97
160	0.185	0.285	0.285	11.69	14.83	92.69
200	0.382	0.581	0.582	23.50	17.65	88.25

Table B.6: Effect of adsorbent dose on the adsorption of Cr (VI) for carbonized charcoal.

Adsorption Conc. (dose) (g/100ml)	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
0.25	0.183	0.182	0.183	7.63	28.93	90.46
0.50	0.015	0.013	0.014	0.91	15.82	98.86
0.75	0.009	0.008	0.009	0.71	10.57	99.11
1.00	0.004	0.004	0.004	0.51	7.93	99.36

Table B.7: Effect of adsorbent dose on the adsorption of Cr (VI) for activated carbon.

Adsorption Conc. (dose) (g/100ml)	Absorbance			Final concentration Ce (mg/L)	Adsorption Capacity qe (mg/g)	Cr(VI) Percentage removal
	Trial 1	Trial 2	Average			
0.25	0.141	0.142	0.142	6.00	29.6	92.50
0.50	0.008	0.007	0.008	0.67	15.87	99.16
0.75	0.004	0.003	0.004	0.51	10.65	99.36
1.00	0.001	0.001	0.001	0.39	7.96	99.51

Table B.8: Effect of contact time for acid treated activated carbon.

Time (min)	Absorbance			Final Conc. (mg/L)	q_t (mg/g)	qe mg/g	Cr (VI) Percent removal	Log(q_e-q_t)	t/q_t
	Trial 1	Trial 2	Average						
15	0.734	0.736	0.735	29.545	5.045	7.957	63.07	0.464	2.973
30	0.621	0.622	0.622	25.090	5.491		68.64	0.392	5.463
45	0.598	0.597	0.598	24.135	5.587		69.83	0.375	8.054
60	0.476	0.477	0.477	19.323	6.068		75.85	0.276	9.888
75	0.312	0.312	0.312	12.760	6.724		84.05	0.091	11.154
90	0.274	0.275	0.275	11.288	6.871		85.89	0.036	13.099
105	0.023	0.022	0.023	1.265	7.874		98.42	-1.081	13.335
120	0.008	0.006	0.007	0.628	7.937		99.22	-1.699	15.119
135	0.006	0.005	0.006	0.589	7.941		99.26	-1.796	17.000
150	0.002	0.002	0.002	0.430	7.957		99.46	-	18.851
165	0.002	0.002	0.002	0.430	7.957		99.46	-	20.736

Table B.9: Langmuir isothermal model parameters for acid treated AC.

Initial Cr (VI) conc. (mg/l)	Absorbance			Final concentration C_e (mg/L)	$1/C_e$	Adsorption Capacity q_e (mg/g)	$1/q_e$
	Trial 1	Trial 2	Average				
80	0.017	0.017	0.017	1.026	0.975	7.903	0.127
120	0.026	0.026	0.026	1.384	0.723	11.861	0.084
160	0.048	0.050	0.049	2.299	0.435	15.770	0.063
200	0.240	0.238	0.239	9.856	0.101	19.014	0.053

Table B.10: Freundlich isotherm model parameters for acid treated AC.

Initial Cr (VI) conc. (mg/l)	Absorbance			Final concentration C_e (mg/L)	Log C_e	Adsorption Capacity q_e (mg/g)	Log q_e
	Trial 1	Trial 2	Average				
80	0.007	0.017	0.017	1.026	0.011	7.897	0.897
120	0.026	0.026	0.026	1.384	0.141	11.861	1.074
160	0.048	0.050	0.049	2.299	0.362	15.770	1.198
200	0.240	0.238	0.239	9.856	0.994	19.014	1.279

Appendix C: Some vital pictures in this thesis study.

Initial Cr (VI), 80mg/L

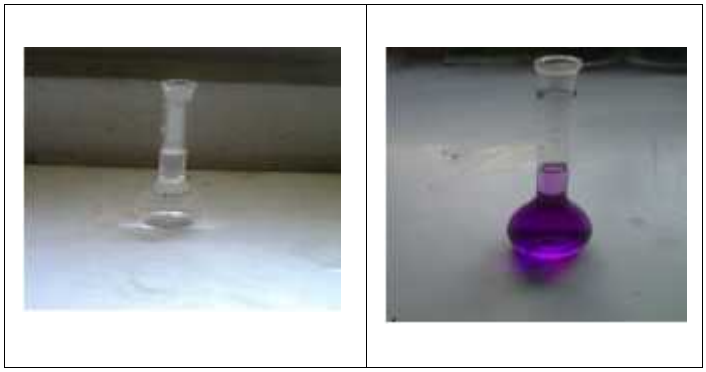
200mg/L respectively

adding of activated carbon

Mechanical shaker

Filtration by using wattman filter paper

Filtered solution

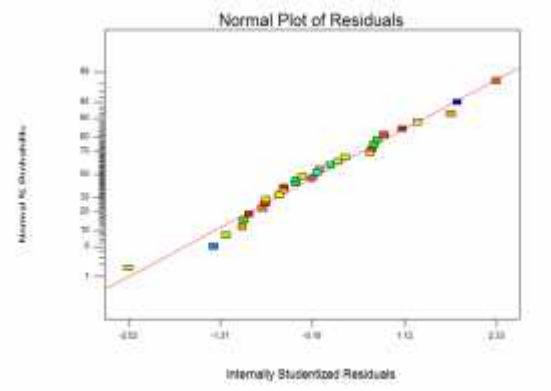


Adding 2ml drop of

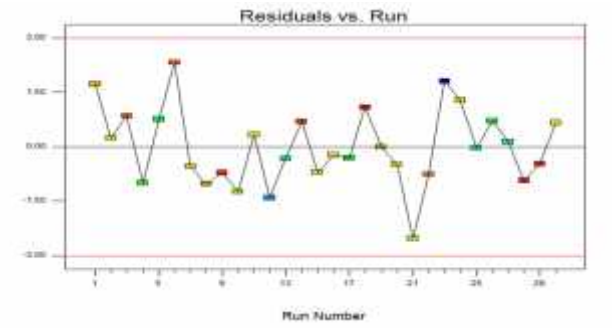
1, 5 DPC & $3MH_2SO_4$ Colure change

Ultra violet spectrophotometer to measure the reaming Cr (VI) ions

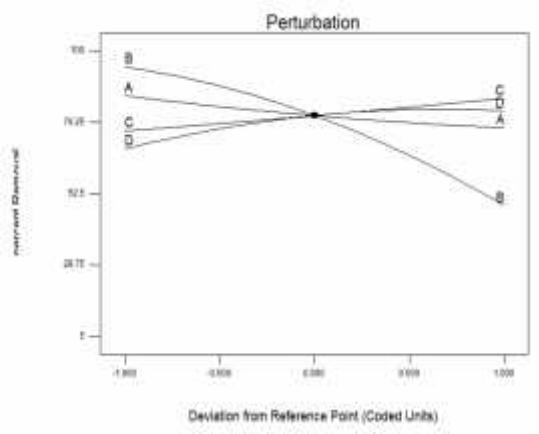
Appendix D: Results from the statistical analysis.

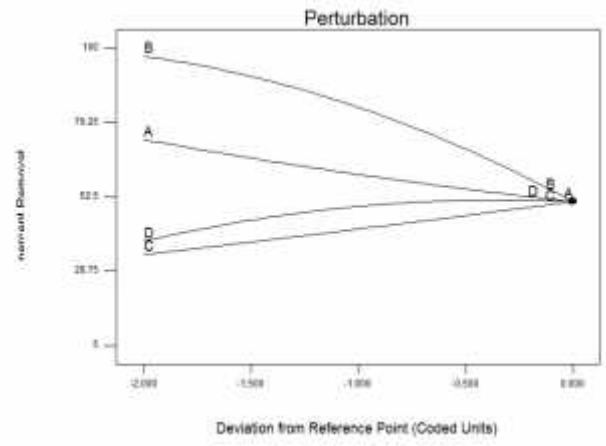


It is almost linear line (Ok)

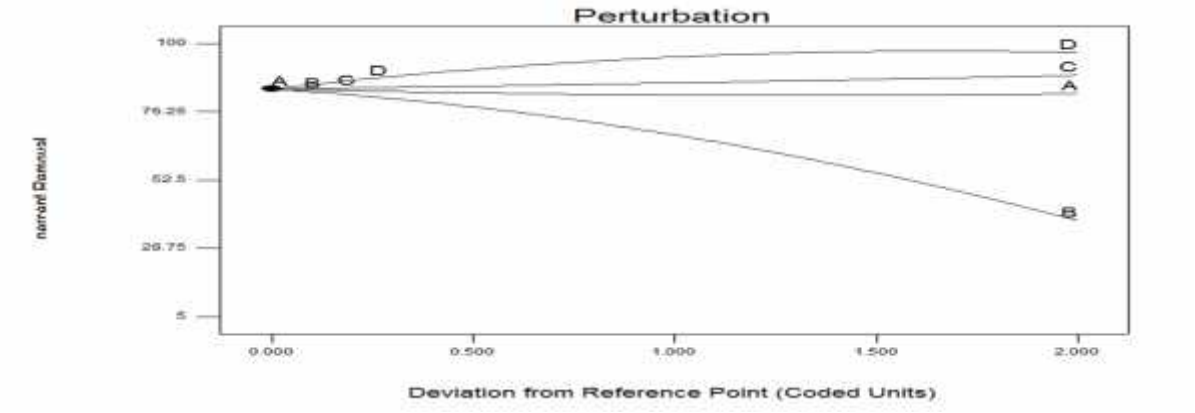


Random pattern (Ok)





When all factorse at low level



When all factorse at hight level